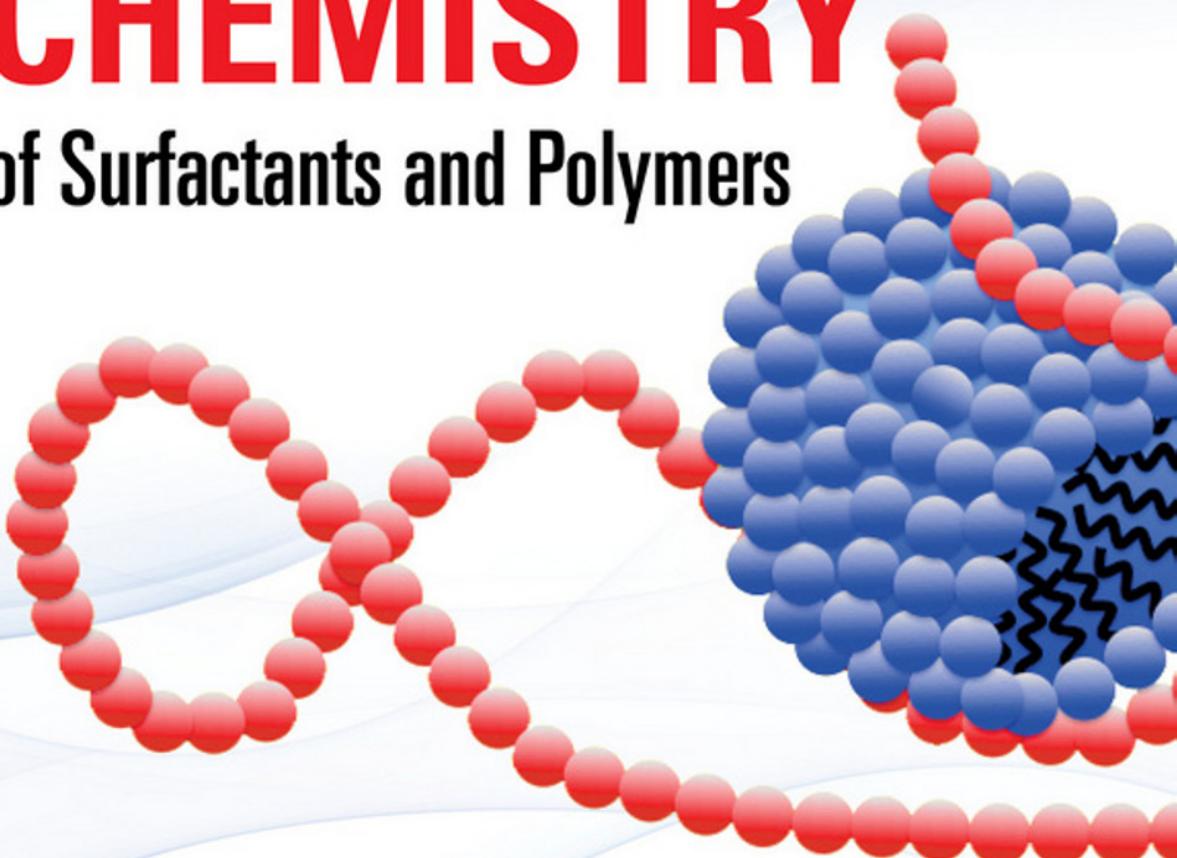


Bengt Kronberg • Krister Holmberg • Björn Lindman

SURFACE CHEMISTRY

of Surfactants and Polymers



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Surface Chemistry of Surfactants and Polymers

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Preface

Knowledge of the surface chemistry of surfactants and polymers is of fundamental importance in areas as diverse as detergents, oil recovery, paints, paper coatings, food, and pharmaceuticals. The solution and interfacial behavior of a single surfactant, or a single polymer, is important, but many formulations are complex mixtures of several different surfactants and one or more polymers. Together, the surfactants and the polymers used in the formulation provide the stability, rheological behavior, deposition, and so on, needed for the specific application. The performance of such products depends to a large extent on the interplay between the different species in the formulation. Hence, knowledge about physicochemical properties of both surfactants and polymers and not least about polymer–surfactant interactions is essential in order to make formulation work more of a science than an art.

This book deals with solution and interfacial properties of surfactants and polymers. Chapters 1–12 cover basic concepts and self-assembly in solution as well as at interfaces. In Chapters 13–17 the systems are more complex in that they comprise mixtures; mixtures of surfactants or combinations of polymers and surfactants. Chapters 18–25 cover colloidal systems as well as some applications.

The background of this book is the success of our previous book *Surfactants and Polymers in Aqueous Solution*, which has been published in two editions, translated into several languages, and reprinted more than 10 times. That book was first published in 1998 and considering the rapid development of surface chemistry/soft matter physics we felt that there was a need for a renewal of the content. The present book is an entirely new book, updating the field and including new aspects, although the fundamental parts of the book are based on the concepts from the previous book.

This book has a practical rather than a theoretical scope. It is written as a reference book for scientists and engineers both in industry and academia. It is also intended as a textbook for courses for researchers in industry and for graduate courses at universities. There are books on surfactants and books dealing with water-soluble polymers but to our knowledge our previous book *Surfactants and Polymers in Aqueous Solution* is the only one that treats both in a comprehensive way. This new book carries on the legacy of the previous book in this aspect.

In covering both surfactants and polymers in one book the reader is given a common description of their physicochemical behavior, which is a major advantage compared to having to consult one book on surfactants and one on polymers, written by different authors with different ways of treating the topics.

The intention has been to make a book that is easy to read and useful as a source of information. We have refrained from much of the fundamental description of the physical

chemistry behind the phenomena but appropriate reference to thorough theoretical treatises is given. We believe in the power of figures to illustrate complex matters and the book is rich in illustrations. Each of the 25 chapters ends with a bibliography section in which the reader is referred to other literature for more in-depth study.

We hope the readers of the book will find it useful and we welcome suggestions for improvements for coming editions.

Acronyms

Common acronyms of surfactants, surfactant raw materials, and surfactant types.

Acronym	Full name
AE	(Fatty) alcohol ethoxylates
AES	(Fatty) alcohol ether sulfates, (fatty) alcohol ethoxy sulfates
AO	(Fatty) amine oxides
AOS	α -Olefin sulfonates
AOT	Sodium bis(2-ethylhexyl)sulfosuccinate
APE	Alkylphenol ethoxylates (ethoxylated alkylphenols)
APG	Alkyl polyglucosides (in reality a misnomer; should rather be alkyl oligoglucosides; the head group typically only comprises two or less than two glucose units)
AS	(Fatty) alcohol sulfates (sulfated primary alcohol)
CTAB	Cetyltrimethylammonium bromide, $C_{16}H_{33}N(CH_3)_3^+Br^-$
DEA	Diethanolamine, $(HOCH_2CH_2)_2NH$
DPPC	Dipalmitoylphosphatidylcholine
DTAB	Dodecyltrimethylammonium bromide, $C_{12}H_{25}N(CH_3)_3^+Br^-$
ECH	Epichlorohydrin
EO	Ethylene oxide
LAS or LABS	Linear alkylbenzene sulfonates (the C_{12} compound is by far the most common)
LDAO	Lauryldimethylamine oxide, $C_{12}H_{25}N^+(CH_3)_2-O^-$
MEA	Monoethanolamine, $HOCH_2CH_2NH_2$
NP	Nonylphenol, $C_9H_{19}-C_6H_4-OH$
NP-E10	Nonylphenol with 10 oxyethylene units, $C_9H_{19}-C_6H_4-(OCH_2CH_2)_{10}-OH$
PEG	Poly(ethylene glycol), $HO(CH_2CH_2O)_nH$
Pluronic	EO-PO block copolymers, $HO(CH_2CH_2O)_n-(CH_2CH(CH_3)O)_m-(CH_2CH_2O)_nH$
PO	Propylene oxide
POE	Polyoxyethylene
PPO	Poly(propylene glycol), $HO(CH_2CH(CH_3)O)_nH$
Quat	Quaternary ammonium compound with at least one long-chain alkyl
SAS	Secondary <i>n</i> -alkanesulfonates, paraffin sulfonates
SDS	Sodium dodecyl sulfate, $C_{12}H_{25}OSO_3^-Na^+$
Span	Sorbitan alkanoates
TEA	Triethanolamine, $(HOCH_2CH_2)_3N$
Tween	Ethoxylated sorbitan alkanoates

1

Types of Surfactants, their Synthesis, and Applications

Definition of a Surfactant

Surfactant is a widely used contraction for surface active agent, which literally means active at a surface. The term *surface active* means that the surfactant reduces the free energy of surfaces and interfaces. Expressed differently, they reduce the surface and the interfacial tensions. This is not an unique quality, however. Most water-soluble organic compounds give a reduction of the surface and interfacial tensions when added to an aqueous solution but the effect is normally much less pronounced than for surfactants. The unique behavior of a surfactant is that it self-assembles at interfaces and forms tightly packed structures: monolayers at the air–water and the oil–water interface, and monolayers and aggregates at the solid–water interface. Such self-assembled layers drastically change the character of the interface. Surfactant self-assembly at the air–water interface, commonly referred to as the “surface,” is dealt with in Chapter 12; the assembling at the oil–water interface, which is key to formation of emulsions, is treated in Chapter 24; and assembly at the solid–water interface, *adsorption*, is described in depth in Chapter 8. Surfactants also self-assemble in water, usually forming *micelles* at very low concentration and other aggregates, called *surfactant liquid crystals*, at higher concentration. These are treated in Chapters 4 and 6, respectively.

The term surfactant is usually associated with relatively low molecular weight substances. The molecular weight is typically below 500 Da but may be larger for nonionic surfactants with long polyoxyethylene tails. There also exist polymeric surface active agents and these may be called polymeric surfactants. However, more often they are referred to as surface active polymers and that terminology is used in this book. Several chapters deal with surface active polymers.



Figure 1.1 Schematic illustration of a surfactant

Surfactants are *amphiphilic* molecules. The word has a Greek origin with *amphi* meaning “both” and *phil* meaning “like”; that is, surfactants are molecules that like both a polar and a nonpolar environment. This is due to their structure. All surfactants have at least one polar headgroup that wants to be in water and at least one hydrophobic tail that prefers to be in an apolar environment; hence, the tendency to go to interfaces. Figure 1.1 shows the structure of a surfactant with one polar head group and one hydrophobic tail.

A surfactant may be viewed as a molecule consisting of a lyophilic and a lyophobic part. The lyophilic moiety is soluble in a specific fluid whereas the lyophobic moiety is insoluble in this fluid. When the fluid is water, which is usually the case, the terms hydrophilic and hydrophobic parts are normally used.

The term *amphiphile* or *amphiphilic compound* is sometimes used in the same sense as the word surfactant. Amphiphilic compounds are also very common in nature. All biological systems contain surface active substances. However, these molecules are usually called polar lipids rather than surfactants. Thus, implicit in the name is that a surfactant is a man-made compound in some sense, although the molecule may have a natural origin, as is discussed later in this chapter.

The hydrophobic tail is almost always based on one or more carbon chains and the chains may be linear, branched, or cyclic. The only exception to carbon chains as hydrophobic backbone is siloxane chains. There exist both high molecular weight and low molecular weight amphiphilic compounds based on the $-\text{Si}-\text{O}-$ unit; these are discussed in Chapters 10 and 20, respectively.

Surfactants Adsorb at Interfaces

The term interface denotes a boundary between any two immiscible phases; the term surface indicates that one of the phases is a gas, usually air. Altogether five different interfaces exist:

1. Solid–vapor *surface*
2. Solid–liquid
3. Solid–solid
4. Liquid–vapor *surface*
5. Liquid–liquid

The driving force for a surfactant to adsorb at an interface is to lower the free energy of that phase boundary. The interfacial free energy per unit area represents the amount of work required to expand the interface. The term interfacial tension is often used

Table 1.1 Examples of interfaces involving at least one liquid phase

Interface	Type of system	Product
Solid–liquid	Suspension, sol, slurry	Solvent-borne paints, colloidal silica, cement slurries
Liquid–liquid	Emulsion	Bitumen emulsions, milk, cream
Liquid–vapor	Foam, aerosol	Shaving cream, fire fighting foams, clouds

instead of interfacial free energy per unit area. Thus, the surface tension of water is equivalent to the interfacial free energy per unit area of the boundary between water and the air above it. When that boundary is covered by surfactant molecules, the surface tension (or the amount of work required to expand the interface) is reduced. The denser the surfactant packing at the interface, the larger is the reduction in surface tension.

This book is concerned with events at interfaces that involve at least one liquid phase, which means three out of the five interfaces listed above. The liquid is usually, but not always, water. Phenomena occurring at these three interfaces, as well as in the bulk liquid, may be referred to as *wet surface chemistry*. *Dry surface chemistry* is also very important—heterogeneous catalysis is a prime example—but that science is not discussed here. Examples of the different “wet” interfaces and of products in which these interfaces are important are given in Table 1.1.

The systems indicated in Table 1.1 are all examples of dispersions, that is, systems with one phase, called the dispersed phase, finely distributed in another phase, the continuous phase. In many formulated products several types of systems are present at the same time. Water-based paints and paper coating formulations are examples of familiar but, from a colloidal point of view, very complicated systems, containing both solid–liquid (dispersed pigment particles) and liquid–liquid (latex or other binder droplets) interfaces. In addition, foam formation is a common (but unwanted) phenomenon at the application stage. All the interfaces are stabilized by surfactants.

As mentioned above, the tendency to accumulate at interfaces is a fundamental property of a surfactant. In principle, the stronger the tendency, the better is the surfactant. The tendency for a surfactant to accumulate at a boundary depends on the surfactant structure and also on the nature of the two phases that meet at the interface. Therefore, there is no universally good surfactant, suitable for all uses. The choice will depend on the application. A good surfactant should have low solubility in the bulk phases. Some surfactants (and several surface active macromolecules) are only soluble at the oil–water interface. Such compounds are difficult to handle but are very efficient in reducing the interfacial tension.

There is, of course, a limit to the surface and interfacial tension lowering effect by the surfactant. Usually that limit is reached when micelles start to form in the bulk solution. Table 1.2 illustrates what a good surfactant can do in terms of reducing surface and interfacial tensions. The values given are typical of what is attained by normal light-duty liquid detergents. With special formulations, so-called ultra-low interfacial tension, that is, values in the range of 10^{-3} mN/m or below, can be obtained. An example of a system

4 Surface Chemistry of Surfactants and Polymers

Table 1.2 Typical values of surface and interfacial tensions at room temperature (mN/m)

Water-air	72–73
10% aqueous NaOH-air	78
Aqueous surfactant solution-air	28–30
Decane-air	24
Benzene-air	29
Decane-water	51
Benzene-water	35
Hydrocarbon-aqueous surfactant solution	1–5

giving ultra-low interfacial tension is a three-phase system comprising a microemulsion in equilibrium with excess water and oil phases. Such systems are of interest in oil recovery and also in detergency; these are discussed in Chapter 25.

Surfactants Aggregate in Solution and at Interfaces

As discussed, one characteristic feature of surfactants is their tendency to adsorb at interfaces. Another fundamental property of surface active agents is that unimers in solution tend to form aggregates, so-called micelles. (The free or unassociated surfactant is referred to in the literature either as *monomer* or *unimer*. In this text unimer is used and the term monomer is restricted to the polymer building block.) Micelle formation, or micellization, can be viewed as an alternative mechanism to adsorption at the interfaces for removing the hydrophobic tail from contact with water, thereby reducing the free energy of the system. It is an important phenomenon, since surfactant molecules behave very differently when present in micelles than they do as free unimers in solution. Surface and interfacial tension lowering and dynamic phenomena, such as wetting and foaming, are governed by the concentration of free unimers in solution. The micelles can be seen as a reservoir for the surfactant unimers. The exchange of surfactant molecules between micelles and bulk solution is fast, with residence times in micelles typically much below milliseconds.

Micelles are generated already at a very low surfactant concentration in water. The concentration at which micelles start to form is called the critical micelle concentration (CMC) and is an important characteristic of a surfactant. A CMC of 10 mM, a reasonable value for an ionic surfactant, means that the unimer concentration will never exceed this value, regardless of the amount of surfactant added to the solution. Surfactant micellization is discussed in detail in Chapter 4.

In a micelle, the surfactant hydrophobic tail is in the interior and the polar head group is directed towards the solvent. The micelle, therefore, is a polar aggregate of high water solubility and without surface activity. When a surfactant adsorbs from aqueous solution at a hydrophobic surface, it normally orients its hydrophobic tail towards the surface and exposes its polar head group to the water. The surface has now become hydrophilic and, as a result, the interfacial tension between the surface and water has been reduced. Adsorption at hydrophilic surfaces often results in more complicated surfactant assemblies. Surfactant adsorption at hydrophilic and hydrophobic surfaces is discussed in Chapter 8.

All Surfactants Contain at Least One Polar Head Group and at Least One Hydrophobic Tail

The hydrophobic part of a surfactant may be branched or linear, it may be cyclic and quite often it is an alkylaryl. The polar head group is usually, but not always, attached at one end of the alkyl chain. The number of carbon atoms in the hydrophobic tail is usually 8–18. The degree of chain branching, the position of the polar head group and the length of the chain are parameters of importance for the physicochemical properties of the surfactant.

The polar part of the surfactant may be ionic or nonionic and the choice of polar head group determines the properties to a large extent. For nonionic surfactants the size of the head group can be varied at will; for the ionics the size is more or less a fixed parameter. As will be discussed many times throughout this book, the relative size of the hydrophobic tail and the polar head group, not the absolute size of either of the two, is decisive in determining the physicochemical behavior of a surfactant in water.

The vast majority of surfactants contains only one polar head group. Recently, there has been considerable research interest in certain dimeric surfactants, containing two hydrophobic tails and two head groups linked together via a short spacer. These species, generally known under the name *gemini* (Latin for “twin”) surfactants, are not yet of commercial importance. They show several interesting physicochemical properties, such as very high efficiency in lowering surface tension and very low CMC. The low CMC values of gemini surfactants can be illustrated by a comparison of the value for the conventional cationic surfactant dodecyltrimethylammonium bromide (DTAB) (16 mM) and that of the corresponding gemini surfactant, having a two carbon linkage between the monomers (0.9 mM). The difference in CMC between monomeric and dimeric surfactants could be of considerable practical importance. A typical gemini surfactant is shown in Figure 1.2. Gemini surfactants are further discussed in a separate section of this chapter.

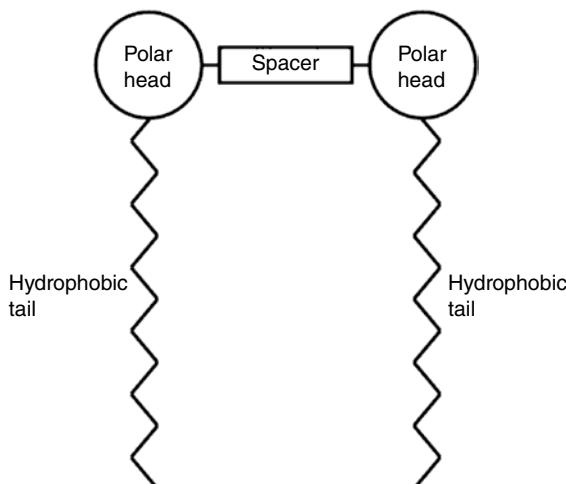


Figure 1.2 A *gemini* surfactant

6 Surface Chemistry of Surfactants and Polymers

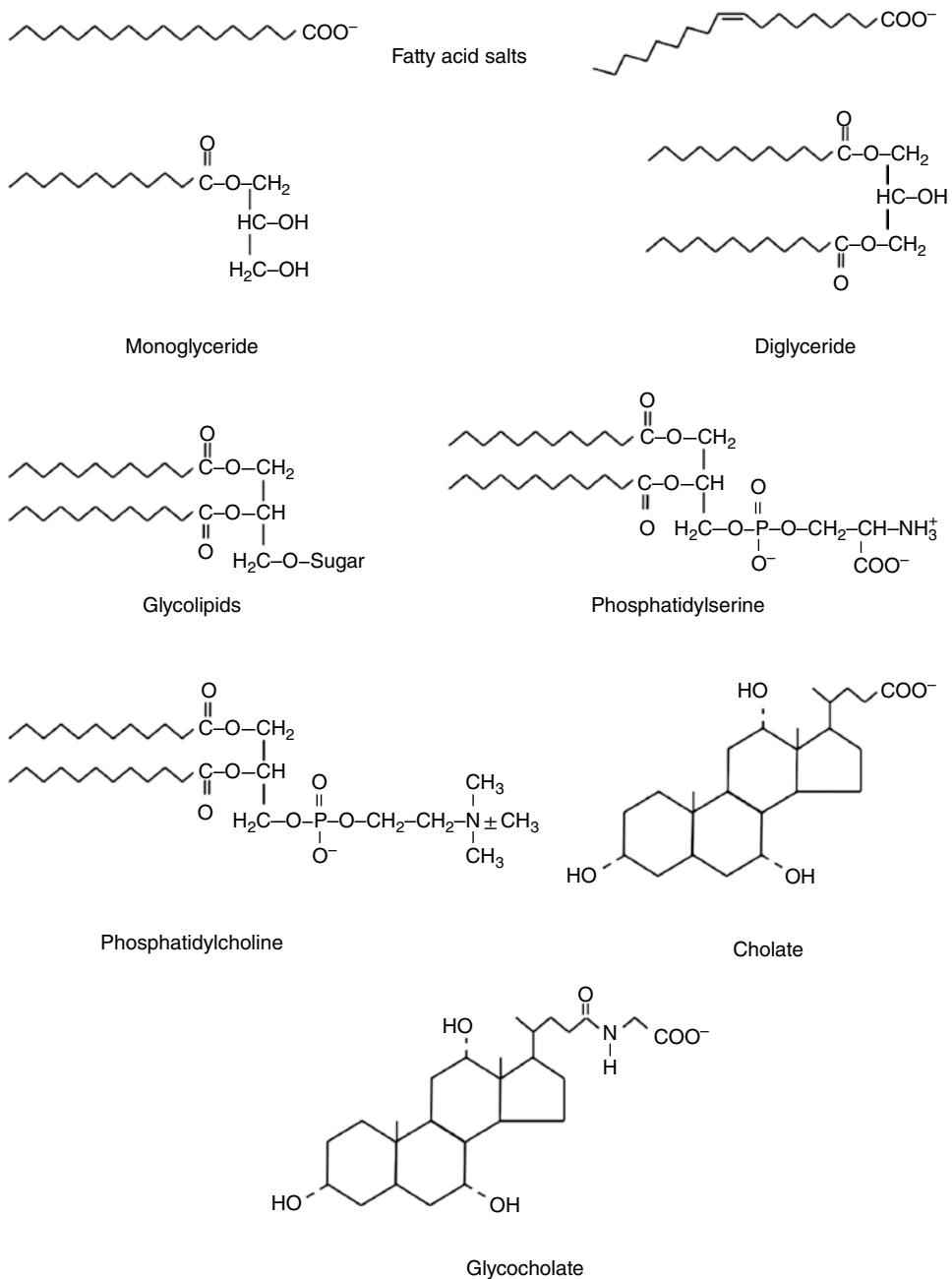


Figure 1.3 Examples of polar lipids

Surface Active Compounds are Plentiful in Nature

Nature's own surfactants are usually referred to as polar lipids. These are abundant in all living organisms. In biological systems the surface active agents are used in very much the same way as surfactants are employed in technical systems: to overcome solubility problems, as emulsifiers, as dispersants, to modify surfaces, and so on. There are many good examples of this in biological systems: bile salts are extremely efficient solubilizers of hydrophobic components in the blood, while mixtures of phospholipids pack in ordered bilayers of surfactant liquid crystal type and such structures constitute the membranes of cells. Figure 1.4 gives examples of important polar lipids. The only important example of a surfactant being obtained directly, without chemical conversion, from nature is lecithin. (The term lecithin is not used in a strict way in the surfactant literature. It is sometimes used synonymously with phosphatidylcholine and it sometimes refers to phospholipids in general.) Lecithin is extracted from phospholipid-rich sources such as soybean and egg.

Microorganisms are sometimes efficient producers of surface active agents. Both high molecular weight compounds, for example, lipopolysaccharides, and low molecular weight polar lipids can be produced in good yields, particularly when the microorganism is fermented on a water-insoluble substrate. Surface active polymers of this type are dealt with in Chapter 10. Figure 1.4 gives the structures of a low molecular weight acylated sugar, a trehalose lipid obtained from the cell walls of *Mycobacterium tuberculosis*, a glycolipid from *Pseudomonas aeruginosa* called rhamnolipid (or more specifically, a di-rhamnolipid), and a surface active polypeptide derivative produced from *Bacillus subtilis*. These and several other low molecular weight amphiphilic lipids have proven to be effective surfactants. Surface active agents produced from bacteria and yeasts have attracted considerable interest in recent years and much effort has been directed towards improving the fermentation and, not least, the work-up procedure. Although considerable process improvements have been made, commercial use of these products is still limited due to their high price. Their main use is in the cosmetics sector.

Surfactant Raw Materials may be Based on Petrochemicals or Oleochemicals

For many years there has been a strong trend towards *green surfactants*, particularly for the household sector. In this context, the term *natural surfactant* is often used to indicate some natural origin of the compound. However, no surfactants used in any substantial quantities today are truly natural. With few exceptions they are all manufactured by organic synthesis, usually involving rather hard conditions, which inevitably give by-products. For example, monoglycerides are certainly available in nature but the surfactants sold as monoglycerides are prepared by glycerolysis of triglyceride oils at temperatures well above 200°C, yielding di- and triglycerol derivatives as by-products. Alkyl glucosides are abundant in living organisms but the surfactants of this class, often referred to as APGs (alkyl polyglucosides), are made in several steps that by no means are natural.

A more adequate approach to the issue of origin is to divide surfactants into oleochemically based and petrochemically based. Surfactants based on oleochemicals are made from

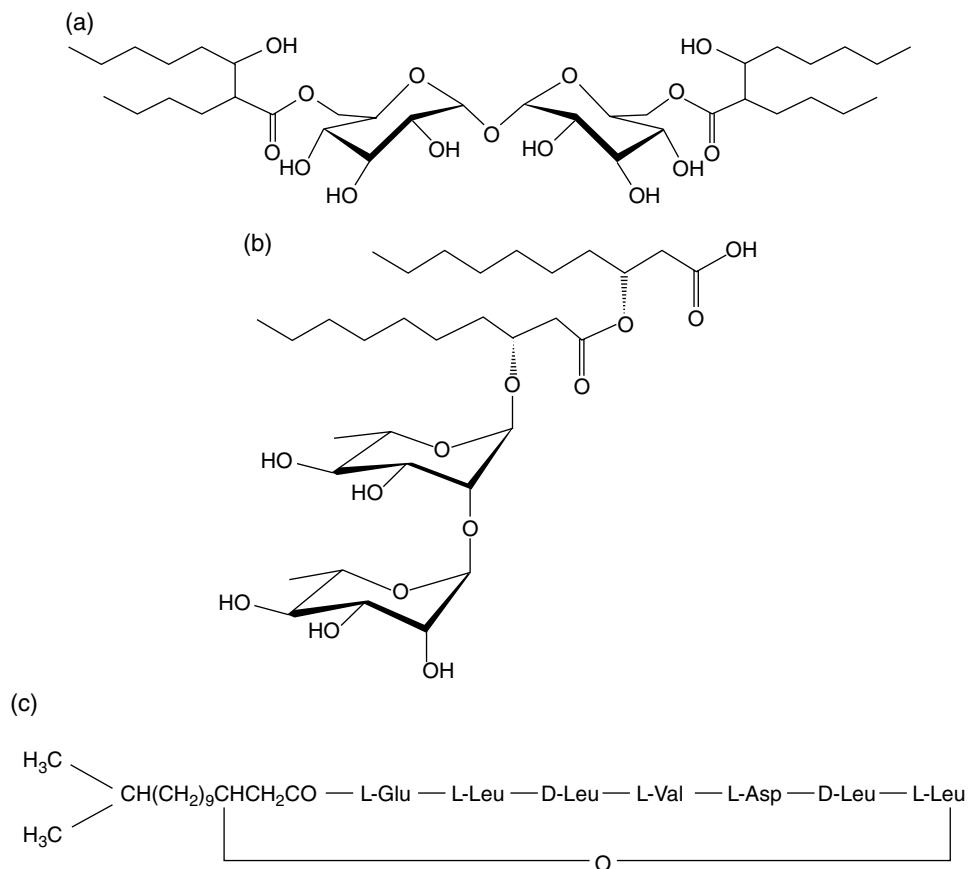


Figure 1.4 Examples of surface active polar lipids produced by fermentation: (a) a trehalose lipid; (b) a rhamnolipid; and (c) a cyclic polypeptide derivative. (The hydrocarbon chains in structures (a) and (b) are only schematic; in reality they are longer than shown here.)

renewable raw materials, most commonly vegetable oils. Surfactants from petrochemicals are made from small building blocks, such as ethylene, produced by cracking of naphtha. Quite commonly, a surfactant may be built up by raw materials from both origins. Fatty acid ethoxylates are one example out of many.

Sometimes the oleochemical and the petrochemical pathways lead to essentially identical products. For example, linear alcohols in the C_{10} – C_{14} range, which are commonly used as hydrophobes for both nonionics (alcohol ethoxylates) and anionics (alkyl sulfates, alkyl phosphates, etc.), are made either by hydrogenation of the corresponding fatty acid methyl esters or via Ziegler–Natta polymerization of ethylene using triethyl aluminum as catalyst. Both routes yield straight-chain alcohols and the homologue distribution is not very different, since it is largely governed by the distillation process. Both pathways are used in very large scale operations.

It is not obvious that the oleochemical route will lead to a less toxic and more environmentally benign surfactant than the petrochemical route. By-products that may be allergenic or toxic to aquatic organisms can be generated by both routes. However, from the carbon dioxide cycle point of view, chemical production based on renewable raw materials is always preferred. In terms of *Carbon Footprint*, that is, the amount of greenhouse gas emissions caused by a product, today a popular measure of the impact made on the environment, oleochemically-based surfactants are preferred.

Linear long-chain alcohols are often referred to as fatty alcohols, regardless of their source. Branched alcohols are also of importance as surfactant raw material. They are invariably produced by synthetic routes, the most common being the so-called Oxo process, in which an olefin is reacted with carbon monoxide and hydrogen in the presence of a soluble rhodium catalyst to give an aldehyde (the hydroformylation reaction), which is subsequently reduced to the alcohol by catalytic hydrogenation. Recent advances in the process technology have made it possible to obtain tailor-made higher olefin fractions from lower and higher linear alpha olefins via isomerization and disproportionation. A mixture of branched and linear alcohols is obtained and the ratio between the two can be varied to some extent by the choice of catalyst and reaction conditions.

The different routes to higher molecular weight primary alcohols are illustrated in Figure 1.5.

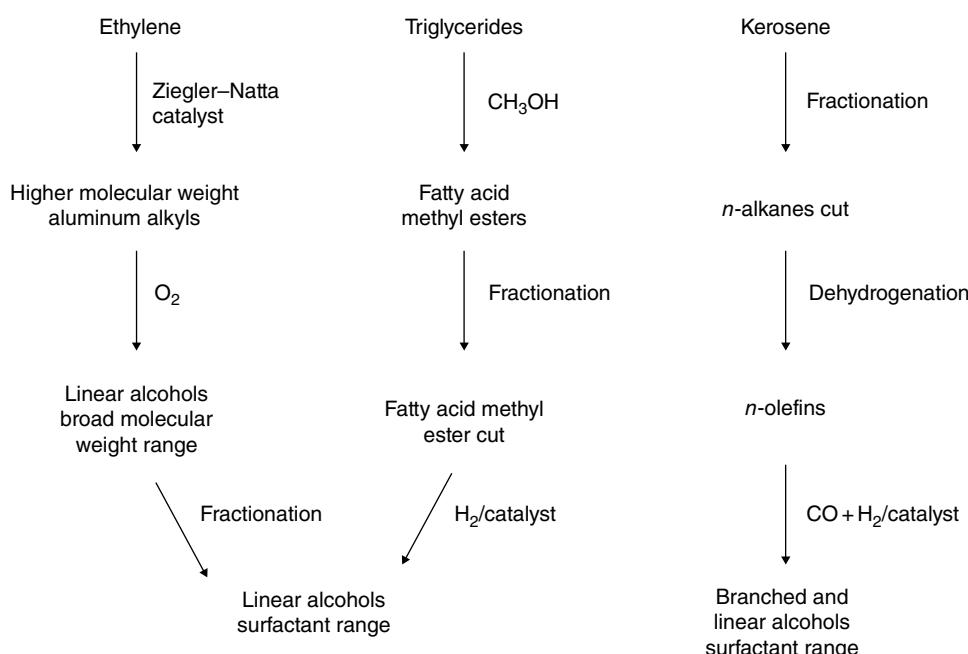


Figure 1.5 Different pathways for preparation of primary alcohols of interest as surfactant building block; from left to right: Ziegler–Natta polymerization of ethylene; reduction of fatty acid methyl esters; hydroformylation of higher olefins (the Oxo process)

Surfactants are Classified by the Polar Head Group

The primary classification of surfactants is made on the basis of the charge of the polar head group. It is common practice to divide surfactants into the classes anionics, cationics, nonionics, and zwitterionics. Surfactants belonging to the latter class contain both an anionic and a cationic charge under normal conditions. In the literature they are often referred to as amphoteric surfactants but the term *amphoteric* is not always correct and should not be used as synonymous to *zwitterionic*. An amphoteric surfactant is one that changes its state of ionization with pH. Among normal organic substances, simple amino acids are well-known examples of amphoteric compounds. However, many of the amino acid-based surfactants, nowadays of increasing interest because of their natural origin, are not amphoteric. They are N-acyl derivatives of the amino acid, which means that the basic character of the α -amino group is lost. Thus, they are anionic surfactants unless they are based on lysine or some other dibasic amino acid, in which case they become amphoteric. Some zwitterionic surfactants retain their charges over the whole pH range. Surfactants with a quaternary ammonium as the cationic group and a sulfonate salt as the anionic group, such as the sulfobetaines, are examples of that. Normal betaine surfactants (see below), on the other hand, are based on a quaternary ammonium group and a carboxylate group, the latter becoming protonated at low pH. Thus, a betaine surfactant is zwitterionic at high and medium pH but cationic at low pH.

Most ionic surfactants are monovalent but there are also important examples of divalent anionic amphiphiles. For the ionic surfactants the choice of counterion plays a role in determining the physicochemical properties. Most anionic surfactants have sodium as counterion but other cations, such as lithium, potassium, calcium, protonated amines, and quaternary ammonium compounds, are used as surfactant counterions for specific purposes. For example, potassium or ammonium as the counterion instead of sodium gives higher solubility in organic solvents, which is sometimes an advantage. The counterion of cationic surfactants is usually a halide, acetate, or methyl sulfate. The counterion used with a cationic surfactant often plays an important role for the physicochemical properties of a formulation. Large polarizable ions, that is, singly charged ions with low charge density ("soft" or *chaotropic* ions) such as iodide or thiocyanate, interact much more strongly with interfaces than do small or multiply charged ions ("hard" or *kosmotropic* ions) such as chloride, acetate, and sulfate. This effect is related to the *Hofmeister series* in which electrolytes are ordered according to their ability to *salt in* or *salt out* a solute. The relation between the Hofmeister series and solubility of a solute in aqueous solution is further discussed on page 25.

The hydrophobic group is normally a hydrocarbon (alkyl or alkylaryl) but may also be a polydimethylsiloxane or a fluorocarbon. The two latter types of surfactants are particularly effective in nonaqueous systems.

For a few surfactants there is some ambiguity as to classification. For example, amine oxide surfactants are sometimes referred to as zwitterionics, sometimes as cationics, and sometimes as nonionics. Their charge is pH dependent and in the net neutral state they may either be seen as having distinct anionic and cationic charges or as dipolar nonionic compounds. Fatty amine ethoxylates, which contain both an amino nitrogen atom (cationic polar group) and a polyoxyethylene chain (nonionic polar group), may be included in either the cationics or the nonionics class. The nonionic character dominates when the

polyoxyethylene chain is very long, whereas for medium and short chains the physicochemical properties are mainly those of cationic surfactants. Surfactants containing both an anionic group, such as sulfate, phosphate, or carboxylate, and a polyoxyethylene chain are also common. These surfactants, known as ether sulfates and so on, usually contain short polyoxyethylene chains, typically two or three oxyethylene units, and are therefore categorized as anionics.

Anionics

Carboxylate, sulfate, sulfonate, and phosphate are the polar groups found in anionic surfactants. Figure 1.6 shows structures of the more common surfactant types belonging to this class.

Anionics are used in a larger volume than any other class of surfactant. A rough estimate of the worldwide surfactant production is 20 million metric tons per year. Soap is the largest single surfactant followed by linear alkylbenzene sulfonate. Anionics in total represent roughly 70% of the surfactant consumption. Even if soap is excluded, as is often the case in the statistics, anionics is still the dominating class. One reason for their popularity is the ease and low cost of manufacture. Anionics are used in most detergent formulations and the best detergency is obtained by alkyl and alkylaryl chains in the C₁₂–C₁₈ range.

The counterions most commonly used are sodium, potassium, ammonium, calcium, and various protonated alkyl amines. Sodium and potassium impart water solubility, whereas calcium and magnesium promote oil solubility. Amine/alkanol amine salts give products with both oil and water solubility.

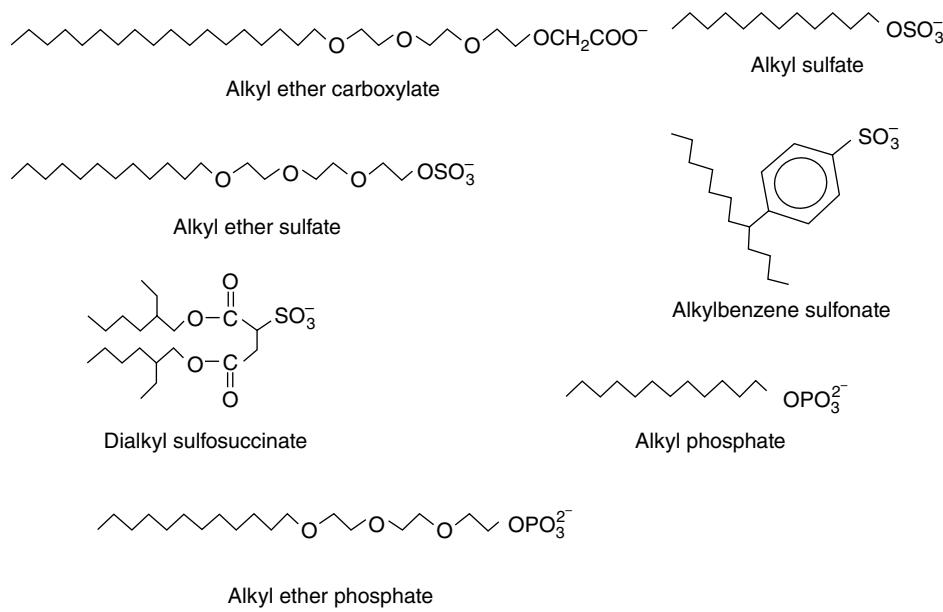
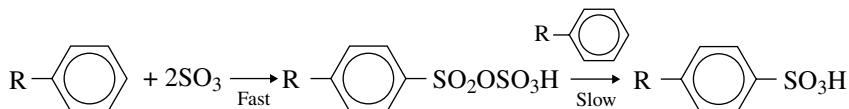


Figure 1.6 Common anionic surfactants

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As mentioned above, soap is still the largest single type of surfactant. It is produced by saponification of natural oils and fats. Soap is a generic name representing the alkali metal salt of a carboxylic acid derived from animal fats or vegetable oils. Soap bars are usually based on mixtures of fatty acids obtained from tallow, coconut, and palm oil. Under the right conditions soaps are excellent surfactants. Their sensitivity to hard water is a major drawback, however, and has constituted a strong driving force for the development of synthetic surfactants. The vast majority of soap produced goes into soap bars but soap also has specific niche applications. One important such application is as foam control agent in laundry detergents, where it suppresses the foam produced by the regular surfactants in the formulation, typically a combination of an alkylbenzene sulfonate and a fatty alcohol ethoxylate. A very specific use of the lithium salt of a fatty acid, that is, lithium 12-hydroxy-stearic acid, is as the major constituent of greases.

Alkylbenzene sulfonates is the largest class of synthetic surfactants. They are widely used in household detergents, as well as in a variety of industrial applications. They are made by sulfonation of alkylbenzenes. In large-scale synthesis, sulfur trioxide is the sulfonating agent of choice but other reagents, such as sulfuric acid, oleum ($H_2SO_4 \cdot nSO_3$), chlorosulfonic acid ($ClSO_3H$), or amidosulfonic acid (sulfamic acid, H_2NSO_3H), may also be used and may be preferred for specific purposes. Industrial synthesis is usually carried out in a continuous process, using a falling film reactor. The first step of the synthesis results in the formation of the pyrosulfonic acid, which slowly and spontaneously reacts further to give the sulfonic acid:



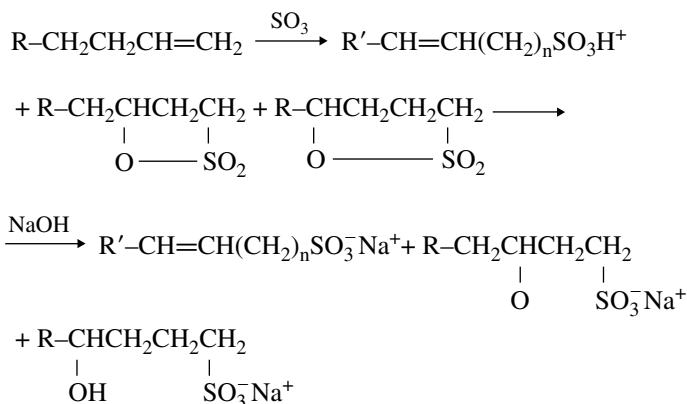
The sulfonic acid is subsequently neutralized, usually by caustic soda, to give the surface active alkylbenzene sulfonate salt. Due to the bulkiness of the alkyl substituent, the process gives almost exclusively *p*-sulfonation. R in the scheme above is typically an alkyl group of 12 carbon atoms. Originally, alkylbenzenes as surfactant intermediates were based on branched alkyls but these have now almost entirely been replaced by their linear counterparts, thus giving the name linear alkylbenzene sulfonate (LABS or LAS). Faster biodegradation has been the main driving force for the transition to chains without branching. Alkylbenzenes are made by alkylation of benzene with an *n*-alkene or with alkyl chloride using HF or AlCl₃ as catalyst. The reaction yields a mixture of isomers with the phenyl group attached to one of the nonterminal positions of the alkyl chain.

Sulfonation with sulfur trioxide as reactant, together with the closely related sulfation process to make sulfated alcohols, see below, is one of the largest chemical operations worldwide. The total annual production of sulfonated/sulfated surfactants is around five million metric tons. The second largest process for making surfactants is ethoxylation, the key step in the production of nonionic surfactants.

Other sulfonate surfactants that have found use in detergent formulations are paraffin sulfonates and α -olefin sulfonates, the latter often referred to as AOSs. Both are complex mixtures of compounds with varying physicochemical properties. Paraffin sulfonates, or secondary *n*-alkane sulfonates, are usually prepared by sulfoxidation of paraffin hydrocarbons with sulfur dioxide and oxygen under UV (ultraviolet) irradiation. In an

older process, which is still in use, paraffin sulfonates are made by sulfochlorination. Both processes are free radical reactions and, since secondary carbon atoms give much more stable radicals than primary carbon atoms, the sulfonate group will be introduced more or less randomly on all nonterminal carbon atoms along the alkane chain. A C₁₄–C₁₇ hydrocarbon cut, sometimes called the *Euro cut* because paraffin sulfonates have by tradition mainly been produced in Europe, is normally used as hydrophobe raw material. Thus, the product obtained will be a very complex mixture of both isomers and homologues.

α -Olefin sulfonates are prepared by reacting linear α -olefins with sulfur trioxide, typically yielding a mixture of alkene sulfonate (60–70%), 3- and 4-hydroxyalkane sulfonates (around 30%) and some disulfonate and other species. The two main α -olefin fractions used as starting material are C₁₂–C₁₆ and C₁₆–C₁₈. The ratio of alkene sulfonate to hydroxy-alkane sulfonate is to some degree governed by the ratio of SO₃ to olefin: the higher the ratio, then the more alkene sulfonic acid will be formed. Formation of hydroxyalkane sulfonic acid proceeds via a cyclic sultone, which is subsequently cleaved by alkali. The sultone is toxic and it is important that its concentration in the end product is very low. The route of preparation can be written as follows:



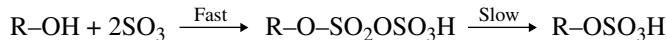
An important alkyl sulfonate surfactant is sodium di(2-ethylhexyl)sulfosuccinate, often referred to by its American Cyanamid trade name Aerosol OT, or AOT. This surfactant, with its bulky hydrophobe structure (Figure 1.6), is particularly useful for preparation of water-in-oil microemulsions, as discussed in Chapter 17. Isethionate surfactants, with the general formula R-COOCH₂CH₂SO₃[−]Na⁺, are fatty acid esters of the isethionic acid salt. They are among the mildest sulfonate surfactants and are used in cosmetics formulations.

Very crude sulfonate surfactants are obtained by sulfonation of lignin, petroleum fractions, alkynaphthalenes or other low-cost hydrocarbon fractions. Such surfactants are used in a variety of industrial applications as dispersants, emulsifiers, demulsifiers, defoamers, wetting agents, and so on.

Sulfated alcohols and sulfated alcohol ethoxylates constitute another important group of anionics, widely used in detergent formulations. They are monoesters of sulfuric acid and the ester bond is a labile linkage, which splits with particular ease at low pH where the hydrolysis is autocatalytic. Both linear and branched alcohols, typically with 8–16 carbon atoms, are used as raw material. The linear 12-carbon alcohol leads to the dodecylmonoester of sulfuric acid and, after neutralization with caustic soda, to sodium dodecyl sulfate (SDS),

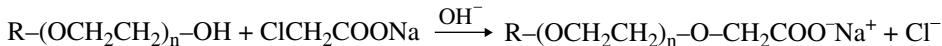
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which is by far the most important surfactant within this category. The alcohol ethoxylates used as intermediates are usually fatty alcohols with two or three oxyethylene units. The sulfation process is similar to the sulfonation discussed above. Sulfur trioxide is the reagent used for large-scale production and, analogous to sulfonation, the reaction proceeds via an intermediate pyrosulfate:



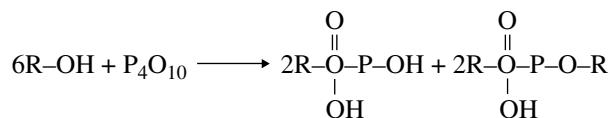
Synthesis of sulfate esters of ethoxylated alcohols proceeds similarly. In this reaction, 1,4-dioxane is usually formed in non-negligible amounts. Since dioxane is toxic, its removal by subsequent evaporation is essential. These surfactants are usually referred to as ether sulfates. Such surfactants are good at producing foams and have low toxicity to the skin and eye. They are popular in hand dishwashing and shampoo formulations.

Ethoxylated alcohols may also be transformed into carboxylates, that is, to give ether carboxylates. These have traditionally been made from sodium monochloroacetate using the Williamson ether synthesis:



The Williamson synthesis usually does not proceed quantitatively. A more recent synthetic procedure involves oxygen or peroxide oxidation of the alcohol ethoxylate in alkaline solution using palladium or platinum catalyst. This reaction gives conversion of the ethoxylate in very high yield, but may also lead to oxidative degradation of the polyoxyethylene chain. Ether carboxylates have found use in personal care products and are also used as a cosurfactant in various liquid detergent formulations. Like ether sulfates, ether carboxylates are very tolerant to high water hardness. Both surfactant types also exhibit good lime soap dispersing power, which is an important property for a surfactant in personal care formulations. Lime soap dispersing power is usually defined as the number of grams of surfactant required to disperse the lime soap formed from 100 g of sodium oleate in water with a hardness equivalent of 333 ppm of calcium carbonate (CaCO_3).

Phosphate-containing anionic surfactants, both alkyl phosphates and alkyl ether phosphates, are made by treating the fatty alcohol or fatty alcohol ethoxylate with a phosphorylating agent, usually phosphorus pentoxide (P_4O_{10}). The reaction yields a mixture of mono- and diesters of phosphoric acid, and the ratio between the esters is governed by the ratio of the reactants and the amount of water in the reaction mixture:



All commercial phosphate surfactants contain both mono- and diesters of phosphoric acid but the relative amounts vary from one producer to another. Since the physicochemical properties of the alkyl phosphate surfactants depend on the ratio of the esters, alkyl phosphates from different suppliers are less interchangeable than other surfactants. Phosphorus oxychloride (POCl_3) can also be used as a phosphorylating agent to produce

Box 1.1 Important facts about anionic surfactants

- They constitute the largest class of surfactant
- They have limited compatibility with cationic surfactants (shorter surfactants have better compatibility)
- They are generally sensitive to hard water and the sensitivity decreases in the order carboxylate>phosphate>sulfate \cong sulfonate
- A short polyoxyethylene chain between the anionic group and the hydrophobic tail improves hard water tolerance
- A short polyoxypropylene chain between the anionic group and the hydrophobic tail improves solubility in organic solvents (but may reduce the rate of biodegradation)
- Alkyl sulfates are rapidly hydrolyzed at low pH in an autocatalytic process. The other types are hydrolytically stable unless extreme conditions are used

alkyl phosphate surfactants. Also with POCl_3 a mixture of mono- and diesters of phosphoric acid is obtained.

Phosphate surfactants are used in the metal working industry, where advantage is taken of their anticorrosive properties. They are also used as emulsifiers in plant protection formulations. Finally, some important facts about anionic surfactants are given in Box 1.1.

Nonionics

Nonionic surfactants have either a polyether or a polyhydroxyl unit as the polar group. Polyether-based surfactants dominate and the polyether consists of oxyethylene units made by polymerization of ethylene oxide (EO). Strictly speaking, the prefix “poly” is a misnomer. The typical number of oxyethylene units in the polar chain is 5–10, although some surfactants, for example, those used as dispersants, often have much longer oxyethylene chains. Ethoxylation is usually carried out under alkaline conditions. Any material containing an active hydrogen can be ethoxylated. The most commonly used starting materials are fatty alcohols, alkylphenols, fatty acids, and fatty amines. Esters, for example, triglyceride oils, may be ethoxylated in a process that in a one-pot reaction involves alkaline ester hydrolysis followed by ethoxylation of the acid and alcohol formed and subsequent partial condensation of the ethoxylated species. Castor oil ethoxylates, used for animal feed applications, constitute an important example of triglyceride-based surfactants.

Examples of polyhydroxyl-based (polyol-based) surfactants are sucrose esters, sorbitan esters, alkyl glucosides, and polyglycerol esters, the latter type actually being a combination of polyol and polyether surfactant. Polyol surfactants may also be ethoxylated. A common example is fatty acid esters of sorbitan (known under the trade name of Span) and the corresponding ethoxylated products (known as Tween). The five-membered ring structure of sorbitan is formed by dehydration of sorbitol during manufacture. The sorbitan ester surfactants are edible and, hence, useful for food and drug applications. Acetylenic glycols, surfactants containing a centrally located acetylenic bond and hydroxyl groups at the adjacent carbon atoms, constitute a special type of hydroxyl-based surfactant that have found use as antifoam agent, particularly in coatings applications.

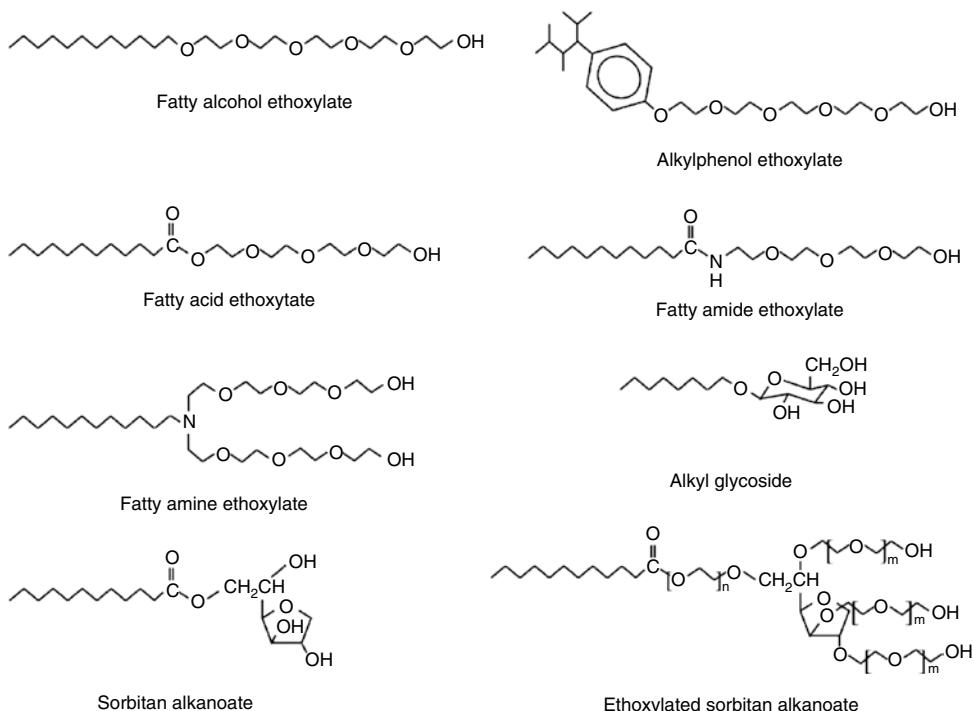
**Figure 1.7** Common nonionic surfactants

Figure 1.7 gives structures of the more common nonionic surfactants. As is discussed below, a commercial oxyethylene-based surfactant consists of a very broad spectrum of compounds, broader than for most other surfactant types. Fatty acid ethoxylates constitute particularly complex mixtures with high amounts of free poly(ethylene glycol) (PEG) and fatty acid as by-products. The single most important type of nonionic surfactant is fatty alcohol ethoxylates. They are used in liquid and powder detergents, as well as in a variety of industrial applications. They are frequently used to stabilize oil-in-water emulsions and their use as emulsifier is discussed in some detail in Chapter 24. Fatty alcohol ethoxylates can be regarded as hydrolytically stable in the pH range 3–11. They undergo a slow oxidation in air, however, and some oxidation products, such as aldehydes and hydroperoxides, are more irritating to the skin than the intact surfactant. Throughout this text fatty alcohol ethoxylates are referred to as C_mE_n with m being the number of carbon atoms in the alkyl chain and n being the number of oxyethylene units. Some important facts about nonionic surfactants are given in Box 1.2.

Polyoxyethylene-based surfactants can be tailor-made with high precision with regard to the average number of oxyethylene units added to a specific hydrophobe, for example, a fatty alcohol. However, the ethoxylation invariably gives a broad distribution of chain lengths. If all hydroxyl groups, that is, those of the starting alcohol and of the glycol ethers formed, had the same reactivity, a Poisson distribution of oligomers would be obtained. Since the starting alcohol is slightly less acidic than the glycol ethers, its deprotonation is disfavored, leading to a lower probability for reaction with ethylene oxide. The reaction scheme is given in Figure 1.8.

Box 1.2 Important facts about nonionic surfactants

- They are the second largest class of surfactant
- They are normally compatible with all other types of surfactants
- They are not sensitive to hard water
- Contrary to ionic surfactants, their physicochemical properties are not markedly affected by electrolytes
- The physicochemical properties of ethoxylates are very temperature dependent. Contrary to most organic compounds they become less water soluble – more hydrophobic – at higher temperatures. The reason for this unusual behavior is discussed in Chapter 7. Polyol-based nonionics exhibit the normal temperature dependence, that is, their solubility in water increases with temperature.

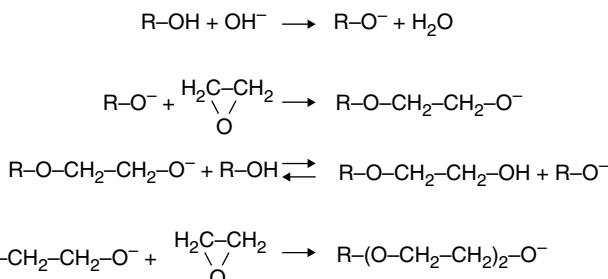


Figure 1.8 Base catalyzed ethoxylation of a fatty alcohol, $R-OH$

Hence, a considerable amount of unethoxylated alcohol will remain in the reaction mixture, also with relatively long ethoxylates. This is sometimes a problem and considerable efforts have been made to obtain a narrower homologue distribution. The distribution can be affected by the choice of ethoxylation catalyst and it has been found that alkaline earth hydroxides, such as $Ba(OH)_2$ and $Sr(OH)_2$, give a much narrower distribution than KOH, probably due to some coordination mechanism. Also Lewis acids, for example, $SnCl_4$ and BF_3 , give narrow distributions. Acid catalyzed ethoxylation suffers, however, from the drawback of 1,4-dioxane being formed in considerable quantities as by-product. Therefore, this process can only be used to prepare short ethoxylates. In Figure 1.9 the homologue distribution of a conventional alcohol ethoxylate, using KOH as catalyst, is compared with ethoxylates prepared using a Lewis acid and an alkaline earth hydroxide as catalyst.

So-called *peaked ethoxylates* have a growing share of the market. Typical advantages of ethoxylates with peaked distribution are that:

1. The low content of free alcohol reduces smell.
2. The low content of free alcohol reduces “pluming” during spray drying.
3. The low content of low oxyethylene homologues increases solubility.
4. The low content of high oxyethylene homologues reduces viscosity.
5. In alkyl ether sulfates, the low content of alkyl sulfate reduces skin irritation.

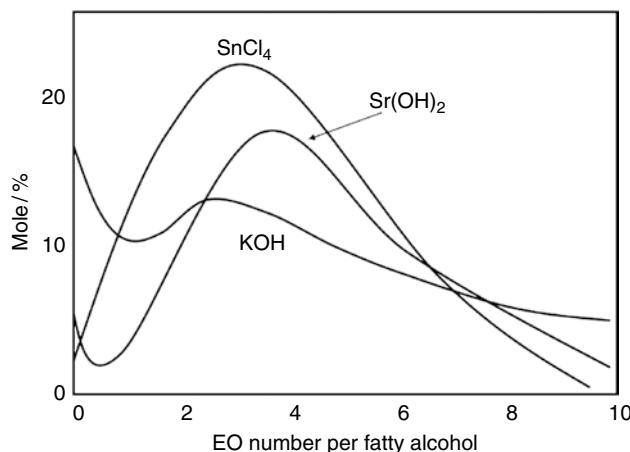


Figure 1.9 Typical homologue distribution of a fatty alcohol reacted with four moles of EO using different ethoxylation catalysts

Ethoxylated alkylphenols have a narrower homologue distribution than the alcohol ethoxylates. The phenolic hydroxyl group is a considerably stronger acid than the alcoholic hydroxyl of the first ethoxylate formed. This means that the phenolic hydroxyl will be preferentially deprotonated, which, in turn, means that there is virtually no unreacted alkylphenol left even in alkylphenol ethoxylates with only few oxyethylene units.

As mentioned in Box 1.2, nonionic surfactants containing polyoxyethylene chains exhibit reverse solubility versus temperature behavior in water. On raising the temperature two phases eventually appear. The temperature at which this occurs is referred to as the cloud point, alluding to the fact that the solution becomes turbid. The cloud point depends on both the hydrophobe chain length and the number of oxyethylene units; it can be determined experimentally with high accuracy. In the manufacture of polyoxyethylene-based surfactants, cloud point determination is used as a way to monitor the degree of ethoxylation. The onset of turbidity varies somewhat with surfactant concentration and in the official test method the cloud point is determined by heating a 1% aqueous solution to above clouding and then monitoring the transition from turbid to clear solution on slow cooling of the sample. For surfactants with long polyoxyethylene chains, the cloud point may exceed 100°C. For such surfactants determinations are often made in electrolyte solutions, since most salts lower the cloud point. Clouding of nonionic surfactants is discussed in detail in Chapter 7.

Ethoxylated triglycerides, for example, castor oil ethoxylates, have an established position on the market and are often regarded as *semi-natural surfactants*. A niche type of product is the fatty acid methyl ester ethoxylates, made from the fatty acid methyl ester by ethoxylation, usually using hydrotalcite, a magnesium–aluminum hydroxycarbonate, as catalyst. The methyl ester ethoxylates have the advantage over alcohol ethoxylates of being much more soluble in aqueous solution. Surfactants that combine high water solubility with proper surface activity are needed in various types of surfactant concentrates.



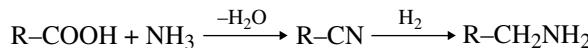
Alcohol ethoxylates with the terminal hydroxyl group replaced by a methyl or ethyl ether group constitute another category of niche products. Such *end-capped nonionics* are made by O-alkylation of the ethoxylate with alkyl chloride or dialkyl sulfate or by hydrogenation of the corresponding acetal. Compared with normal alcohol ethoxylates, the end-capped products are more stable against strong alkali and against oxidation. They are also low foaming, which is important in many applications.

Cationics

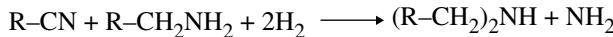
The vast majority of cationic surfactants are based on the nitrogen atom carrying the charge. Both amine and quaternary ammonium-based products are common. The amines only function as a surfactant in the protonated state; therefore, they cannot be used at high pH. Quaternary ammonium compounds, *quats*, on the other hand, are not pH sensitive. Nonquaternary cationics are also much more sensitive to polyvalent anions. As discussed previously, ethoxylated amines (Figure 1.7) possess properties characteristic of both cationics and nonionics. The longer the polyoxyethylene chain, then the more nonionic is the character of this surfactant type.

Figure 1.10 shows the structures of typical cationic surfactants. The diester quat represents an environmentally friendly type, which during the 1980s and 1990s almost completely replaced dialkyl quats as textile softening agents. The diester quats most commonly used for fabric softening generally show very limited water solubility and form lamellar phases and liposomes at low concentration. The low water solubility in combination with the hydrolytic instability makes formulation of softener products a demanding task. Diester quats used as rinse cycle softeners are usually formulated together with additives such as a hydrophilic alcohol ethoxylate and/or a water miscible solvent, such as isopropanol.

The main synthesis procedure for nonester quaternary ammonium surfactants is the nitrile route. A fatty acid is reacted with ammonia at high temperature to yield the corresponding nitrile, a reaction that proceeds via an intermediate amide. The nitrile is subsequently hydrogenated to primary amine using a cobalt or nickel catalyst:



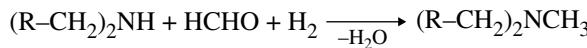
Secondary amines can be produced either directly from the nitrile or in a two-stage reaction from the primary amine. In the one-stage route, which is believed to proceed via an intermediate imine, ammonia is continuously removed from the reaction in order to promote secondary amine formation:

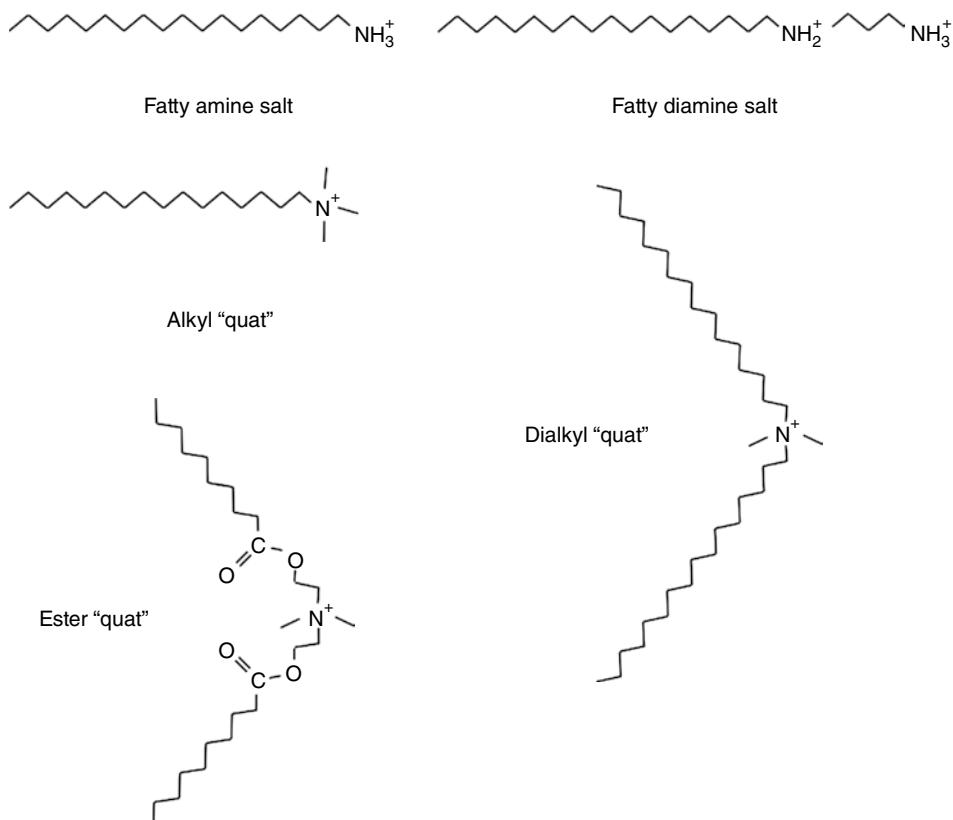


Primary amines can be converted to long-chain 1,3-diamines by cyanoethylation followed by hydrogenation:



Primary or secondary long-chain alkyl amines can be methylated to tertiary amines, for example, by reaction with formaldehyde under reducing conditions:



**Figure 1.10** Common cationic surfactants

Ethylene oxide can also be used as an alkylating agent to convert primary or secondary amines to tertiary amines with the general structures $\text{R}-\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ and $(\text{R}-\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{OH}$, respectively.

Quaternary ammonium compounds are usually prepared from the tertiary amine by reaction with a suitable alkylating agent, such as methyl chloride, methyl bromide, or dimethyl sulfate, the choice of reagent determining the surfactant counterion:



Ester-containing quaternary ammonium surfactants, *ester quats*, are prepared by esterifying a fatty acid (or a fatty acid derivative) with an amino alcohol followed by N-alkylation as above. The process is illustrated here for triethanolamine as the amino alcohol and dimethyl sulfate as methylating agent:

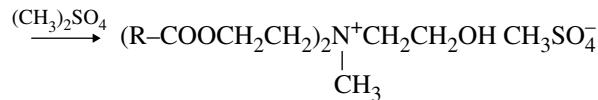
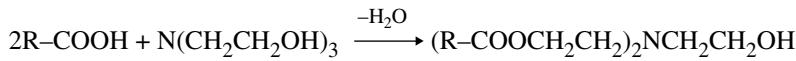


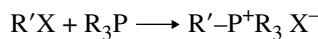
Table 1.3 Applications of cationic surfactants related to their adsorption at surfaces

Surface	Application
Steel	Anticorrosion agent
Mineral ores	Flotation collector
Stones	Road surfacing with bitumen emulsion
Inorganic pigments	Dispersant
Plastics	Antistatic agent
Fibers	Antistatic agent, fabric softener
Hair	Conditioner
Fertilizers	Anticaking agent
Bacterial cell walls	Bactericide

Box 1.3 Important facts about cationic surfactants

- They are the third largest class of surfactant
- They have limited compatibility with anionics (shorter surfactants have better compatibility)
- Hydrolytically stable cationics show higher aquatic toxicity than most other classes of surfactants
- They adsorb strongly to most surfaces and their main uses are related to this interaction

Nitrogen-based compounds constitute the vast majority of cationic surfactants. However, phosphonium, sulfonium, and sulfoxonium surfactants also exist. The first two are made by treatment of an alkyl chloride with trialkyl phosphine or dialkyl sulfide, respectively, as is shown here for phosphonium surfactant synthesis:



Sulfoxonium surfactants are prepared by hydrogen peroxide oxidation of the sulfonium salt. The industrial use of non-nitrogen cationic surfactants is small, since only rarely do they give performance advantages over their less expensive nitrogen counterparts. Phosphonium surfactants carrying one long-chain alkyl and three methyl groups have found use as biocides.

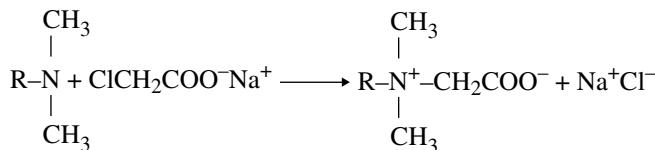
The majority of surfaces, metals, minerals, plastics, fibers, cell membranes, and so on, are negatively charged. The prime uses of cationics relate to their tendency to adsorb at these surfaces. In doing so, they change the character of the surface. Some examples are given in Table 1.3, while some important facts about cationic surfactants are given in Box 1.3.

Zwitterionics

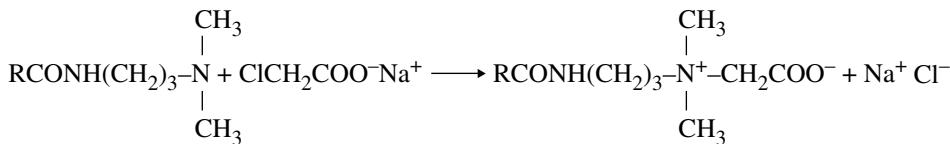
Zwitterionic surfactants contain two charged groups of different sign. Whereas the positive charge is almost invariably ammonium, the source of negative charge may vary, although carboxylate is by far the most common. Zwitterionics are often referred to as *amphoteric*s, but as was pointed out on page 10, the terms are not identical.

The change in charge with pH of the truly amphoteric surfactants naturally affects properties such as foaming, wetting, detergency, and so on. These will, therefore, depend strongly on the solution pH. At the isoelectric point the physicochemical behavior often resembles that of nonionic surfactants. Below and above the isoelectric point there is a gradual shift towards the cationic and anionic character, respectively. Surfactants based on sulfate or sulfonate (and a quaternized nitrogen as positive charge) remain zwitterionic down to very low pH values due to the very low pK_a values of the monoalkyl ester of sulfuric acid and of the alkyl or alkylaryl sulfonic acid, respectively.

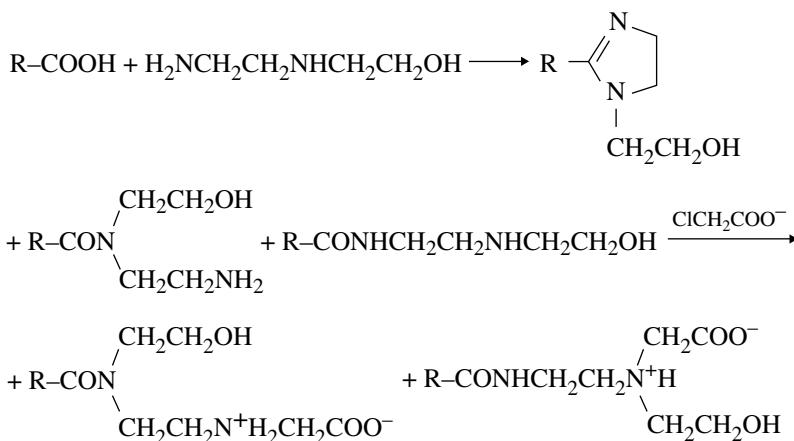
Common types of zwitterionic surfactants are N-alkyl derivatives of simple amino acids, such as glycine ($\text{NH}_2\text{CH}_2\text{COOH}$), betaine ($(\text{CH}_3)_2\text{NCH}_2\text{COOH}$) and amino propionic acid ($\text{NH}_2\text{CH}_2\text{CH}_2\text{COOH}$). They are usually not prepared from the amino acid, however, but by reacting a long-chain amine with sodium chloroacetate or a derivative of acrylic acid, giving structures with one and two carbons, respectively, between the nitrogen and the carboxylate group. As an example, a typical betaine surfactant is prepared by reacting an alkylidimethyl amine with sodium monochloroacetate:



Amidobetaines are synthesized analogously from an amidoamine:



Another common type of zwitterionic surfactant, usually referred to as an imidazoline, is synthesized by reaction of a fatty acid with aminoethylethanolamine followed by treatment with chloroacetate. The nomenclature for this surfactant type is a bit confused; it was believed that the products contained an imidazoline ring, but later investigations have shown that the five-membered ring is cleaved during the second synthesis step. A typical reaction sequence is:



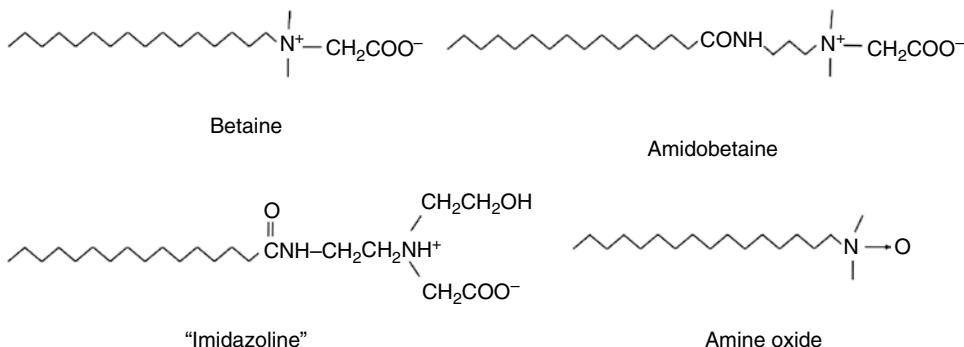


Figure 1.11 Common zwitterionic surfactants. The arrow from the nitrogen to the oxygen atom in the formula of the amine oxide indicates that electrons are pulled away from the nitrogen atom. Sometimes the formula is written with a normal bond between the two heteroatoms, in which case there is a positive sign on the nitrogen and a negative sign on the oxygen

Box 1.4 Important facts about zwitterionic surfactants

- They are the smallest class of surfactant (partly due to high price)
- They are normally compatible with all other types of surfactants
- They are not sensitive to hard water
- They are generally stable in acids and bases. The betaines, in particular, retain their surface activity at high pH, which is unusual
- Most types show very low eye and skin irritation. They are, therefore, well suited for use in shampoos and other personal care products

Zwitterionics as a group are characterized by having excellent dermatological properties. They also exhibit low eye irritation and are frequently used in shampoos and other cosmetic products. Since they possess no net charge, zwitterionics, similar to nonionics, function well in high electrolyte formulations. A traditional use of the products has been in alkaline cleaners. Figure 1.11 shows examples of typical zwitterionics and Box 1.4 summarizes some general information about the surfactant class. As mentioned previously, amine oxide surfactants, or more correctly N-oxides of tertiary amines, are sometimes categorized as zwitterionics, sometimes as nonionics, and sometimes as cationics. They basically behave as nonelectrolytes but at low pH or in the presence of an anionic surfactant an amine oxide surfactant will pick up a proton and behave as a cationic surfactant. A 1:1 salt will form between the anionic surfactant and the protonated amine oxide and this salt is very surface active. Amine oxides are prepared by hydrogen peroxide oxidation of the corresponding tertiary amine. They are good foam boosters and frequently used in cleaning formulations.

Hydrotropes and Solubilization

Hydrotropes are substances that increase the solubility of sparingly soluble organic molecules in water. The term, which was coined almost 100 years ago, is widely used in connection with liquid formulations but the meaning of the term differs depending on the application. In cleaning

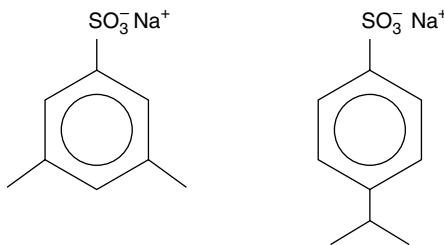


Figure 1.12 Sodium xylene sulfonate (left) and sodium cumene sulfonate (right)

formulations, which volume-wise may be the most important, the term hydrotrope has a very broad meaning, ranging from cosolvents, such as glycol ethers, to hydrophilic surfactants, such as medium-chain alkyl phosphates or short alkyl glucosides. In a stricter sense a hydrotrope is a compound that shows some amphiphilicity, yet does not exhibit the distinct break on the surface tension versus concentration plot that is indicative of a cooperative self-assembly process in solution. Thus, by the definition of a surfactant mentioned at the beginning of this chapter, a true hydrotrope is not a surfactant. The most common traditional hydrotropes are short-chain alkylbenzene sulfonates. Two representative examples of such compounds are shown in Figure 1.12. Both sodium cumene sulfonate and sodium xylene sulfonate decrease the surface tension to approximately 40 mN/m but they do not self-assemble into micelles. When the alkyl chain of a sodium alkylbenzene sulfonate has four or more carbon atoms a distinct self-association at a certain concentration can be detected by techniques such as light scattering or NMR diffusometry. Such compounds should be regarded as surfactants.

Alkylnaphthalene sulfonates are alternatives to alkylbenzene sulfonates and give approximately the same effect. Aromatic carboxylic acids are also used as hydrotropes. Sodium salicylate is a typical example of such a compound.

Transfer of a poorly water soluble substance into an aqueous formulation is a very important issue in formulation science and the use of a hydrotrope is not the only way to do this. There are three main approaches:

1. Formulation of a dispersed system, such as an oil-in-water emulsion or a solid suspension. Emulsions and suspensions are dealt with in Chapters 21 and 24.
2. Formulation of a microemulsion, that is, a macroscopic one-phase system that on the microscopic level exhibits distinct hydrophilic and hydrophobic domains. Microemulsions are presented in Chapter 17.
3. Formulation of a system that is homogeneous on both the macroscopic and the microscopic level. Use of a water-miscible organic solvent to improve the solubility of a lipophilic compound is the prime example.

Use of a hydrotrope may relate to either approach 2 or approach 3 depending on in how broad a sense the term is used. A hydrophilic surfactant, often referred to as a cosurfactant, is commonly used for formulating a microemulsion, that is, a system of type 2 above. The cosurfactant can be seen as a hydrotrope in that formulation. Use of a cosolvent such as a glycol ether falls within category 3 and the glycol ether may also be regarded as a hydrotrope. A classical hydrotrope such as xylene or cumene sulfonate is a borderline case and may be classified into either type 2 or type 3 of the formulation approaches listed above. The term *coupling agent* is sometimes used synonymously with hydrotrope.

Apart from the ways to improve the aqueous solubility mentioned above, that is, use of a cosolvent, a classical hydrotrope or a hydrophilic surfactant, one must be aware of yet another parameter of importance: the electrolyte. An electrolyte can be either *salting in* or *salting out*. Salting in electrolytes help solubilize poorly soluble organic substances in water and the effect can be substantial. The order in which salts appear on this scale is given by the Hofmeister series, named after a famous paper from the late 1800s in which ions were classified in order of their ability to salt out proteins. The Hofmeister series for anions is:



For cations it is:



The further to the right in the two series, the more beneficial is the ion for solubilization of an organic compound. A common example of the use of the Hofmeister series is in biochemistry, where proteins are made to precipitate from an aqueous solution by addition of ammonium sulfate, the salt of the two ions furthest to the left in the two series. Salts of ions at the right end of the series are good at increasing the solubility of a protein. However, such salts, for example, guanidinium thiocyanate, are so efficient structure breakers that they may disrupt the intramolecular noncovalent interactions, which means that the protein loses its secondary structure and becomes randomly coiled. (Urea, a small, uncharged molecule, behaves in the same way as guanidinium salts; also, nonionic molecules can act as salting in reagents.)

Cosolvents such as glycol ethers are needed in large amounts in order to give proper effect. Also hydrotropes of the type shown in Figure 1.12 have to be added in relatively large amounts in order to solubilize a hydrophobic organic substance. Typical hydrotrope concentrations are 1 M and the cosolvents are used in even higher concentrations. Surfactants, on the other hand, are effective as solubilizers at concentrations several orders of magnitude lower. Figure 1.13 shows solubilization of a hydrophobic organic dye using either a surfactant, a classical hydrotrope or a glycol ether as additive. The order of efficacy is very clear: surfactant > hydrotrope > cosolvent.

The mechanism of solubilization is clearly different for a cosolvent and for a surfactant. The cosolvent changes the solvency by affecting the character of the solvent. The change may be quantified by the use of solubility parameters. Replacing water by a water–glycol ether mixture leads to a reduction of the hydrogen bonding and the polar contributions of the solubility parameter, which, in turn, means that the dispersion contribution gains in importance. This is favorable for dissolution of most hydrophobic organic compounds.

Hydrotropes destroy the ordered packing of self-aggregated surfactants just as urea and chaotropic ions do with proteins, as discussed above. Thus, cumene sulfonate and other traditional hydrotropes are very efficient in reducing the extension of liquid crystalline phases that often appear in concentrated surfactant solutions (Chapter 6). The liquid crystalline phases are highly viscous and difficult to handle, so addition of a hydrotrope is common in many cleaning formulations. Another important use of hydrotropes in surfactant-based formulations is to raise the cloud point of long-chain fatty alcohol ethoxylates. These hydrophobic nonionic surfactants are very effective in removing oily soil but

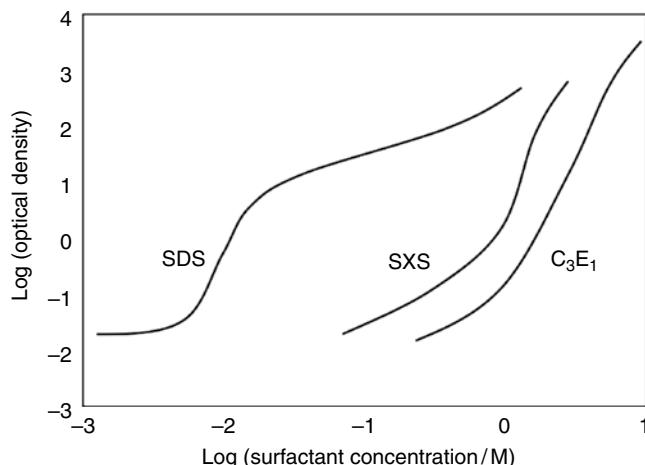


Figure 1.13 Solubilization of an organic dye (Disperse Red 13) in aqueous solution as a function of amount of added SDS (left), sodium xylene sulfonate (middle) and ethylene glycol monopropyl ether (right). The solubilization is quantified by the optical density given on the y-axis. (Adapted with permission from Bauduin, P., Renoncourt, A., Kopf, A., et al. (2005) Unified concept of solubilization in water by hydrotropes and cosolvents. *Langmuir*, 21, 6769–6775. Copyright © 2005, American Chemical Society.)

Table 1.4 Cloud point (°C) of solutions of 1% alcohol ethoxylate with addition of 1% hydrotrope

Fatty alcohol ethoxylate	No hydrotrope	Butyl glucoside	Octyl glucoside	Decyl glucoside	Undecyl glucoside	Sodium toluene sulfonate
C ₁₁ E ₅	27	28	59	52	35	36
C ₁₃ E ₆	<0	9	48	37	9	9

(From Matero, A., Mattsson, Å. and Svensson, M. (1998) APGs as hydrotropes. *Journal of Surfactants and Detergents*, 1, 485–489.)

the best surfactants often have very low cloud points. The role of the hydrotrope in such formulations is to bring the cloud point to above working temperature. Cumene sulfonate and similar compounds are efficient in doing so but hydrophilic surfactants, such as short-chain alkyl phosphates and hydrophilic alkyl glucosides, are often even more efficient. The hydrophilic surfactant in such a formulation is usually termed a *cosurfactant* but it clearly acts as a hydrotrope. As is illustrated in Table 1.4, the cosurfactant needs to be fine-tuned for the specific application.

Gemini Surfactants have Special Features

A gemini surfactant may be viewed as a surfactant dimer, that is, consisting of two amphiphilic molecules connected by a spacer. The general structure is shown in Figure 1.2. Gemini surfactants are also referred to as twin surfactants, dimeric surfactants, or bis-surfactants.

The spacer chain, which can be hydrophilic or hydrophobic, rigid or flexible, should bind the two moieties together at, or in close proximity to, the head groups. Connecting two surfactant moieties towards the end of their hydrophobic tails results in a so-called *bola-form* surfactant and the physicochemical properties of such species are very different from those of gemini surfactants. Most gemini surfactants are composed of two identical halves, but unsymmetrical geminis have also been synthesized, either having different hydrophobic tail lengths or different types of polar groups (*heterogemini surfactants*), or both. Higher oligomers of single surfactants, that is, tris-surfactants, tetra-surfactants, and so on have also been synthesized. These are difficult to prepare, however, and may not be so practically interesting.

Gemini surfactants have not yet reached the market in large-scale quantities. They are, however, attracting considerable attention, both in industry and in academia. Some gemini surfactants, in particular symmetrical cationic ones, are made from readily available raw materials by a straightforward synthesis, as is discussed here.

Figure 1.14 shows examples of gemini surfactants. Compounds I–III are cationics differing in the type of spacer unit connecting the two ionic moieties. The spacer of compound I is hydrophobic and flexible, that of compound II is hydrophilic and flexible, and that of compound III is hydrophobic and rigid. Compound IV is an ester-containing cationic gemini surfactant and compound V is an anionic one. Finally, compounds VI and VII are examples of heterogemini surfactants. For the regular cationic gemini surfactants, such as compound I, which by far are the most studied, the nomenclature used in the literature is m-n-m, where m is the number of carbons in the hydrophobic tails and n the number of carbons in the spacer unit.

Synthesis

Regular cationic geminis, such as compounds I–III of Figure 1.14, are conveniently prepared by reacting an alkyldimethylamine with an α,ω -dihalo compound. Dibromo reagents are very reactive and are usually employed in laboratory synthesis but the corresponding dichloro compounds may be preferred in large-scale preparation:



where R is an alkyl of normal surfactant chain length such as $C_{12}H_{25}$, X can be alkylene to give a hydrophobic, flexible spacer, $CH_2CH(OH)CH_2$ or $CH_2(CH_2OCH_2)_nCH_2$ to give a hydrophilic flexible spacer, or $CH_2-\Phi-CH_2$ to give a hydrophobic, rigid spacer (Φ denotes a phenyl ring, i.e., in the simplest case C_6H_4).

For the specific (but important) case when X equals CH_2CH_2 in the formula above the dihalo compound is not reactive enough. The preferred synthesis route is then:



Ester-containing gemini surfactants, such as compound IV of Figure 1.14, are of interest because the ester bond is easily hydrolyzed in the sewage plant. Their preparation route is analogous to that of the stable gemini surfactants with the alkyldimethyl reactant ($R-N(CH_3)_2$ in the formula above) replaced by the N,N-dimethylaminoethyl ester of a fatty acid ($R-COO-CH_2CH_2-N(CH_3)_2$).

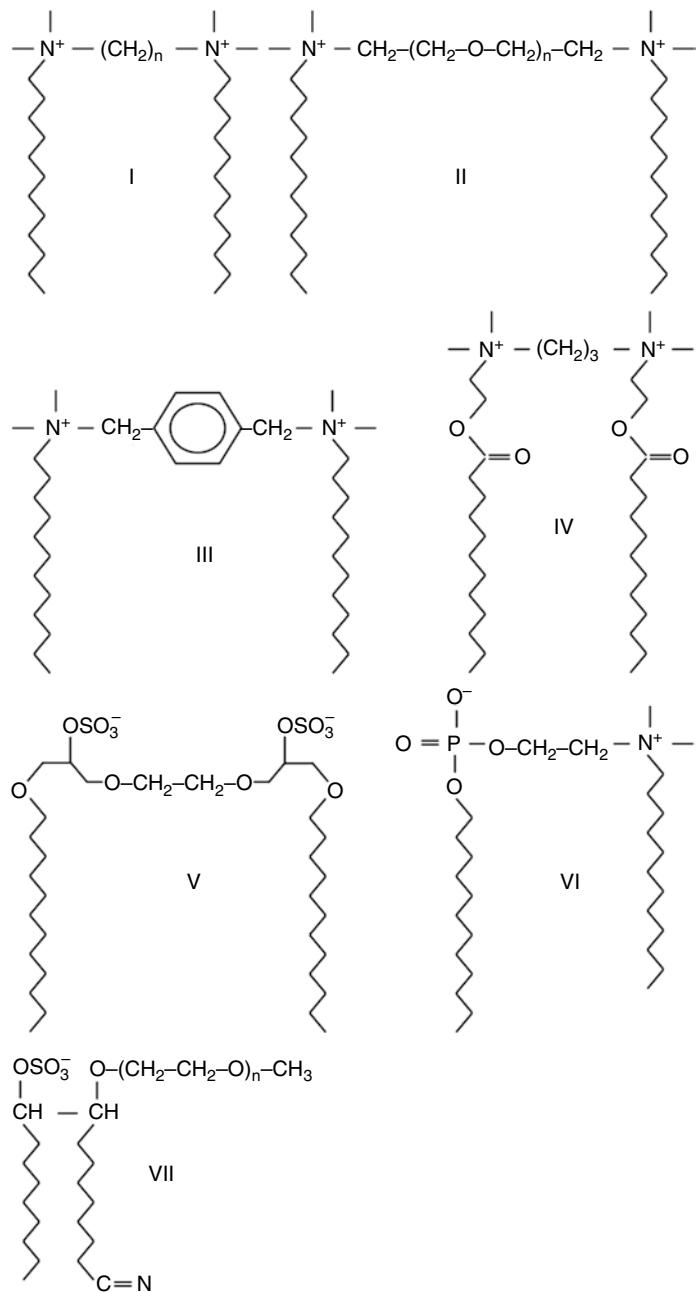


Figure 1.14 Structures of gemini surfactants. Compounds I–IV are cationic gemini surfactants, compound V is an anionic gemini surfactant, and compounds VI and VII are examples of heterogemini surfactants

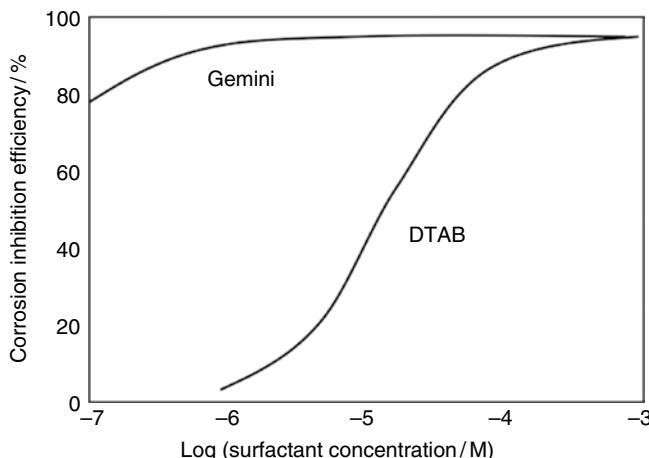


Figure 1.15 Comparison between a regular cationic surfactant, DTAB, and a gemini surfactant with C12 hydrophobic tails and a tetramethylene spacer (12-4-12) with respect to efficiency to protect mild steel being exposed to 1 M HCl solution for 4 h. (Adapted with permission from Mahdavian, M., Tehrani-Bagha, A.R. and Holmberg, K. (2011) Comparison of a cationic gemini surfactant and the corresponding monomeric surfactant for corrosion protection of mild steel in hydrochloric acid. Journal of Surfactants and Detergents, **14**, 605–613. Copyright © 2011, Springer.)

Gemini Surfactants are More Efficient

As mentioned on page 5, gemini surfactants self-assemble at very low concentrations compared to the corresponding monomeric surfactants. The low CMC values of gemini surfactants are an indication that they can be used in lower concentration than normal surfactants of the same hydrophobic tail length. This is indeed the case and has been demonstrated for a variety of applications. A striking example, illustrated in Figure 1.15, is in corrosion protection. As the curves show, both a regular cationic surfactant and the gemini surfactant can provide very effective corrosion protection but the gemini surfactant can be used in several orders of magnitude lower amount.

Cleavable Surfactants are Attractive from an Environmental Point of View

Background

The term *cleavable surfactant* generally refers to a surfactant with a labile bond intentionally included in the molecular structure. Traditionally, the presence of an inherently labile bond in a surfactant was considered a substantial disadvantage but, much due to the increased concern for the environment, the negative attitude towards surfactants that contain a labile bond has changed. Among the surfactant workhorses—anionics such as alkylbenzene sulfonates and alkyl sulfates, nonionics such as fatty alcohol ethoxylates and alkylphenol ethoxylates, and cationics such as alkyl quats and dialkyl quats—only alkyl

sulfates are not chemically stable under normal conditions. Alkyl sulfates are monoesters of sulfuric acid, which are readily hydrolyzed under acidic conditions to release sulfuric acid. The produced acid will, in turn, accelerate breakdown of the surfactant. This autocatalytic degradation of a surfactant such as SDS is well known among those who formulate surfactant-containing products and has often been regarded as a substantial disadvantage with this specific surfactant. The general attitude used to be that weak bonds in a surfactant may cause handling and storage problems and should, therefore, be avoided.

For a couple of decades, environmental concern has been one of the main driving forces for the development of new surfactants and their rate of biodegradation is a major issue. One of the main approaches taken to produce readily biodegradable surfactants is to build into the structure a bond with limited stability. For practical reasons the weak bond is usually the bridging unit between the polar head group and the hydrophobic tail of the surfactant, which means that the degradation immediately leads to destruction of the surface activity of the molecule, an event usually referred to as the *primary degradation* of the surfactant. Biodegradation then proceeds along various routes depending on the type of primary degradation product. The ultimate decomposition of the surfactant, often expressed as amount of carbon dioxide evolved during four weeks exposure to appropriate microorganisms, counted as a percentage of the amount of carbon dioxide that could theoretically be produced, is the most important measure of biodegradation (page 53).

There are many possible types of cleavable bonds and a wide range of cleavable surfactants can be designed with respect to stability and cleavage properties. The majority of cleavable surfactants contain a hydrolyzable bond, for which the breakdown can be induced by a change in pH. In the environment bonds susceptible to hydrolysis are often degraded by enzymatic catalysis but only few published investigations deal with the breakdown of cleavable surfactants *in vitro*. Cleavable surfactants with the bond breakage induced by other triggers, such as UV light, ozone, or an increase in temperature, have also been developed.

Environmental concern is the main driving force behind the concept of cleavable surfactants but there are also other incentives. The use of a cleavable surfactant can be a way to avoid complications, such as foaming or formation of unwanted, stable emulsions, that may occur in industrial processes involving surfactant-based formulations. If the weak bond is present between the polar and the apolar part of the molecule, cleavage will lead to one water-soluble and one water-insoluble product. Both moieties can usually be removed by standard work-up procedures. This approach has been of particular interest for surfactants used in preparative organic chemistry and in various biochemical applications. A related application is the use of a cleavable cationic surfactant as a transient biocide.

Another use of surfactants with limited stability is to have the cleavage product impart a new function. For example, a surfactant used in personal care formulations may decompose on application to form products beneficial to the skin. A surfactant used for cleaning of rain clothes, tents, and so on may decompose during the washing process and the hydrophobic moiety released, for example a fatty alcohol, will deposit on the textile and act as a hydrophobizing agent. Surfactants that after cleavage impart a new function are sometimes referred to as *functional surfactants*.

Finally, surfactants that in a controlled way break down into nonsurfactant products may find use in specialized applications, for example in the biomedical field. For instance, cleavable surfactants that form vesicles or microemulsions can be of interest for drug delivery, provided the metabolites are nontoxic.

Alkali-Labile Surfactants

The ester bond is the typical linkage to use in the design of alkali-labile surfactants. The concept is by no means new. PEG esters of fatty acids, also referred to as fatty acid ethoxylates, have been commercially available for a long time. This surfactant class has an ester group between the polar head group and the hydrophobic tail. Fatty acid esters of sugars constitute another established type of ester surfactants. Sorbitan esters of fatty acids, known under their trade name Span, are one well-known example and sucrose esters are another. Other established ester-containing surfactants are dialkylsulfosuccinates, α -sulfo fatty acid methyl esters, methyl ester ethoxylates, ethoxylated triglycerides, and sulfated triglycerides.

Normal Ester Quats

Cationic surfactants have traditionally been stable molecules. However, when environmental concern became an important issue it soon became clear that the traditional “quats,” with a large use as fabric softeners, exhibited a slow rate of biodegradation and considerable aquatic toxicity. The toxicity is not unexpected considering that cationic surfactants in general are potent microbicides and frequently used as such. The response from the industry was to change the surfactant used in fabric softener formulations from normal stable “quats” to “ester quats.” The structures of both can be found in Figure 1.10.

What is meant by ester quats are surfactants based on esters between one or more fatty acids and a quaternized amino alcohol. Figure 1.16 shows examples of three different ester quats, all containing two long-chain and two short substituents on the nitrogen atom. The figure also shows the “parent,” noncleavable quat. As can be seen, the ester-containing surfactants contain two carbon atoms between the ester bond and the nitrogen that carries the positive charge. Cleavage of the ester bonds of surfactants II–IV yields a fatty acid soap in addition to a highly water-soluble quaternary ammonium diol or triol. These degradation products exhibit low fish toxicity and are degraded further by established metabolic pathways. The overall ecological characteristics of ester quats are much superior to those of traditional quats as represented by compound I of Figure 1.16.

The switch from stable dialkyl quats to dialkylester quats in softener formulations, which mainly took place during the 1990s, may represent the most dramatic change of product

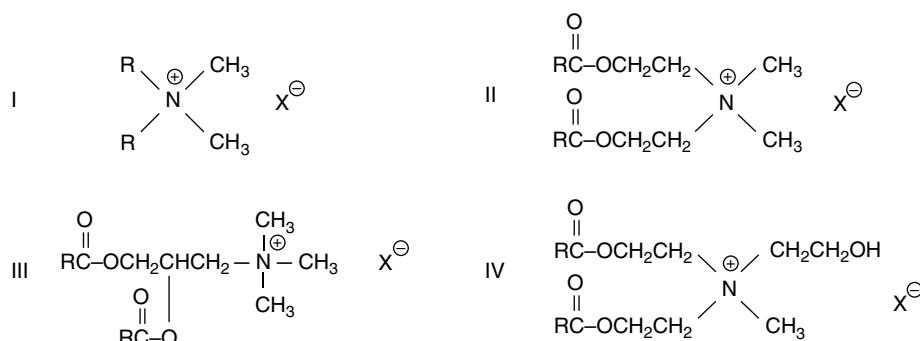


Figure 1.16 Structures of one conventional quaternary ammonium surfactant (I) and three ester quats (II–IV). R is a long-chain alkyl and X is Cl, Br, or CH_3SO_4^-

type in the history of surfactants and was entirely environment-driven. Ester quats have also fully or partially replaced traditional quats in other applications of cationic surfactants, such as hair care products and various industrial formulations.

The cationic charge close to the ester bond renders normal ester quats unusually stable to acid and labile to alkali. The hydrolysis rate is at minimum at pH 3–4 and accelerates strongly above pH 5–6. Formulations containing ester quats must, therefore, be maintained at low pH. The pH dependency of the hydrolysis rate is even more pronounced for betaine esters, for which the mechanism of hydrolysis is discussed in more detail in the following section.

Betaine Esters

The rate of alkali-catalyzed ester hydrolysis is influenced by adjacent electron-withdrawing or electron-donating groups. A quaternary ammonium group is strongly electron withdrawing. The inductive effect will lead to a decreased electron density at the ester bond; hence, alkaline hydrolysis, which starts by a nucleophilic attack by hydroxyl ions at the ester carbonyl carbon, will be favored. Compounds II–IV of Figure 1.16 all have two carbon atoms between the ammonium nitrogen and the $-\text{O}-$ oxygen of the ester bond. Such esters undergo alkaline hydrolysis at a faster rate than esters lacking the adjacent charge but the difference is not very large. If, on the other hand, the charge is at the other side of the ester bond, the rate enhancement is much more pronounced. Such esters are extremely labile on the alkaline side but very stable even under strongly acidic conditions. The large effect of the quaternary ammonium group on the alkaline and acid rates of hydrolysis is due to a stabilization/destabilization of the ground state, as illustrated in Figure 1.17. The charge repulsion, involving the carbonyl carbon atom and the positive charge at the nitrogen atom, is relieved by hydroxide ion attack but augmented by protonation. The net result is that, compared with an ester lacking the cationic charge, the rate of alkaline hydrolysis is increased 200-fold whereas the rate of acid hydrolysis is decreased 2000-fold. For surface active betaine esters based on long-chain fatty alcohols the rate of alkaline hydrolysis is further accelerated due to micellar catalysis, as is discussed later in this chapter. The presence of large, polarizable counterions, such as bromide, can completely outweigh the micellar catalysis, however.

The extreme pH dependence of surface active betaine esters makes them interesting as cleavable cationic surfactants. The shelf life is long when stored under acidic conditions and the hydrolysis rate will subsequently depend on the pH at which they are used. Single chain surfactants of this type have been suggested as *temporary bactericides* for use in

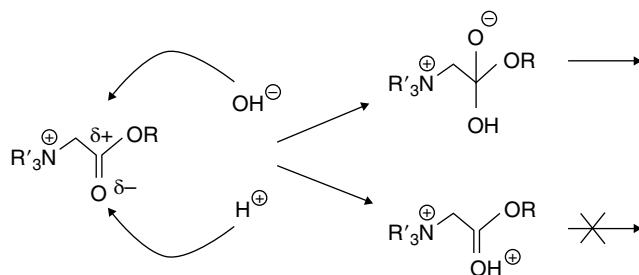


Figure 1.17 Mechanisms for acid- and base-catalyzed cleavage of a betaine ester

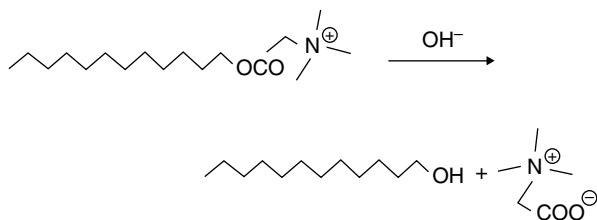


Figure 1.18 Alkaline hydrolysis of a betaine ester surfactant into a fatty alcohol and betaine

hygiene products, for disinfection in the food industry, and in other applications where only a short-lived bactericidal action is wanted. Figure 1.18 illustrates the breakdown of a betaine ester with bactericidal action into harmless products, fatty alcohol, and betaine, an amino acid. The concept is also of interest for formulations in the cosmetics area, where the skin irritation of stable quats can be a problem. A possible medical application of betaine ester surfactants that is described in the literature is for DNA compaction, that is, folding of the large DNA molecule so that it can pass through a cell membrane. Normal cationic surfactants are effective for this purpose but their toxicity limits their *in vivo* use. Betaine ester surfactants have also been evaluated for emulsion polymerization. The subsequent decomposition of the surfactant is a way to produce emulsifier-free latex. The patent literature also contains examples of betaine esters containing two long tails for use as fabric softeners.

Acid-Labile Surfactants

As mentioned above, SDS is labile on the acidic side and relatively stable at high pH. However, SDS was developed long before the concept of “cleavable surfactants” was introduced. In more recent times a number of surfactants have been developed, and reached the market, where the intention has been to design a surfactant that is stable under the normal alkaline conditions of the washing process but breaks down at low pH. However, none of these research lines have resulted in a dramatic change of a product class, as was the case when the stable quats were replaced by ester quats.

Acetals

Surfactants containing an acetal or a ketal linkage between the polar head group and the hydrophobic tail are well known on the market. They may be cyclic, as the compound in Figure 1.19, or acyclic, as in APGs (Figure 1.20). Both acetal and ketal surfactants are very stable in an alkaline environment but break down relatively easily under acidic conditions. The cyclic compounds are more susceptible to acid hydrolysis than the acyclic ones and ketal surfactants are, in general, more labile than the corresponding acetal surfactants. As an example, a ketal surfactant kept at pH 3.5 was cleaved to the same extent as an acetal surfactant of similar structure kept at pH 3.0. The lower stability of the ketal linkage is due to the greater stability of the carbocation formed during ketal hydrolysis compared to that formed during acetal hydrolysis. However, the biodegradation of acetal surfactants has been found to be faster than for ketal surfactants of similar structure.

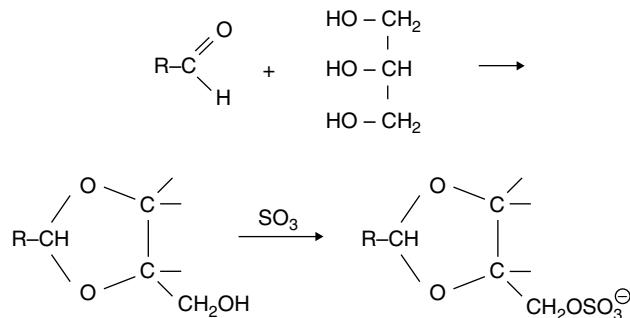


Figure 1.19 Preparation of a sulfated acetal surfactant from a fatty aldehyde and glycerol

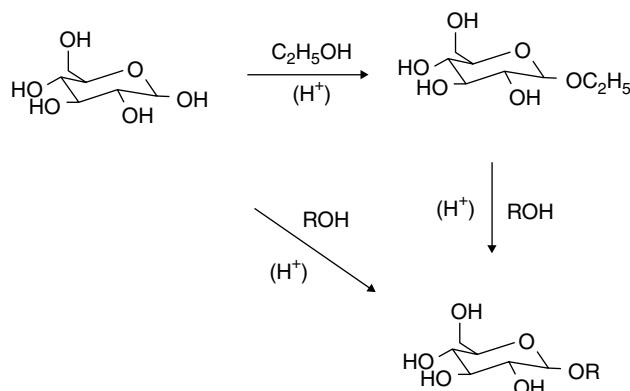


Figure 1.20 Preparation of alkyl glucoside surfactants

Both acetal and ketal surfactants may be cationic, anionic, or nonionic. It has been found that the 1,3-dioxolane ring, which is present in cyclic acetal and ketal surfactants, corresponds to approximately two oxyethylene units with regard to effect on the CMC and adsorption characteristics. Thus, when an acetal surfactant is made from glycerol and the remaining hydroxyl group subsequently sulfated, the physicochemical properties resemble those of the well-known ether sulfates of the general formula $R-(OCH_2CH_2)_2OSO_3Na$. This is interesting since commercial alkyl ether sulfates typically contain two to three oxyethylene units.

The acyclic acetal surfactant APG is synthesized by direct reaction of glucose with fatty alcohol, using a large excess of alcohol in order to minimize sugar oligomerization. Alternatively, it is made by transacetalization of a short-chain alkyl glucoside, such as ethyl or butyl glucoside, with a fatty alcohol. The latter procedure is used for APGs with longer alkyl tails. An acid catalyst is used in both processes. Either glucose or a degraded starch fraction is used as starting material. Figure 1.20 illustrates the synthesis.

Alkyl glucosides can also be made by enzymatic synthesis, using β -glucosidase as catalyst, which yields only the β -anomer (and gives low yield). The corresponding β -anomer can be obtained by β -glucosidase catalyzed hydrolysis of the racemate. There are considerable differences between the α,β -mixture obtained by organic synthesis and the pure enantiomers

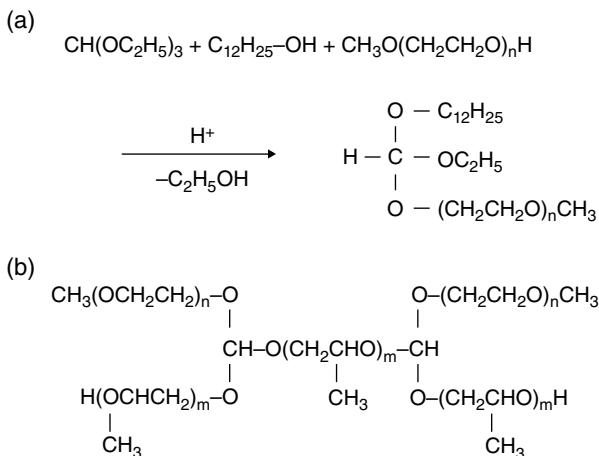


Figure 1.21 (a) Synthesis of an ortho ester-based surfactant; (b) structure of an ortho ester-based block copolymer

obtained by the bio-organic route. The β -anomer of *n*-octyl glucoside has found use as a surfactant in biochemical work.

Ortho Esters

Surfactants containing the ortho ester bond have been explored in recent years. They are typically prepared by transesterification of a low molecular weight ortho ester (such as triethyl orthoformate) with a fatty alcohol and a methyl-capped PEG. Due to the trifunctionality of the ortho ester, a complex mixture of species is obtained. The synthesis is shown in Figure 1.21.

Furthermore, if the reactant alcohol is difunctional, cross-linking will occur and a large network will be formed. An example based on poly(propylene glycol) (PPG) and PEG is also shown in Figure 1.21. Such PEG–PPG block copolymers exhibit higher biodegradation rates than conventional block copolymers without ortho ester linkages between the segments. By varying the number and types of substituents (fatty alcohol, alkyleneoxy group, end blocking), the properties of the ortho ester-based surfactant or block copolymer can be tailor-made.

Hydrolysis of ortho esters occurs by a mechanism analogous to that of acetals and ketals and gives rise to one mole of formate and two moles of alcohol. Ortho ester-based surfactants undergo acid-catalyzed cleavage much more readily than acetal-based surfactants under the same conditions. For instance, a water-soluble ortho ester based on octanol and monomethyl-PEG is hydrolyzed to 50% in two hours at pH 5. The structure of the surfactant has been found to influence the hydrolysis rate and, in general, a more hydrophilic surfactant has a higher decomposition rate.

Overview

As illustrated by the discussion above, there exists a wide range of cleavable surfactants suitable for different applications. One of the most decisive factors for choosing surfactant type is the pH required for the application in question. Figure 1.22 summarizes the susceptibility

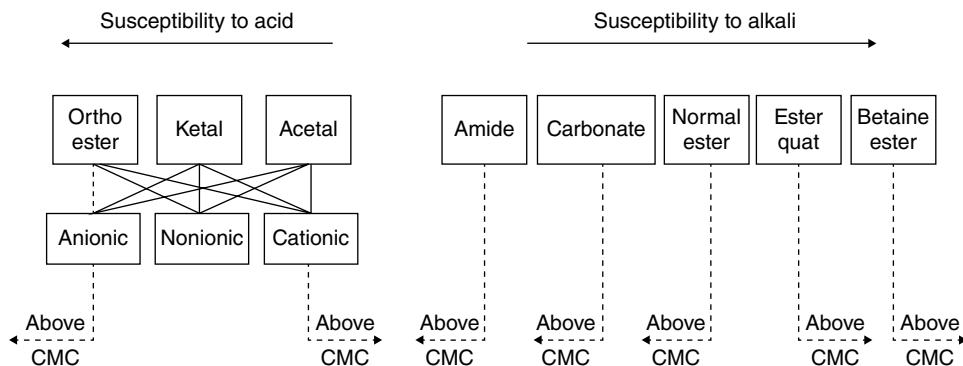


Figure 1.22 Hydrolysis characteristics of different types of hydrolysable surfactants. (Redrawn from Stjernholm, M. (2005) Biodegradable surfactants containing hydrolyzable bonds. PhD thesis. Chalmers University of Technology, Göteborg, Sweden.)

to acid and alkaline hydrolysis of the different types of surfactants discussed above, as well as some more types, including the effects of surfactant aggregation on the hydrolysis rate. This effect is further discussed and illustrated in the next section of this chapter. The figure is based on collected data from the literature and on assumptions based on extrapolation of such data.

Self-Aggregation of a Surfactant may Increase or Decrease the Hydrolysis Rate of Surfactants Containing a Labile Bond

Surfactants aggregate to form micelles and the concentration at which the first micelle is formed is called the CMC. A micellized surfactant will experience a different environment than a surfactant unimer in solution. As will be seen, micellization may cause either an increase or a decrease in the rate at which a cleavable surfactant degrades by hydrolysis. An increase in reaction rate is often referred to as *micellar catalysis*. The opposite behavior could, correspondingly, be called *micellar inhibition*.

Most quantitative treatments of micellar rate effects are based on the so-called pseudophase model. In this model, the surfactant aggregates and the bulk aqueous solution are regarded as distinct reaction regions, or pseudophases. Provided that the exchange of material between the bulk and the micellar pseudophase is fast enough that the reaction does not disturb the equilibrium distribution of the reactants, which is true for most thermal reactions, the observed reaction rate will be the weighted sum of the rates in the micellar and the aqueous pseudophases. A schematic representation of the pseudophase model of a bimolecular reaction is shown in Figure 1.23.

Since a cleavable surfactant is itself one of the reactants, the influence of micelle formation on the degradation of such a surfactant constitutes a special case of micellar catalysis (or inhibition). Depending on their molecular structures, the cleavage products might gradually change the properties of the system as the reaction proceeds; for example, the effective CMC of the surfactant, and thus the fraction of aggregated molecules, may be raised or lowered. The character of the aggregates with respect to shape, charge, or lifetime may also change. Such variations with time may influence the reaction kinetics significantly.

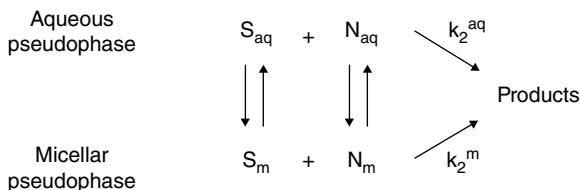


Figure 1.23 Schematic illustration of the two-site principle of the pseudophase model. S and N represent the reactants and indices aq and m denote the aqueous and micellar pseudophases, respectively. k_2^{aq} and k_2^m are the rate constants in the respective pseudophases. (With permission from Bunton, C.A., Nome, F., Quina, F.H. and Romsted, L.S. (1991) Ion binding and reactivity at charged aqueous interfaces. Accounts of Chemical Research, **24**, 357–364. Copyright 1991, American Chemical Society.)

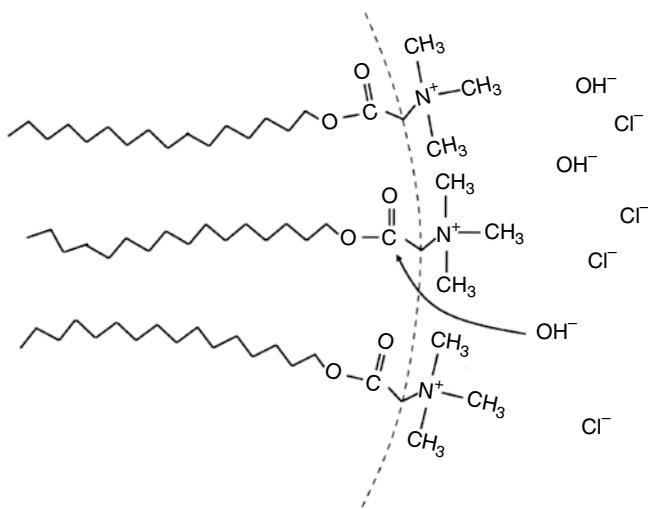


Figure 1.24 Micellar catalysis is caused by an increased concentration of hydroxyl ions in the vicinity of the surface of the cationic micelle. If chloride as counterion is replaced by a more polarizable anion, such as bromide, access of the hydroxyl ion will be more limited and the rate of hydrolysis will decrease

Increased Hydrolysis Rate—Micellar Catalysis

Cationic ester-containing surfactants, such as ester quats and betaine esters, are subject to micellar catalysis and hydrolyze faster when present in micelles than as free unimers in solution. This is due to an increased hydroxyl ion concentration around the micelle, that is, the local effective pH in the vicinity of the micelle surface is higher than in the bulk. Figure 1.24 illustrates the phenomenon for a betaine ester surfactant.

Figure 1.25 shows the pseudo-first-order rate constants for alkaline hydrolysis of a series of betaine esters with different lengths of the alkyl tail. The observed pronounced concentration dependence of the hydrolysis rate can be explained by micellar catalysis, that is, by

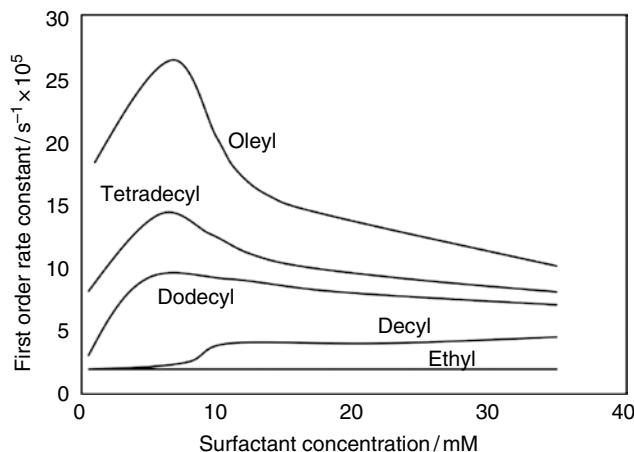


Figure 1.25 Concentration dependence of the pseudo-first-order rate constants in a 100 mM phosphate buffer at pH 7.5 and 37°C for surface active betaine esters with hydrophobic tails of different sizes. For comparison, the rate constant for a non-surface active betaine ester (ethyl betainate) is included. (Reprinted with permission from Lundberg, D. and Holmberg, K. (2004) NMR studies on hydrolysis kinetics and micellar growth in solutions of surface-active betaine esters. *Journal of Surfactants and Detergents*, 7, 239. Copyright © 2004, Springer.)

the locally elevated pH in the micellar pseudophase. The reaction rate will thus be substantially higher when the surfactant is present at a concentration above the CMC compared to the rate observed for a unimeric surfactant or a betaine ester that is not surface active under the same conditions. The decrease in reaction rate observed at higher concentrations for the C₁₂–C_{18:1} compounds is a consequence of competition between the reactive hydroxyl ions and the inert surfactant counterions at the micellar surface. The chloride ions are more polarizable than hydroxyl ions and, thus, show a stronger affinity to the charged micellar surface. The decrease in rate at higher concentration will be even stronger if bromide is the counterion. Addition of extra salt may completely eliminate the micellar catalysis. The hydroxyl ions may then not be able to compete with the other anions for a place in the micellar pseudophase.

Decreased Hydrolysis Rate—Micellar Inhibition

Figure 1.26 illustrates alkaline hydrolysis of a noncharged ester surfactant above and below the CMC. As can be seen, the half-life of the surfactant is constant at concentrations below the CMC, while above the CMC there is a linear increase of the half-life. This means that below the CMC the values are in accordance with pseudo-first-order kinetics and above the CMC they express zero-order kinetics, that is, the rate is independent of the concentration of the reacting species. This implies that only surfactant molecules present as unimers are cleaved. Those residing in micelles are protected from hydrolysis. (Above the CMC the unimer concentration will, under the assumption that the micellar dissociation is faster than

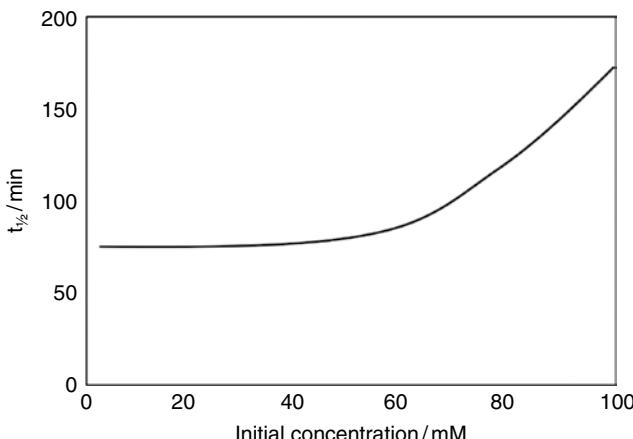


Figure 1.26 Half-life of a non-charged ester surfactant, tetra(ethylene glycol) monoester of octanoic acid ($C_7H_{15}CO-(OCH_2CH_2)_4-OH$) as a function of initial surfactant concentration. The surfactant has a CMC of 50 mM. (With permission from Stjernsdahl, M. and Holmberg, K. (2003) *Synthesis and chemical hydrolysis of surface-active esters*. Journal of Surfactants and Detergents, **6**, 311–318. Copyright © 2003, Springer.)

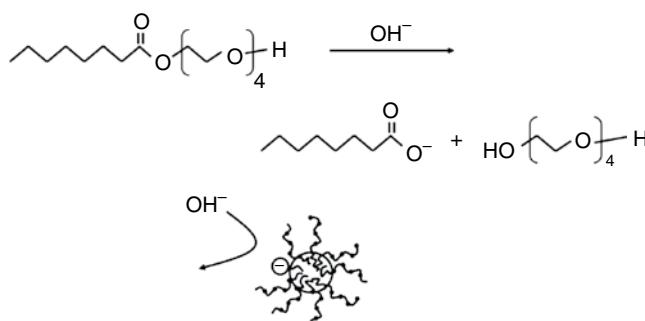


Figure 1.27 Hydrolysis of the ester surfactant present as unimers generates an anionic surfactant, which will enter the micelle and render it a negative charge. Hydroxyl ions are repelled by the negatively charged micelle in analogy with the attraction of hydroxyl ions to positively charged micelles, as illustrated in Figure 1.24

the hydrolysis reaction, be practically constant.) Evidently, aggregation into micelles protects these nonionic ester surfactants from undergoing alkaline ester hydrolysis, that is, the opposite to what happens to the cationic ester-containing surfactants discussed above. It is likely that the effect is due to the fact that hydrolysis of the unimers in bulk generates a fatty acid soap, that is an anionic surfactant. Anionic and nonionic surfactants readily combine into mixed micelles, as is discussed in Chapter 13; thus, the micelles will gradually build up a negative charge. Hydroxyl ions will be repelled by such negatively charged aggregates, as is illustrated in Figure 1.27.

Use of Polymerizable Surfactants is a Way to Immobilize the Surfactant

Polymerizable surfactants are examples of what is sometimes referred to as *functional surfactants*, that is surfactants that possess one characteristic property besides that of pronounced surface activity. The interest in polymerizable surfactants originates from the fact that surfactant action may be needed at some stage of an operation but unnecessary, or even unwanted, at some later stage. The problems with residual surfactants may be environmentally related, such as with slowly biodegradable surfactants in sewage plants. The problems may also be of a technical nature because the presence of surface active agents in the final product may affect the product performance in a negative way.

The paint area is a good example where surfactants are needed at one stage but unwanted at a later stage. Surfactants are used in paints as emulsifier for the binders, as dispersant for the pigments, and to improve wetting of the substrates. In the dried paint film, the presence of surfactant frequently causes problems, however, since the surfactant acts as an external plasticizer in the film, imparting softness and flexibility. This could be taken advantage of had the plasticizer been evenly distributed in the coating. However, due to its surface activity, the surfactant will migrate out of the bulk phase and concentrate at the interfaces. It has been shown that surfactant molecules go to the film–air interface, where they align with their hydrophobic tails pointing towards the air (Figure 1.28). (The surfactant may also align at the film–substrate interface, but the extent at which this happens will depend on the nature of the substrate.) As an example, calculations from Electron Spectroscopy for Chemical Analysis (ESCA) (or X-ray Photoelectron Spectroscopy (XPS)) spectra show that the dried film from a lacquer containing 1% surfactant may have an average surface surfactant concentration of 50%. The overall bulk concentration of surfactant is still approximately 1%, since the modified surface region is a very thin layer when compared to the thickness of the whole film. The surfactant surface layer constitutes a so-called weak boundary layer when a second coating is applied, sometimes leading to poor adhesion of a second lacquer layer or to poor quality when the surface is printed.

It is also known that during the drying of emulsion paints the surfactant may undergo phase separation, forming lumps, tenths of microns wide, distributed throughout the film. Atomic force microscopy studies have revealed that these surfactant lumps can extend far down into the film. On exposure to water the surfactant is washed out of the film, with the result being that deep cavities appear where the lumps had been. Such film defects can severely reduce the protective action of a coating on wood.

A way to overcome the problems associated with the presence of surfactant in the final product is to have the surfactant chemically bound to the latex particle or, alternatively, to

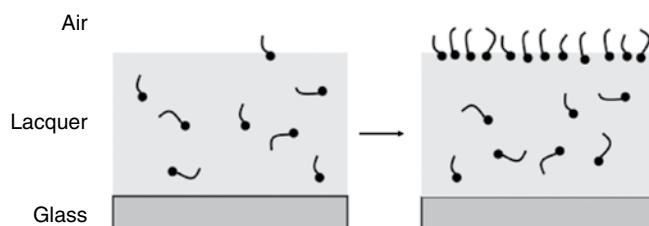


Figure 1.28 Migration of surfactant in a lacquer film leads to enrichment at the surface

make the surfactant polymerize during the setting or curing stage. In principle, the surfactant may either undergo homopolymerization or copolymerize with some other component of the system. In paints and lacquers, the obvious other component is the binder.

A completely different way to avoid the problem of residual surfactant in the end product is to use cleavable surfactants, that is, surfactants that spontaneously break down at some stage. This concept was discussed in a previous section of this chapter.

Mode of Surfactant Polymerization

Homopolymerization versus Copolymerization

In a formulation containing reactive surfactant, homopolymerization of the amphiphile may take place if the concentration is high enough. However, in most technical formulations the surfactant concentration is too low to allow substantial homopolymerization in the bulk phase. The reactive surfactant will instead copolymerize with another component in the bulk. A monolayer of surfactant, on the other hand, may homopolymerize when adsorbed at an interface, as is shown below. The palisade layer may either form by adsorption from an aqueous solution or by migration through a film, as discussed above.

Autoxidative versus Nonautoxidative Polymerization

Autoxidation, that is, oxygen-induced curing, may take place both during copolymerization in the bulk phase and during homopolymerization of a surface monolayer. A surfactant capable of undergoing autoxidation is shown in Figure 1.29. The surfactant is a monoethanolamide ethoxylate of an unsaturated fatty acid. The fatty acid originates from an unsaturated triglyceride, such as linseed oil or tall oil. Such surfactants belong to the class fatty acid ethoxylates that was discussed under the section Nonionics earlier in this chapter and illustrated in Figure 1.7. Surfactants that can undergo autoxidation are of

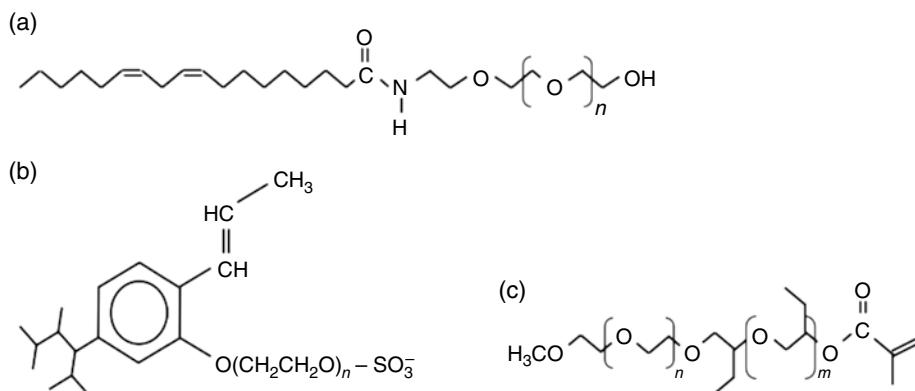


Figure 1.29 Examples of polymerizable surfactants: (a) a monoethanolamide ethoxylate of an unsaturated fatty acid capable of undergoing autoxidative polymerization; (b) a sulfated nonylphenol ethoxylate derivative capable of undergoing free-radical polymerization; and (c) a copolymer based on polyoxyethylene and polyoxybutylene segments with a methacrylate group at the hydrophobic end, also capable of undergoing free radical polymerization

particular interest in combination with alkyd resins, which also contain unsaturated fatty acid residues. The autoxidation, that is, the curing of the alkyd-based film containing reactive surfactant, is normally catalyzed by cobalt or manganese salts.

Nonautoxidative polymerization includes UV curing or thermally induced curing with the use of free radical initiators, such as benzoyl peroxide or potassium persulfate. Similar to autoxidation, both bulk and surface curing may occur. Surfactants based on activated vinyl groups, such as acrylate and methacrylate esters, are typical examples of this class. Examples of surfactants capable of rapid free radical curing are also shown in Figure 1.29.

Position of the Polymerizable Group

In principle, the reactive group may be present either in the polar, hydrophilic or in the apolar, hydrophobic part of the surfactant molecule.

In emulsion systems the solubility characteristics of the initiator are important. The distribution of the initiator between the oil and the water phases should be such that it is predominantly present in the phase where the polymerizable function is located. Thus, surfactants with a polymerizable bond in the polar head group are best served with a water-soluble initiator whereas an oil-soluble initiator is preferred when the polymerizable bond is situated in the hydrocarbon part.

In general, polymerization at the polar end of nonionic surfactants requires relatively severe conditions and often gives poor yield. When the same functional group is present in the hydrophobic tail, the reactivity in a two-phase system is much higher. Cross-linking of the polar groups should also be avoided if the surfactant after polymerization is supposed to provide steric stabilization, for example, in the stabilization of dispersed systems. The entropy term, which is the main driving force behind steric stabilization, will be reduced if the freedom of motion of the polar head groups is restricted.

Cross-linking of the hydrophobic tails is also the best choice in those cases where the surfactant polymerizes when adsorbed at a hydrophobic surface. Adsorption at such surfaces occurs with the surfactant hydrophobic chains close together, an orientation that should facilitate formation of inter-chain bonds.

Applications of Polymerizable Surfactants

Emulsion Polymerization

Polymerizable surfactants are of interest in emulsion polymerization, for example, in the conversion of vinyl chloride to poly(vinyl chloride) and of acrylates and vinyl acetate to latices for coatings. Use of a reactive surfactant in vinyl chloride polymerization leads to poly(vinyl chloride) with improved shear stability. In latices, polymerizable surfactants can bring about several advantages such as:

- improved stability against shear, freezing, and dilution;
- reduced foaming;
- reduced problems with competitive adsorption (see below);
- improved adhesion properties of the film;
- improved water and chemical resistance of the film.

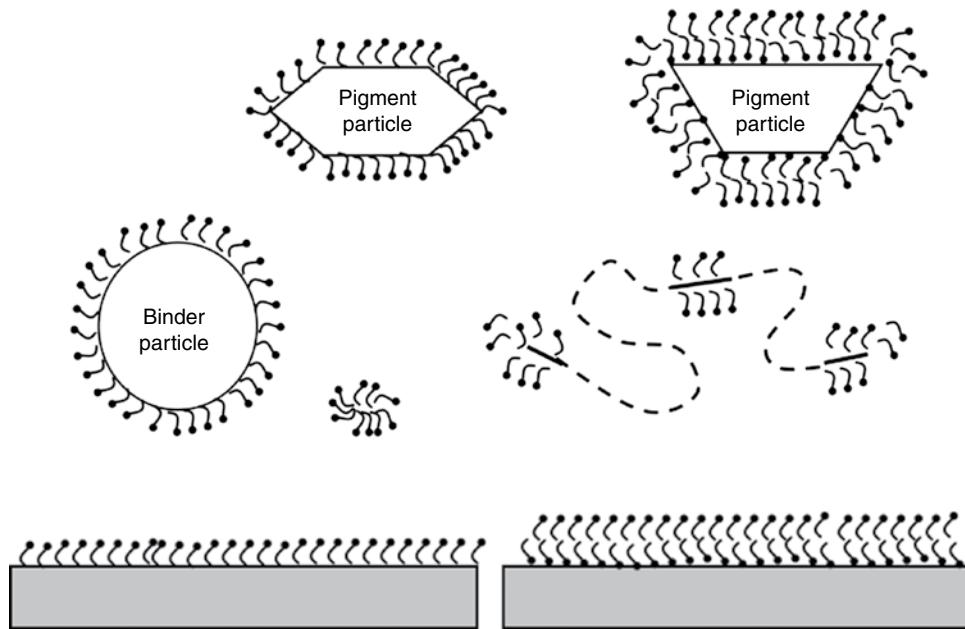


Figure 1.30 The surfactant may adsorb at many different surfaces in a paint formulation

Competitive adsorption is a serious problem in many paint systems, as well as in many other surfactant-containing formulations. A pigmented latex coating contains a variety of interfaces at which surfactants may adsorb, such as binder–water, pigment–water, substrate–water, and air–water. In addition, the surfactant molecules may assemble in micelles or form aggregates together with hydrophobic segments of the associative thickener, which is normally present in today's latex paints. The situation is illustrated in Figure 1.30. Since different surfactants are normally introduced into the system together with the individual components, for example, emulsifier (often a mixture of an anionic and a nonionic surfactant) with the binder, pigment dispersant with the pigment, wetting agent added directly to the formulation, and so on, the situation becomes very complex and competitive adsorption is a potential problem in all pigmented emulsion paints and in many related systems. The surface active agent used as the emulsifier for the binder may desorb from the emulsion droplet and adsorb at the pigment surface. The pigment dispersing agent may go the other way. Such an exchange is known to occur and to cause problems in terms of instability and unwanted rheological behavior. Competitive adsorption in general is discussed in Chapter 13.

Alkyd Emulsions

Alkyd resins are traditionally used in formulations based on organic solvents, such as white spirit or xylene, in which the alkyd is molecularly dissolved. Emulsions of alkyds came later and can be seen as the response by the alkyd industry to environmental demands. Stable emulsions can be made from most alkyds, provided the resin viscosity is not too

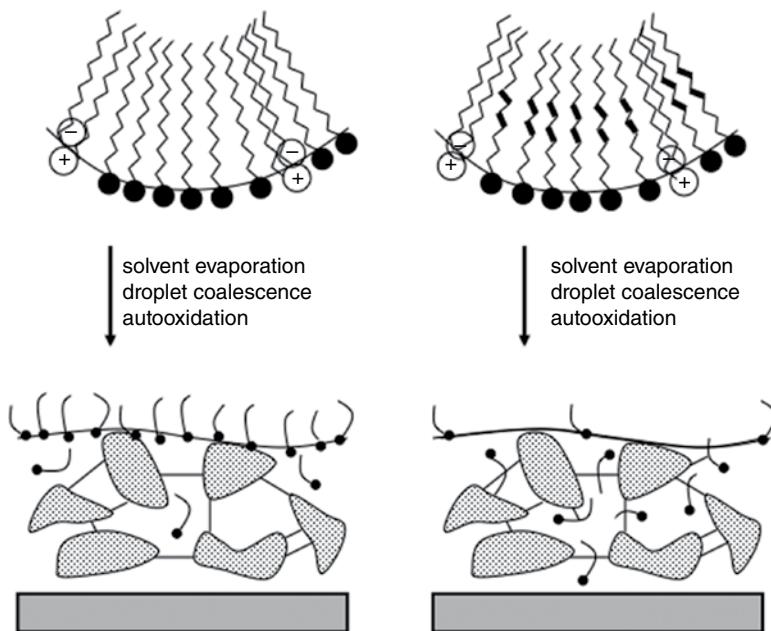


Figure 1.31 Curing of an alkyd emulsion based on (left) a conventional surfactant and (right) a reactive surfactant containing homoconjugated double bonds in the hydrophobic tail. Whereas the conventional, unreactive surfactant migrates to the surface, most of the reactive surfactant molecules become chemically bound to the resin network. (With permission from Holmberg, K. (1992) Polymerizable surfactants. Progress in Organic Coatings, **20**, 325–337. Copyright Elsevier Limited.)

high and sufficient shear forces are applied in the emulsification. It has been found that by using emulsifiers capable of participating in the autoxidative drying of the binder, the film properties can be considerably improved. Surfactant (a) of Figure 1.29 is an example of a surfactant that can copolymerize with the alkyd binder during autoxidative curing of the film. Such copolymerization is a way to reduce the above-mentioned problems with free surfactant molecules in the film. Figure 1.31 depicts schematic representations of the curing process with a conventional emulsifier and with a surfactant capable of copolymerizing with unsaturated fatty acid chains of the binder.

Surface Modification

Modification of solid surfaces can be achieved by an adsorbed layer of reactive surfactant on the surface, as illustrated in Figure 1.32. Provided that the surfactant molecules are extensively cross-linked, such a thin surface film will be attached irreversibly. In this way, hydrophobic surfaces can be made hydrophilic or a specific functionality can be introduced.

For example, low-density polyethylene films can be hydrophilized with surfactants having one or two polymerizable groups, such as methacrylate or diacetylene. Adsorption can be made from buffer solution and the subsequent polymerization of the adsorbed monolayer achieved by UV irradiation. Particularly good results are often obtained with surfactants of

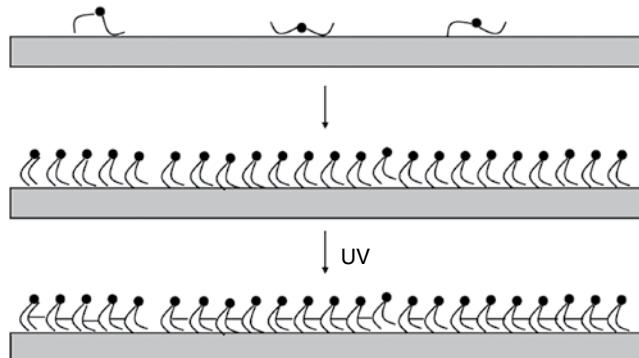


Figure 1.32 Surface modification with a UV-curable surfactant

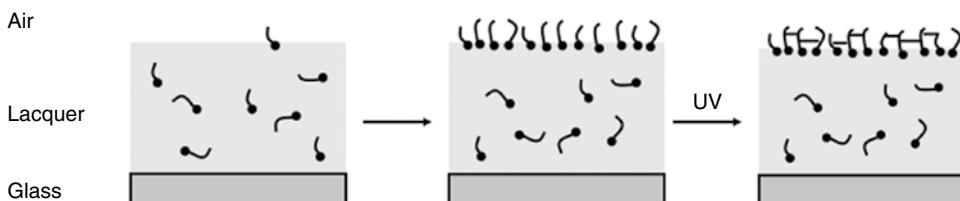


Figure 1.33 Surface modification of a lacquer film through migration of the surfactant to the film–air interface, followed by UV curing

the twin-tail type, that is, having a hydrophobic part consisting of two hydrocarbon chains. This structure gives optimal packing on planar surfaces since the surfactants have a value of the critical packing parameter close to one (Chapter 6). Proper alignment of the surfactants at the surface is believed to be vital for effective cross-linking to occur. There is experimental evidence that surfactants that contain two polymerizable functions give better result in terms of permanent hydrophilization than surfactants containing only one reactive group. Most likely, surfactants with more than one polymerizable group give a cross-linked network of higher molecular weight.

Paint and lacquer films can also be surface-modified by migration of a dissolved surfactant to the film–air interface during the drying or curing stage followed by crosslinking. The principle is shown in Figure 1.33 for a UV-polymerizable surfactant. As an example, a fluorocarbon surface layer can be obtained by dissolving a small amount, less than 1%, of a polymerizable fluorosurfactant in a lacquer and cross-linking the surfactant monolayer formed at the surface. Such a surface becomes extremely water repellent with a minimal use of the costly and not so environmentally benign fluorinated surfactant.

Surfactant Self-Assemblies

The homopolymerization of reactive surfactants in the form of assemblies, such as micelles or liquid crystals, has been attempted as a way to freeze the structure and prepare various types of nano-sized materials. Polymerization of micelles has not been entirely successful,

however. With both spherical and rod-like micelles the polymerized aggregates were of much larger size than the original structures. With liquid crystals and, in particular, with vesicles, the results are more promising. Stable vesicles, of interest for drug administration, have been prepared by free radical polymerization of preformed vesicles. Such vesicles need not to be based entirely on polymerizable surfactants. Incorporation of smaller amounts, 10–30%, of reactive species into a phospholipid-based vesicle formulation leads to vesicles with much improved stability.

Special Surfactants Give Extreme Surface Tension Reduction

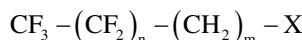
The vast majority of surfactants have the hydrophobic part of the molecule made up of a hydrocarbon chain, either aliphatic or alkylaryl. With a suitable choice of polar head group, the minimum surface tension that can be achieved with such surfactants is in the order of 26–28 mN/m. Such surface activity is sufficient for most uses of surface active agents. However, there are some applications where a lower surface tension of aqueous solutions is required. The spreading of aqueous foams on top of burning oil and the spreading of water-based formulations on surfaces of polyolefins are two relevant examples.

Two types of specialty surfactants are used to achieve extreme reduction of surface tension: silicone surfactants and fluorinated surfactants. The former type is based on polydimethylsiloxane as the apolar group, while the latter contains a fluorocarbon or a combination of fluorocarbon and hydrocarbon as the hydrophobic tail. Silicone surfactants are either low molecular weight or high molecular weight compounds. The low molecular weight silicone surfactants are excellent wetting agents and are discussed in Chapter 20. The high molecular weight compounds are treated together with other surface active polymers in Chapter 10.

Fluorinated surfactants are normally of low molecular weight and have the general structure:



or



where X can be any polar group, charged or uncharged. The fluorocarbon chain is usually rather short, with n typically being 5–9. Fluorinated carboxylates are common. Due to the inductive effect exerted by the electronegative fluorine atoms, these compounds are strong acids and, hence, relatively insensitive to low pH or hard water. There are also perfluorinated block copolymers, analogous to EO–PO block copolymers (Chapters 7 and 10), on the market.

Fluorinated surfactants are used for various applications where wetting and spreading of aqueous solutions are difficult. Another use of fluorinated surfactants is to render surfaces, for example, paper or textiles, both hydrophobic and lipophobic. Fluorinated surfactants, like silicone surfactants but unlike hydrocarbon-based surfactants, are also surface active in organic solvents and are, therefore, used as surfactants in paints and other nonaqueous formulations. The main disadvantage with fluorinated surfactants, besides their high price, is their poor biodegradability.

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2

Environmental and Health Aspects of Surfactants

Environmental Concern is a Strong Driving Force for Surfactant Development

All major types of surfactants, alkylbenzene sulfonates, alkyl sulfates, alcohol ethoxylates, and so on, have been around for decades. The only major class of surfactant that does not have a long tradition is the ester quats, which entered the market on a large scale in the 1980s and 1990s. The ester quats replaced the stable dialkyl quats and the transition was entirely environmentally driven. (The structures of ester quats and dialkyl quats are given in Figure 1.10.) The stable dialkyl quats, until then dominating the market for fabric softeners, did not meet the requirements in terms of biodegradability and aquatic toxicity that came into force at the time. The ester quats, with bonds in the structure susceptible to enzymatic hydrolysis, were much better in this respect.

The change from stable quats to ester quats represents a major environmentally driven substitution of one class of surfactants for another. Another major change was the replacement of branched alkylbenzene sulfonates by linear alkylbenzene sulfonates but that transition occurred much earlier, in the 1960s and 1970s. The branched alkylbenzene sulfonates were very resistant to microbial degradation, which in the early days of laundry detergent formulations was seen as an asset. The linear alkylbenzene sulfonates, often referred to as LABS or LAS, took over from the branched products and it was environmental concern, not performance, that was the driving force. A third example of an environmentally driven transition from one class of surfactant to another is the replacement of alkylphenol ethoxylates by fatty alcohol ethoxylates. Alkylphenol ethoxylates, typically octyl- and nonylphenol-based products, are excellent surfactants but suffer from slow rate of biodegradation and considerable aquatic toxicity. Fatty alcohol ethoxylates are more

environmentally benign. Replacing alkylphenol ethoxylates by fatty alcohol ethoxylates is not a trivial task, however. The bulkiness of the alkyl chain and the presence of π -electrons in the hydrophobic part of the alkylphenol ethoxylates are attractive from a performance point of view and there are applications where the replacement by fatty alcohol ethoxylates has proven to be difficult.

The trend towards more environmentally benign surfactants continues. Besides the constant challenge of finding ways to minimize the manufacturing cost for existing surfactants, the market pull for “greener” products is the overriding driving force for surfactants development. Some general trends are:

- to synthesize the surfactant from natural building blocks; this is further dealt with below;
- to use starting materials—natural or synthetic—that give proper rate of biodegradation;
- to insert one or more weak bonds into the structure; the ester quats are good examples but the concept is broader than that and *cleavable surfactants* were discussed on pages 29–36;
- to make more efficient surfactants, that is, surfactants that can be used in lower amounts; gemini surfactants (pages 26–29) are one example, polymeric surfactants (Chapter 10) are another.

The Polar Head Group

Two main types of natural products have been investigated as surfactant polar head group, polyols, such as sugars, and amino acids. These are briefly discussed here.

Polyol Surfactants

Fatty acid esters of sugars, or more correctly polyols, have been around for a long time. A well-known product type is sorbitan esters (sorbitan alkanoates), often referred to by the trade name Span. Span, and its ethoxylated “relative” Tween, are excellent surfactants both in terms of performance and from an environmental point of view. The structures of Span and Tween can be found in Figure 1.7.

Esters of glycerol, also a natural polyol, are well established on the market, too. The polar head group in these surfactants is not monomeric glycerol but slightly oligomerized glycerol with the condensation primarily, but not exclusively, involving primary hydroxyl groups. A representative example of a glycerol ester surfactant is shown in Figure 2.1a.

More recently there has been an interest in fatty acid esters of glucose. Such surfactants can either be produced by organic synthesis, which leads to a mixture of products with the acyl group attached at different positions on the ring, or by a lipase catalyzed process, in which the esterification occurs specifically at the six-position of the glucose. Such a surfactant is also shown in Figure 2.1b. A high selectivity can be achieved by an organic synthesis route if protecting groups are used, but such procedures tend to be expensive. Starting from sugar acetals and fatty acids, monoesters of sugars can be obtained in good yield, after a deprotection step, from several starting materials, both mono- and disaccharides. All sugar esters are very labile on the alkaline side but fairly resistant to acid. Their degradation products, that is, sugar and fatty acid, are both very natural products; thus, sugar esters are ideal candidates as food surfactants. Sugar esters seem to undergo rapid

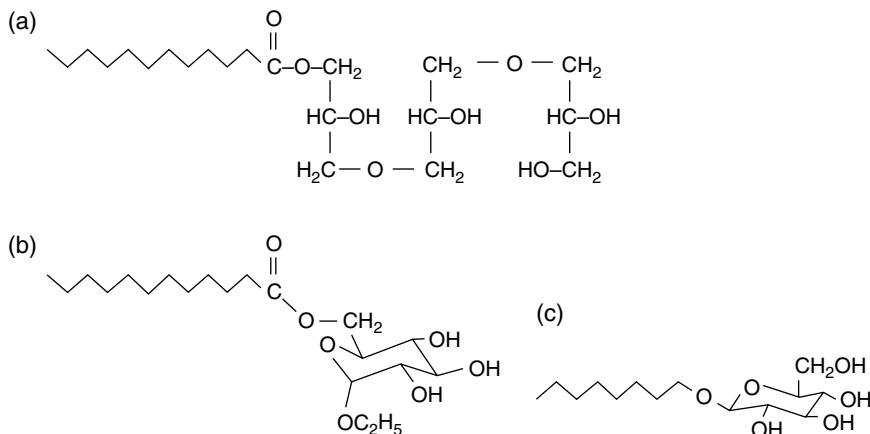


Figure 2.1 Three examples of polyol surfactants: (a) triglycerol ester of dodecanoic acid; (b) ethyl glucoside ester of dodecanoic acid; and (c) octyl glucoside

biodegradation regardless of the sugar head group size or the acyl chain length. Sulfonated sugar esters have also been prepared and evaluated. These anionic surfactants were found to undergo less rapid biodegradation.

During the last decades much effort has been directed to explore alkyl polyglucosides (APGs) as surfactants for different types of application. The synthesis of APGs was discussed on pages 34–35 and shown in Figure 1.21. As with the glucose esters, APGs can be synthesized either by an organic synthesis route, in which case a mixture of products is obtained, or by enzymatic synthesis, which leads to a more well-defined product. The biochemical route gives poor yield, however, and so far it cannot compete with the organic process.

The parent alkyl glucoside is shown in Figure 2.1c. The hydrophobic tail is based on a fatty alcohol of the same type as is used in the main type of nonionic surfactant, the fatty alcohol ethoxylates. In reality, the sugar part is never exactly one glucose unit unless the preparation method is a bioorganic one. The glucose is partly oligomerized and the degree of oligomerization can be tailored to give the right size of the head group to balance the hydrophobic tail, just like the number of oxyethylene units can be tailored in the ethoxylation of a fatty alcohol. Alkyl glucosides are stable at high pH but sensitive to low pH, where they hydrolyze to sugar and fatty alcohol. A sugar unit is more water soluble and less soluble in hydrocarbons than the corresponding polyoxyethylene unit; hence, APGs and other polyol-based surfactants are more lipophobic than their polyoxyethylene-based surfactant counterparts. This makes the physicochemical behavior of APG surfactants in oil–water systems distinctly different from that of conventional nonionics. Furthermore, APGs and other polyol surfactants do not show the inverse solubility versus temperature relationship that normal nonionics do. This makes an important difference in solution behavior between APGs and polyoxyethylene-based surfactants. The main attractiveness of APGs lies in their favorable environmental profile: the rate of biodegradation is usually high and the aquatic toxicity is low. In addition, APGs exhibit favorable dermatological properties, being very mild to skin and eye. The mildness makes this surfactant class attractive for personal care products but APGs have also found a range of technical applications.

Box 2.1 Characteristics of polyol surfactants

- Aerobic and anaerobic biodegradation is fast
- Aquatic toxicity is low
- Hydroxyl groups are strongly lipophobic. At the same time surfactants with long enough hydrocarbon chains are strongly hydrophobic. Polyol surfactants, therefore, have a high tendency to remain at the oil–water interface
- The effect of temperature on solution behavior is small and opposite to that of ethoxylates. Mixtures of polyol surfactants (larger fraction) and ethoxylates (smaller fraction) can be formulated so that a mixed nonionic surfactant with phase behavior unaffected by temperature is obtained

Polyol surfactants have many attractive properties: they are mild to the skin, they exhibit low aquatic toxicity and high rate of biodegradation, and they show good tolerance to high electrolyte concentrations. Characteristic properties of polyol surfactants in general are summarized in Box 2.1.

Amino Acid-Based Surfactants

Many of the 20 standard amino acids (the α -amino acids that are used in the biosynthesis of proteins) have been explored as a surfactant raw material and several of these have been thoroughly investigated. Some are established on the market, particularly in personal care products. Simple α -amino acids, such as glycine and alanine, have two functional groups, a carboxyl group and a primary amino group. In principle, a surfactant can be made by attaching the hydrophobe moiety at either of these, as shown in Figure 2.2. The carboxyl group may be derivatized by reaction with a fatty alcohol to give a surface active ester-amine (*path 1*) or with a long-chain amine to yield an amphiphilic amidoamine (*path 2*). In the latter reaction, care must be taken to avoid reaction with the α -amino group of the amino acid. This can be accomplished by protecting the α -amino group.

Alternatively, the α -amino group can be derivatized. This may be done by amidation with a fatty acid or, more conveniently, with a reactive derivative of a fatty acid. The product is an amidoacid (*path 3*). The α -amino group may also be alkylated with a long-chain alkyl halide, transforming it to a secondary (or tertiary) amine (*path 4*). The product is a long-chain amino acid.

Derivatization of the carboxyl group, that is, *paths 1* and *2*, will give a long-chain amine, which is protonated and surface active at neutral and acidic pH. Its special feature compared to regular fatty amines is that it contains a bond close to the polar head group, an ester or an amide linkage that is easily cleaved by enzymatic catalysis. Thus, it can be expected that such long-chain amines will be more readily degradable than normal amines. The amidoacid formed by *path 3* is by far the most common type of amino acid derivative and there exist many commercial products based on this synthesis route. Examples of important such products are glycinate, sarcosinate, glutamate, and aspartate. The glutamates and aspartates are based on dicarboxylic amino acids, thus their long-chain N-acyl derivatives are dicarboxylic surfactants with strong chelating capability.

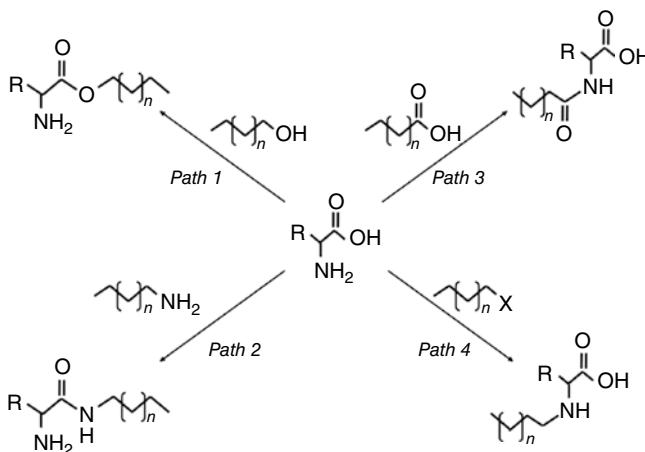


Figure 2.2 Synthesis routes for amino-acid based surfactants. (Reprinted with permission from Bordes R. and Holmberg, K., Copyright 2014.)

The Hydrocarbon Tail

Triglyceride oils are the most important natural source for surfactant hydrophobes. As shown in Figure 2.3, a very large variety of surfactants are made from triglyceride as starting material.

Sterols are another class of natural hydrophobes of interest as surfactant building blocks. The special feature of sterol-based surfactants is the large hydrophobic group of fully natural origin which, due to its rather planar four-ring structure, may induce good packing at interfaces. Phytosterol is the common name for sterols of plant origin and they are today used as surfactant raw material. Their structure is similar to that of cholesterol, the prime example of sterols from animal sources. The sterols contain a secondary hydroxyl group that can be ethoxylated and sterol ethoxylates are used in cosmetics products. Compared to fatty acids and other products originating from triglycerides, the use of sterols as surfactant raw material is small, however.

Biodegradability

Surfactants should be regarded as toxic to aquatic organisms, even at low concentrations, and should, therefore, be removed from wastewater before entering receiving waters. In the sewage treatment plants surfactants and other organic molecules are destroyed through the biological action of living organisms. The microorganisms carrying out the biodegradation are able to metabolize organic substances and convert them into less complex chemicals by a series of enzymatic reactions. Under aerobic conditions microorganisms convert organic substances into carbon dioxide, water, and biomass. A product that does not undergo natural biodegradation persists in the environment.

In the industrialized world the majority of surfactants will pass through a sewage treatment plant. In these plants the chemicals are exposed to aerobic biodegradation; this is also the case when the chemicals are released into natural water. Therefore, most

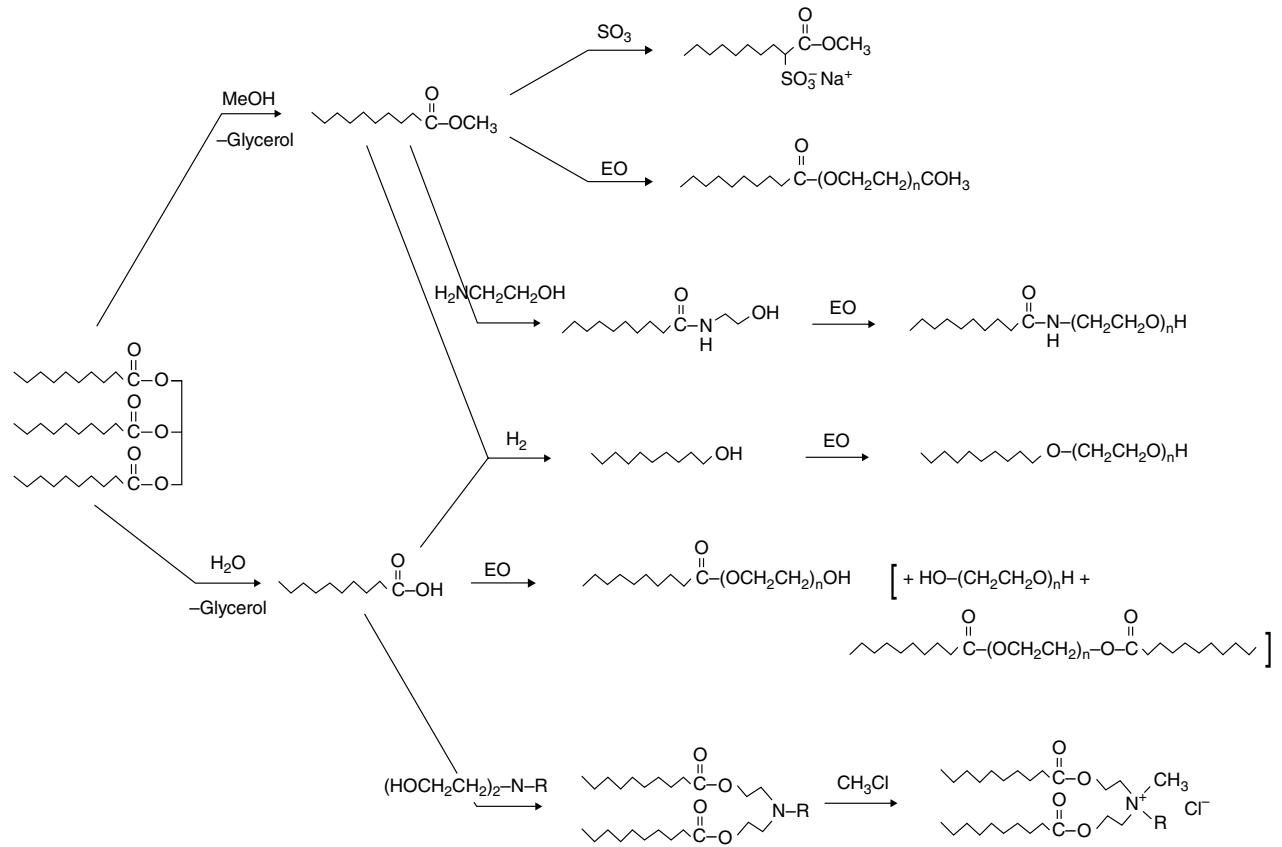


Figure 2.3 A surfactant product tree originating from triglyceride oils

biodegradation methods for surfactants are based on aerobic conditions. Certain terms are commonly used when discussing biodegradability. *Ultimate biodegradation* is the complete breakdown of the surfactant into carbon dioxide, water, inorganic materials (also called mineralization), and cellular matter. In *ready biodegradation* the term “ready” has a very specific meaning originally defined by the Organisation for Economic Co-operation and Development (OECD). *Readily biodegradable* means that the substance reaches a specific level of ultimate biodegradation within a specified time frame using a ready biodegradability test method. For surfactants the most common test method is the *Closed Bottle Test*. This test is performed using two bottles with a certain amount of active sludge added—one with and one without the compound to be tested—and the difference in the amount of gas (carbon dioxide) evolved is a measure of the biodegradation of the test substance. *To qualify as readily biodegradable, 60% biodegradation, calculated on the theoretical amount, should be reached within 28 days under aerobic conditions.*

The term inherent biodegradation is used for substances that do not fulfill the demands for ready biodegradation but are degraded to a certain extent within a specified time frame. It is considered that if a substance is degraded to, say, 20% within a test period, there is reason to believe that it should break down completely given sufficient time.

The Rate of Biodegradation Depends on the Surfactant Structure

Several parameters are of importance for the rate of biodegradation of a surfactant. Firstly, the surfactant needs to have a reasonable solubility in water. Very lipophilic amphiphiles, such as fluorinated surfactants, accumulate in lipid compartments in organisms and break down very slowly. Most surfactants have enough water solubility that bioaccumulation of the intact molecule is not a problem. However, the initial degradation may lead to intermediates with very limited water solubility. A well-known example of this is the class of alkylphenol ethoxylates, which degrade by oxidative cleavage from the hydroxyl end of the polyoxyethylene chain. This means that alkylphenol ethoxylates with polar head groups of just a few oxyethylene units will form. These are very lipophilic and biodegrade at a very low rate. Analyses of fish in waters exposed to nonylphenol ethoxylates have shown high levels of nonylphenol with two and three oxyethylene units in lipid tissues. Such findings were one of the reasons for the strong concern about the environmental effects of this surfactant class. Fatty alcohol ethoxylates break down more readily because the metabolism can take at least three different routes. The breakdown can start with attack on the terminal hydroxyl group, by oxidation at the terminal end of the alkyl chain, or by cleavage of the ether bond adjacent to the hydrophobic tail (central scission). In surfactants with straight alkyl chains, the central scission dominates. If this pathway is blocked by large substituents in the vicinity of the ether bond, degradation from the two ends may be more important. Central scission of an alcohol ethoxylate normally involves oxidation of the ether bond to an ester bond followed by hydrolysis. The primary metabolites are then a fatty acid and a poly(ethylene glycol). The fatty acid is subsequently degraded by so-called β -oxidation, in which two carbons at a time are removed by the action of coenzyme A. The β -oxidation can cope with a moderate amount of branching (particularly if the

substituents are small). When quaternary carbons are present alternative degradation routes have to be employed.

All natural fatty alcohols are linear and, therefore, present no problems in terms of biodegradation. The synthetic fatty alcohols can have varying amounts of branching and the substituents are usually methyl groups, sometime ethyl groups. The degree of branching varies depending on the process used for the synthesis of the fatty alcohol. To comply with regulations most fatty alcohols used for surfactant production today have greater than 80% linear species.

If the hydrophobic tail is linear, its complete breakdown is fast, considerably faster than the degradation of the poly(ethylene glycol) part. The length of the polyoxyethylene part of nonionic surfactants is, therefore, critical for the overall biodegradation rate; the longer the chain, the slower is the rate. This is due to the fact that large, hydrophilic substances pass slowly through the cell membranes.

Besides water solubility it is essential that the surfactant contains bonds that can easily be broken down by enzymatic catalysis. Most, if not all, chemical bonds will ultimately break down in nature but it is important that the rate is high enough that unacceptable concentrations of a surfactant or its metabolites are not generated in the environment. To speed up the rate of biodegradation one strategy used by the surfactant manufacturers is to build a bond susceptible to enzymatic hydrolysis into the surfactant structure. Typical examples of such bonds are esters and amides, the breakdown of which are catalyzed by esterases/lipases and peptidases/acylases, respectively. The concept of *cleavable surfactants* was discussed in some detail in Chapter 1. It may have been anticipated that the ether bond of nonionic surfactants would be a problem, since ether-splitting enzymes are not common in nature. This is evidently not the case, however. As mentioned above, under aerobic conditions the ether bond may be oxidized to an ester bond. An alternative degradation process is that hydroperoxides are generated in α -position to the ether bond and the breakdown proceeds from there via aldehydes and acids.

Considerable effort has been put into finding correlations between branching in the hydrophobic tail and rate of biodegradation. It is clear that extensive branching of the hydrocarbon tail often leads to a reduced rate of biodegradation but the exact role of the substituents in hindering the breakdown process is not fully understood. Some branching patterns seem to be more troublesome than others and the effect is probably specific to the enzyme in question. It seems that methyl branching is less of a problem than branching involving longer alkyl chains but if many methyl branches appear in a row, such as in poly(propylene glycol) derivatives, they are still problematic. A very good example of the importance of linearity of alkyl chains is the difference in rate of biodegradation between alkylbenzene sulfonates with linear or branched alkyl chains. As mentioned briefly previously, branched alkylbenzene sulfonates, which are based on tetra-1,2-propylene as alkyl chain, were once the bulk surfactant in household detergents—cheap, efficient, and chemically stable. When environmental aspects became an issue, these surfactants were replaced by their counterparts with linear alkyl chains. The linear alkylbenzene sulfonates break down satisfactorily under aerobic conditions. Their rate of anaerobic biodegradation is relatively slow, however, a fact which is currently subject to some concern. A commercial linear alkylbenzene sulfonate consists of a large number of isomers having the alkyl chain connected to the aromatic ring at different nonterminal positions. In-depth biodegradation studies have revealed considerable differences in the rates of degradation of the different isomers.

In addition, the position of the branching along an aliphatic hydrocarbon chain seems to be critical. Branching on a carbon two atoms away from a cleavable bond (such as in 2-ethylhexyl ethers, carboxylic esters, acetals, and sulfates) is less harmful than branching on the carbon one atom away. This is of importance because the oxo alcohols, which are widely used as a surfactant raw material, contain a large portion of 2-alkyl branching. However, considerably more work is needed before it will be possible to predict the biodegradation characteristics by inspection of the chemical formula of a surfactant alone.

For surfactants with a hydrolyzable bond in the structure a correlation may be expected between the biodegradation rate and the rate of chemical hydrolysis or, at least, of enzymatic hydrolysis. This is not necessarily the case, however. In a study made with four homologue pure octanoic acid monoesters of tetra(ethylene glycol) with different substitution pattern no correlation was found between the three types of degradation, as is illustrated in Figure 2.4.

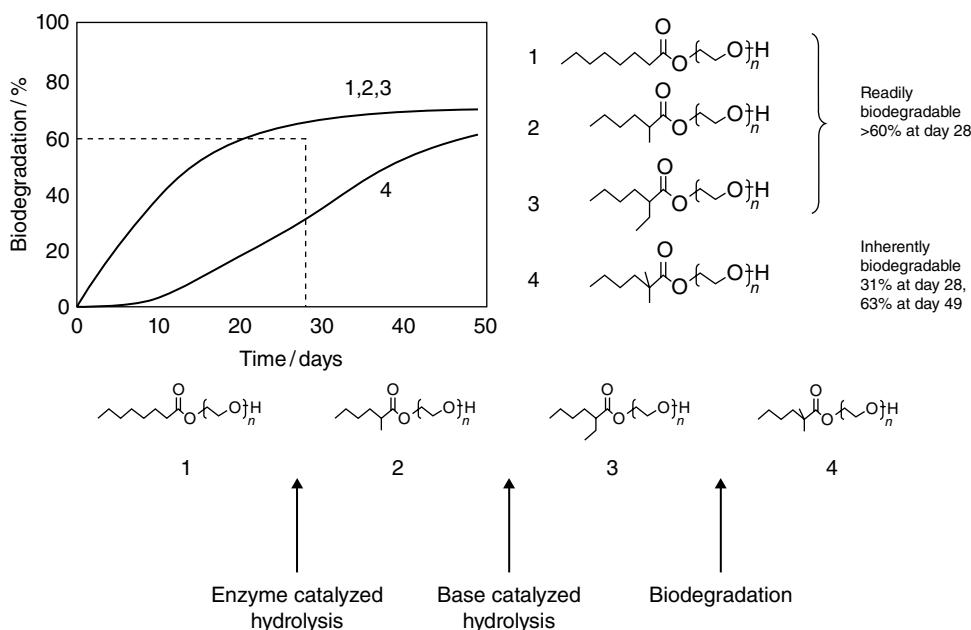


Figure 2.4 While the biodegradation rate was the same for the unsubstituted ester surfactant as for the surfactants with a methyl or an ethyl substituent in the α -position, two methyl substituents resulted in a surfactant with a much reduced rate of biodegradation. The dividing line in terms of rate of enzymatic breakdown went between the unsubstituted and the monomethyl substituted surfactant and that for chemical hydrolysis went between the monomethyl and the monoethyl substituted species. (With permission from Stjerndahl, M., van Ginkel, C.G. and Holmberg, K. (2003) Hydrolysis and biodegradation studies of surface-active esters. Journal of Surfactants and Detergents, **6**, 319–324, Copyright © 2003, Springer, and Lundberg, D., Stjerndahl, M. and Holmberg, K. (2008) Surfactants containing hydrolysable bonds. Advances in Polymer Science, **218**, 57–82, Copyright © 2008, Springer.)

Aquatic Toxicity

Aquatic toxicity may be measured on fish, daphnia, or algae. Toxicity is given as LC₅₀ (for fish) or EC₅₀ (for daphnia or algae), where LC and EC stand for lethal and effective concentration, respectively. *Values below 1 mg/l after 96 h testing on fish and algae and 48 h on daphnia are considered toxic.* Environmentally benign surfactants should preferably be above 10 mg/l.

Bioaccumulation

Hydrophobic organic compounds are persistent in nature, as all biodegradation requires some kind of aqueous environment. Bioaccumulation can be measured directly in fish but is more often calculated from a model experiment. Partitioning of the compound between two phases, octanol and water, is measured and the logarithm of the value obtained, log P , is used. (This is a common procedure for assigning hydrophobicity values to organic substances and tables of log P values are available in the literature). A surfactant is considered to bioaccumulate if:

$$\log P_{\text{oct/w}} > 3 \quad (2.1)$$

The vast majority of surfactants have log P values below 3. Bioaccumulation, therefore, is not considered to be a crucial issue.

Log P values for many surfactants have been collected. It has been found that these values can be used as an indication of the surfactant hydrophilicity; the lower the log P value, then the higher the hydrophilicity. Values of surfactant hydrophilicity are often helpful in formulation work and the surfactant literature contains several other procedures to assign a hydrophilicity number to a surfactant based on experiments. Another well-known standard for the same purpose is the hydrophilic–lipophilic balance (HLB) concept, which is widely used in the selection of emulsifier. The HLB of surfactants is discussed in some detail in Chapter 24. There is a reverse relationship between log P and HLB, the higher the HLB value, then the lower the log P value. The critical packing parameter (CPP) concept (Chapter 4) is yet another way to assign a hydrophilicity number to the surfactant hydrophilicity.

Other Regulatory Concerns

Tests for aquatic toxicity, ready biodegradation, and bioaccumulation by no means give the complete picture of the environmental impact of a surfactant. A number of other relevant parameters are listed in Box 2.2. In addition, the formulated end-product often contains mixtures of surfactants or a blend of surfactant and polymer. Since it is well-known that the physicochemical behavior of a surfactant may be very different in such mixtures than alone in solution, it is reasonable to believe that the biological effects may also be different. In order to obtain the full picture, ecological tests should be carried out on each individual end-product.

Box 2.2 Relevant factors besides aquatic toxicity, ready biodegradability, and bioaccumulation for assessment of surfactant ecotoxicity

- Anaerobic biodegradation (alkylbenzene sulfonates, alkylphenol ethoxylates, and EO–PO block copolymers are examples of surfactants with very slow anaerobic biodegradation)
- Chronic toxicity
- Effect on function of sewage plants
- Toxicity in the production of surfactants
- Life cycle aspects
- Technical effect, that is, the more effective the surfactant, the smaller amount is needed; therefore, biotoxicity per effect unit is the relevant measure (this is particularly relevant for the formulated end product)

Dermatological Aspects of Surfactants

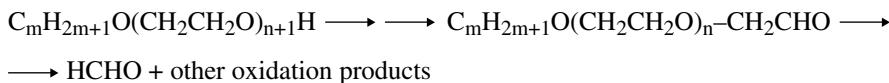
Dermatological effects of surfactants are important issues that are subject to much current concern. A large fraction of dermatological problems in normal working life can be related to exposure of unprotected skin to surfactant solutions. These solutions are often cleaning formulations of different kinds but may also be cutting fluids, rolling oil emulsions, and so on. Skin irritation of various degrees of seriousness is common, and in rare cases allergic reactions may also appear. Whereas skin irritation is normally induced by the surfactant itself, the sensitization causing the allergic reaction is usually caused by a by-product. A well-known example of a severe allergic reaction is the so-called *Margarine disease* that struck The Netherlands in the 1960s and which was subsequently traced to a by-product of a new surfactant that had been added to a margarine brand as an anti-spattering agent, that is, a surfactant that keeps the water droplets finely dispersed during frying. Sensitizing agents are electrophiles and react with nucleophilic groups of proteins, creating unnatural protein derivatives that the body then detects as foreign. The margarine surfactant contained an appreciable amount of an unreacted intermediate, a maleic anhydride derivative, which could be ring-opened in the body by protein amino or thiol groups.

The physiological effects of surfactants on the skin are investigated by various dermatological and biophysical methods, starting with the surface of the skin and progressing via the horny layer and its barrier function to the deeper layer of the basal cells. At the same time, subjective sensations, such as “feeling” of the skin, are recorded by verbalization of tactile sense and experience. Surfactant classes that are generally known to be mild to the skin are polyol surfactants (for example, alkyl glucosides), zwitterionic surfactants (such as betaines and amidobetaines), and isethionates. Such surfactants are frequently used in cosmetics formulations.

For homologous series of surfactants there is usually a maximum in skin irritation at a specific chain length of the hydrophobic tail. For instance, in a comparative study of alkyl glucosides in which the C₈, C₁₀, C₁₂, C₁₄ and C₁₆ derivatives were evaluated, a maximum irritation effect was obtained with the C₁₂ derivative. Such a maximum is normally also obtained when it comes to the biocidal effect of surfactants. This probably reflects the fact that the biological effect, caused by surfactant action on the mucous membrane or the bacterial surface, respectively, is favored by high surface activity and high unimer concentration.

Since an increasing chain length of the hydrocarbon tail of the surfactant leads to an increased surface activity and to a reduced critical micelle concentration (CMC), that is, a reduced unimer concentration, there will somewhere be an optimum in hydrocarbon chain length (assuming the same polar head group for all surfactants).

Alcohol ethoxylates are relatively mild surfactants but not as mild as polyol-based non-ionic such as alkyl glucosides. It seems that the dermatological effect seen with alcohol ethoxylates is usually not caused by the intact surfactant but by oxidation products formed during storage. All ethoxylated products undergo autoxidation to give hydroperoxides on methylene groups adjacent to the ether oxygens. Hydroperoxides formed at methylene groups in the polyoxyethylene chain are too unstable to be easily isolated. The hydroperoxide with the $-OOH$ group at carbon number 2 of the hydrophobic tail is relatively stable, however, and has been isolated in an amount of around 1% after storage of a normal fatty alcohol ethoxylate for one year. This hydroperoxide exhibited considerable skin irritation. Another oxidation product of some dermatological concern that has been isolated is the surfactant aldehyde $C_mH_{2m+1}O(CH_2CH_2O)_{n+1}H$. This aldehyde is not very stable, however, and further oxidation leads to a break-down of the polyoxyethylene chain with formaldehyde formed as one of many degradation products. Both the surfactant aldehyde and formaldehyde are irritating to the skin and eye.



An indirect way to monitor the autoxidation of alcohol ethoxylates is to measure the change in cloud point with time. Figure 2.5 shows an example of such a storage test. As can be seen from this figure, both of the surfactants investigated show a considerable drop in cloud point on storage at 40°C.

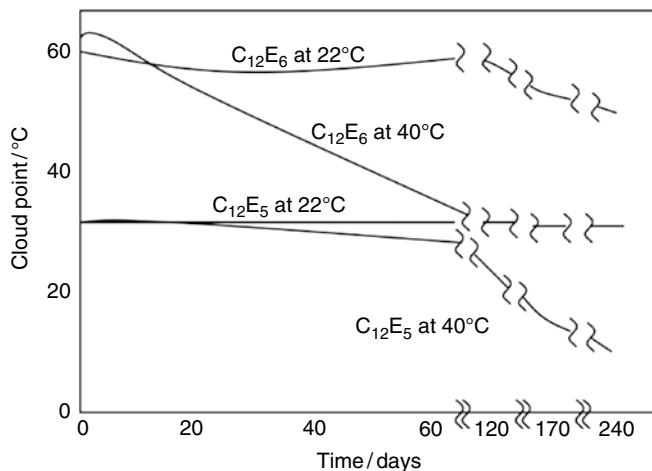


Figure 2.5 Cloud point versus time curves for the storage of 1% solutions of the surfactants $C_{12}E_5$ and $C_{12}E_6$, both "homologue pure", measured at two different temperatures. (With permission from Blute, I., Svensson, M., Holmberg, K., et al. (1999) Solution behavior of a surfactant aldehyde—the oxidation product of an alcohol ethoxylate. Colloids and Surfaces A, **150**, 105–113. Copyright Elsevier.)

Anionic surfactants are, in general, more skin irritating than nonionics. For instance, sodium dodecyl sulfate (SDS), although used in some personal care products such as toothpastes, has relatively high skin toxicity. Sodium alkyl ether sulfates are much milder than sodium alkyl sulfates, which is one of the reasons why the ether sulfates are the most commonly used anionic surfactant in hand dishwashing formulations. (Their good foaming ability is another reason for their widespread use in such products.) The better dermatological characteristics of alkyl ether sulfates when compared to alkyl sulfates is one of the main reasons for the interest in ethoxylates with narrow homologue distribution, that is, *peaked ethoxylates*, discussed on page 17. With a peaked ethoxylate as the intermediate to be sulfated, the content of the more aggressive alkyl sulfate will be considerably lower than when a standard ethoxylate with a broad homologue distribution is used.

The effect of surfactants on the skin is often evaluated in the so-called Modified Duhring Chamber test. Figure 2.6 shows typical results for a sodium alkyl ether sulfate (sodium laureth sulfate), an alkyl glucoside (decyl glucoside), and combinations of the two. As can be seen, the skin irritation decreases linearly with an increasing amount of polyol surfactant. In other cases already small additions of a mild surfactant may cause very large improvements in dermatological properties. Such a *synergistic effect* is probably related to a strong reduction in CMC of the formulation due to mixed micelle formation. Some amphoteric surfactants, such as betaines, are known to give very pronounced reduction of the skin irritation of anionics such as alkyl ether sulfates. This is probably due to protonation of the carboxyl group of the betaine surfactant, transforming it into a cationic surfactant, and subsequent packing into mixed micelles together with the anionic surfactant. Thus, the energy gain in the mixed micelle formation (Chapter 13) induces protonation of the carboxylate group of the betaine surfactant already at a pH level far above the pK_a value.

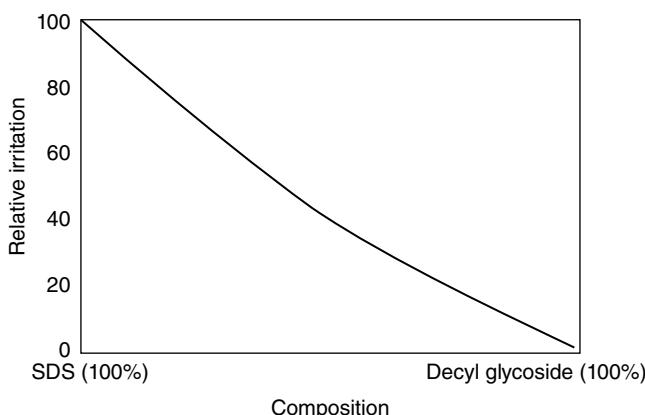


Figure 2.6 Modified Duhring Chamber test with relative irritation scores for erythema formation. (With permission from Tesmann, H., Kahre, J., Hensen, H. and Salka, B.A. (1997) Alkyl polyglycosides in personal care products, in Alkyl Polyglycosides: Technology, Properties and Applications (eds K. Hill, W. von Rybinski and G. Stoll), Wiley-VCH, Weinheim, pp. 71–98. Copyright 1997, Wiley-VCH.)

REACH

The surfactants and detergents industries have been under intense environmental scrutiny since the 1960s due to the problems caused by poor biodegradation of surfactants in wastewater treatment plants discussed above. Europe, in particular, has always been at the forefront of environmental legislation and the safety of detergents.

The detergents industry has been among the most proactive in dealing with the new legislation. In 1999 a collaboration was established between the International Association for Soaps, Detergents and Maintenance products (AISE) and the European Chemical Industry Council (CEFIC). This partnership known as HERA was intended to carry out *Human and Environmental Risk Assessments* on all the ingredients used in household cleaning products. The data from the HERA efforts were to a large extent proprietary and not publically available, however. The European Union wanted a more extensive risk assessment than HERA had provided; the assessment should cover all chemicals not only surfactants and, not least, the data should be publicly available. Those ambitions lead to an intense debate between environmentalists and industry and eventually, after many compromises, resulted in REACH.

REACH stands for Registration, Evaluation, Authorization and Restriction of Chemicals. It is a European Union regulation from December 2006. REACH addresses the production and use of chemicals in general, not only surfactants, and deals with their potential impact on both human health and the environment. REACH has been described as the most complex legislation in the European Union's history. It is the strictest law to date regulating chemical substances and it affects industries throughout the world. REACH entered into force in June 2007, with a phased implementation over one decade. When REACH is fully in force, it will require all companies manufacturing chemicals in the European Union or importing chemical substances into the European Union in quantities of one tonne or more per year to register these substances with the European Chemicals Agency in Helsinki, Finland. The legislation also covers chemical substances that are contained in products, which means that companies from a wide range of businesses will be affected. From a surfactant perspective this means that REACH covers not only the production and import of the surface active substances but also covers laundry detergents, water-borne paints, bitumen emulsions, and so on. All types of formulations containing surfactants are subject to the legislation.

The industry was invited to preregister existing compounds and 143 000 chemical substances marketed in Europe were preregistered by the December 2008 deadline. The full registration is a long process and the European Chemicals Agency initially set three major deadlines for the process, with priority given by tonnage manufactured or imported. The deadlines are 1 December 2010, 1 June 2013 and 1 June 2018 for annual volumes exceeding 1000, 100 and 1 tonne, respectively. The procedure is illustrated by Figure 2.7. Registration is mandatory both for production and for import of chemicals and products containing chemicals (such as formulations). In the language of REACH: *no registration—no market*.

In order to simplify the registration and, not least, in order to minimize the animal testing procedures, so-called Substance Information Exchange Forums (SIEFs) have been formed among companies producing the same chemicals. The companies are encouraged to join forces and share the cost and effort of creating a registration dossier. This means that the producers of specific chemicals, such as surfactants, carry out the registration work as a joint effort.

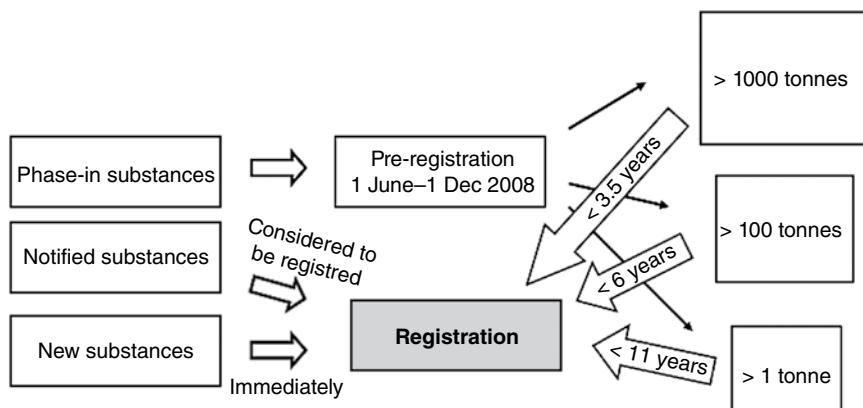


Figure 2.7 Schematic of the registration procedure within REACH

Surfactants are different from many other chemicals in that they are usually not well defined. As an example, laureth-2 sulfate, a commonly used surfactant in liquid cleaning formulations, is formally $C_{12}H_{25}-\left(OCH_2CH_2\right)_2-OSO_3^- Na^+$. In reality the product consists of a blend of a large number of different molecules. The hydrophobic tail will be a mixture of C_{10} , C_{12} and C_{14} homologues, and will probably also contain detectable amounts of C_{16} species as well. The number of oxyethylene groups may formally be two but the product will contain species with no oxyethylene units up to at least five or six oxyethylene units. There will be a small, but detectable amount of nonsulfated molecules, that is, nonionic amphiphiles. It is, of course, not possible to register all these components individually. The way this is being handled is that surfactants are registered by classes. Alkyl ether sulfates is one such class and laureth-2 sulfate is a member of that class. Thus, the producers of alkyl ether sulfates take on the joint effort of creating the registration dossier for this surfactant class.

The same applies for other surfactant classes but there is one important exception. Polymers are exempt from the REACH registration. Polymers, according to the REACH terminology, are substances that contain four or more repeating units. This means that polymeric surfactants, also called surface active polymers, are not subject to REACH registration. It also means that the vast majority of nonionic surfactants are exempt. For instance, within the largest class of nonionics, the fatty alcohol ethoxylates, more than 95% of the surfactants contain four or more oxyethylene units. (However, the producers of fatty alcohol ethoxylates must still register the use of the reactants, fatty alcohol and ethylene oxide.)

In the United States the Toxic Substances Control Act (TSCA) from 1976 provides the Environmental Protection Agency (EPA) with authority to require testing and reporting of surfactants and many other chemicals. The TSCA also requires US manufacturers and importers of chemicals to notify the EPA after obtaining information about potential risks of injury to health or the environment of any of their products. There are, however, major differences between REACH and TSCA in that the legislation in REACH is proactive—no registration, no market—and the test results are made publicly available. It is likely that the United States, as well as many other countries outside Europe, will eventually adjust their environmental legislation in the direction of REACH's policy.

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3

Two Fundamental Forces in Surface and Colloid Chemistry

Two fundamental forces in surface and colloid chemistry are highlighted in this chapter. They are the electrostatic interaction and the hydrophobic effect. The electrostatic interaction is essential because it influences most of the processes where ions are involved. It is important to have an understanding of the basic physical chemistry related to this interaction; the first part of the chapter is devoted to this topic. The second part of this chapter deals with the hydrophobic effect, which is of major importance for the self-assembly of all types of surfactants and polymers in bulk and at interfaces and for the solubility of most types of organic substances in water.

Counterion Binding Affects Self-Assembly and Adsorption of Surfactants and Polymers

A charged surface in water needs to be surrounded by counterions in order to attain electroneutrality. Hence, micelles with ionic surfactants, polyelectrolytes, or any charged surface, are always in equilibrium with a solution that contains the counterions. The counterions are not free to move around in the solution and this immobilization is termed counterion binding. If only energy governed the counterions would be located just adjacent to the charges of the surface, as illustrated in Figure 3.1a. This is not optimal, however, since it corresponds to low entropy. Maximum entropy would be achieved in a situation illustrated in Figure 3.1b, where all counterions are evenly spread out in the solution. In reality, the situation is found to be somewhere in between these two extremes, as illustrated in Figure 3.1c. This diffuse layer of counterions is termed the double layer. Hence, there is an electrostatic force trying to tie the counterions to the surface and there

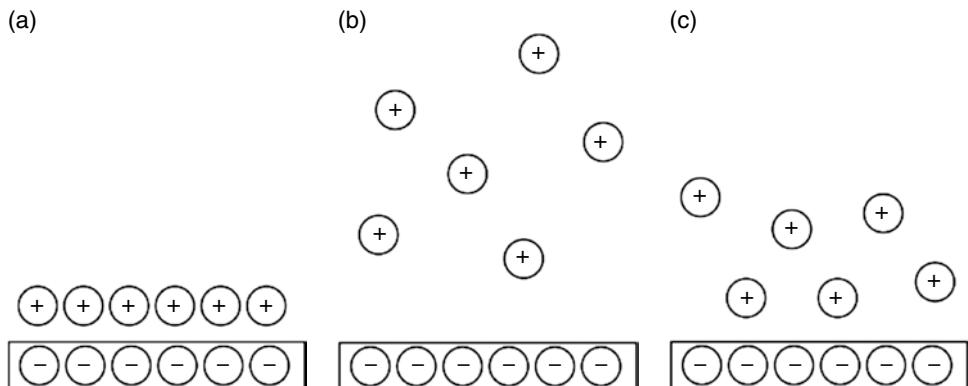


Figure 3.1 Distribution of counterions above a surface or a charged polymer: (a) when only energy governs; (b) when only entropy governs; and (c) for a combination of (a) and (b), i.e. when the free energy governs

is an entropic force trying to disperse the counterions in the surrounding solution. In cases where the counterions have high affinity to the surface, *high counterion binding*, the system is more towards the situation shown in Figure 3.1a. For ions showing lower affinity for the surface, that is, more towards the situation in Figure 3.1b, it is said to be *low counterion binding*.

When the surface charge increases, then the electrostatic force acting on the counterions increases and, hence, the counterion binding is increased. Therefore, the entropy of the counterions decreases on increasing the surface charge density (Figure 3.2). In the following sections the implications of this on (i) surfactant micellization, (ii) surfactant adsorption at hydrophobic surfaces, (iii) polyelectrolytes in solution, and (iv) colloidal stability are discussed.

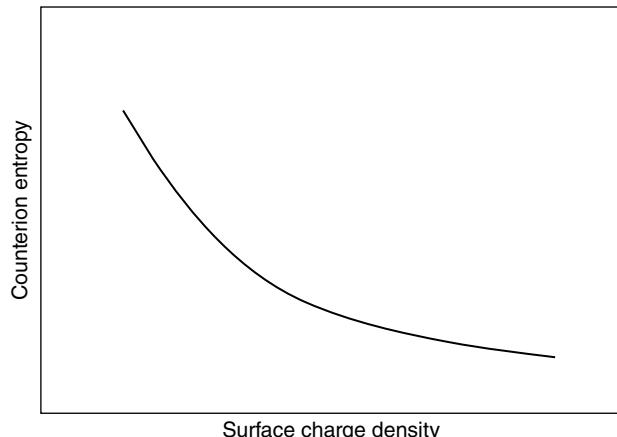


Figure 3.2 When the surface charge density increases the counterion binding also increases; this, in turn, decreases the entropy of the counterions

High affinity of the counterions for the surface is driven by a strong interaction of the ions with the surface. The distribution of counterions can be calculated from the Poisson–Boltzmann equation, which takes the two opposing forces, electrostatic attraction and entropy, into account.

In addition to this simple electrostatic interaction there may be other interactions affecting the ion distribution, mainly dispersion forces, correlated with the polarizability of the ions, and hydrophobic interactions for less polar counterions.

Micelle Formation and Interaction of Micelles

Consider the micellization of an ionic surfactant in two steps. The first step is micelle formation of the ionic surfactant without the counterions, i.e. self-assembly of the surfactant ions. In this step a highly charged surface is formed and there will be some Coulombic repulsion between the surfactant head groups. In the second step the counterions are associated with the surface of the micelle in a diffuse layer, as depicted in Figure 3.1c. This step lowers the entropy and hence counteracts the micelle formation.

The surface of the micelle is of high charge and hence there is a considerable counterion binding, resulting in low entropy (Figure 3.2). Micellization is therefore opposed by the counterion binding to the micelle. It is not primarily the lateral repulsion between the surfactant head groups that opposes the micelle formation but rather the counterion binding. This is the reason why ionic surfactants have a much higher critical micelle concentration (CMC) compared to nonionic surfactants (of the order of 100 times).

Adding a medium-chain alcohol (or a nonionic surfactant) to such systems results in a decrease of the CMC. The reason is that the added molecules decrease the surface charge density and, hence, the counterion binding is decreased, resulting in higher entropy of the counterions (Figure 3.2). Thus, the effect obtained by adding a medium-chain alcohol is not to shield the lateral repulsion between the surfactant head groups but rather to decrease the surface charge density, which in turn lowers the counterion binding.

Similarly, when adding a surfactant of opposite charge the CMC is drastically decreased. The surface charge is reduced and counterions are freed from the micelle. Thus, the lowering of the CMC with a surfactant of opposite charge is not an effect of complex formation between the surfactants but rather a result of the release of counterions from the micelle surface.

Micelle formation in the presence of an oppositely charged polyelectrolyte or at an oppositely charged surface are two further examples where the entropy of the counterions is a dominant factor. In the first case, the polymer facilitates the formation of micelles, as the polymer replaces the small counterions of the micelle and at the same time the micelle replaces the counterions of the polymer. This implies that the formation of micelles is facilitated resulting in a lower CMC. Thus, the interaction between a micelle and a polyelectrolyte of opposite charge is not mainly due to an electrostatic attraction but is driven by the release of bound counterions from both the polymer and the micelle.

Also, in the second case, that is, formation of micelles at an oppositely charged surface, the process is dominated by the entropy of the counterions (Chapter 8). Here, too, the driving force is the release of counterions, from both the surface and the micelle.

A diagnostic tool for this phenomenon is to add salt. Salt present in the bulk solution reduces the entropy penalty due to the binding of the counterions, since the difference

between the interfacial and bulk ion concentrations will be reduced. Hence, all the phenomena described above are influenced by an increase in ionic strength. Salt addition will decrease the CMC as the salt will swamp the bound counterions. Hence, the surfactant will behave more like a nonionic surfactant. The consequence is that it is more favorable to form a micelle, leading to a lowering of the CMC. Similarly, the drastic decrease in CMC on adding a surfactant of opposite charge will be hampered by salt, since the gain in entropy due to the freeing of counterions is now smaller. The association of micelles with polymers or surfaces of opposite charge will also be hampered as there is less gain in entropy when salt is present.

An important consequence of the discussion above is that addition of salt will increase the critical packing parameter (CPP) of the surfactant (Equation 6.2 provides a definition of the CPP). Adding salt will decrease the entropy loss from the counterion binding (due to the swamping effect of the salt), allowing a closer packing of the surfactant molecules in the micelle. This results in a lower effective cross-sectional area per surfactant head group. Hence, the CPP increases on salt addition. The surfactant aggregates therefore change shape on addition of salt going from spherical towards elongated micelles and further on to lamellar aggregates. Thus, it is not a screening of the electrostatic head group repulsion that changes the aggregate shape in solution but rather a regulation of the surface charge density due to the loss of entropy of the counterions when a surfactant aggregate is formed.

Adsorption of Surfactants at Nonpolar Surfaces

The process of adsorption of ionic surfactants at hydrophobic solid surfaces, or at the liquid/air interface, is very much akin to the process of micelle formation. The driving force for adsorption is the hydrophobic effect, that is, the transfer of the surfactant hydrocarbon part from an aqueous environment to the apolar environment in the adsorbed layer (Figure 8.2). The transfer of a surfactant molecule from the aqueous environment to the surface is also accompanied by the attraction of its counterion to the surface. In the bulk solution the surfactant is totally dissociated, hence the counterions lose entropy on adsorption of a surfactant molecule. This entropy loss is higher the larger the surface charge density. The surface charge density increases as the adsorption progresses, thus the counterion binding increases with the adsorption leading to a gradual lowering of the counterion entropy (Figure 3.2). Hence, the adsorption is counteracted by an increasing counterion binding.

The adsorption reaches a limiting value when the entropic contribution from the counterions balances the contribution from the hydrophobic effect. As discussed in Chapter 8, the limiting adsorption of ionic surfactants is not determined by packing constraints at the surface but rather by this balance between the entropic contribution from the counterions (counteracting adsorption) and the energetic contribution from the surfactant ion (promoting adsorption).

Also, in such systems adding salt is a good diagnostic tool for elucidating the forces at play. Addition of salt will decrease the entropy loss on adsorption and, consequently, increase the adsorption of an ionic surfactant at a hydrophobic surface. Therefore, the adsorption reaches a limiting value at higher surface charge, that is, at higher adsorbed amount, when salt is present (Figure 8.5). The reason lies in the fact that the entropy penalty of counterion binding is now smaller due to the presence of extra ions in the bulk solution.

Also in this case, the addition of salt increases the CPP of the surfactant. The surface area per surfactant head group decreases, giving a higher CPP (Equation 6.2).

Polymer Systems

The effect of counterions is also evident in polymer solutions. Charging a neutral polymer, for example, drastically increases its solubility. This is due to the counterions that are, at least partially, released from the polymer and, hence, greatly contribute to the entropy of the system. The degree of expansion of a polyelectrolyte increases with the degree of ionization. The conventional view is that the expansion of a polyelectrolyte is due to repulsion between the ionized groups. It is, however, more correct to discuss in terms of entropy of the counterions and the effect of the charge density of the polymer. This can be understood from Figure 3.2 where the x -axis now represents the charge density of the polymer. Hence, if the polymer at a certain degree of ionization expands, the charge density will become lower (going to the left in the diagram). Then there is a lower degree of counterion binding and, hence, a higher entropy. This expansion is counteracted by a lowering in entropy of the polymer chain itself (due to a smaller number of available conformations) and, therefore, a balance between the two contributions is obtained. Again, addition of salt is a powerful diagnostic tool for assessing the importance of counterions. Addition of salt reduces the solubility of a polyelectrolyte because the entropy gain of releasing counterions is smaller when there already are ions in the aqueous phase.

The formation of complexes between two oppositely charged polyelectrolytes, or between a polyelectrolyte and an oppositely charged micelle, are further examples of the role of the counterions. The driving force for complex formation is the freeing of the counterions from both the polyelectrolytes and the micelles. Note that it is not a simple electrostatic driving force, as the electrostatic interactions are already present before the complex is formed, that is, between the polyelectrolyte/micelle and the counterions. Adding salt to such a system simply lowers the driving force of complex formation and at one point the complex will dissolve (provided that the polyelectrolyte is soluble in the salt solution).

A similar situation occurs when a polyelectrolyte adsorbs to a surface of opposite charge. Here, also, the driving force is due to the freeing of bound counterions, both from the surface and from the polymer. Adding salt has the effect of decreasing the adsorbed amount (Figure 11.9 and Figure 11.11).

Finally, the strong swelling of polyelectrolyte gels compared to uncharged gels originates from the entropic contribution from the counterions. Here, too, addition of salt counteracts the swelling. This phenomenon can be illustrated with the behavior of cross-linked polyacrylates, a type of hydrogel often referred to as *superabsorbent polymers* or SAPs and frequently used in diapers. A SAP can swell up to 1000 times its weight when exposed to distilled water. With salt present in the water, as is the case for urine, the swelling capacity may be reduced by a factor of 10 or more.

In all the examples discussed above, both in the surfactant and the polymer systems, an increase of the valency of the counterions will have a drastic effect. For example, micelle formation occurs at a much lower concentration with divalent than with monovalent counterions. The higher the valency of the counterion, the fewer ions are needed for charge neutralization, which means that the entropy penalty of counterion binding will be lower, rendering a lower CMC.

Colloidal Stability

One of the two main routes to stabilize a colloid is to provide charges at the particle surface (Chapter 18). This is termed *electrostatic stabilization*. The basic physics is the creation of an osmotic barrier with the aid of the counterions. As mentioned previously, a charged particle has counterions close to the surface (Figure 3.1c) and when two such particles approach each other the counterion concentration will be high between the particles where the two double layers overlap (Figure 18.5a). This locally high counterion concentration between the particles causes the surrounding water to diffuse into the region between the particles, attempting to separate them. Therefore, the driving force for electrostatic stabilization of a dispersion is the osmotic force of water, which seeks to dilute this region where there is a high concentration of counterions.

It is now easy to understand that the addition of salt will make such a colloidal dispersion unstable. Upon adding salt there will be a lower concentration gradient between the region between the particles and the bulk solution. Hence, the osmotic force, that is, the driving force for water molecules to enter this region, is reduced.

The presence of di- or trivalent ions will lower the osmotic suction force because there will be fewer ions between the approaching particles, which means that the concentration gradient of ions between the area between the particles and the bulk will be smaller. This leads to a much reduced colloidal stability. In fact, high valency salts, such as FeCl_3 , are commonly used as flocculants.

The Hydrophobic Effect is due to the High Energy Density of Water

The molecular mechanism of the hydrophobic effect has been a source of great controversy. It is generally accepted that introducing a hydrocarbon into water is associated with structuring, or ordering, of water in the vicinity of the hydrocarbon. This ordering causes a decrease in the entropy. Experimentally it has been found that the enthalpy change upon transferring a hydrocarbon from a hydrocarbon environment into water is negligible. Hence, there is a large and positive free energy change when a hydrocarbon is introduced into water according to:

$$\Delta G(\text{large}) = \Delta H(\text{small}) - T\Delta S(\text{large and negative}) \quad (3.1)$$

This large and positive free energy change leads to low solubility of the hydrocarbon in water.

The simplest model, now abandoned, states that Equation 3.1 is solely due to the structuring of water around the hydrophobe. The problem with this model is that it does not consider the temperature dependence. Structuring should be strongly temperature dependent, since order is broken up on heating. An ordering, that is, a decrease in entropy, is associated with a change in the heat capacity (ΔC_p) according to:

$$\frac{d\Delta S}{dT} = -\frac{\Delta C_p}{T}. \quad (3.2)$$

Therefore, the process of transferring a hydrocarbon from a hydrocarbon environment into water should be associated with a significant change in heat capacity. Since $\Delta C_p = dH/dT$, it

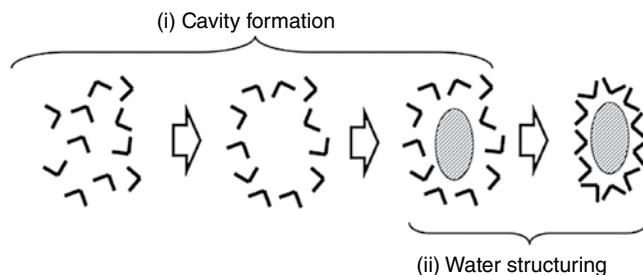


Figure 3.3 An attempt to illustrate the two contributions in the transfer of a hydrocarbon into water. The cavity formation contribution is the creation of a cavity in the water and insertion of the hydrocarbon molecule into the cavity. The water structuring contribution is a relaxation of the water molecules around the hydrocarbon into a more ordered state. The same principles apply to any hydrocarbon moiety, for instance the hydrocarbon tail of a surfactant

can be realized that the enthalpy term in Equation 3.1 must also be strongly temperature dependent. Therefore, this term cannot be ignored and it is only by coincidence that it is around zero at room temperature.

According to a more modern view, the transfer of a hydrocarbon molecule or moiety into water is associated with two contributions, namely (i) cavity formation in the water in order to accommodate the hydrophobe and (ii) structuring of water around the hydrophobe (Figure 3.3). As will be seen below it turns out that the latter favors mixing whilst the former is the source of the hydrophobic effect, giving low solubility of hydrocarbons in water.

- i. *Cavity formation requires large energy.* Transferring a hydrophobic molecule or moiety into water requires a cavity in the water in order to accommodate the hydrophobe. The formation of a cavity requires the breaking, or bending, of hydrogen bonds and this, in turn, is associated with a large and positive enthalpy. The entropy contribution to this process is negligible, hence the free energy of cavity formation is also large and positive. The cavity formation is the main cause of the low solubility of the hydrophobe in water and is the source of the hydrophobic effect. This is discussed in thermodynamic terms in the next section. The cavity formation contribution also involves the insertion of the hydrophobe into the water, hence there is also a contribution to the energy originating from the dispersion force between the hydrocarbon and the water molecules.
- ii. *Water structuring increases the solubility in water.* The structuring of water around a hydrophobe is associated with a large and negative entropy, which is accompanied by a large and negative enthalpy, resulting in a small and negative free energy. This is termed enthalpy–entropy compensation. As will be shown in the following section, any process where structure is built up, or destroyed, is associated with large entropy and enthalpy contributions resulting in a small free energy change. The free energy of water structuring is negative and is, therefore, a contribution that increases the solubility of a hydrocarbon in water, that is, it counteracts the hydrophobic effect.

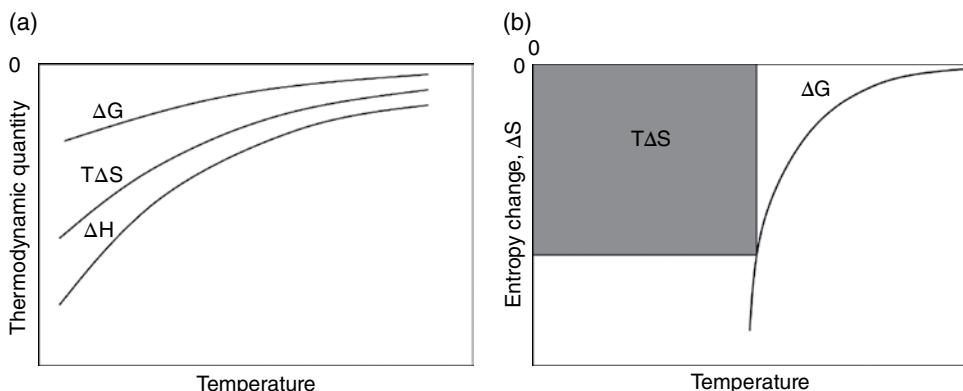


Figure 3.4 (a) Temperature dependence of the thermodynamic functions for a process where structuring is involved (b) and the entropy for the same process plotted versus the absolute temperature. (With permission from Patterson, D. and Barbe, M. (1976) Enthalpy-entropy compensation and order in alkane and aqueous systems. Journal of Physical Chemistry, **80**, 2435–2436. Copyright 1976, American Chemical Society.)

Ordering of the Water Leads to an Enthalpy–Entropy Compensation

To understand the hydrophobic effect it is helpful to consider the thermodynamics of the ordering of water. When introducing a hydrocarbon into water, the water molecules become ordered, hence the entropy decreases. This ordering, or entropy, is expected to decrease with temperature and eventually vanish at high temperatures. Figure 3.4b illustrates that the entropy effect decreases rapidly when the temperature is put on an absolute scale. The area under the ΔS curve is equal to ΔG according to:

$$\Delta G = \int_T^\infty \Delta S dT \quad (3.3)$$

The shaded area, that is, the rectangle in Figure 3.4b, is equal to $T\Delta S$. Hence, the enthalpy of transferring the hydrocarbon is equal to the total area, that is:

$$\Delta H = T\Delta S + \Delta G \quad (3.4)$$

From the relative areas in Figure 3.4b this gives, for the structuring of water when transferring a hydrocarbon from a hydrocarbon environment into water, the following picture: $T\Delta S$ large and negative, ΔH large and negative, and ΔG small and negative, all quantities decreasing rapidly with temperature (Figure 3.4a).

Comparing with experimental results, however, the enthalpy differs by a constant value, independent of temperature (Figure 3.5). This discrepancy is attributed to the energy required to form a cavity in the water in order to accommodate the hydrocarbon.

The fascinating conclusion is, therefore, that the structuring of water around a hydrophobe *increases* its solubility. The source of the poor solubility of hydrocarbons in water lies in the creation of a cavity in order to accommodate the hydrophobe. The creation of a cavity requires a large and positive enthalpy that is independent on temperature (Figure 3.5b).

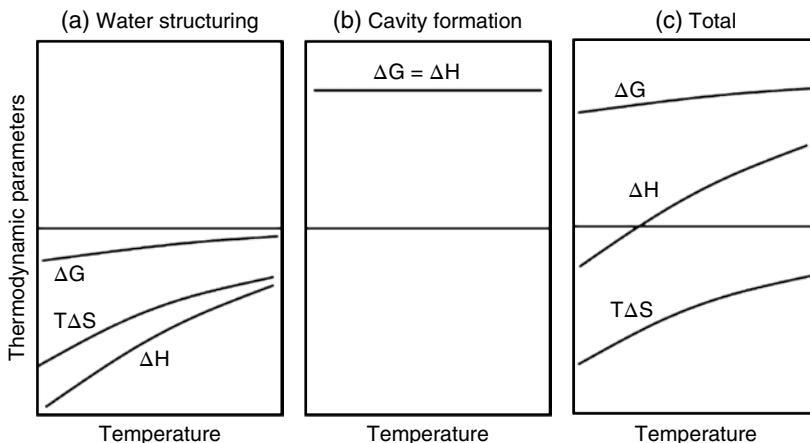


Figure 3.5 Schematic drawing of the thermodynamic parameters $T\Delta S$, ΔH , and ΔG for the transfer of a hydrophobic molecule from a nonpolar environment into water; (a) contribution due to water structuring, (b) contribution due to cavity formation in water, and (c) the sum of the two contributions, which corresponds to experimental results. Note that in (c) the enthalpy contribution is around zero at room temperature, which is the situation illustrated by Equation 3.1

Notice that this enthalpy of cavity formation is the same, irrespective of whether or not the molecule is a hydrophobe. For hydrophilic molecules, however, energy is regained because there are possibilities for the inserted molecule to interact with the water, by, for example, hydrogen bonding or dipole–dipole interaction, hence lowering ΔH . This ability to lower the energy is much less for hydrophobic molecules, giving rise to the poor interaction with water, with low solubility as a consequence. This is the mechanism behind the hydrophobic effect.

The Solubility of Hydrocarbons Increases due to Water Structuring

Shinoda first showed that the free energy of water structuring around a hydrophobic molecule is negative and, therefore, contributes to an increased solubility of hydrocarbons in water, that is, it counteracts the hydrophobic effect. The solubility (x) of a compound in water is equivalent to the transfer of that compound from its (almost) pure state to the water. Plotting the aqueous solubility (as the logarithm, $\ln x$) of a compound versus $1/T$ should give a straight line since:

$$\frac{\Delta G}{T} = -R \ln x = \frac{\Delta H}{T} - \Delta S \quad (3.5)$$

Here the slope of the straight line gives us the ΔH , that is, the enthalpy associated with transferring the compound into water. Shinoda showed that the solubility of hydrocarbons in water increases due to the formation of water structure around the hydrophobe (Figure 3.6). At very high temperatures (above about 180°C), the experimental solubility follows the expected straight line. At lower temperatures, however, there is a marked deviation from the straight line as shown in the figure. This deviation is due to the structuring of water around the hydrophobe. As seen in the diagram, the deviation is such that it increases the

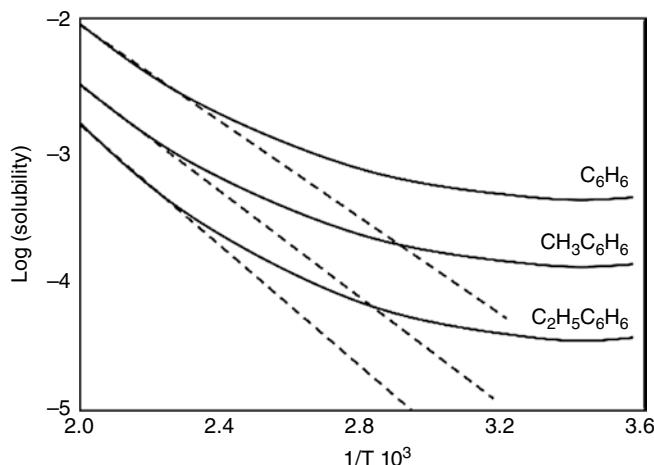


Figure 3.6 The solubility of some hydrocarbons in water as a function of $1/T$, illustrating that only at high temperatures one obtains the expected straight line according to Equation 3.5. At lower temperatures the structuring of water increases the solubility (going from the dashed lines to the solid lines). (With permission from Shinoda,K. (1992) Characteristic property in aqueous solutions: Effect of iceberg formation of water surrounding solute on the solubility (or CMC) and its peculiar temperature dependence. Advances in Colloid and Interface Science, **41**, 81–100. Copyright Elsevier.)

solubility, which is contrary to the earlier conception of water structuring being the cause of the hydrophobic effect. Note that the slope of the experimental line gives the enthalpy of transfer. Hence, at room temperature the enthalpy of transfer is near zero as given by Equation 3.5 and as indicated in Figure 3.5c.

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4

Surfactant Self-Assembly: General Aspects and Spherical Micelles

Amphiphilic Molecules Self-Assemble

As described in Chapter 1, surfactant molecules are amphiphilic, that is, possess both hydrophilic and hydrophobic parts. The amphiphilicity drives in any aqueous system self-assembly. This leads to a range of different structures, a few of which are shown in Figure 4.1.

Systems containing amphiphiles are best classified into homogeneous, or single-phase, systems and heterogeneous systems of two or more phases. The single-phase systems can, in turn, be divided into isotropic solutions, solid phases, and liquid crystalline phases. The solid crystalline phases have, as crystals in general, both long-range and short-range order, but the degree of short-range order varies between different phases. Isotropic solution phases are characterized by disorder over both short and long distances, whereas liquid crystalline phases or mesophases have a short-range disorder but some distinct order over larger distances. In both isotropic solutions and liquid crystals the state of the amphiphile alkyl chains can be denoted as “liquid like.” In crystals formed below the “chain melting temperature” the state is more or less “solid like.” The more important amphiphile systems can be arranged as shown in Table 4.1

Here we stress the difference between homogeneous and heterogeneous systems, the former having a single phase, whereas the latter contain two or more phases; in this case one phase can be dispersed in another forming a dispersion. A well-known example is emulsions, which are dispersions of oil in water. Dispersions are, in contrast to the homogeneous phases, not at equilibrium and always have the tendency to separate into the constituent phases with time. The distinction is made between phases, which are thermodynamically stable, and dispersions, which are kinetically stable.

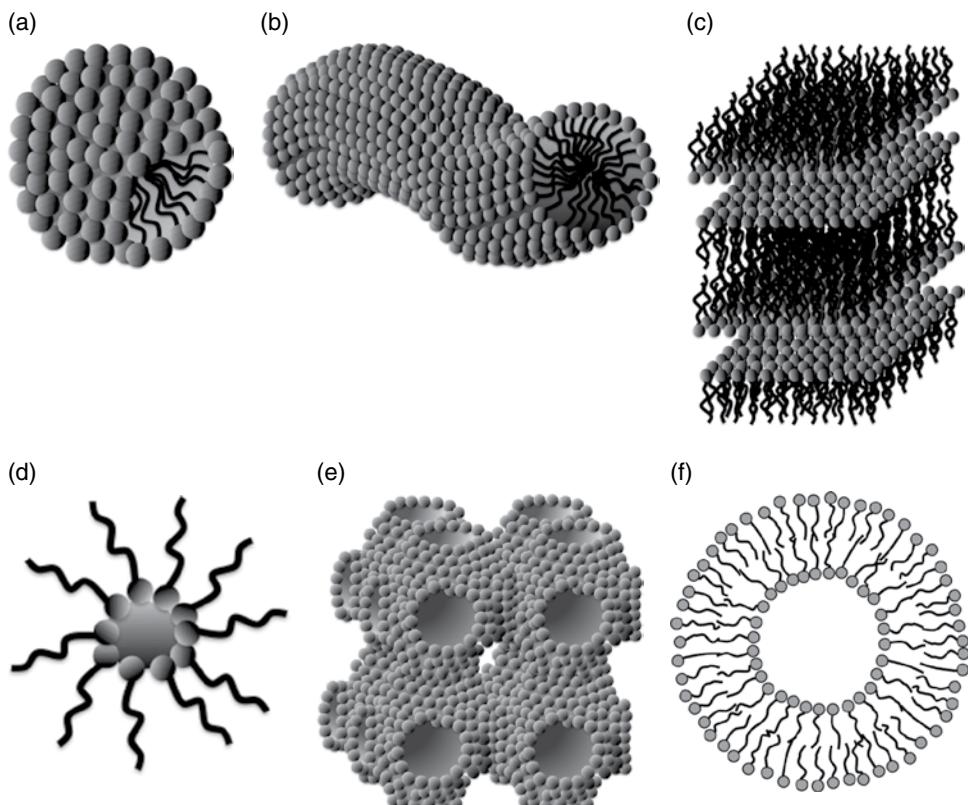


Figure 4.1 Surfactant self-assembly leads to a range of different structures, of which a few are shown. (a) Spherical micelles with an interior composed of the hydrocarbon chains and a surface of polar head groups (pictured as spheres) facing water. Spherical micelles are characterized by a low surfactant number (CPP) and a strongly positive spontaneous curvature. The hydrocarbon core has a radius close to the length of the extended alkyl chain. (b) Cylindrical micelles with an interior composed of the hydrocarbon chains and a surface of the polar head groups facing water. The cross-section of the hydrocarbon core is similar to that of spherical micelles. The micellar length is highly variable, so these micelles are polydisperse. (c) Surfactant bilayers which build up lamellar liquid crystals have a hydrocarbon core with a thickness of about 80% of the length of two extended alkyl chains. (d) Reversed or inverted micelles have a water core surrounded by the polar head groups. The alkyl chains together with the organic solvent make up the continuous medium. Like “normal” micelles they can grow into worm-like micelles. (e) A bicontinuous structure with the surfactant molecules aggregated into connected films characterized by two curvatures of opposite sign. The mean curvature is small (zero for minimal surface structures). (f) Vesicles are built from bilayers similar to those of the lamellar phase and are characterized by two distinct water compartments, one forming the core and one the continuous medium. Vesicles may have different shapes and there may also be reversed vesicles

Table 4.1 Different surfactant systems

a) Thermodynamically stable phases		
Short-range disorder	Short-range disorder	Short-range order
Long-range disorder	Long-range order	Long-range order
<i>Isotropic solutions</i>	<i>Liquid crystals</i>	<i>Solid crystals</i>
Micellar solutions (dilute, concentrated)	Lamellar Hexagonal Cubic (several) Others (several)	Classical crystals “Gels”
Reversed micellar		
Microemulsions		
Vesicle solutions		
b) Thermodynamically unstable phases		
	Emulsions Suspensions Vesicles Liposomes Foams	

Amphiphilic properties have a much broader significance than only surfactant systems. Polar lipids behave very much in the same ways as surfactants, as do block copolymers. Other amphiphilic polymers, like graft copolymers, show a distinctly different self-assembly behavior. There are also several biomacromolecules with amphiphilic character like many proteins and lipopolysaccharides. In some cases, the significance of amphiphilicity has been overlooked, as for DNA and cellulose. Thus, the formation of the DNA double helix and the aqueous insolubility of cellulose are due to the partial hydrophobic character of these biopolymers.

We will return to the different aggregate structures in Chapter 6 and to different dispersions in several chapters. Discussed now are the basic aspects of self-assemblies with the spherical micelle as example.

Surfactants Start to Form Micelles at the CMC

When measuring different physicochemical properties of an aqueous solution of a surfactant or lipid that is polar enough to be water soluble up to relatively high concentrations, many peculiarities are encountered, as exemplified in Figure 4.2 for an ionic surfactant.

At low concentrations, most properties are similar to those of a simple electrolyte. One notable exception is the surface tension, which decreases rapidly with surfactant concentration. At some higher concentration, which is different for different surfactants, unusual changes are recorded. For example, the surface tension, and also the osmotic pressure, take on an approximately constant value, while light scattering starts to increase and self-diffusion starts to decrease. All the observations suggest and are consistent with a change-over from a solution containing single surfactant molecules or ions, unimers, to a situation where the surfactant occurs more and more in a self-assembled or self-associated state. We will examine in detail the structures formed as well as the underlying mechanisms and will here only note two general features. The concentration for the onset of self-assembly

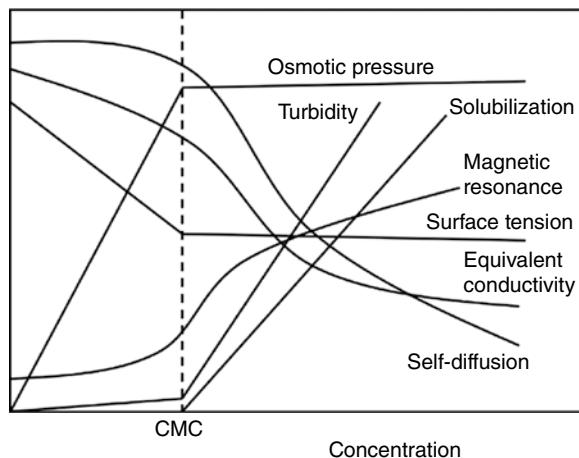


Figure 4.2 Schematic representation of the concentration dependence of some physical properties for solutions of a micelle-forming surfactant. (With permission from Lindman, B. and Wennerström, H. (1980) *Micelles. Amphiphile aggregation in aqueous solution*. Topics in Current Chemistry, **87**, 1–83. Copyright © 1980, Springer.)

is quite well defined and becomes more so the longer the alkyl chain of the surfactant. The first-formed aggregates are generally approximately spherical in shape. The aggregates are called micelles, and the concentration where they start to form is the critical micelle concentration, abbreviated CMC. An illustration of a micelle's structure is given in Figure 4.3.



Figure 4.3 An illustration of a spherical micelle (of dodecyl sulfate) emphasizing the liquid-like character with a disordered hydrocarbon core and a rough surface

The CMC is the single most important characteristic of a surfactant, useful *inter alia* in consideration of the practical uses of surfactants. We will now consider how different factors influence the CMC but will first make a note on how to measure it. The two most common and generally applicable techniques are surface tension and solubilization, the solubility of an otherwise insoluble compound. For an ionic amphiphile, the conductivity also offers a convenient approach to obtain the CMC. However, as a very large number of physicochemical properties are sensitive to surfactant micellization, there are numerous other possibilities, such as self-diffusion measurements and nuclear magnetic resonance (NMR) and fluorescence spectroscopy. As will be seen, CMC is not an exactly defined quantity, which causes difficulties in its determination. For long-chain amphiphiles, an accurate determination is straightforward and different techniques give the same results. However, for short-chain, weakly associating, amphiphiles this is not so and great care must be taken not only in the measurements but also in evaluating the CMC from experimental data.

CMC Depends on Chemical Structure

A list of CMC values of selected ionic surfactants at 25°C is given in Table 4.2.

In Table 4.3 CMC values for nonionic surfactants are given.

From these and other data, several general remarks about the variation of the CMC with the surfactant chemical structure can be made:

1. The CMC decreases strongly with increasing alkyl chain length of the surfactant (Figure 4.4 and Figure 4.5). As a general rule the CMC decreases by a factor of about two for ionics (without added salt) and by a factor of about three for nonionics on adding one methylene group to the alkyl chain. (This is sometimes referred to as Traube's rule.) Comparisons between different classes of surfactants are best made at a fixed number of carbons in the alkyl chain.
2. The CMCs of nonionics are much lower than for ionics. The relation depends on the alkyl chain length, but two orders of magnitude is a rough starting point.
3. Besides the major difference between ionics and nonionics, the effects of the head group are moderate. Cationics typically have slightly higher CMCs than anionics. For nonionics of the oxyethylene variety, there is a moderate increase of the CMC as the polar head becomes larger.
4. The valency of the counterion is significant. While simple monovalent inorganic counterions give approximately the same CMC, increasing the valency to two gives a reduction of the CMC by roughly a factor of four. Organic counterions reduce the CMC compared to inorganic ones, the more so the larger the nonpolar part.
5. While alkyl chain branching and double bonds, aromatic groups, or some other polar character in the hydrophobic part produce sizeable changes in the CMC, a dramatic lowering of the CMC (one or two orders of magnitude) results from perfluorination of the alkyl chain. Partial fluorination interestingly may increase the CMC; for example, fluorination of the terminal methyl group roughly doubles the CMC. The anomalous behavior of partially fluorinated surfactants is due to unfavorable interactions between hydrocarbon and fluorocarbon groups.

Table 4.2 CMC values of selected ionic surfactants

Surfactant	CMC/M
Dodecylammonium chloride	1.5×10^{-2}
Dodecytrimethylammonium chloride	2.0×10^{-2}
Decytrimethylammonium bromide	6.5×10^{-2}
Dodecytrimethylammonium bromide	1.6×10^{-2}
Hexadecyltrimethylammonium bromide	9.2×10^{-4}
Dodecylpyridinium chloride	1.5×10^{-2}
Sodium tetradecyl sulfate	2.1×10^{-3}
Sodium dodecyl sulfate	8.3×10^{-3}
Sodium decyl sulfate	3.3×10^{-2}
Sodium octyl sulfate	1.3×10^{-1}
Sodium octanoate	4.0×10^{-1}
Sodium nonanoate	2.1×10^{-1}
Sodium decanoate	1.1×10^{-1}
Sodium undecanoate	5.6×10^{-2}
Sodium dodecanoate	2.8×10^{-2}
Sodium <i>p</i> -octylbenzene sulfonate	1.5×10^{-2}
Sodium <i>p</i> -dodecylbenzene sulfonate	1.2×10^{-3}
Potassium perfluoroctanoate	2.9×10^{-2}

Table 4.3 CMC for nonionic surfactants

Surfactant	CMC/M
C_6E_3	1.0×10^{-1}
C_8E_4	8.5×10^{-3}
C_8E_5	9.2×10^{-3}
C_8E_6	9.9×10^{-3}
$C_{10}E_5$	9.0×10^{-4}
$C_{10}E_6$	9.5×10^{-4}
$C_{10}E_8$	1.0×10^{-3}
$C_{12}E_5$	6.5×10^{-5}
$C_{12}E_6$	6.8×10^{-5}
$C_{12}E_7$	6.9×10^{-5}
$C_{12}E_8$	7.1×10^{-5}
$C_8\phi E_9$	3.4×10^{-4}
$C_8\phi E_{10}$	3.4×10^{-4}
β -D- C_8 glucoside	2.5×10^{-2}
β -D- C_{10} glucoside	2.2×10^{-3}
β -D- C_{12} glucoside	1.9×10^{-4}

Oxyethylene surfactants are abbreviated as C_mE_n with m being the number of carbon atoms in the alkyl chain and n the number of oxyethylene groups.

ϕ denotes an aromatic group.

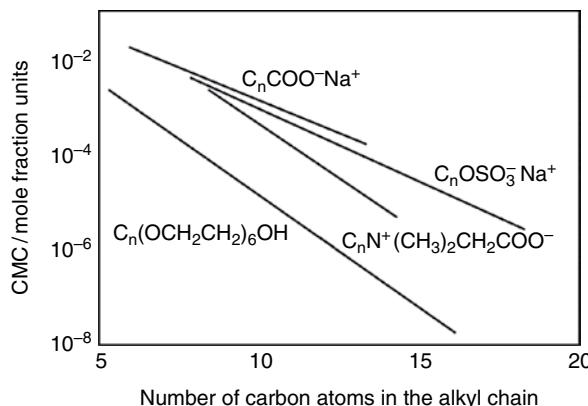


Figure 4.4 The logarithm of the CMC varies linearly with the number of carbon atoms in the alkyl chain of a surfactant. The slope is larger for nonionic and zwitterionic surfactants than for ionic surfactants (without added electrolyte). (With permission from Lindman, B. and Wennerström, H. (1980) *Micelles. Amphiphile aggregation in aqueous solution*. Topics in Current Chemistry, **87**, 1–83. Copyright © 1980, Springer.)

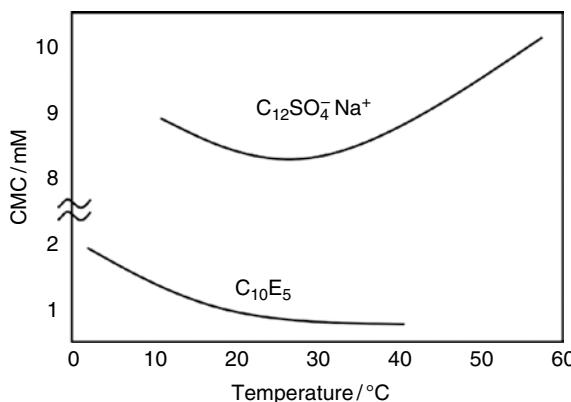


Figure 4.5 The temperature dependence of the CMC of an ionic and a nonionic surfactant

Temperature and Cosolutes Affect CMC

It is a characteristic feature of micellization of ionic surfactants that CMC is to a first approximation independent of temperature, as illustrated in Figure 4.5. The CMC varies in a nonmonotonic way by about 10–20% over a wide range. The shallow minimum around 25°C can be compared with a similar minimum in the solubility of hydrocarbons in water. Nonionic surfactants of the polyoxyethylene type deviate from this behavior and show typically a monotonic, and much more pronounced, decrease in CMC with increasing temperature. As is discussed in some detail in Chapter 7, this class of nonionics behaves differently from other surfactants with respect to temperature effects.

We turn next to the effect of cosolutes on the CMC, which is an important and broad issue that we will come back to repeatedly. An especially important matter is the effect of

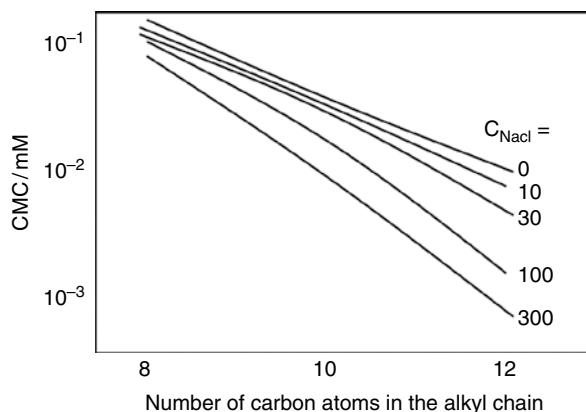


Figure 4.6 Effect of sodium chloride addition (in mM) on the CMC of different sodium alkyl sulfates; predictions from electrostatic theory (Poisson–Boltzmann equation) give the same values as experiments. (Adapted with permission from Gunnarsson, G., Jönsson, B. and Wennerström, H. (1980) Surfactant association into micelles. An electrostatic approach. *Journal of Physical Chemistry*, **84**, 3114–3121. Copyright 1980, American Chemical Society.)

added electrolyte on the CMC of ionics. This is illustrated in Figure 4.6 for the simplest and generally most important case of adding a 1:1 inert electrolyte to a solution of a monovalent surfactant.

The following features are noted:

1. Salt addition gives a dramatic lowering of the CMC, which may amount to an order of magnitude.
2. The effect is moderate for short-chain surfactants but is much larger for long-chain ones.
3. As a consequence, at high salt concentrations the variation of CMC with the number of carbons in the alkyl chain is much stronger than without added salt. The rate of change at high salt concentrations becomes similar to that of nonionics.
4. The salt effects (like many other aspects of ionic surfactant self-assembly) can be quantitatively reproduced from a simple model of electrostatic interactions, the Poisson–Boltzmann equation. An intuitive account of this was presented in Chapter 3.

It can be further added that:

5. The effect of added salt depends strongly on the valency of added ions of the same charge as the surfactant counterion.
6. For nonionics, simple salts produce only small variations in CMC with both increases and decreases possible.

Other lower molecular weight cosolutes produce changes in the CMC to a very different extent depending on polarity of the cosolute. Both increases and decreases in the CMC are possible. Small or moderate increases may result from the addition of highly water-soluble compounds, such as urea and ethanol, the reason being that water is the most effective solvent for surfactant self-assembly. (Urea is well known for decreasing hydrophobic

interactions, a familiar example being the denaturation of proteins.) More common and more interesting are the decreases in CMC observed for many uncharged cosolutes. The effect depends on cosolute polarity and on any amphiphilic character it may have. The addition of simple alcohols with a longer alkyl chain give a significant reduction of the CMC. The alcohols are less polar than water and are distributed between the bulk solution and the micelles. The more preference they have for the micelles, the more they stabilize them. The alcohol will act basically as any added nonionic amphiphile, like a nonionic surfactant, in lowering the CMC (cf. Chapter 13).

The Solubility of Surfactants may be Strongly Temperature Dependent

There are many important and intriguing temperature effects in surfactant self-assembly. One, which is of great practical significance, is the dramatic temperature-dependent solubility displayed notably by many ionic surfactants. The solubility may be very low at low temperatures and then increase by orders of magnitude in a relatively narrow temperature range. The phenomenon is generally denoted as the Krafft phenomenon and the temperature for the onset of the strongly increasing solubility the Krafft point or Krafft temperature. The temperature dependence of surfactant solubility in the region of the Krafft point is illustrated in Figure 4.7.

The Krafft point may vary dramatically with subtle changes in the surfactant chemical structure but some general remarks can be made for alkyl chain surfactants:

1. The Krafft point increases strongly as the alkyl chain length increases. The increase is not regular but displays an odd–even effect as the number of carbons varies.

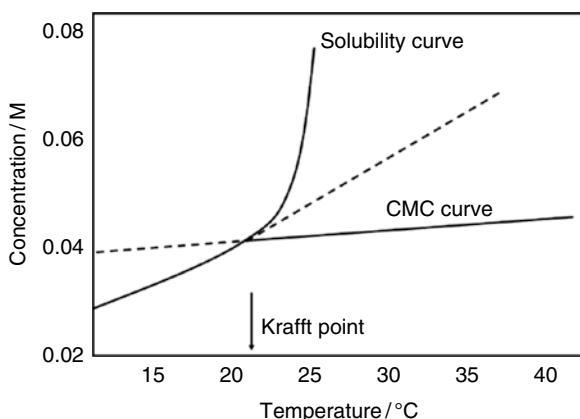


Figure 4.7 Temperature dependence of surfactant solubility in the region of the Krafft point; the dashed lines give the expected extrapolations of the CMC and unimer solubility curves. (Adapted from Shinoda, K., Nakagawa, T., Tamamushi, B.-I. and Isemura, T. (1963) Colloidal Surfactants, Some Physicochemical Properties, Academic Press, London. With permission from Elsevier.)

2. The Krafft point is strongly dependent on the head group and the counterion. Salt addition typically raises the Krafft point, while many other cosolutes decrease it. There are no general trends for the counterion dependence. Thus, for example, for alkali alkanoates the Krafft point increases as the atomic number of the counterion decreases, while the opposite trend is observed for alkali sulfates and sulfonates. Problems with high Krafft points are common also for cationic surfactants. For such surfactants, the Krafft point is typically higher for bromide than for chloride and still higher for iodide. With divalent counterions, the Krafft point is in general much higher.

The Krafft phenomenon is best discussed from the interplay between the temperature dependence of the surfactant unimer solubility and the temperature dependence of the CMC. As learnt above, the latter temperature dependence is very weak and we can consider here that the CMC is to a good approximation independent of temperature. On the other hand, we expect the dissolution of the surfactant into the constituent solvated ions to increase markedly with temperature, as for simple salts. If this solubility is below the CMC, no micelles can form and the total solubility is limited by the (low) unimer solubility. If, on the other hand, the unimer solubility reaches the CMC, micelles may form. It is a characteristic feature of micellization, as will be seen later, that as the micelle concentration increases there is virtually no change in the free unimer activity (or concentration). This, together with a very high micelle solubility, explains why a quite small increase in unimer solubility (resulting here from a temperature increase) leads to a dramatic increase in the overall surfactant solubility.

The Krafft point is determined by the energy relationship between the solid crystalline state and the micellar solution. It appears that the micellar solutions vary only weakly between different cases, like different counterions, while the solid crystalline state may change dramatically due to packing effects. Looking for an understanding of the Krafft phenomenon we have, therefore, to look into packing effects and ionic interactions in the solid state.

If the solubility of a surfactant is very low it will clearly not be operative in various applications. Since a longer-chain surfactant is generally more efficient, there is commonly a delicate compromise in the design of surfactants. Attempts to lower the Krafft point should mainly be directed towards the conditions in the solid state. Besides changing counterion, which is not always possible, we should look into the packing conditions of the hydrophobic chains. The development of surfactants with a lower Krafft point is generally based on making the packing conditions in the solid state less favorable in one of the following ways:

1. Introduction of a methyl group, or some other chain branching, in the alkyl chain.
2. Introduction of a double bond in the alkyl chain.
3. Introduction of a polar segment, usually an oxyethylene group, between the alkyl chain and the ionic group.

These are also common approaches to manufacturing surfactants compatible with hard water; the presence of calcium ions significantly increases the Krafft point of anionic surfactants, an important limitation in using these surfactants, for example, in cleaning in hard water. Control of chain melting is also very important in biological systems, notably biological membranes, and is achieved by controlling chain unsaturation.

Driving Forces of Micelle Formation and Thermodynamic Models

Hydrophobic Interactions

We have come back several times to the important characteristic of surfactants and polar lipids—the amphiphilicity. Water does not interact favorably with the hydrophobic groups and there is a driving force for expelling them from the aqueous environment (Chapter 3). This may be achieved by a macroscopic phase separation or by hiding the nonpolar groups in some other way. There are numerous other examples of hydrophobic effects and hydrophobic interactions, as illustrated in Figure 4.8.

For a hydrocarbon in water there is a strong driving force for transfer to a hydrocarbon phase or some other nonpolar environment. When a polar group is attached to the hydrocarbon an opposing force is created, which counteracts phase separation. If the opposing force is weak, phase separation will still result. If it is very strong compared to the hydrophobic effect, on the other hand, the amphiphile will occur as single molecules or as small aggregates, like dimers. It is the common intermediate situation with balance between hydrophobic and hydrophilic interactions that we are concerned with in surfactant self-assemblies.

The hydrophobic interaction increases with the increasing alkyl chain length of an alkane or the hydrophobic group of a surfactant. Indeed, the decrease in solubility of an alkane with the number of carbons very much parallels the change in CMC that was discussed above.

We have noted that micellization (and surfactant self-assembly in general) is some intermediate between phase separation and simple complex formation, and this is illustrated in the ways that micellization has been modeled in thermodynamic analyses. Micelle formation is generally discussed in terms of one of the following models.

Phase Separation Model

In this model, micelle formation is considered as akin to a phase separation, with the micelles being the separated (pseudo-)phase and the CMC the saturation concentration of surfactant in the unimeric state. Surfactant addition above the CMC consequently only affects the micelle concentration but not the unimer concentration. In many physicochemical investigations we observe a number average over the different states that a surfactant molecule can occupy. The phase separation model is particularly simple for interpretation of experimental observations. Below the CMC we have only unimers and the average of a quantity Q is simply:

$$\langle Q \rangle = Q_{\text{aq}} \quad (4.1)$$

For a concentration above the CMC we get, since $C_{\text{mic}} = C_{\text{tot}} - \text{CMC}$ and $C_{\text{aq}} = \text{CMC}$:

$$\langle Q \rangle = p_{\text{mic}} Q_{\text{mic}} + p_{\text{aq}} Q_{\text{aq}} = \left(1 - \frac{\text{CMC}}{C_{\text{tot}}}\right) Q_{\text{mic}} + \frac{\text{CMC}}{C_{\text{tot}}} Q_{\text{aq}} \quad (4.2)$$

For concentrations sufficiently above the CMC, $\langle Q \rangle$ approaches Q_{mic} .

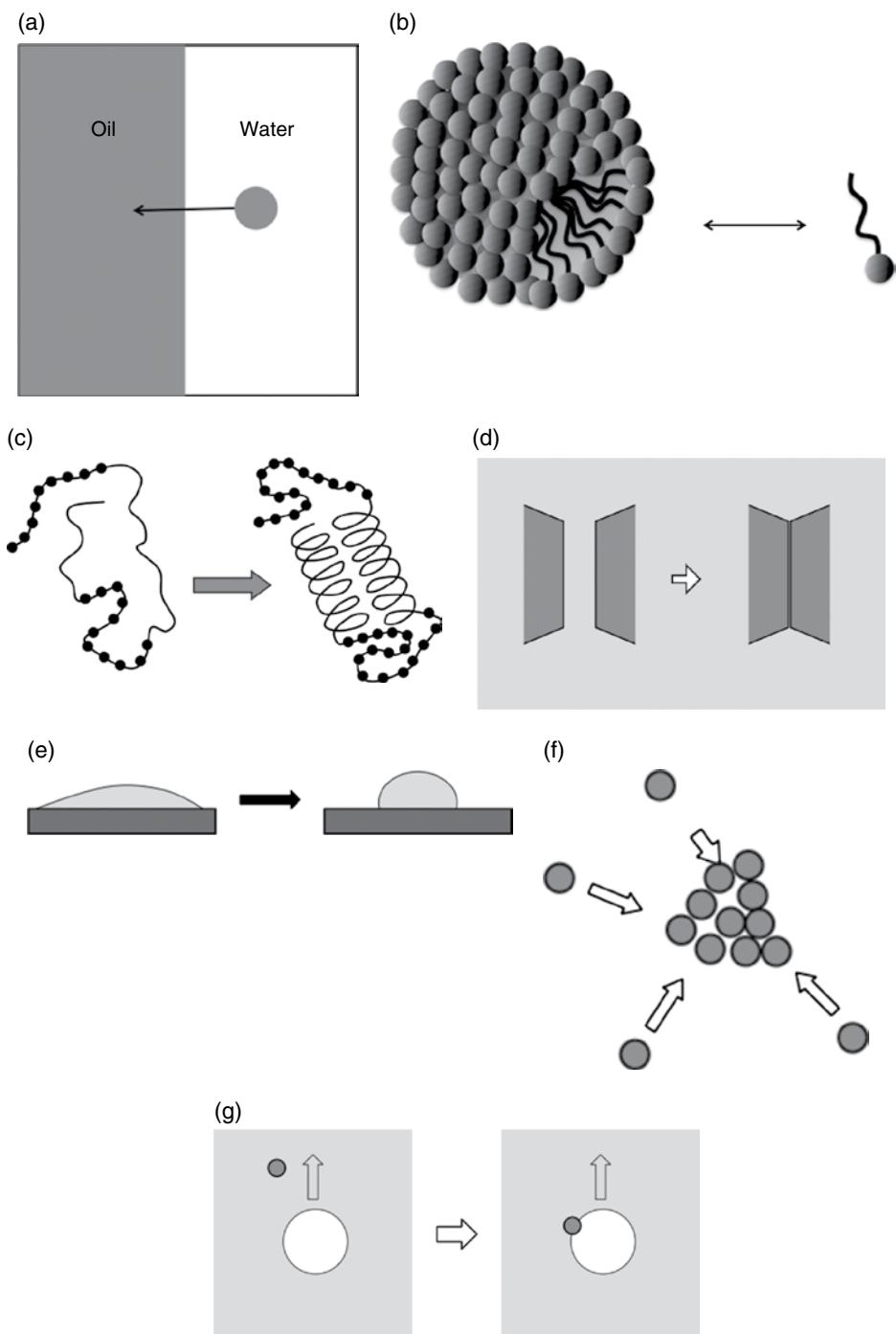


Figure 4.8 Illustrations of the effects of hydrophobic interactions, that is, the tendency to eliminate contacts between water and nonpolar molecules or surfaces: (a) water and oil are immiscible, with a strong driving force to expel hydrocarbon molecules from water; (b) self-assembly of surfactant molecules; (c) folding of proteins; (d) strong adhesion between nonpolar surfaces in water; (e) nonwetting of water on hydrophobic surfaces; (f) rapid coagulation of hydrophobic particles in water; (g) attachment of hydrophobic particles to air bubbles (mechanism of froth flotation). (Adapted from Israelachvili, J. (1991) Intermolecular and Surface Forces, 2nd edn, Academic Press, London. With permission from Elsevier.)

The phase separation model is simple to apply, illustrative, and sufficient for many considerations. As may be expected, it becomes a better approximation the higher the aggregation number.

Mass Action Law Model

Here we assume a single micellar complex in equilibrium with the unimeric surfactant:

$$n A_1 = A_n \quad (4.3)$$

$$\frac{A_n}{(A_1)^n} = K \quad (4.4)$$

In this model, the aggregation number may be obtained from the variation in Q_{obs} around the CMC. The more gradual the change, the lower the aggregation number and the more appropriate the mass action law model is with respect to the phase separation model. The fraction of added surfactant that goes to the micelles is plotted in Figure 4.9 as a function of the total surfactant concentration for different aggregation numbers. For very high aggregation numbers, N , there is a close to stepwise change and the variation in the limit is the same as predicted by the phase separation model. In reality, micelles are not monodisperse but there is a distribution of aggregation numbers, and micelles are formed in a stepwise process.

As written, this treatment considers nonionic surfactants. To account for the association of the counterions to the micelles, we can add the relevant (stepwise if needed) equilibria for the counterions. This is normally not a reasonable approach, however, since the treatment in terms of equilibrium constants assumes short-range interactions and formation of well-defined complexes. The distribution of counterions is governed by electrostatic interactions, which are long range. It is, therefore, not possible to assign definite characteristics of “micellar-bound” counterions. This does not mean that counterion binding or association may not be a useful concept. However, we should be aware of the limitations and analyze findings in terms of appropriate models.

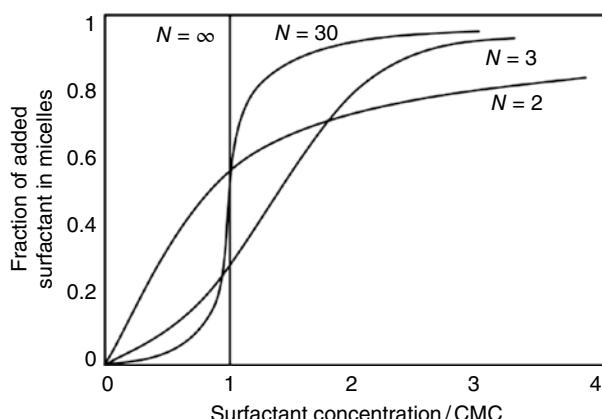


Figure 4.9 The fraction of added surfactant that goes to the micelles as a function of the total surfactant concentration for different aggregation numbers, N

The Association Process and Counterion Binding can be Monitored by NMR Spectroscopy

A complete characterization of the self-association of a surfactant would include giving the concentration of all the different species as a function of the total surfactant concentration. We cannot easily measure the concentration of micelles of all different aggregation numbers but we can obtain some suitable averages. Consider the unimer concentration, the concentration of micellized surfactant, the concentration of bound and free counterions, and the hydration of micelles. Using counterion and surfactant specific electrodes we can obtain counterion and surfactant activities that provide information on the distribution between micellar and unimeric states. Even more complete information is obtained if we measure the self-diffusion coefficients of surfactant molecules, micelles, counterions, and water molecules. These can nowadays be obtained in a single fast experiment using NMR methodology. A representative example is given in Figure 4.10 for the case of decylammonium dichloroacetate.

Self-diffusion coefficients constitute one example where the observed quantity is a weighted average over the different environments (micellar and unimeric) so that

$$D_{\text{obs}} = p_{\text{mic}} D_{\text{mic}} + p_{\text{free}} D_{\text{free}} \quad (4.5)$$

or

$$D_{\text{obs}} = \frac{(C_{\text{mic}} D_{\text{mic}} + C_{\text{free}} D_{\text{free}})}{C_{\text{tot}}} \quad (4.6)$$

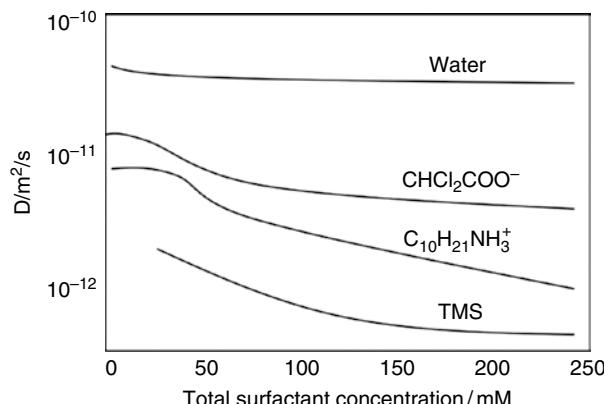


Figure 4.10 Dependence on the surfactant concentration of the self-diffusion coefficients of surfactant ions (decylammonium), counterions (dichloroacetate), water molecules, and micelles (approximated by the diffusion of added TMS); the CMC is 26 mM. (Adapted with permission from Stilbs, P. and Lindman, B. (1981) Determination of organic counterion binding to micelles through Fourier transform NMR self-diffusion measurements. *Journal of Physical Chemistry*, **85**, 2587–2589. Copyright 1981, American Chemical Society.)

D, p and C denote, respectively, the self-diffusion coefficient, the fraction of molecules in a given environment, and the concentration. D_{free} is obtained from data below the CMC and D_{mic} from measurements on probe molecules confined to the micelles. In the study of Figure 4.10, a low (to avoid perturbation of the micellization) concentration of sparingly soluble tetramethylsilane (TMS) is used. Since micelles are large entities, their D values are very much lower than those of single unimeric molecules.

As can be seen in Figure 4.10, the rate of self-diffusion is very different for the different molecules at concentrations well above the CMC. We can directly read out that water molecules are least associated with the (slowly moving) micelles while TMS molecules are almost exclusively located in micelles. A quantitative analysis of the surfactant and counterion diffusion data gives the results presented in Figure 4.11.

There are some important general features, generally applicable for ionic surfactants, that we should note:

1. With a good approximation, all surfactant molecules are in the unimeric state below the CMC.
2. Above the CMC, the surfactant unimer concentration decreases and may reach values well below the CMC.
3. The free counterion concentration increases at a lower rate above than below the CMC.
4. If we normalize the micellar bound counterion concentration (C_{mic}^c) to the micellar surfactant concentration (C_{mic}^s), we obtain the degree of counterion binding, β :

$$\beta = \frac{C_{\text{mic}}^c}{C_{\text{mic}}^s} \quad (4.7)$$

It is an important result that β remains constant when we vary the micelle concentration over orders of magnitude. The latter observation is often referred to as a counterion

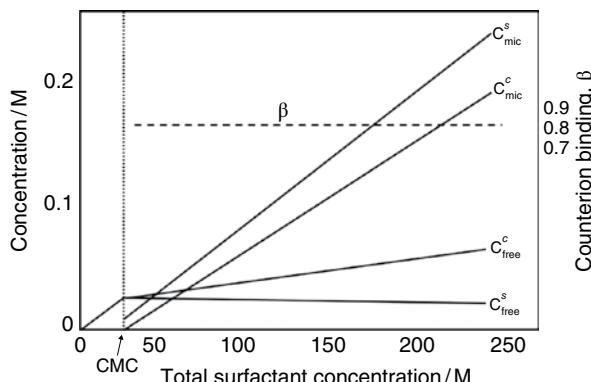


Figure 4.11 Concentrations of micellar and free unimeric surfactant ions (s) and counterions (c) as a function of the total surfactant (decylammonium dichloroacetate) concentration; β is the degree of counterion binding. (Adapted with permission from Stilbs, P. and Lindman, B. (1981) Determination of organic counterion binding to micelles through Fourier transform NMR self-diffusion measurements. *Journal of Physical Chemistry*, **85**, 2587–2589. Copyright 1981, American Chemical Society.)

condensation, meaning that counterion association is on a level that gives a certain critical effective charge density. β then remains approximately constant, even on large variations of the conditions, not only for micelle concentration but also for added salt and temperature. The counterion condensation phenomenon is common to all systems of high charge densities, including also polyelectrolytes and charged surfaces. It is very well understood from electrostatic theory (Poisson–Boltzmann equation, Chapter 3).

Hydrophobic Compounds can be Solubilized in Micelles

A nonpolar compound is insoluble in water. Typically the solubility stays very low until the CMC is reached, while above the CMC it increases rapidly and almost linearly with the surfactant concentration (Figure 4.12).

Solubilization is one of the most important phenomena for surfactant solutions, with a direct bearing on *inter alia* detergency and the formulation of pharmaceuticals. This was discussed in Chapter 1 and illustrated by Figure 1.13. We will come back to it repeatedly, for example when we discuss phase diagrams, which give quantitative information on the capacity of micelles to incorporate different molecules. In order to study the solubilization equilibria and thus obtain information on the thermodynamics of solubilization, the mentioned self-diffusion technique is the most general and useful approach.

Surface tension measurements on impure surfactants provide an illustration of solubilization. If the surface tension is measured for sodium dodecyl sulfate SDS solutions, one frequently obtains a minimum (Figure 12.10). On purification, the minimum is eliminated. The explanation is that SDS often contains some dodecanol (due to hydrolysis). The latter is more surface active than SDS and becomes concentrated at the air–water interface. However, as soon as micelles start to form there is a large micellar surface available as well. Dodecanol is removed from the surface by solubilization and the surface tension increases. We return to these aspects in Chapter 8 when surfactant absorption is discussed.

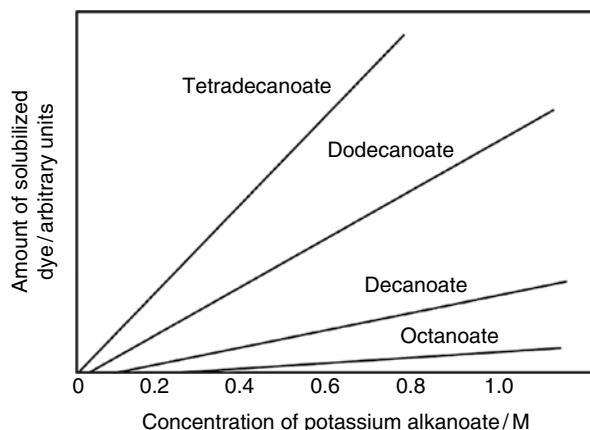


Figure 4.12 Amount of a dye solubilized in solutions of potassium alkanoates. (Adapted from Shinoda, K., Nakagawa, T., Tamamushi, B.-I. and Isemura, T. (1963), Colloidal Surfactants, Some Physicochemical Properties, Academic Press, London. With permission from Elsevier.)

Micelle Size and Structure

With a good approximation, micelles can, in a wide concentration range above the CMC, be viewed as microscopic liquid hydrocarbon droplets covered with the polar head groups that interact with water. It appears that the radius of the micelle core constituted of the alkyl chains is close to the extended length of the alkyl chain, that is, in the range of 1.5–3.0 nm. Why is this so?

The driving force of micelle formation is the elimination of the contact between the alkyl chains and water. The larger the spherical micelle, the more efficient this is, since the volume-to-area ratio increases. Decreasing the micelle size always leads to an increased hydrocarbon–water contact. However, if the spherical micelle was made so large that no surfactant molecule could reach from the micelle surface to the center, one would either have to create a void or some surfactant molecules would lose the contact with the surface, introducing polar groups in the center. Both alternatives are unsatisfactory.

We should note that the fact that the micelle radius equals the length of an extended surfactant molecule does not mean that the surfactant molecules are extended. Only one needs to be extended (in an all *trans* state) to fulfill the requirements mentioned, and the majority of the surfactant molecules are in a disordered state with many gauche conformations. Spectroscopic studies have been used to characterize the state of the alkyl chains in micelles in detail. This state is indeed very close to that of the corresponding alkane in a neat liquid oil. The liquid-like state is clearly expressed by molecular dynamics. Thus, chain isomerism occurs on a time scale of a few tens of a picosecond, only slightly slower than for liquid alkanes. Due to the constraints involved in the attachment to the micelle surface, the motion is slightly anisotropic.

We emphasize that a micelle may, for many purposes, be considered as a microscopic droplet of oil. This explains the large solubilization capacity towards a broad range of non-polar and weakly polar substances. We note, however, that the locus of solubilization will be very different for different solubilizates. While a saturated hydrocarbon will be rather uniformly distributed over the micelle core, an aromatic compound, being slightly surface active, also like a long-chain alcohol, tends to prefer the surface region and to orient in the same way as the surfactant itself.

At the surface of the micelle we have the associated counterions, which amount to 50–80% of the surfactant ions; as noted above, a number quite invariant to the conditions. Simple inorganic counterions are very loosely associated with the micelle. The counterions are very mobile and there is no specific complex formed with a definite counterion–head group distance. Rather, the counterions are associated to the micelle as a whole by long-range electrostatic interactions. They remain hydrated to a great extent; cations, especially, tend to keep their hydration shell.

Some water of hydration is thus accounted for by the associated counterions and, furthermore, the polar head groups are extensively hydrated. On the other hand, water molecules are effectively excluded from the micelle core. There is, due to packing limitations, some inevitable exposure of the hydrocarbon chains at the micelle surface, but even a short step inwards the probability of finding water molecules becomes very low.

The micelle size, as expressed by the radius of a spherical aggregate, may be obtained *inter alia* from various scattering experiments and from micelle self-diffusion. A related and equally important characteristic of a micelle is the micelle aggregation number, that is, the number of surfactant molecules in one micelle. This is best determined in fluorescence quenching experiments. To take an example, the aggregation number of SDS micelles at

25°C is 60–70. The aggregation number is quite well defined with only a narrow distribution. Micelles of all aggregation numbers exist in equilibrium but for aggregation numbers deviating markedly from the average the probability is very small. For this reason, the mass action law model offers a good description. In fact, as mentioned above, by analyzing experimental observations around the CMC using this model some information on the micelle aggregation numbers is obtained.

Based on the mass action law model and the general relationship between the free energy change and the equilibrium constant,

$$\Delta G^\circ = -RT \ln K \quad (4.8)$$

the approximate relationship for micelle formation can be derived:

$$\Delta G^\circ = RT \ln CMC \quad (4.9)$$

Here ΔG° represents the free energy difference between a unimer in the micelle and some suitably chosen reference state. This is a convenient starting point for thermodynamic considerations.

A Geometrical Consideration of Chain Packing Is Useful

We came above to a simple characterization of the micelle core as a hydrocarbon droplet with a radius, R_{mic} , equaling the length of the extended alkyl chain of the surfactant. We also noted that, since the cross-section area per chain decreases radially towards the center, only one chain can be fully extended while the others are more or less folded. The aggregation number, N , can be expressed as the ratio between the micellar core volume, V_{mic} , and the volume, v , of one chain:

$$N = \frac{V_{\text{mic}}}{v} = \frac{4\pi}{3} \frac{R_{\text{mic}}^3}{v} \quad (4.10)$$

We can alternatively express the aggregation number as the ratio between the micellar area, A_{mic} , and the cross-sectional area, a , of one surfactant molecule:

$$N = \frac{A_{\text{mic}}}{a} = 4\pi \frac{R_{\text{mic}}^2}{a} \quad (4.11)$$

Putting these aggregation numbers equal gives:

$$\frac{v}{a R_{\text{mic}}} = \frac{1}{3} \quad (4.12)$$

Since R_{mic} cannot exceed the extended length of the surfactant alkyl chain:

$$\ell_{\text{max}} = 1.5 + 1.265 n_c \quad (4.13)$$

(1.5 Å is the van der Waals radius of a methyl group and 1.265 the projected length along the chain of a carbon–carbon bond). For a spherical micelle:

$$\frac{v}{a \ell_{\text{max}}} \leq \frac{1}{3} \quad (4.14)$$

The ratio $v/a \ell_{\max}$, which gives a geometric characterization of a surfactant molecule, is very useful when discussing the type of structure formed by a given amphiphile. It is denoted as the critical packing parameter (CPP) or the surfactant number. The concept is further discussed in Chapter 6.

Kinetics of Micelle Formation

We have already noted that micelles are formed in a stepwise process, so the elementary step is the equilibrium between a unimer and a micellar aggregate:



The “on” rate constant, k^+ , is diffusion controlled and depends little on surfactant and micelle size. The “off” rate constant, k^- , on the other hand, decreases strongly with alkyl chain length, and depends on micelle size, and so on. Because of the cooperativity in micelle formation there is a very deep minimum in the size distribution curve. This leads to a two-step approach to equilibrium after a perturbation. In a fast step, quasi-equilibrium is reached under the constraint of a constant total number of micelles. The redistribution of unimers between abundant micelles is a fast process. To reach a true equilibrium, the number of micelles must change. Because of the stepwise process this also involves the very rare intermediate micelles. Therefore this process is slow.

From fast kinetic measurements, two relaxation times are determined that characterize molecular processes in micellar solutions: t_1 measures the rate at which surfactant molecules exchange between micelles, while t_2 measures the rate at which micelles form and disintegrate. As an example, t_1 is of the order of $10\mu s$ for SDS, while t_2 is longer than a millisecond. Both relaxation processes become much slower as the surfactant alkyl chain length increases.

Surfactants may Form Aggregates in Solvents Other than Water

In strongly *polar organic solvents*, such as formamide and ethylene glycol, micelles are formed with qualitatively the same features as in water. However, the CMC is much higher; for example, in formamide the CMC values are two orders of magnitude higher than in water. It is a general feature, also exemplified by smaller micelle radii and aggregation numbers, that self-assembly is much less cooperative in the organic polar solvents.

The association of amphiphilic compounds is of low cooperativity in *nonpolar solvents* and typically leads only to small aggregates, dimers, trimers, and so on. However, introduction of even quite small amounts of water can induce a cooperative self-assembly leading to reverse micelles. We will return to this point later.

General Comments on Amphiphile Self-Assembly

In water, aggregation results from the insolubility of the nonpolar parts in water. The packing of the hydrocarbon chains results from the drive to minimize contact with water. Aggregation is opposed by the hydrophilic interaction, giving a repulsion between the polar head groups on the micelle surface. The head groups will arrange themselves to minimize the unfavorable repulsions.

The self-assembly of an amphiphile depends on the strength of the opposing force. It must be strong enough to compete with the alternative behavior, which is macroscopic phase separation, but must also be limited in magnitude, as otherwise the unimeric state will be the most stable one. Examples of head groups giving amphiphiles that are too weak are hydroxyl, aldehyde, ketone, and amine. For a long-chain alcohol, macroscopic phase separation results rather than micelle formation.

For ionic surfactants, the counterion dissociation plays a major role. Because of the counterions, macroscopic phase separation becomes entropically very unfavorable and there is a strong tendency to form small micelles.

Cosolutes may affect amphiphile self-assembly in many different ways. They can, for example, stabilize the micelles by reducing the polar interactions. For ionic surfactants, we can neutralize the charges by adding an oppositely charged surfactant, we can “screen” the repulsions between head groups, or rather even out the uneven counterion distribution by adding electrolyte, or we can dilute the charges by introducing a nonionic amphiphile, like a long-chain alcohol. In all cases, we observe a marked reduction of the CMC and, as discussed in Chapter 6, an increase in micelle size.

Self-assembly and micelle formation have, however, a broader significance. Mixed polymer–surfactant solutions have many applications and an important role of the polymer chains in many systems is to promote micelle formation. A macromolecular cosolute will be much more effective in reducing the CMC than a low molecular weight one. This is discussed in some detail in Chapter 14.

Likewise, surfactant adsorption at hydrophilic solid surfaces is best regarded as a process of surfactant self-assembly. This will be dealt with in Chapter 8.

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5

Introduction to Phase Diagrams

Phase identification and phase diagrams have become very powerful tools in understanding the behavior of both surfactants and polymers in solution. Furthermore, when complemented with spectroscopic methods, such as structure determination using nuclear magnetic resonance (NMR), the determination of phase diagrams of surfactant systems has become the first choice for the formulator. This chapter is a brief presentation of the principles of phase diagrams, on a descriptive level, without going into the thermodynamics that forms the rules. It starts with two components and continues with three or more components.

The Phase Rule Regulates the Number of Phases

Firstly, it is necessary to distinguish between intensive and extensive variables. Intensive variables, such as concentration or temperature, do not depend on the size of the system, whereas extensive variables depend on the size. Examples of extensive variables are the number of moles, mass, or volume.

The phase rule was formulated by Gibbs in the 1870s. It relates the number of degrees of freedom (F), that is, the number of intensive variables that can be independently varied, to the number of components (C) and the number of phases (P):

$$F = C - P + 2 \quad (5.1)$$

Consider initially a single component system, that is, $C=1$. Within a single-phase region there are two degrees of freedom ($F=1-1+2=2$); hence, both the temperature and pressure must be specified in order to define the system. When two phases are in equilibrium there is only one degree of freedom ($F=1-2+2=1$); hence, either the temperature or the

pressure is sufficient to specify the system (along the coexistence line). Note that the Gibbs phase rule says nothing about the relative amounts of the phases in equilibrium. At the triple point there is no degree of freedom ($F=1-3+2=0$), which thus occurs only at one specific temperature and pressure.

For a two-component system, $C=2$. Within a single-phase region there are three degrees of freedom ($F=2-1+2=3$); hence, the temperature, pressure, and composition must be specified to define the system. When two phases are in equilibrium there are two degrees of freedom ($F=2-2+2=2$); hence, the temperature and the pressure are sufficient to specify the system, as the composition of the two phases are given by the boundary lines.

For a three-component system, $C=3$. Within a single-phase region there are four degrees of freedom ($F=3-1+2=4$); hence, the temperature, pressure, and two compositions must be specified to define the system. When two phases are in equilibrium there are three degrees of freedom ($F=3-2+2=3$); hence, the temperature, pressure, and one composition are sufficient, as the system is limited by the boundary lines. For three phases in equilibrium we have ($F=3-3+2=2$). Hence, only temperature and pressure are needed to specify the system. The compositions of the three phases are fixed.

As noted, the intensive variables are pressure, temperature, and composition. In the following we will always consider phase diagrams at a fixed pressure. This is justified by the fact that in practice we are rarely interested in varying the pressure and, furthermore, the aggregation processes considered are to a good approximation independent on pressure.

Binodal and Spinodal—Metastable and Unstable

Figure 5.1 shows a typical phase diagram where two components are miscible at high, but not at low temperatures. The increased miscibility with temperature is due to an increased thermal movement of the molecules (corresponding to an increase in entropy) overcoming the adverse interaction between the two components A and B. Increasing the concentration

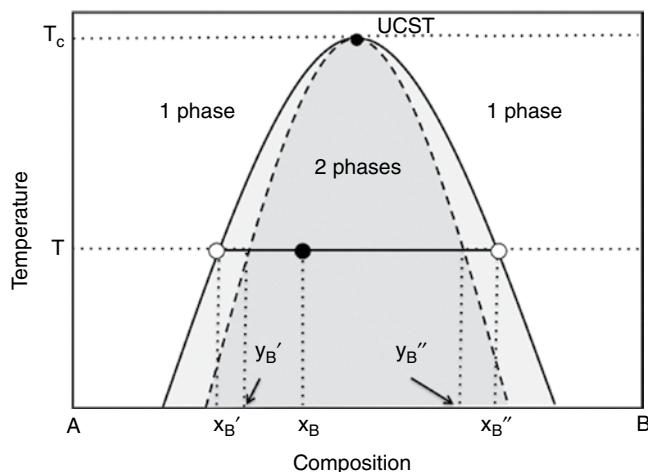


Figure 5.1 Binary phase diagram showing the binodal (solid) and spinodal (dashed) lines

of component B in the figure, at the indicated temperature, T, one reaches a point of phase separation, x'_B . This concentration is the miscibility limit of B in A. It often manifests as a clouding, since drops of composition x''_B form in the solution and clouds the solution until the phases separates due to a difference in density.

Increasing the concentration of component B further, one reaches the point of instability, y'_B . This is the concentration limit to which the solution can be supersaturated, that is, between the solid and dashed lines we could have a metastable solution that is not phase separated. Going beyond the dashed line this is impossible. Here the solution is unstable and will separate under all circumstances. The dashed line giving the limits between unstable and metastable is termed the *spinodal*, whereas the solid line giving the limits between a homogenous solution and a phase separated state is termed the *binodal*, or coexistence curve. The binodal and spinodal meet at the critical point, T_c , termed the *upper critical solution temperature*, UCST. Polymer solutions, especially solutions of polymers of high molecular weights, are easily supersaturated due to their slow kinetics; hence, the spinodal is often determined. Finally, increasing the concentration of component B further we reach point x''_B , where the solution becomes homogeneous. This is the other end of the limit of the solubility gap and represents the solubility of component A in B.

Having a composition inside the phase separation area we have two solutions at different compositions in equilibrium. The horizontal line in the two-phase region that is tying the two phases together at a constant temperature is termed a *tie-line*. The relative amounts of the two phases, which can be expressed in terms of volume or mass, are related to the composition of the phases, x'_B and x''_B , through the *lever rule*:

$$\frac{w'_B}{w''_B} = \frac{x''_B - x'_B}{x_B - x'_B} \quad (5.2)$$

Here, w'_B and w''_B are the volumes, or masses, of the two coexisting phases. Hence, by determining the volume, or mass, of the phases for a couple of compositions inside the two-phase region one can calculate the phase boundaries.

Some systems separate on heating and thus have a reverse phase behavior to that in Figure 5.1. Then there is a *lower critical solution temperature*, LCST, below which there is no phase separation. In this book we will encounter aqueous solutions of oxyethylene containing surfactants and polymers that phase separate on heating (Chapter 7). Figure 5.2 shows schematically polymer solutions that separate either on cooling or heating. The figure shows that for polymer solutions the UCST or LCST are not found at 50/50 polymer–solvent ratio but rather at lower polymer concentrations. This critical concentration increasingly shifts toward infinitely dilute polymer solution as the molecular weight goes to infinitely high values, which is illustrated in Figure 9.9.

The temperature at which phase separation starts is called the cloud point (by convention for a 1 wt% solution), due to the increased turbidity of the polymer solution as this temperature is reached. Note the difference between the critical point and the cloud point. The latter is the temperature at which phase separation occurs for a specific polymer concentration, normally 1%, whereas the former is the minimum, or maximum, temperature/concentration for phase separation in the phase diagram.

In a two-component system of surfactant and water there can be many different homogenous phases as is exemplified in Figure 5.3. These phases are liquid, liquid crystalline

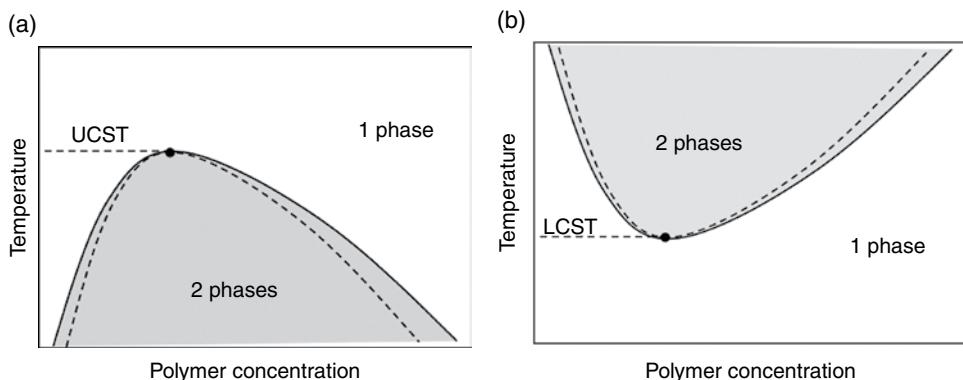


Figure 5.2 Schematic phase diagrams of polymer–solvent systems that phase separate on (a) cooling and (b) heating; the solid lines are the binodals and the dashed lines are the spinodals

(also termed mesophases) or solid in character. Each individual phase needs to be separated by a two-phase region, which is often very narrow. This is a necessary criterion in the construction of phase diagrams in general. For convenience and clarity reasons, however, the two-phase regions are not always included in the phase diagrams.

The Gibbs Triangle

In systems with three components, the phase diagrams become more complex. It is most common to consider the phase behavior at constant temperature and to use the Gibbs' triangle (Figure 5.4). Here each apex represents the pure components. Hence, being positioned on the axis A–B, for example, we have systems with only components A and B

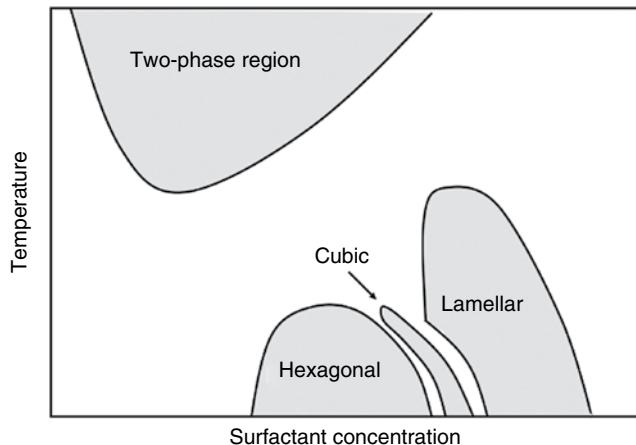


Figure 5.3 Schematic phase diagram of a nonionic surfactant containing a polyoxyethylene moiety showing hexagonal, cubic, and lamellar mesophases (between the mesophases the narrow two-phase regions are indicated)

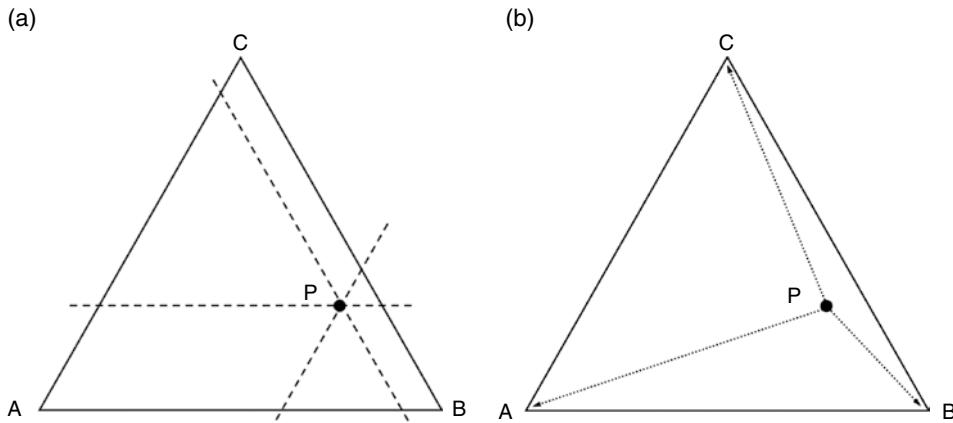


Figure 5.4 The Gibbs triangle with three components A, B, and C at a fixed temperature. The amounts of the different components at a point P are given by the relative distance from the opposite base. (a) A sample represented by the point P is composed of 10% A, 60% B, and 30% C. (b) Dilution with the pure components is represented by the dotted lines

present. The composition of a sample in the figure can be read by determining the relative distance to the corners. The closer you are to one corner the higher is the concentration of that component. The dashed lines through the point P in Figure 5.4a that are parallel to the base lines of the triangle illustrate this.

Diluting with one of the pure components, will move us from point P towards the corner of that component at constant ratio of the other two components, as shown by the dotted lines in Figure 5.4b.

Phase Behavior and the Gibbs Triangle

Considering the phase rule for a system with three components (Equation 5.1), we realize that a single homogeneous phase is represented by an area; two phases in equilibrium are represented by a line, that is a tie-line, and three phases in equilibrium are represented by three points, that is, three fixed compositions. Figures 5.5a–c display schematic phase diagrams where components A and B are not miscible but component C is miscible in both A and B. In the two-phase region the solutions in equilibrium are tied together with tie-lines. One rule in the construction of a phase diagram is that tie-lines are not allowed to cross. Furthermore, tie-lines are not allowed to emerge from the same point. The point where the compositions of the two solutions merge is termed the *plait point* and is marked in the figures. In Figure 5.5a, component C has equal affinity for A and B, resulting in horizontal tie-lines. In Figure 5.5b, component C has a higher affinity for component B than for A, resulting in tie-lines that connect solutions that are rich in A with solutions that contain considerable amount of both B and C but only small amounts of A. The type of phase separation depicted in Figure 5.5a and b is termed *segregative phase separation*.

Under certain conditions not only two but three phases are in equilibrium, as is illustrated in Figure 5.5c. The phase rule then states that there are no extra degrees of freedom.

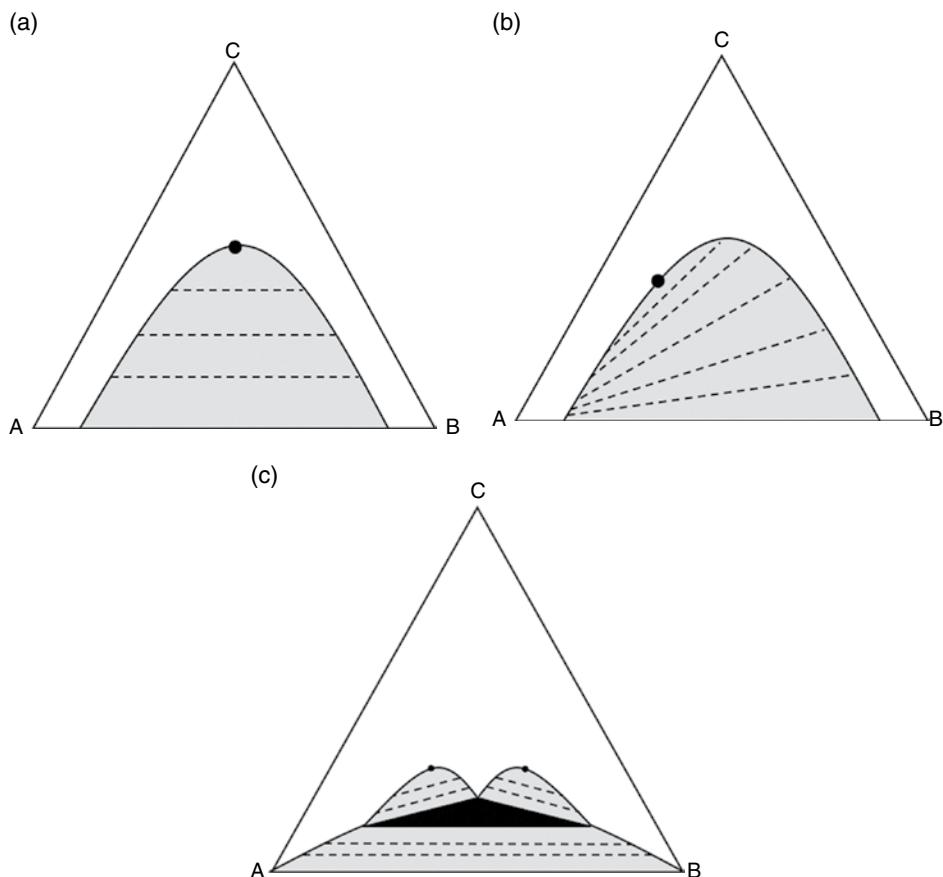


Figure 5.5 Gibbs triangle phase diagram for a system where A and B do not mix and where C is a solvent for both A and B. Equal partitioning of component C in A and B (a), component C has a higher affinity for B than for A giving tie-lines that connect solutions with high concentration of C in B with solutions that have low concentration of C in A (b). The appearance of a three-phase triangle (in black), which always borders two-phase regions (Note that the tie-lines in the two-phase region are always parallel to the base line of the three-phase triangle.) (c)

The three phases in equilibrium therefore have an invariant composition. In the Gibbs triangle the three-phase region is represented by a triangle where the phases in equilibrium are represented by the apexes of the triangle. Formulations with compositions that fall inside the three-phase triangle will de-mix into three solutions, each with a composition represented by the corners of the triangle (Figure 5.5c). The only variable is the relative amounts of the three phases in equilibrium. In fact, a lever rule can also be constructed for the three-phase triangle. Note that the sides of a three-phase triangle always need to be in contact with a two-phase region. Also note that the extrapolation of the two-phase boundaries must either both pass into the three-phase triangle or must both pass into the adjacent two-phase regions (Schreinemakers' rule).

Examples of How to Read Phase Diagrams

We will now give some examples of how to read phase diagrams. The first example is a polymer–solvent system and we want to deposit the polymer at a surface by adding a nonsolvent. Through phase diagram considerations we conclude that in order to have a proper polymer deposition we need to choose the system such that the affinity of the solvent for the nonsolvent needs to be greater than it is for the polymer. This is illustrated in Figure 5.6, showing two cases where the affinity of the solvent for the nonsolvent is, respectively, higher and lower than for the polymer, as indicated by the tie-lines. Let us assume that we start at point A in both cases, that is, a polymer solution in a good solvent. We then add the nonsolvent. In the first case when hitting the two-phase region, the tie-lines lean down towards the polymer corner (Figure 5.6a). Hence, upon dilution with the nonsolvent the polymer-rich phase becomes even richer in polymer while the other solution phase becomes more depleted of the polymer. In the other case, where the solvent affinity is larger for the polymer than for the nonsolvent (Figure 5.6b), we get a phase separation where the composition of the polymer-rich phase hardly changes upon dilution with the nonsolvent. That phase will keep a substantial amount of solvent regardless of the dilution with the nonsolvent. In both cases the polymer-rich phase will become smaller in volume as the dilution progresses.

A second example concerns solubilization of decanol in a surfactant solution. Figure 5.7a shows a Gibbs triangle for the system sodium cholate–decanol–water. In the two-phase region, at low surfactant concentrations, there is a separation into an almost pure organic phase, decanol, and one phase that can be considered as a microemulsion (Chapter 17). The microemulsion phase encompasses the whole two-phase region. Having a composition at the black dot in Figure 5.7a and diluting with water will give a phase separation. Decanol, saturated with water, will separate out and be in equilibrium with a microemulsion phase. Most likely the decanol will be in the form of emulsion droplets, dispersed in the microemulsion phase and stabilized by the surfactant. Emulsions always form with the highest surfactant concentration in the continuous phase (Bancroft's rule page 434), that is, the

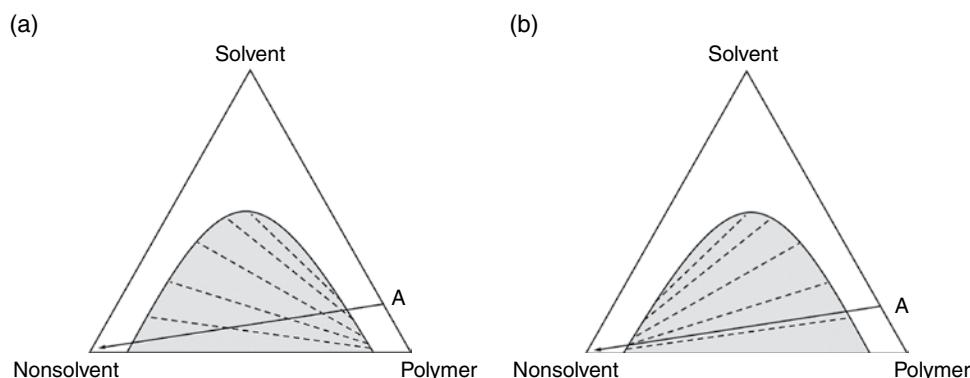


Figure 5.6 Deposition of polymer on a surface by adding a nonsolvent: (a) the affinity of the solvent for the nonsolvent is higher than for the polymer and (b) the affinity of the solvent for the nonsolvent is lower than for the polymer (the solid line is the dilution path)

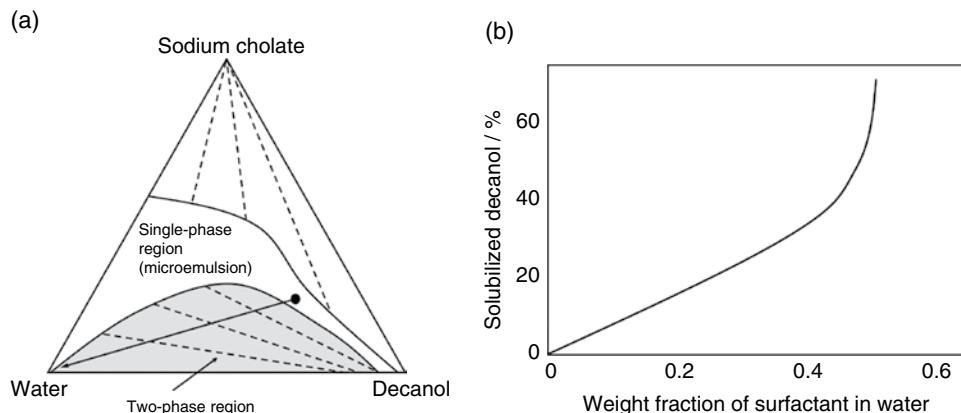


Figure 5.7 A three-component system (water-deanol-sodium cholate) that separates at low surfactant concentrations (a) into one phase of almost pure decanol and one phase which is a microemulsion; (b) the data replotted as the amount of solubilized decanol (%) as a function of surfactant concentration in the aqueous phase. (Data from Ekwall, P. (1975) Composition, properties and structures of liquid crystalline phases in systems of amphiphilic compounds, in *Advances in Liquid Crystals*, vol. 1 (ed. G.H. Brown), Academic Press, London, pp. 1–142.)

microemulsion phase in Figure 5.7a. The solution behavior in Figure 5.7a resembles that of forming an Ouzo emulsion (Figure 24.10).

The data in the phase diagram indeed represent the solubilization of decanol in the surfactant solution and can be replotted as in Figure 5.7b, where the maximum solubilized amount of decanol is plotted as a function of the surfactant concentration in the aqueous phase.

In a third example we have a surfactant that dissolves in the oil phase (Figure 5.8a). Here the system separates into an almost pure water phase and a microemulsion phase. On dilution with water the composition of the microemulsion phase stays almost invariant and the water phase increases in size, as shown by the arrow in the diagram. Such a system is of interest when we want a microemulsion to be in contact with water irrespective of the size of the water reservoir. An example is cleaning applications where the water-soluble dirt is transported to the aqueous phase and the organic dirt into the microemulsion phase. Figure 5.8b shows the amount of solubilized water in xylene as a function of surfactant concentration in the organic phase as obtained from the phase diagram in Figure 5.8a.

A fourth example is shown in Figure 5.9, which displays the phase behavior of the system $\text{EO}_{19}\text{PO}_{43}\text{EO}_{19}$ -*p*-xylene-water. Here, one can imagine going from the surfactant-water baseline towards the surfactant-xylene baseline at a constant concentration of surfactant according to the dotted line drawn in the figure. This “cut” illustrates the richness in the phases of this particular system. Note also that the phase diagram is not complete, since below the dashed line there are two- and three-phase regions. Comparing the phase diagrams in Figure 5.8 and Figure 5.9 (where the same organic phase is used) we realize the importance of the surfactant molecular structure for the formation of various mesophases.

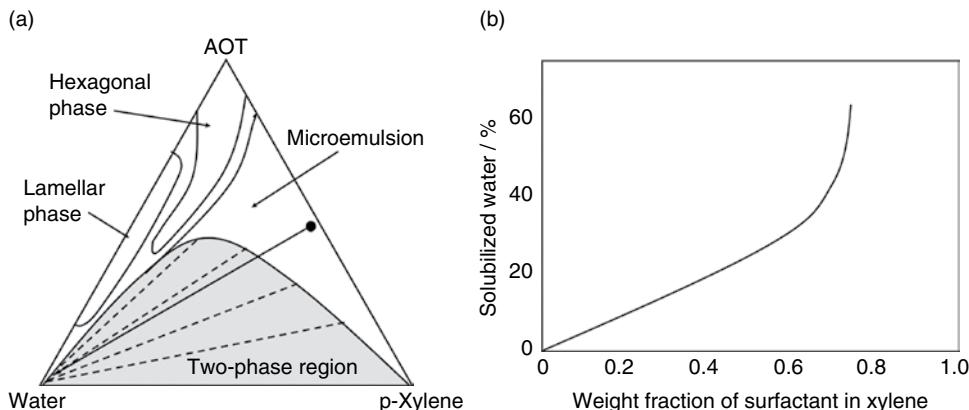


Figure 5.8 A three-component system (water, *p*-xylene and sodium bis(2-ethylhexyl) sulfosuccinate (Aerosol-OT)) that separates at low surfactant concentrations into (a) one almost pure water phase and one microemulsion phase; (b) the data replotted as the amount of solubilized water (%) as a function of surfactant concentration in the organic phase. (From Ekwall, P., Mandell, L. and Fontell, K. (1979) Some observations in binary and ternary aerosol OT systems. *Journal of Colloid and Interface Science*, **33**, 215–235.)

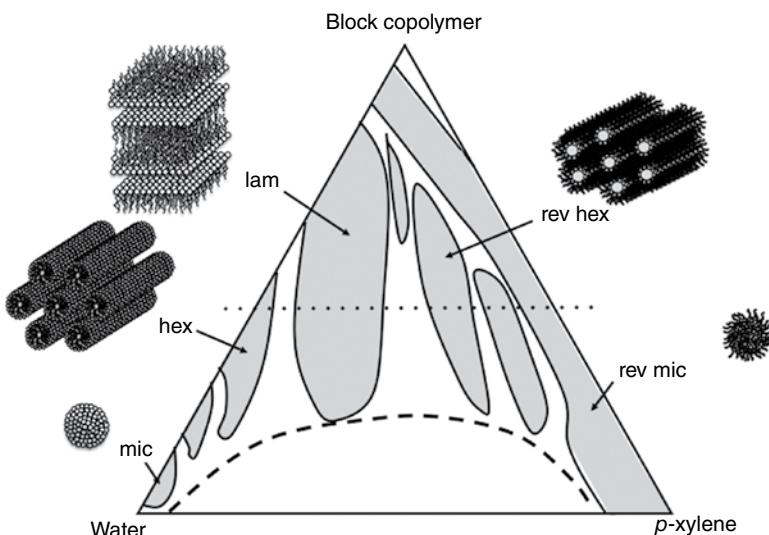


Figure 5.9 Phase diagram for the system $\text{EO}_{19}\text{PO}_{43}\text{EO}_{19}$ –water–*p*-xylene. The one-phase regions not identified in the figure are different cubic liquid crystalline phases. The white area under the dashed line contains two or three phases in equilibrium. (With permission from Alexandridis, P., Olsson, U. and Lindman, B. (1998) A record nine different phases (four cubic, two hexagonal, and one lamellar lyotropic liquid crystalline and two micellar solutions) in a ternary isothermal system of an amphiphilic block copolymer and selective solvents (water and oil). *Langmuir*, **14**, 2627–2638. Copyright 1998, American Chemical Society.)

Temperature is an Important Parameter

To illustrate the temperature dependence, important mainly for nonionic surfactants, a stack of isothermal phase diagrams can be given in a triangular prism, as depicted in Figure 5.10.

As in the case of four-component systems (next section), one may choose to investigate the phase behavior at equal amounts of oil and water (Figure 5.11). Here the surfactant corner could be a single surfactant, or a mixture of surfactants. (Or a mixture of a surfactant and another amphiphile, such as a long-chain alcohol.)

Figure 5.12 shows two examples of such cuts. In Figure 5.12a the surfactant is a pure substance, giving a horizontal fish, whereas in Figure 5.12b the surfactant is of technical quality with a broad homologue distribution. In the latter case the fish is twisted upwards, towards higher temperatures, as the surfactant concentration is lowered. This is due to an uneven partitioning of the hydrophobic and hydrophilic species between the oil and water phases. The hydrophobic species are solubilized in the oil phase rendering the surfactant at the interface more hydrophilic (page 432–433). As the surfactant concentration increases, more of the hydrophobic species are located at the interface, thus lowering the transition temperature. Such phenomena are further dealt with in Chapters 24 and 25 on emulsions, detergency, and microemulsions.

A third representation is commonly termed the “Shinoda cut” after its originator and presents the temperature dependence of the phases at a constant concentration of amphiphile,

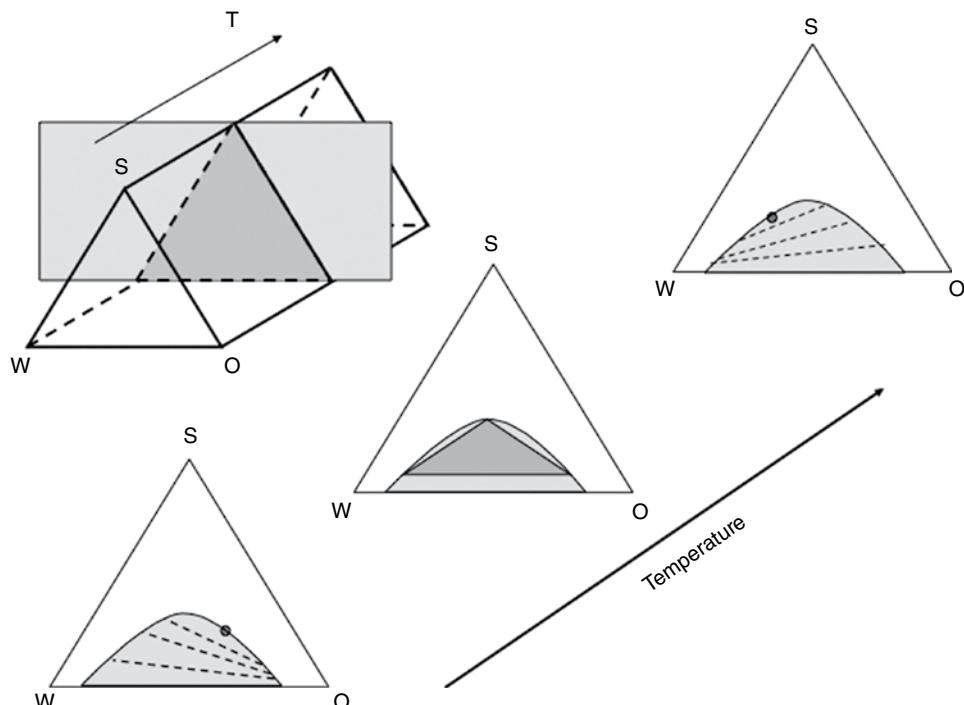


Figure 5.10 Three-dimensional representation of phase diagrams of a ternary system where the temperature is one variable

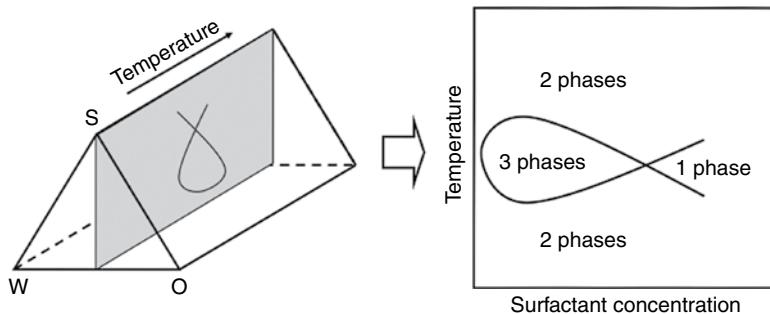


Figure 5.11 Construction of a “fish diagram” where the cut is such that the oil/water ratio is constant at 1:1

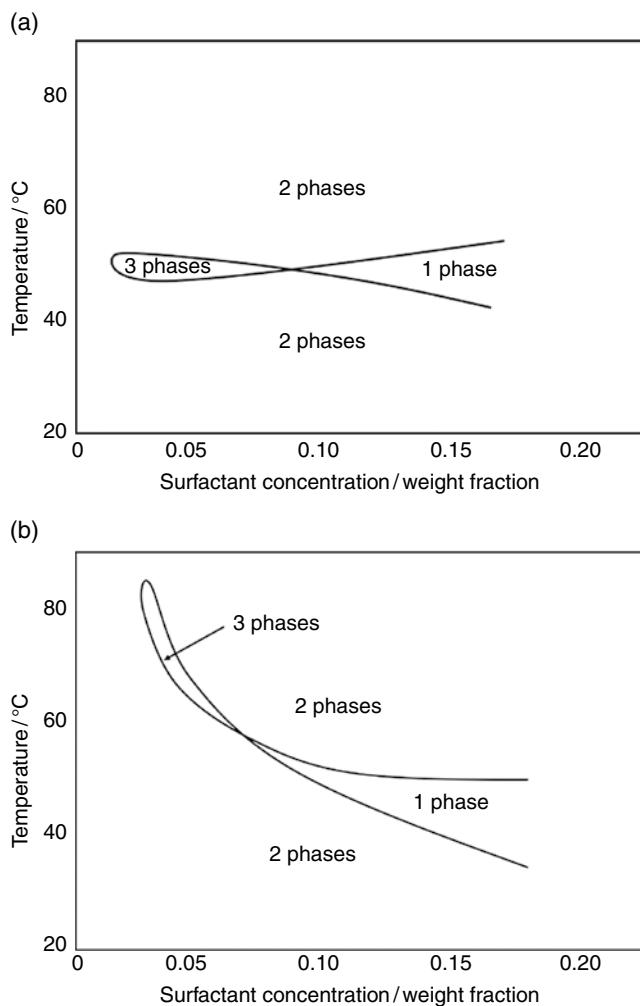


Figure 5.12 Two examples of fish diagrams. The system is water-n-octane- $C_{12}E_6$ and the surfactant is homologue pure (a). The same system as in (a) but with a technical surfactant (b). (With permission from Jacobs, B., Sottmann, T. and Strey, R. (2000) Efficiency boosting with amphiphilic block copolymers: a new approach to microemulsion formulation. *Tenside Surfactants Detergents*, **37**, 357–364. Copyright 2000, Carl Hanser Verlag GmbH & Co.)

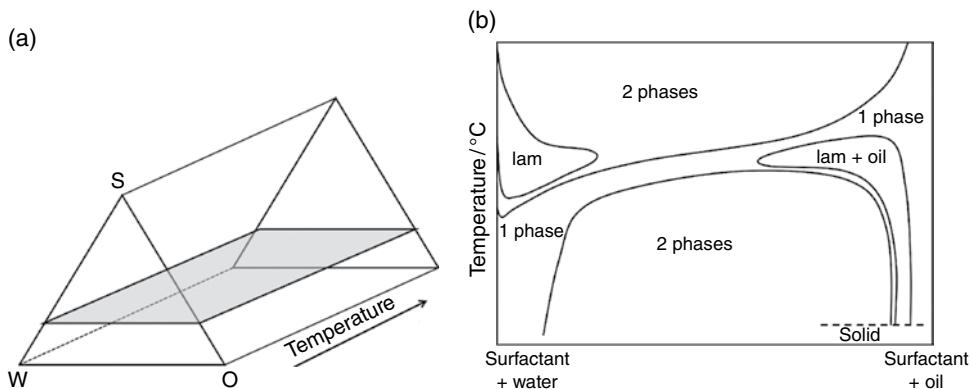


Figure 5.13 The temperature dependence of nonionic systems is often represented by Shinoda cuts, which are performed at a constant concentration of the amphiphile (a). Here exemplified with the system $C_{12}E_5$ -tetradecane–water (further discussed in Chapter 17) (b). (With permission from Licherfeld, F., Schmeling, T. and Strey, R. (1986) Microstructure of microemulsions of the system water-*n*-tetradecane-alkyl polyglycol ether ($C_{12}E_5$). Journal of Physical Chemistry, **90**, 5762–5766. Copyright 1986, American Chemical Society.)

typically between 5 and 15%, as shown in Figure 5.13a. An example is shown in Figure 5.13b for the system $C_{12}E_5$ -tetradecane–water.

A fourth representation, where temperature is one parameter, is to use a constant ratio of surfactant/water and increase the oil content or, alternatively, a constant ratio of surfactant/oil and increase the water content. Examples of such cuts are shown in Figure 5.14. These cuts are used for evaluation of the stability ranges of oil-in-water and water-in-oil microemulsions, respectively.

Four Components can be Represented by Pseudo-Phase Diagrams

A four-component system can at fixed temperature be represented by a tetrahedron as is illustrated in Figure 5.15. In order to have a two-dimensional representation, one ties two components together. If, for example, the fourth component is a salt, then it may be included in the water phase. In this way a pseudo three-component system is created. If, on the other hand, the fourth component is an amphiphile, for example, a cosurfactant, then it is normally put together with the surfactant, thus forming a mixed amphiphile system, as is depicted in Figure 5.15a. Cosurfactant here means any other amphiphilic compound, such as an alcohol or another surfactant. One should be aware, however, that this type of construction is not straightforward in a thermodynamic sense and none of the guiding rules regarding the construction of phase diagrams, outlined above, are valid.

The total amphiphile concentration, in weight fraction, is normally given the symbol γ , where:

$$\gamma = \frac{m_{\text{surfactant}} + m_{\text{co-surfactant}}}{m_{\text{water}} + m_{\text{oil}} + m_{\text{surfactant}} + m_{\text{co-surfactant}}} \quad (5.3)$$

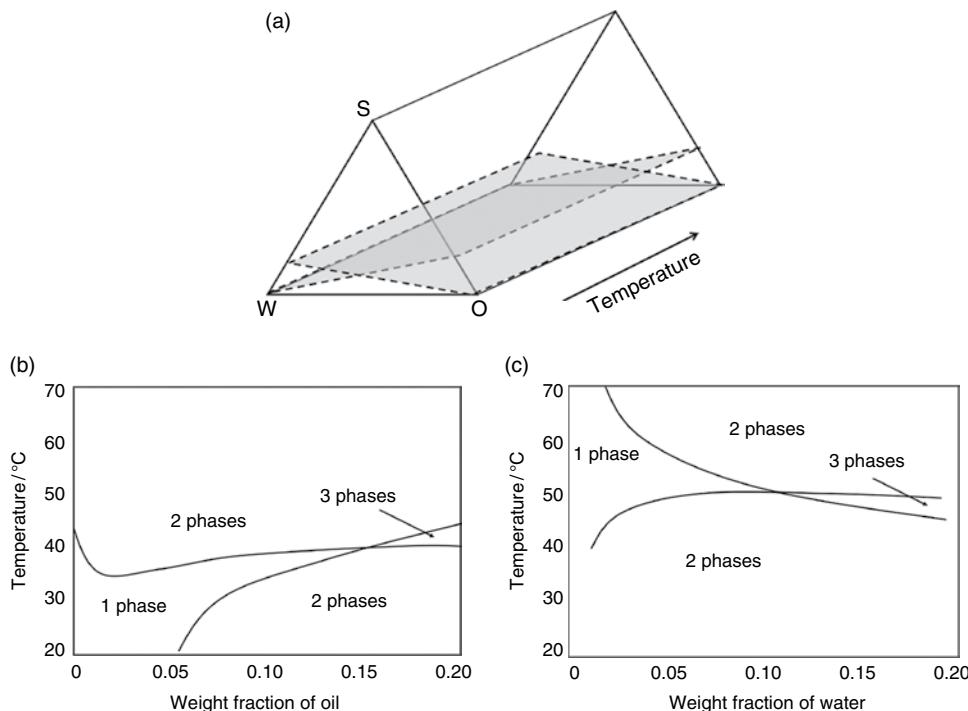


Figure 5.14 (a) Two cuts where either the surfactant/water or the surfactant/oil ratio is held constant. (b) Keeping the surfactant:water ratio constant and increasing the oil content, forming an o/w microemulsion, and (c) keeping the surfactant:oil ratio constant and increasing the water content forming a w/o microemulsion. The system is $C_{10}E_5$ -n-octane-water. (With permission from Sottmann, T. and Stubenrauch, C. (2009) Phase behavior, interfacial tension and microstructure of microemulsions, in Microemulsions—Background, New Concepts, Applications, Perspectives (ed. C. Stubenrauch), John Wiley & Sons, Ltd, Chichester, pp. 1–47. Copyright 2009, Wiley-Blackwell.)

Here, m_i is the mass of component i .

Another useful parameter is the amphiphile composition, that is, the fraction of cosurfactant in a mixed amphiphile system. This is denoted δ and is defined as:

$$\delta = \frac{m_{\text{co-surfactant}}}{m_{\text{co-surfactant}} + m_{\text{surfactant}}} \quad (5.4)$$

This nomenclature is used in Chapter 17, which deals with microemulsions.

In some cases it is required that a surfactant system be evaluated with respect to the formation of a microemulsion. In these cases, “one component” is a mixture of oil and water in a 50/50 ratio, as exemplified in Figure 5.15b. Such cuts are schematically shown in Figure 5.16. In these representations one normally finds a three-phase region bordered by two-phase regions. At higher surfactant concentrations the three-phase region converts into a one-phase region—a microemulsion—sometimes termed the *surfactant phase*. The

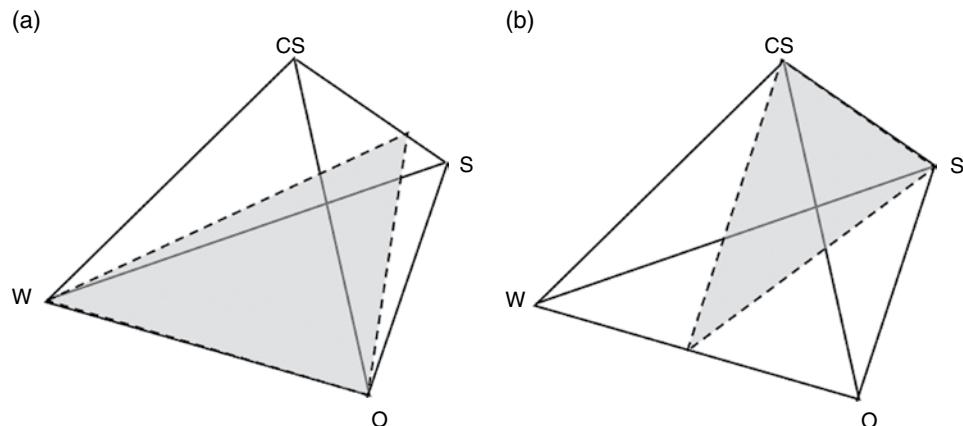


Figure 5.15 Representation of four components in a tetrahedron; the shaded area represents cuts at (a) a constant ratio of surfactant (*S*) to cosurfactant (*CS*) and (b) a constant ratio of water (*W*) to oil (*O*)

boundary lines of the phase regions resemble the symbol of a fish and this cut is, therefore, sometimes termed a “fish cut”.

In Figure 5.16a the surfactant and the cosurfactant partition equally between the oil and water phases, hence the three-phase region is symmetrically positioned on a line that passes through the o/w apex. This gives a fish lying in a horizontal direction if the amphiphile composition (δ) is plotted as a function of total amphiphile concentration (γ), as shown in Figure 5.16b.

In Figure 5.16c, on the other hand, the symmetry line does not pass through the o/w apex. This renders a skewed and tilted fish, as shown in Figure 5.16d. This is due to an uneven partitioning of the surfactant and the cosurfactant between the oil and water phases; this is further discussed later in relation to Figure 24.2. Such uneven distribution of surfactant and cosurfactant is of great importance in formulating surfactant systems.

Note the similarity of the fish diagrams in Figure 5.16 with the fish diagram when the temperature is used as a variable (Figure 5.12). This is not surprising, as a nonionic surfactant becomes hydrophobic when increasing the temperature. Likewise, changing the amphiphile composition (δ) will alter the hydrophobicity of the mixture.

Complexes Formed from Species of Opposite Charge Represent Complicated Phase Diagrams

Figure 5.17a shows another type of phase behavior, which occurs when two solutes associate, as in the formation of polyelectrolyte complexes from oppositely charged polyelectrolytes (Chapter 9) or the formation of complex between a charged surfactant and an oppositely charged polymer (Chapter 14) or mixtures of oppositely charged surfactants (Chapter 13). Here, an almost pure aqueous phase is in equilibrium with a phase that is rich in the two associating species. This type of phase separation is termed *associative phase separation*.

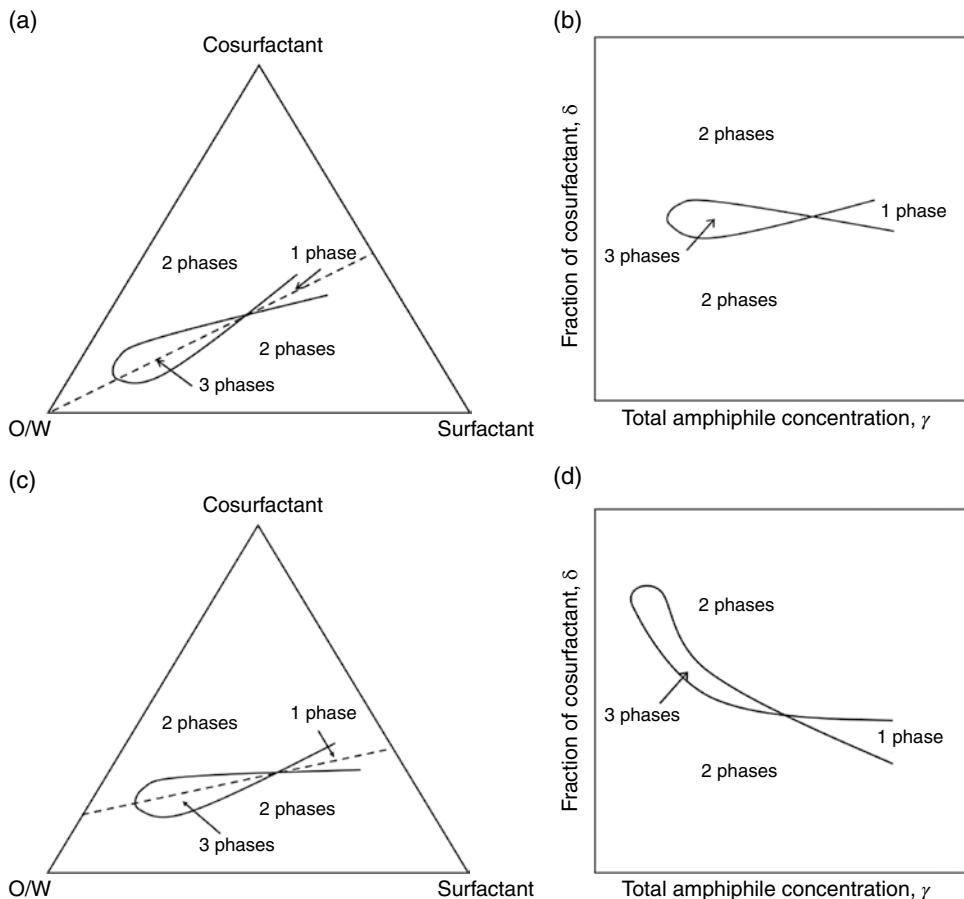


Figure 5.16 A (pseudo-)phase diagram where one corner represents a mixture of oil and water and the other corners represent a cosurfactant (e.g., an alcohol) and a surfactant. The area inside the “fish” is a three-phase region and the area in the tail is a one-phase region (microemulsion). The areas outside the fish are two-phase regions. (a) Equal partitioning of surfactant and cosurfactant between the oil and water phases and (b) replotted as amphiphile composition, δ , versus total amphiphile concentration, γ . (c) and (d) are similar diagrams to (a) and (b) but with the difference that the fish does not point towards the o/w corner, due to unequal partitioning of surfactant and cosurfactant between the water and oil phases

Such systems cannot be considered to be three-component systems, since the effect from the counterions that come with the components is significant. The counterions must be considered as a separate component. Figure 5.17b shows how the components can be split up into (i) water, (ii) one polyelectrolyte, (iii) the other polyelectrolyte (or alternatively a surfactant) of opposite charge, (iv) the complex salt (for example, the polyelectrolyte complex), and (v) the simple salt (that is, the salt formed from the counterions). In the figure the conventional plane is shown, that is, the water, polyelectrolyte and the polyelectrolyte (or surfactant) of opposite charge. The problem with this representation is that the tie-lines

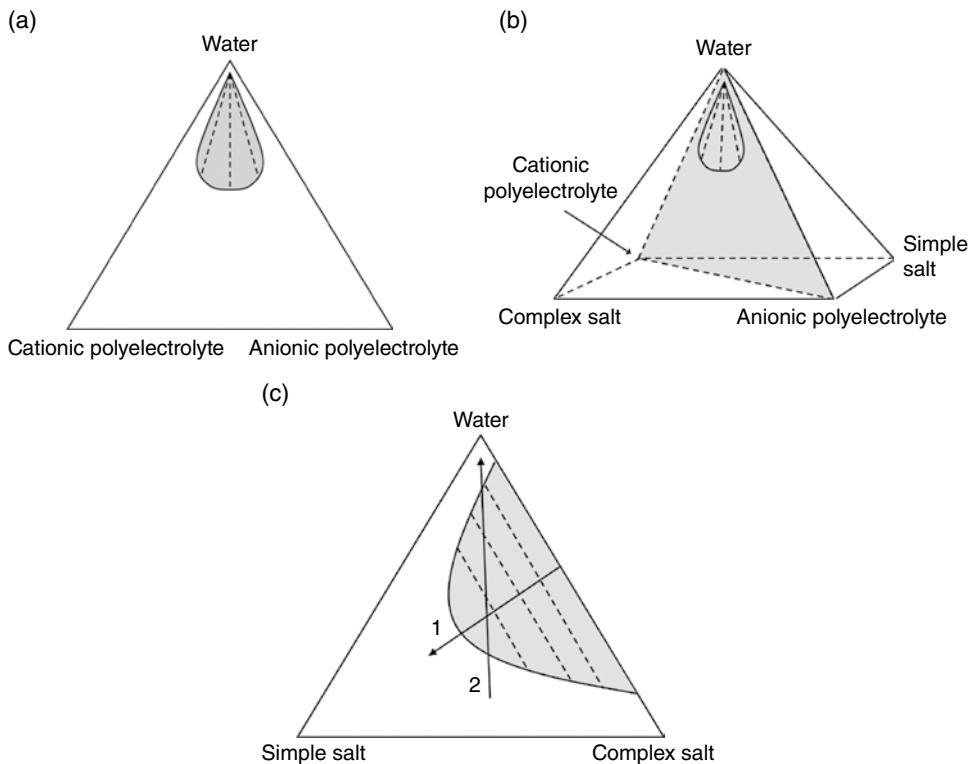


Figure 5.17 Phase diagram obtained when two polymers of opposite charge are mixed: (a) the ordinary representation with the original components at the apices (note that the dashed lines are not tie-lines in a strict sense, see text); (b) a complete representation having the complex as one component and the salt originating from the counterions as another component; (c) is a representation where the polyelectrolyte complex and the salt, formed from the counterions, are components at the apices. (With permission from Ilekti, P., Piculell, L., Tournilhac, F. and Cabane, B. (1988) How to concentrate an aqueous polyelectrolyte/surfactant mixture by adding water. *Journal of Physical Chemistry B*, **102**, 344–351 and Svensson, A., Piculell, L., Cabane, B. and Ilekti, P. (2002) A new approach to the phase behavior of oppositely charged polymers and surfactants. *Journal of Physical Chemistry B*, **106**, 1013–1018. Copyright 1988, American Chemical Society.)

are not in this plane, as is indicated in the figure by the line; the dilute aqueous solution contains most of the simple salt whereas the complex precipitate hardly contains any salt.

An alternative representation is to use water, complex salt, and single salt as components (Figure 5.17c). Now it is seen that when diluting with water (arrow 2 in the figure) the two-phase region grows larger. This is according to expectations because the ionic strength decreases and, hence, the driving force for complex formation increases (Chapter 3 and Figure 9.15). The diagram also shows that on adding salt (arrow 1 in the figure), the two-phase region decreases and ultimately vanishes, as expected from the discussion on the driving force for complex formation in Chapter 3.

The conclusion is then that being inside the two-phase region in Figure 5.17a and diluting with water, the two-phase area (the drop-shaped area) will increase in extension. It should be noted that a phase diagram such as the one depicted in Figure 5.17c implies that the complex must first be formed and cleansed from salts before being used for phase determination.

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6

Surfactant Self-Assembly: Beyond the Spherical Micelle

Micelle Type and Size Vary with Concentration

The spherical micelle discussed in Chapter 4 is but one possibility of an amphiphile self-assembly. The spherical micelle does not form at all for many amphiphiles and for others it occurs only in a limited range of concentration and temperature. In general, we can distinguish between three types of behavior of a surfactant or a polar lipid as the concentration is varied:

1. The surfactant has a high solubility in water and physicochemical properties (viscosity, scattering, spectroscopy, etc.) vary in a smooth way from the critical micelle concentration (CMC) region up to saturation. This suggests there are no major changes in micelle structure but that the micelles remain small and do not depart much from a spherical shape.
2. The surfactant has a high solubility in water but as the concentration is increased there are quite dramatic changes in certain properties. This indicates that there are marked changes in the self-assembly structure.
3. The surfactant has low water solubility and there is a phase separation at low concentrations.

The three cases are characterized by different ranges of existence of the isotropic solution phase. In either case, the new phase formed above saturation may be:

- a liquid crystalline phase,
- a solid phase of (hydrated) surfactant, or
- a second, more concentrated, surfactant solution.

Different phase structures give very different physicochemical properties and, therefore, in any practical use of surfactants it is mandatory to have control over the structure.

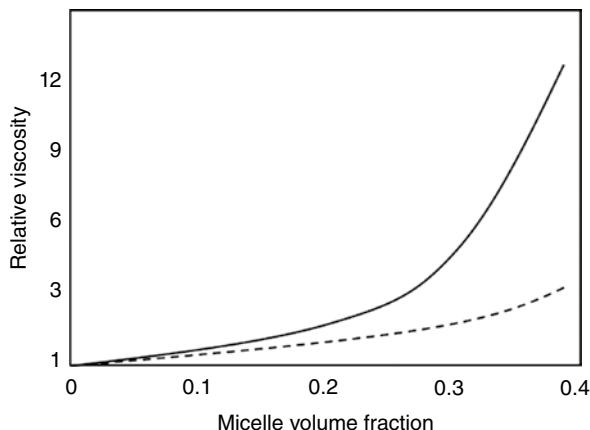


Figure 6.1 Relative viscosity (i.e., solution viscosity divided by that of water) as a function of micelle volume fraction for solutions of spherical micelles. Dashed and solid curves give theoretical predictions for two models of spherical particles, in the latter case taking into account particle-particle interactions. The system exemplified is that of $C_{12}E_5$ micelles with an equal weight of solubilized decane. (With permission from Leaver, M.S. and Olsson, U. (1994) Viscosity of a nonionic microemulsion near emulsification failure. Langmuir, **10**, 3449–3454. Copyright 1994, American Chemical Society.)

The regions of existence of different phases and the equilibria between different phases are described by phase diagrams (Chapter 5). These are significant not only as a basis for applications but also for our general understanding of surfactant self-assembly.

For a relatively short-chain surfactant, like C_8 or C_{10} , a slow and regular variation of relevant properties with concentration, and no phase separation, is usually observed up to high concentrations, say 10–40 wt% (Figure 6.1). The viscosity, which is an important property for uses of surfactants, varies smoothly and approximately as predicted for a dispersion of spherical particles up to high concentrations. By scattering experiments and by nuclear magnetic resonance (NMR) spectroscopy, direct evidence is obtained for small globular aggregates up to the approach of phase separation. For some surfactants it may be that only at micelle volume fractions of the order of 0.3 are appreciable deformations of the micelles seen.

A frequently encountered behavior for longer-chain surfactants, say C_{14} or above, is that at low or intermediate concentrations the viscosity starts to increase rapidly with concentration. This is exemplified in a plot of the (zero shear) viscosity versus concentration in Figure 6.2. Here the micelles grow with increasing concentration, at first to short prolate spheroids or cylinders and then to rod-like or even long thread-like micelles (Figure 6.3).

A third, less common, behavior is the growth to very long thread-like micelles at very low concentrations, sometimes just above the CMC. Growth of micelles is generally a one-dimensional process leading to aggregates with a circular cross-section. The hydrophobic core has a radius, which, as for the spherical micelles and for the same reasons, equals the length of the extended alkyl chain of the surfactant. The linear length of the thread-like micelles can vary over wide ranges, from well below 10 nm to many 100 nm.

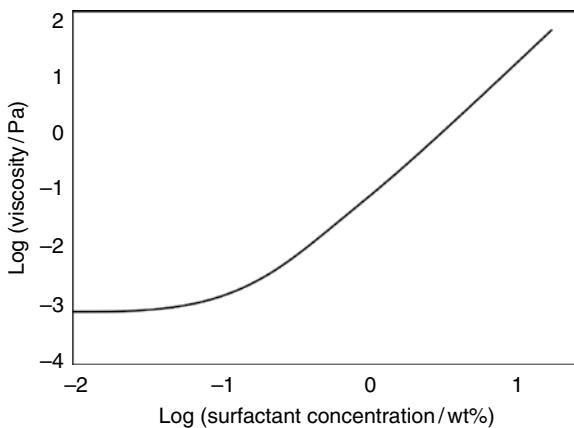


Figure 6.2 For surfactants forming large micelles, the viscosity increases rapidly with surfactant concentration. The increase in zero shear viscosity is plotted on a logarithmic scale as a function of surfactant concentration for $C_{16}E_6$. (Courtesy of U. Olsson, M. Malmsten and F. Tiberg.)

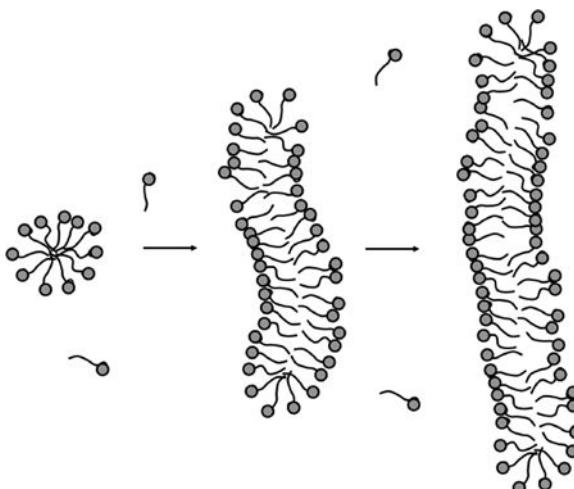


Figure 6.3 At higher concentrations the micelles often grow from spherical aggregates to long elongated micelles, referred to as rod-, worm-, or thread-like micelles

Micellar Growth is Different for Different Systems

Micellar growth is a very common phenomenon and for ionic surfactants the following factors (some of which are exemplified in Figures 6.4 and Figure 6.5) influence the growth:

1. The tendency to grow increases strongly with the alkyl chain length and there is no growth for shorter chains.

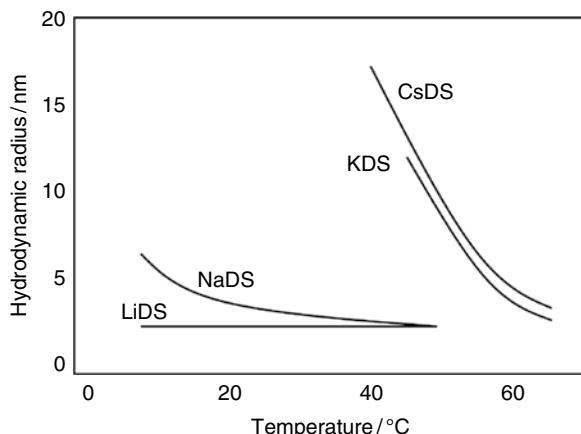


Figure 6.4 The size of micelles of dodecylsulfate (DS) with different counterions. The micelles are characterized by the hydrodynamic radius, which decreases with increasing temperature and is very sensitive to the choice of counterion. Concentrations are: LiDS, 20 g/l and 1 M LiCl; NaDS, 20 g/l and 0.45 M NaCl; KDS, 5 g/l and 0.45 M KCl; CsDS 5 g/l and 0.45 M CsCl. As seen, KDS and CsDS give much more pronounced growth in spite of lower concentrations of surfactant. (Adapted with permission from Missel, P.J., Mazer, N.A., Carey, M.C. and Benedek, G.B. (1982) Thermodynamics of the sphere-to-rod transition in alkyl sulfate micelles, in Solution Behavior of Surfactants (eds K.L. Mittal and E.J. Fendler), vol. 1, pp. 373–388. Copyright 1982, Springer.)

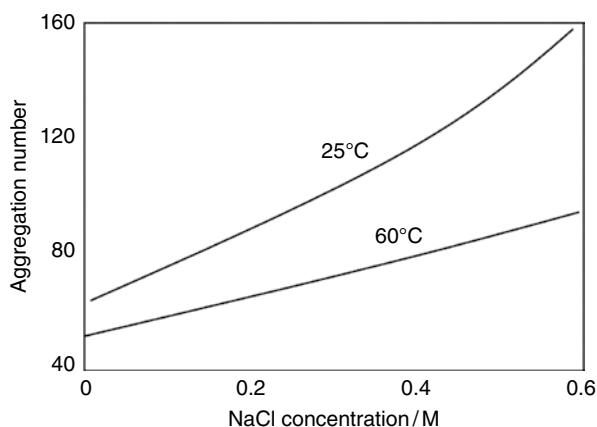


Figure 6.5 The aggregation number of sodium dodecyl sulfate (SDS) micelles increases with decreasing temperature and increasing salt concentration. (With permission from Turro, N.J. and Yekta, A. (1978) Luminescent probes for detergent solutions. Journal of the American Chemical Society, **100**, 5951–5952. Copyright 1978, American Chemical Society.)

2. Micellar growth is strongly dependent on temperature and is promoted by a decrease in temperature. For example, for hexadecyltrimethylammonium bromide, there is micellar growth at 30°C but not at 50°C.
3. While CMC is only slightly dependent on the counterion within a given class, micellar growth displays a strong variation. The dependence of growth on the counterion, however, is very different for different surfactant head groups. For example, for hexadecyltrimethylammonium bromide, there is major micelle growth while there is no growth with chloride as the counterion. For alkyl dodecyl sulfates, growth is insignificant with Li⁺ as the counterion, moderate with Na⁺ but quite dramatic with K⁺ or Cs⁺. With carboxylate as the head group, the opposite variation along the series of alkali ions is observed. Organic counterions may induce dramatic growth at low concentration, as exemplified by salicylate in the presence of long-chain cationic surfactants.
4. In the case of micellar growth, micellar size increases strongly with surfactant concentration.
5. Micelle size is very sensitive to cosolutes. Addition of salt promotes micelle growth for ionic surfactants. Solubilized molecules can have very different effects depending on the surfactant system. However, in general nonpolar solubilizates, such as alkanes, which are located in the micellar core, tend to inhibit micellar growth, while medium-to long-chain alcohols or aromatic compounds, which are located in the outer part of the micelles, tend to strongly induce growth. For example, for hexadecyltrimethylammonium bromide there is no growth on adding cyclohexane while hexanol and benzene give dramatic growth. Large micelles are, contrary to the small spherical micelles, very polydisperse.

For other classes of surfactants there are different characteristics of micellar growth. Nonionic surfactants of the polyoxyethylene type give growth with increasing concentration, which is much more marked the shorter the polar group. With four to six oxyethylene units there is dramatic growth, while with eight or more oxyethylene units there is negligible growth under any conditions. These surfactants show a micellar growth that is much more pronounced at a higher temperature, that is, opposite to other classes of surfactants. This and other unusual features of nonionics are treated in Chapter 7.

Solutions of large micelles show many parallels with solutions of linear polymers and the micelles have been denoted “living polymers.” Because of the polymer-like behavior, concepts and theories developed for polymer solutions have been successfully applied. Differences from polymers, which complicate the comparison, include the strong dependence of the “degree of polymerization” on the conditions (surfactant concentrations, temperature, etc.). Furthermore, under certain conditions, such as very high concentrations, growth may lead to branched structures.

The large micelles can differ strongly in flexibility and may be referred to as rigid rods, or semi-flexible or highly flexible micelles. As for polymers, the flexibility can be characterized by a persistence length. The flexibility of ionic micelles is strongly dependent on electrolyte addition. Thus, salt addition can induce a change from rather rigid rods to very flexible micelles.

In dilute solutions, where the micelles do not overlap they behave as independent entities (Figure 6.6). After the overlap volume fraction (ϕ^*) in the so-called semi-dilute concentration regime, the micelles are entangled and there is a transient network. The

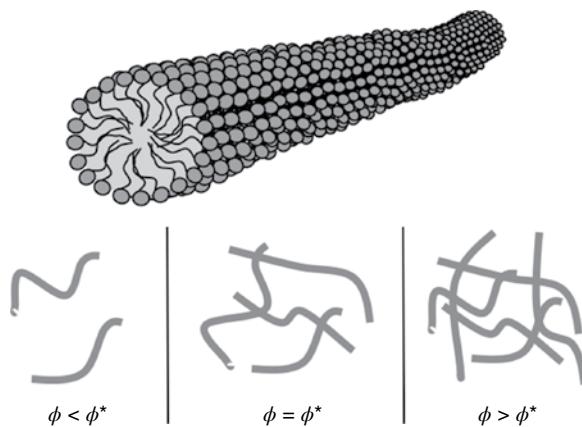


Figure 6.6 There is a close analogy between solutions of long micelles and polymer solutions, including transient networks. The figure illustrates the transition from dilute to semi-dilute solutions and the overlap concentration; ϕ^* is the overlap volume fraction

overlap concentration of the system presented in Figure 6.2 is about 0.1%. The viscosity of solutions of long linear micelles can be analyzed in terms of the motion of the micelles, for example, using the reptation model of polymer systems. In this, the micelles creep like a snake through tubes in a porous structure given by the other micelles. The zero shear viscosity (η) depends on micelle size (aggregation number, N), and volume fraction (ϕ) according to:

$$\eta = \text{constant } N^3 \phi^{3.75} \quad (6.1)$$

The viscosity thus increases very strongly with both micelle size and surfactant concentration.

Linear growth of micelles is the strongly dominating type of growth. Disc-like or plate-like structures may also form, but these micelles are quite small and exist only in a narrow range of conditions (concentration, etc.). Linear growth can, as mentioned, lead to branched structures, which at high enough concentrations may transform into a completely connected surfactant micellar structure, where the concept of distinct micelles loses its meaning. In such a case we use the term bicontinuous structure, since the solutions are continuous not only in the solvent but also in the surfactant.

As we will see below, bicontinuous structures are very significant in many contexts of amphiphile self-assembly. Another type of bicontinuous structure in simple surfactant–water solutions is the “sponge phase,” formed also in quite dilute surfactant solutions (Figure 6.7). This structure may form for all classes of surfactants but in particular for nonionics. We will consider it in more detail in our discussion of these surfactants (Chapter 7). We will also mention that the structure of the sponge phase is related to that of many microemulsions and will, therefore, be further discussed in this context (Chapter 17).

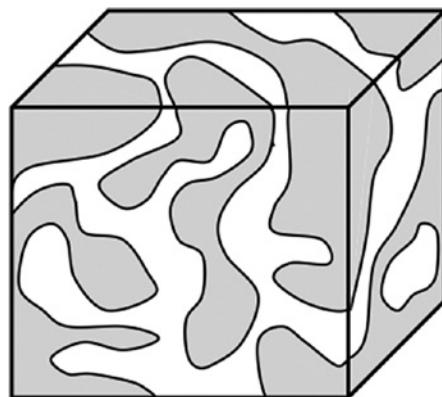


Figure 6.7 The sponge phase. For many surfactants there is an isotropic solution phase where the surfactant forms a connected three-dimensional network. Since both water and the hydrophobic regions are connected over macroscopic distances, such structures are termed bicontinuous

The Shape of the Micelles Affects the Rheology of Solutions of Gemini Surfactants

A very striking feature of gemini surfactants (Chapter 1) is that they start to form micelles at a concentration more than one order of magnitude lower than that of the corresponding “monomeric” surfactant. The low value of the CMC is an important property, implying, for instance, that gemini surfactants are very effective in solubilizing oily components. The efficiency of gemini surfactants, expressed as the C_{20} value, that is, the surfactant concentration at which the surface tension (γ) is lowered by 20 mN/m, is also very high, again when compared with the monomeric species. The effectiveness of geminis, which is given by the value of surface tension at the CMC (γ_{CMC}) is usually also somewhat better than for the corresponding monomeric surfactants. Figure 6.8 shows surface tension plots for a cationic gemini surfactant and for the corresponding monomeric amphiphile.

Gemini surfactants with flexible spacers, both hydrophilic and hydrophobic, generally show lower γ_{CMC} values than the corresponding surfactants with rigid spacers. This is probably due to better packing of the former at the air–water interface.

As mentioned above, gemini surfactants have very low CMC values when compared with conventional surfactants of the same hydrocarbon chain length. CMC ratios as high as 80 between monomeric and dimeric species have been reported. The CMC values are not very dependent on the polarity of the spacer. The values change with the length of the spacer, however, and there is often a CMC maximum at a spacer length of 5–6 carbon atoms. This maximum has been attributed to a change in spacer conformation and its resulting effect on head group hydration and alkyl chain orientation. When the spacer becomes long enough it may twist in order to allow its middle portion to reside in the micelle interior, thus contributing to the hydrophobicity of the surfactant. For geminis with a hydrophilic spacer such as oligo(ethylene glycol) the CMC values keep increasing with

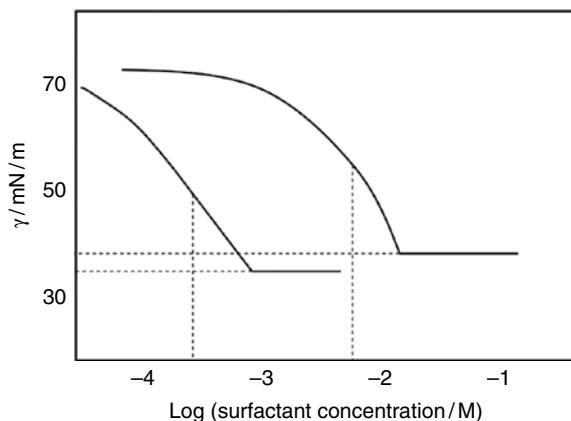


Figure 6.8 Surface tension versus log concentration plots of the gemini surfactant $C_{12}H_{25}N(CH_3)_2-(CH_2)_3-N(CH_3)_2C_{12}H_{25}^{2+}\cdot 2Br^-$ (lower left curve) and the monomeric surfactant $C_{12}H_{25}N(CH_3)_3^+\cdot Br^-$ (upper right curve). (Data reused with permission from Alami, E., Beinert, G., Marie, P. and Zana, R. (1993) Alkanediy- α , ω -bis(dimethylalkylammonium bromide) surfactants. 3. Behavior at the air-water interface. Langmuir, **9**, 1465–1467 Copyright 1993, American Chemical Society, and Tanaka, A. and Ikeda, S. (1991) Adsorption of dedecyltrimethylammonium bromide on aqueous surfaces of sodium bromide solutions. Colloids and Surfaces, **56**, 217–228. With permission from Elsevier.)

increasing spacer chain length. Introduction of a polar substituent, such as a hydroxyl group, on the spacer results in a decrease of the CMC, which is contrary to expectations. This is believed to be due to a more favorable packing in the micelles.

At low concentrations, that is, just above the CMC, cationic gemini surfactants form spherical or nearly spherical micelles just as their monomeric counterparts do. The micellar aggregation number, that is, the number of molecules that make up a micelle, for surfactants with 12 carbon atoms in the hydrophobic tails goes from around 40 for the species with two methylene groups as spacer to around 25 for the surfactant with a 10-methylene spacer unit. The surfactants with a short spacer (two, three and four methylene groups) show a very steep growth with concentration, indicating a transition from spherical to elongated micelles even at very low surfactant concentration. Surfactants with longer spacer units show a much less pronounced micelle growth with increasing concentration, in this respect resembling the behavior of the corresponding monomeric surfactants.

The shape of the micelles governs the solution viscosity. The cationic gemini surfactant 12-2-12 exhibits a dramatic viscosity increase at about 2 wt% surfactant. As can be seen from Figure 6.9, the viscosity increases between six and seven orders of magnitude within a rather narrow concentration range. This is a much more pronounced viscosity increase with concentration than normally encountered with cationic surfactants and can be accounted for by the sharp transition from spherical to thread-like micelles. It can also be noted that thread-like micelles, and thus an increased viscosity, can be induced by use of an applied shear, already at a concentration below that where they form under static conditions. The unusual rheological behavior of gemini surfactants, which takes place at relatively low surfactant concentrations, can have important practical consequences.

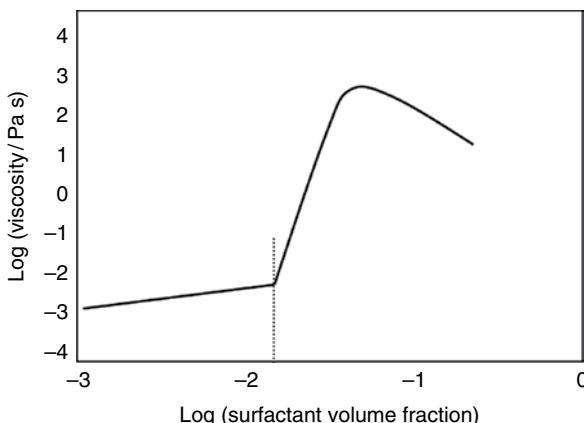


Figure 6.9 Variation of the viscosity with the surfactant volume fraction of solutions of the cationic gemini surfactant $C_{12}H_{25}N(CH_3)_2-(CH_2)_2-N(CH_3)_2C_{12}H_{25}^{2+}\cdot 2Br^-$ (12-2-12) at 20°C. (Adapted with permission from Kern, F., Lequeux, F., Zana, R. and Candau, S.J. (1994) Dynamic properties of salt-free viscoelastic micellar solutions. *Langmuir*, **10**, 1714–1723. Copyright 1994, American Chemical Society.)

Surfactant Phases are Built up by Discrete or Infinite Self-Assemblies

Surfactant micelles and bilayers are the building blocks of most self-assembly structures, the most important of which are illustrated in Figure 4.1, and it is natural to dwell on the distinction between these and give some further examples. As schematically shown in Figure 6.10 we can divide phase structures into two groups, those that are built up of limited or discrete self-assemblies, which may be characterized roughly as spherical, prolate, oblate, or cylindrical (more or less flexible), or infinite or unlimited self-assemblies. In the latter case, the surfactant aggregate is connected over macroscopic distances in one, two, or three dimensions. The hexagonal phases are examples of one-dimensional continuity, the lamellar phase of two-dimensional continuity, while three-dimensional continuity is found for the bicontinuous cubic phases, for the “sponge” phase and, as we shall see in Chapter 17, for many microemulsions.

Phases built up of discrete aggregates include the normal and reversed micellar solutions, micellar-type microemulsions, and certain (micellar-type) normal and reversed cubic phases. However, discrete self-assemblies are also important in other contexts. Adsorbed surfactant layers at surfaces may involve micellar-type structures and the same applies to mixed polymer–surfactant solutions. We will return to these matters later.

Bilayer structures are common both in nature and in applications and have a broad significance. Cooling a lamellar liquid crystalline phase typically leads to a so-called gel phase (with characteristics distinct from polymer-based gels) or a crystal with a bilayer structure. Depending on packing conditions, different arrangements can be found. One example is illustrated in Figure 6.11. In the so-called gel phases, the water between the bilayers is in a liquid-like state.

Other examples of bilayer structures already mentioned are the “sponge” phase and bicontinuous cubic phase. Bilayers may also easily close on themselves to form discrete

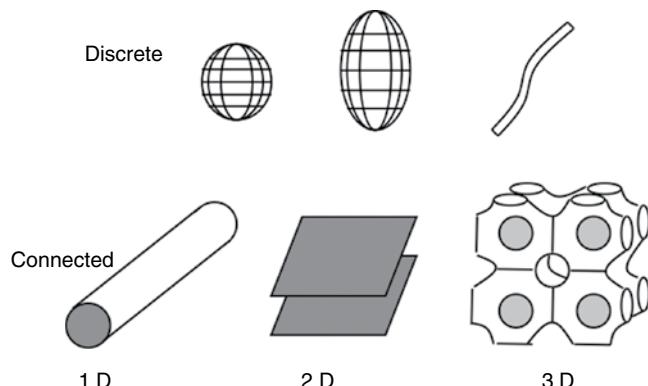


Figure 6.10 Amphiphile self-assembly structures can be divided into discrete micellar-type and connected forms. There may be connectivity in one, two, or three dimensions

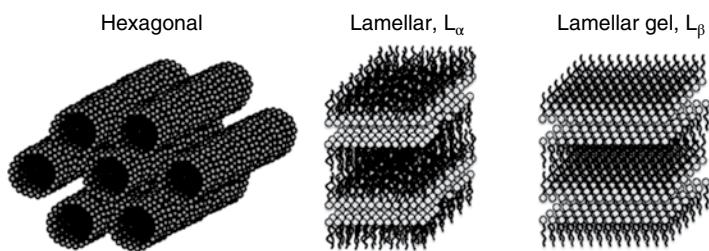


Figure 6.11 Illustration of molecular packing in two liquid crystalline phases, hexagonal (left) and lamellar (middle), and in one phase with the surfactant tails in the solid state (right)

entities, referred to as vesicles or liposomes, the latter normally used for the case of more than one bilayer. Vesicles and liposomes are of interest because of the division into inner and outer aqueous domains separated by the bilayers. Vesicles and liposomes are normally not thermodynamically stable, although there are exceptions for unilamellar vesicles, and they tend to phase-separate into the lamellar phase and a dilute aqueous solution. Lipid bilayers are important constituents of living organisms and form membranes that act as barriers between different compartments. Certain surfactants and lipids may form reversed vesicles, that is, vesicles with inner and outer oleic domains separated by an (reversed) amphiphile bilayer; the bilayer may or may not contain some water.

Micellar Solutions can Reach Saturation

Having considered the different micellar solutions, two questions arise naturally: what limits the range of existence of micelles at higher surfactant concentrations and what happens to the self-assembly structure at saturation? We will now consider the second question and return to the first one later.

Table 6.1 Different systems of notation for the most common liquid crystalline and other phases

Phase structure	Our notation	Other notations
Lamellar	lam	L_a , D, G, neat
Hexagonal	hex	H_1 , E, M_1 , middle
Reversed hexagonal	rev hex	H_2 , F, M_2
Cubic (normal micellar)	cub (cub_m)	I_1 , S_{1c}
Cubic (reversed micellar)	cub (cub_m)	I_2
Cubic (normal bicontinuous)	cub (cub_b)	I_1V_1
Cubic (reversed bicontinuous)	cub (cub_b)	I_2V_2
Gel	gel	L_β
Micellar	mic	L_1 , S
Reversed micellar	rev mic	L_2 , S
Sponge phase (reversed)	spo	L_3 (normal), L_4
Microemulsion	μ em	L, S, μ E
Vesicular	ves	—

Micellar growth to rods can be considered to arise from two mechanisms. In one, there is an internal driving force to form large aggregates with another geometry, and then micelles may grow also at low concentrations. In the other, micellar growth is induced by intermicellar repulsions to allow a better packing of the micelles. This will occur at quite high concentrations, when the micelles come in direct close contact. Often we see a combination of the two mechanisms.

Another way to solve the problem of too strong crowding of micelles is a structural transition, a “crystallization,” into an ordered phase, which may be a solid but is more frequently a liquid crystalline phase. We will now discuss:

- the structures formed;
- phase diagrams of binary surfactant–water mixtures.

There is no generally accepted notation for the different phases occurring in surfactant systems. In Table 6.1 the most common symbols for liquid crystalline phases are given.

Structures of Liquid Crystalline Phases

Micellar Cubic Phase

As can be seen in Figure 6.12, this phase is built up of regular packing of small micelles, which have properties similar to those of small micelles in the solution phase. The micelles are short prolates (axial ratio 1–2) rather than spheres, as this allows a better packing. The phase is highly viscous.

Hexagonal Phase

This phase is built up of (infinitely) long cylindrical micelles arranged in a hexagonal pattern, each micelle being surrounded by six others (Figure 6.11). The radius of the circular

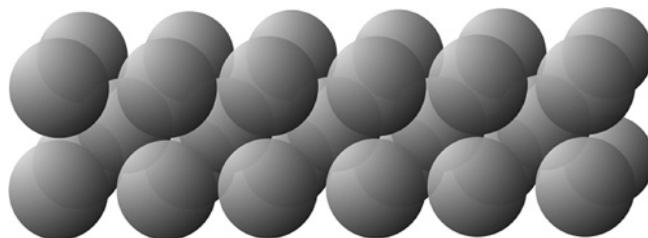


Figure 6.12 A cubic phase built up of discrete micelles. (Adapted from Fontell, K., Fox, C. and Hansson, E. (1985) *On the structure of the cubic phase I in some lipid–water systems*. Molecular Crystals and Liquid Crystals, **1**, 9–17. With permission from Taylor and Francis.)

cross-section (which may be somewhat deformed) is again close to that of the surfactant molecule length. Whereas the micellar cubic phase can be considered to arise from an ordered packing (“crystallization”) of globular micelles, the hexagonal is due to crystallization of rod-like micelles.

Lamellar Phase

This phase is built up of bilayers of surfactant molecules alternating with water layers (Figure 6.11). The thickness of the bilayers is somewhat less than twice the surfactant molecule length. The thickness of the water layer can vary (depending on surfactant) over wide ranges (below a nanometer to micrometers). The surfactant bilayer can range from being stiff and planar to being very flexible and undulating.

Bicontinuous Cubic Phases

There can be a number of different structures, where the surfactant molecules form aggregates that penetrate space, forming a porous connected structure in three dimensions. We can consider structures as either formed by connecting rod-like micelles, similar to branched micelles, or bilayer structures as visualized in Figure 4.1.

Reversed Structures

Except for the lamellar phase, which is symmetrical around the middle of the bilayer, the different structures have a reversed counterpart in which the polar and nonpolar parts have changed role (Figure 6.13). For example, a reversed hexagonal phase is built up of hexagonally packed water cylinders surrounded by the polar heads of surfactant molecules and a continuum of the hydrophobic parts. Reversed (micellar-type) cubic phases and reversed micelles analogously consist of globular discrete water cores surrounded by the surfactant molecules. The radii of these water droplets are typically in the range 20–100 Å.

The phases described are the commonly occurring ones but, in addition, there are other phases of less importance. Some of these involve discrete aggregates of different shapes and different types of mutual organization and some are similar to the hexagonal phase but with alternative arrangements of the cylinders or noncircular cross-sections of the aggregates.

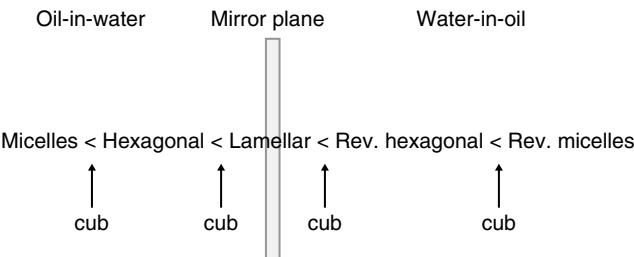


Figure 6.13 The Fontell scheme for the dependence of surfactant liquid crystal structure on composition, illustrating the symmetry of curvature of the surfactant aggregates around the lamellar phase structure, and the four principal locations of cubic phases. (With permission from Fontell, K. (1990) Cubic phases in surfactant and surfactant-like lipid systems. Colloid and Polymer Science, **268**, 264–285. Copyright © 1990, Springer.)

How to Determine Phase Diagrams

In a phase diagram we can read how many phases are formed, which the phases are and what the compositions of the phases are. The determination of a complete phase diagram involves considerable work and skill, and strongly increases in difficulty as the number of components increases. The distinction between solution and liquid crystalline phases is best made from studies of diffraction properties, either light, neutron, or X-ray. Liquid crystalline phases have a repetitive arrangement of aggregates and the observation of a diffraction pattern can firstly give evidence for a long-range order and, secondly, distinguish between alternative structures.

The scattering of normal and polarized light is very useful for identification of different structures. Isotropic phases, that is, solutions and cubic liquid crystals, are clear and transparent while the anisotropic liquid crystalline phases scatter light and appear cloudy to varying degrees. Using polarized light and viewing samples through crossed polarizers give a black picture for isotropic phases, while anisotropic ones give bright images. The patterns in a polarization microscope are distinctly different for different anisotropic phases and can, therefore, be used to identify phases, for example, to distinguish between hexagonal and lamellar phases. Another very useful technique is NMR spectroscopy, especially observations of quadrupole splittings in deuterium NMR. Different patterns are observed for different regions in a phase diagram and allow a direct identification (Figure 6.14). For isotropic phases (micellar solution, sponge phase, cubic phase, or microemulsion) a narrow singlet is observed (Figure 6.14a). If there is a single anisotropic liquid crystalline phase, a doublet is obtained (Figure 6.14b). The magnitude of the “splitting” depends on the degree of anisotropy and is, for example, twice as large for a lamellar phase as for a hexagonal one under comparable conditions. In a two-phase region, with coexistence of two phases, we observe spectra of the two phases superimposed; for one isotropic and one anisotropic phase, we observe one singlet and one doublet (Figure 6.14c), and for two anisotropic phases (lamellar and hexagonal) we observe two doublets (Figure 6.14d). In a three-phase region with two anisotropic and one isotropic phase coexisting, we observe two doublets and one singlet (Figure 6.14e). One narrow and one broad singlet may be observed for the case of one

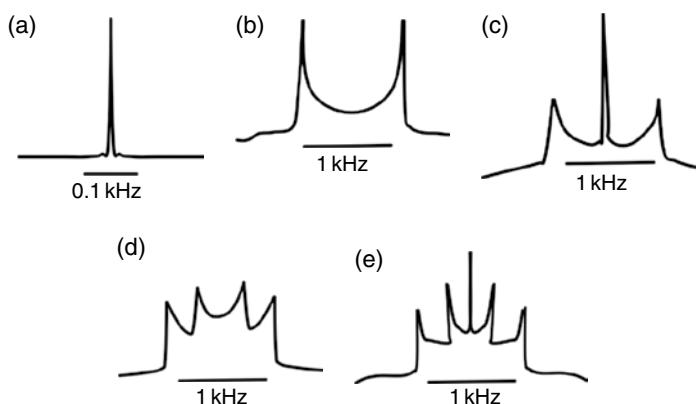


Figure 6.14 NMR spectra of D_2O are helpful in phase diagram determinations. (With permission from Khan, A., Fontell, K., Lindblom, G. and Lindman, B. (1982) Liquid crystallinity in a calcium surfactant system: phase equilibria and phase structures in the system calcium octylsulfate/decan-1-ol/ water. *Journal of Physical Chemistry*, **86**, 4266–4671. Copyright 1982, American Chemical Society.)

anisotropic and one isotropic phase before equilibrium has been reached and the anisotropic phase is dispersed as small microcrystallites.

The viscosity varies strongly between different phases but since it is also strongly dependent on concentration and surfactant it does not allow an unambiguous determination of the phase present in a sample. Characteristically, however, cubic phases are very viscous and often quite stiff, so the clear gel-like appearance of a phase can normally be used to identify a cubic phase. Hexagonal phases, although less viscous than cubic phases, are also of high viscosity and much more viscous than the lamellar phases.

The distinction between normal and reversed phases can typically be made from sample compositions, since normal phases occur on the water-rich side of the lamellar phase and the reversed ones on the water-poor side. Conductivity is most helpful since the conductivity of a solution of water in closed domains is several orders of magnitude lower than if there are aqueous domains connected over macroscopic distances.

In the determination of phase diagrams, we can distinguish between a first step involving the establishment of which phases are forming and their sequence of appearance as a function of concentration, and a second step involving the quantitative determination of the regions of existence of different phases. The first step can, for example, involve macroscopic observations of the effect of the penetration of water into the surfactant crystals. The complete phase diagram determination involves making up a large number of samples with different compositions and firstly establishing whether there is a single homogeneous phase or more than one phase. In the latter case, the next step is to separate the phases, which often is possible by centrifugation; however, the separation can be very difficult or impossible due to high viscosities of phases and/or a small difference in density. (The NMR method mentioned above circumvents this problem as phase identification can be made without macroscopic separation of phases.) Finally, the different phases are identified and the compositions of phases and of multiphase samples are determined by some chemical analysis.

Binary Surfactant–Water Phase Diagrams can be Very Different

For a surfactant, which forms spherical micelles up to high concentrations, the first liquid crystalline phase is the micellar cubic one. At higher concentrations there are structural transitions into hexagonal, bicontinuous cubic, and lamellar. This type of behavior is illustrated schematically in Figure 6.15 and for a single-chain ionic surfactant in Figure 6.16. Binary phase diagrams are presented with the temperature along the ordinate and the composition along the abscissa. The composition may be expressed in different ways: mole ratio, mole fraction, weight fraction, or weight percent. Traditionally, compositions on weight rather than mole basis have been used. This has the disadvantage that molar compositions cannot be directly read out, but since stoichiometric complexes are rare this is not a major disadvantage. Weight-based scales give a more suitable division of diagram area into stability regions of different phases and are the only possibility if the surfactant composition is not exactly known. In Figure 6.16 two-phase regions, which are always present, are included between the different one-phase regions. In the low temperature part of the diagram there are various solid phases, ice and solid surfactant.

The phase diagram of dodecyltrimethylammonium chloride (Figure 6.16) represents a case with little micellar growth, and a relatively low Krafft point; solid phases have little role to play. We can see that the isotropic micellar phase exists at room temperature up to high concentrations (about 40%). The next phase is a cubic phase built up of discrete globular micelles. Between the two phases there is a two-phase region where the two phases coexist. Due to the impossibility of packing globular micelles at high volume fractions, the micelles deform and become elongated to form a hexagonal phase. Thereafter,

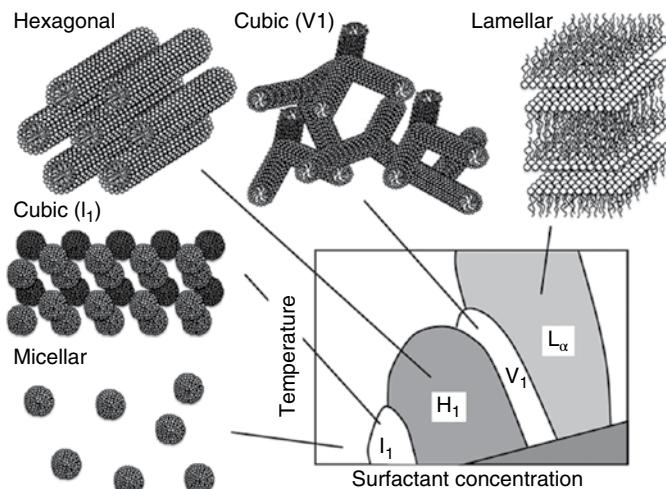


Figure 6.15 Schematic phase diagram for a polar surfactant with a preference for forming spherical micelles; five different phases are formed: from the lower left, isotropic micellar solution, micellar cubic phase, hexagonal, bicontinuous cubic, and lamellar phase (two-phase regions between the different one-phase regions are omitted)

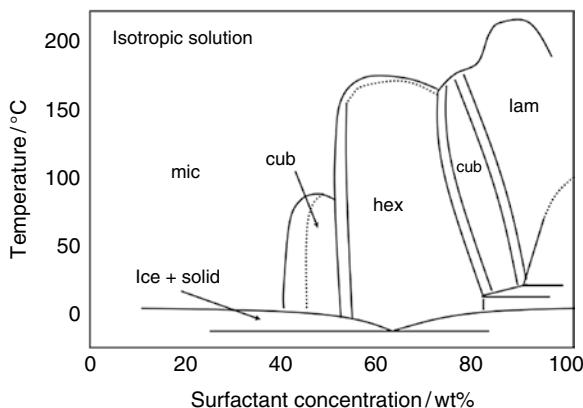


Figure 6.16 Binary phase diagram of dodecyltrimethylammonium chloride–water. Isotropic solutions (*mic*) exist at lower surfactant concentrations and higher temperatures. In addition, there are liquid crystalline phases (cubic, hexagonal, and lamellar) and, at lower temperatures, crystalline phases. (With permission from Balmbra, R.R., Clunie, J.S. and Goodman, J.F. (1969) Cubic mesomorphic phases. *Nature (London)*, **222**, 1159–1160. Copyright 1969, Macmillan Publishers Ltd.)

there is a transformation to a second cubic phase, now of the bicontinuous type. Then we find the lamellar phase and, finally, a solid hydrated surfactant. The sequence of phases found in this case is typical of rather hydrophilic surfactants.

At higher temperatures, the stability relationships between the different phases change. The first cubic phase disappears and at very high temperatures the lamellar phase is the only liquid crystalline phase, forming also for the neat surfactant. At the very highest temperatures, there are only isotropic solutions, of course with major changes in aggregate structures as the composition changes.

An ionic surfactant with a longer alkyl chain (like hexadecyltrimethylammonium bromide) would typically form rod-like or thread-like micelles at higher concentrations. In this case there will be no micellar cubic phase but the first liquid crystalline phase is the hexagonal one.

For double-chain surfactants, the phase diagram looks quite different, as exemplified in Figure 6.17 for the case of dioctadecyldimethylammonium chloride (DODMAC). As for single-chain surfactants, the chain melting temperature depends strongly on chain length. In the case of DODMAC, the chains are long, so melting occurs at a high temperature (about 45°C). The most important feature of phase diagrams of this class of surfactants is the low solubility (often extremely low) in water, pointing to an inability to form micelles. Rather it is typical with a very stable lamellar phase and a broad two-phase region of a dilute solution and a lamellar phase. In addition, for this type of surfactant there is often formation, at higher surfactant concentrations, of a bicontinuous cubic phase and a reversed hexagonal phase.

Transitions between phases in surfactant systems are generally of the first-order type, implying that there is a (smaller or larger) two-phase region between two single-phase regions; sometimes the two-phase region is omitted for simplicity but its existence should

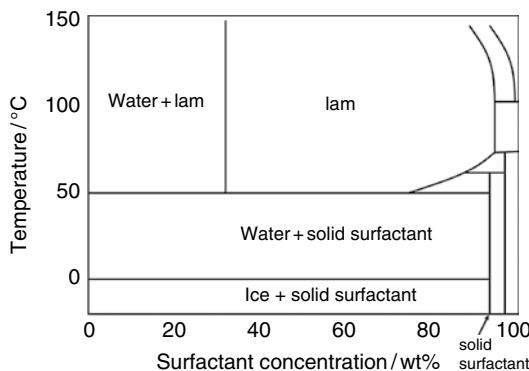


Figure 6.17 The binary phase diagram of DODMAC–water is dominated by a lamellar phase and crystalline hydrates, as well as two-phase regions. (With permission from Laughlin, R.G., Munyon, R.L., Fu, Y.C. and Fehl, A.J. (1990) Physical science of the dioctadecyldimethylammonium chloride–water system. 1. Equilibrium phase behavior. *Journal of Physical Chemistry*, **94**, 2546–2552. Copyright 1990, American Chemical Society.)

not be forgotten. Macroscopic properties are frequently very different in the two-phase region from those in the two single phases.

Three-Component Phase Diagrams are Complex but have a Direct Bearing on Applications

As described in Chapter 5, with three components, at constant pressure we have a maximum of three degrees of freedom: temperature and two concentration variables. It is most common to consider the phase behavior at constant temperature and to use the Gibbs' triangle. Two three-component phase diagrams are illustrated in Figure 6.18 and Figure 6.19. In the first there is an aqueous mixture of a single-chain ionic surfactant and a weakly polar amphiphile. The phase diagram is built up of six different phases: two isotropic solution phases, three liquid crystalline phases, and solid surfactant. Note that in binary mixtures with water, the surfactant forms only micelles and a hexagonal phase. Addition of decanol induces a transition to the lamellar phase and, at higher alcohol concentrations, to reversed structures, reversed hexagonal, and reversed micellar. In addition to the single-phase regions, there are a large number of two-phase and three-phase regions describing the coexistence of the different phases.

The ternary system in Figure 6.19 looks very different. Here we consider a double-chain ionic surfactant, which in mixtures with water gives an extensive lamellar phase as well as a bicontinuous cubic phase and a reversed hexagonal phase; the solubility in water is low. On addition of the oil, there is a transition from the lamellar to reversed hexagonal phases and then to the reversed micellar phase.

The sequence in which phases occur as a function of surfactant concentration or addition of a less polar component generally follows a simple sequence summarized in the Fontell scheme (Figure 6.13). Depending on the system and on temperature, and so on, a smaller

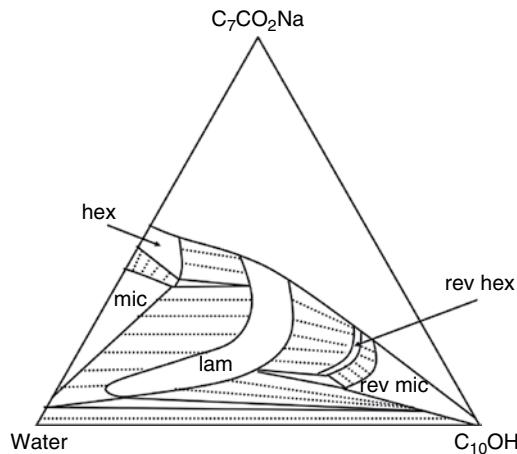


Figure 6.18 Ternary phase diagram of the sodium octanoate-decanol-water system at 25°C. There are two isotropic solution phases, micellar and reversed micellar, and three liquid crystalline phases, hexagonal, lamellar, and reversed hexagonal. The white upper region involves different solid surfactant phases. (With kind permission from Springer Science+Business Media: Adapted from Ekwall, P., Danielsson, I. and Mandell, L. (1960) Assoziations- und phasengleichgewichte bei der Einwirkung von Paraffinkettenalkoholen an wässrigen Lösungen von assoziationskolloiden. Kolloid-Zeitschrift, **169**, 113–124.)

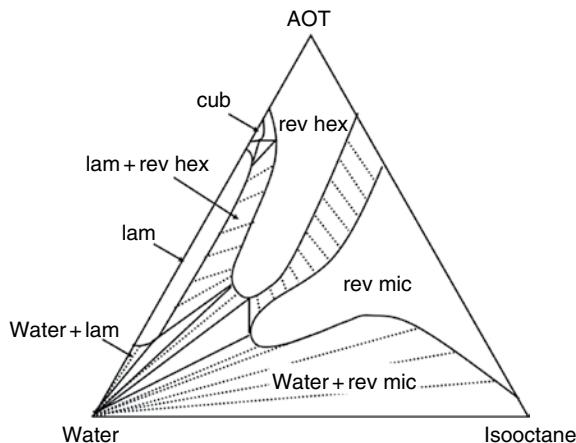


Figure 6.19 Ternary phase diagram of a double-chain anionic surfactant, Aerosol OT, mixed with isoctane and water at 25°C. There are two isotropic solution phases, water (with a low surfactant concentration) and reversed micellar, and three liquid crystalline phases, lamellar, bicontinuous cubic, and reversed hexagonal (K. Fontell, unpublished). (With permission from Evans, D.F. and Wennerström, H. (1994) The Colloidal Domain. Where Physics, Chemistry, Biology, and Technology Meet, VCH, New York, p. 471. Copyright 1994, John Wiley & Sons.)

or larger number of the different phases actually appear. For example, for single-chain surfactants we generally encounter structures from the mirror plane and to the left, while double-chain surfactants give the phases from the mirror plane and to the right.

The phase diagram in Figure 6.20 for a mixture of a cationic and an anionic surfactant shows an additional feature, namely of regions of stable vesicle solutions. Such systems show for stoichiometric mixtures the precipitation of a solid crystal. In addition, there are lamellar and vesicle regions forming with some excess of one surfactant. This is further discussed in the Chapter 13. As discussed in Chapter 5, such a system is not a true three-component system, but more complex.

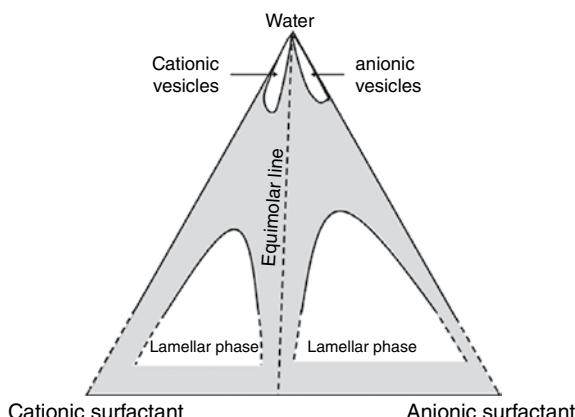


Figure 6.20 The dilute part of the ternary phase diagram for an aqueous mixture of a cationic and an anionic surfactant

Surfactant Geometry and Packing Determine Aggregate Structure: The Packing Parameter is a useful Concept

We have noted the, quite general, rule that single-chain surfactants tend to form micelles and other “normal” structures, while double-chain surfactants prefer to form lamellar phases and reversed structures. We can easily understand this if we try to pack space-filling models of surfactants into different aggregate shapes. We will, for example, find that due to the bulkiness of the hydrophobic part, double-chain molecules cannot be packed into spherical micelles. We also noted in our simple geometrical characterization of chain packing in spherical micelles that the quantity $v/(al_{\max})$ can be at most $1/3$ for a spherical micelle. If we double v by adding a second alkyl chain, keeping the other factors constant, it can easily be understood that structures of other geometries become more favorable.

While relating chemical structure to aggregate structure is much more complex than such a simple geometrical analysis, this is an illustrative and useful starting point, in particular in analyzing trends in phase behavior. Basically, the structure formed is a result of the balance between the polar and the nonpolar parts of a surfactant molecule; this explains the interest in (mainly empirical) scales of hydrophilic–lipophilic balances (HLB), which are briefly discussed in Chapter 24. These are useful classifications of surfactants,

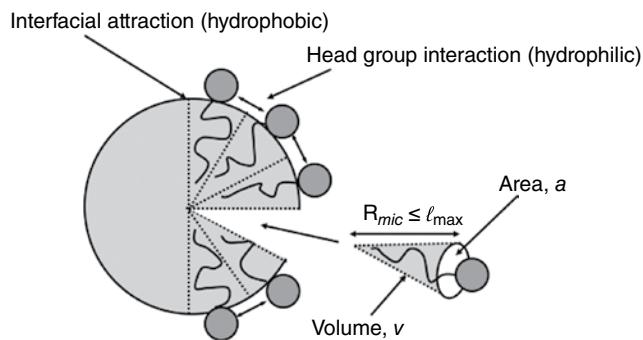


Figure 6.21 The critical packing parameter (CPP) or surfactant number relates the head group area, the extended length and the volume of the hydrophobic part of a surfactant molecule into a dimensionless number $\text{CPP} = v/(al_{\max})$. (Adapted from Israelachvili, J.N. (2011) Intermolecular and Surface Forces, with Applications to Colloidal and Biological Systems, 3rd edn, Academic Press, London. With permission from Elsevier.)

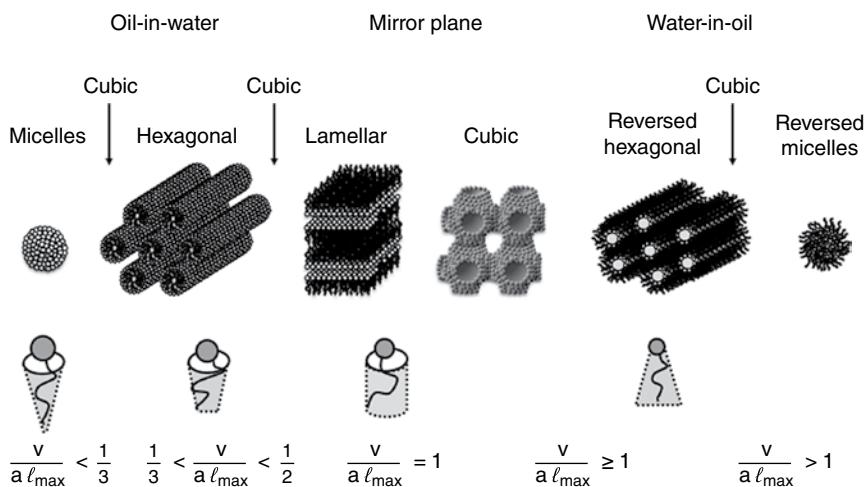


Figure 6.22 Critical packing parameters (CPPs) of surfactant molecules and preferred aggregate structures for geometrical packing reasons

helpful *inter alia* in selecting a surfactant for a certain application, but they do not allow a deeper analysis or understanding. A more general approach is based on the concept of surfactant packing:

$$\text{CPP} = v / (al_{\max})$$

The definition of the critical packing parameter (CPP) or the surfactant number, introduced in Chapter 4, is illustrated in Figure 6.21. Analyses of different geometrical shapes of aggregates, like the one made above for spheres, lead to the simple rules illustrated in Figure 6.22.

There are two factors that are not taken into account in the simple geometrical model but which have a great influence on the aggregate structure. The first of these is the interaction between the head groups in the aggregates. Clearly a strongly repulsive interaction between head groups will drive aggregates to the left in the Fontell scheme while the opposite applies for attractive interactions. This problem can be circumvented by estimating an “effective” head group area. For example, for ionic surfactants, the area per head group is large because of electrostatic repulsions (the counterion entropy effect discussed in Chapter 3). The effective size will be strongly affected by the electrolyte concentration so that a_o decreases on addition of electrolyte. For nonionics, temperature rather than electrolyte concentration is very important for interactions between head groups and is decisive for aggregate structure. We will return to this question in Chapter 7.

Considering which surfactants fall into the different categories of Figure 6.22, we have already noted that $\text{CPP} < 1/3$ and thus spherical micelles are found for single-chain surfactants with a strongly polar head group, such as an ionic head in the absence of an electrolyte. Here we also find nonionics with large head groups. The range of CPP values of $1/3$ – $1/2$ and rod-like structures are characteristic of single-chain ionics with an added electrolyte, single-chain ionics with a strongly bound counterion, or nonionics with an intermediate head group size. Higher CPP values are characteristic of double-chain amphiphiles or nonionics with short head groups. Here we also find many membrane lipids. For ionics, electrolyte addition again increases the CPP value and may drive aggregate structures from bilayers to reversed type structures. The CPP approach neglects interaggregate interactions. Crowding will promote changes from the left to the right in the Fontell scheme (Figure 6.13). Having these limitations in mind, the CPP approach still is very useful in predicting trends of surfactant self-assembly as conditions are changed. Some examples are:

1. On addition of electrolyte to a solution of a single-chain ionic surfactant, the effective area decreases, thus the CPP increases. This leads to growth of micelles into rod-like ones and, at higher salt concentrations, to bicontinuous and lamellar phases.
2. Addition of a long-chain alcohol (or a nonionic surfactant with a small head group) to a solution of an ionic surfactant increases the CPP, since the area per chain decreases; the alcohol contributes mainly to volume and little to area. Therefore, there is for a single-chain ionic surfactant firstly a transition from spherical to rod-like micelles, then the formation of a lamellar phase.
3. Increasing the hydrophobic part of the surfactant increases ν and thus also the CPP. Therefore, single-chain surfactants tend to form micelles while double-chain ones form lamellar phase.
4. Mixing two oppositely charged ionic surfactants gives a reduction of head group area, thus an increase in the CPP, because of charge neutralization. Therefore, a mixture of two such micelle-forming surfactants typically gives lamellar phase.

Surfactant aggregates can be considered to be built up of surfactant films and, depending on the curvature of the films, different structures result. (The curvature is the inverse of the radius of curvature.) The spontaneous curvature is defined here to be positive if the film is curved around the hydrophobic part and negative if it is curved towards the polar part. A normal micelle thus has a positive film curvature while a reversed one has a negative one. Planar films, such as in a lamellar phase, have zero curvature. Many bicontinuous structures

are characterized by a more complex saddle-shaped geometry with two principal radii of curvature with opposite signs. An important case is that of minimal surfaces, where the mean curvature is zero.

Polar Lipids Show the same Phase Behavior as other Amphiphiles

Polar lipids obey the same rules as surfactants and show the same type of phase behavior. In Chapter 1 the chemical structures of a number of different lipids were given and we can easily understand the very different tendencies of associating in water of, for example, a very nonpolar triglyceride and a highly polar bile salt. In fact, triglycerides and diglycerides are generally not amphiphilic enough to be soluble in water and show self-assembly. The other extreme, the bile salt, tends to form only small aggregates, with a large positive spontaneous curvature. Other lipids fall in-between and show different types of self-assembly structures, as exemplified in a number of phase diagrams. (In the literature, these phase diagrams are generally presented with amphiphile and water reversed compared to surfactant phase diagrams, i.e., with the water content increasing from left to right.)

Phospholipids, such as lecithin, behave similarly to other double-chain surfactants in showing a strong preference to form a lamellar phase (Figure 6.23). The lamellar phase can take up water and swell to about 45% water. At higher water contents, there is a coexistence of the lamellar phase and a very dilute aqueous solution. Dispersion of the lamellar phase in water can give liposomes and vesicles. Monoolein (Figure 6.24) also gives a lamellar phase but only in a limited range of concentration and temperature. This system is rather unusual in giving a bicontinuous cubic phase, which, firstly, is stable over wide ranges of concentration and temperature and, secondly, coexists with excess water. In the two-phase region there is a formation of Cubosomes®, dispersed cubic phase (Figure 6.25).

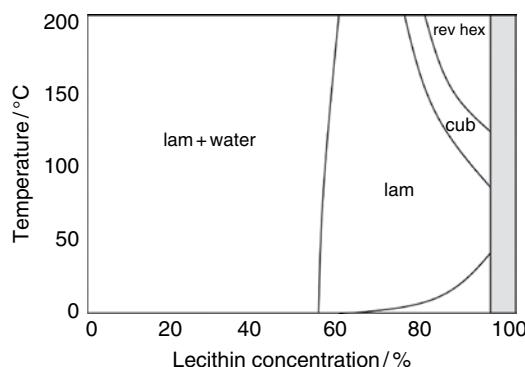


Figure 6.23 The phase diagram of lecithin (from egg yolk) and water is dominated by a lamellar phase, which at higher water contents is in equilibrium with a very dilute aqueous solution.

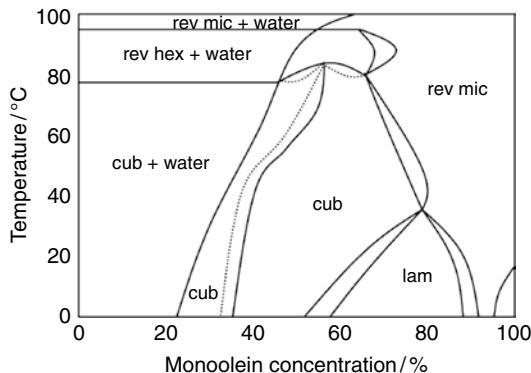


Figure 6.24 The phase diagram of monoolein and water is characterized by a large region of bicontinuous cubic phases. One cubic phase can be in equilibrium with excess water. In addition, there is a lamellar phase and a reversed micellar phase. (Adapted with permission from Kulkarni, C., Wachter, W., Iglesias-Salto, G., Engelskirchen, S. and Ahualli, S. (2011) Monoolein: A Magic Lipid?, *Phys. Chem. Chem. Phys.*, **13**, 3004–3021. Copyright 2011, The Royal Society of Chemistry.)

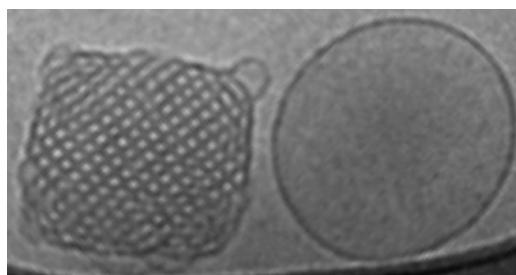


Figure 6.25 As illustrated in this cryogenic transmission electron microscope picture, dispersions of a lamellar phase in water can give unilamellar vesicles while a bicontinuous cubic phase gives Cubosomes®

Bile salts are characterized by very low CPP. They give, therefore, only micellar solutions in mixtures with water and generally no liquid crystalline phases. If we add a bile salt to a less polar lipid, we get the expected changes in aggregate structure. For lecithin, the lamellar phase incorporates some bile salt but is then transformed first to a hexagonal phase and then to a micellar phase. For monoolein, the cubic phase is transformed into the lamellar phase, which at a higher content is transformed into a micellar phase.

Liquid Crystalline Phases may form in Solvents other than Water

We have noted that surfactants have a much stronger tendency to self-assemble into micelles in water than in other polar solvents; this applies, in general, to all types of self-assembly aggregates. Thus, the different liquid crystalline phases have much more limited stability ranges in nonaqueous solvents.

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7

Surfactants and Polymers Containing Oxyethylene Groups Show a Complex Behavior

Polyoxyethylene Chains make up the Hydrophilic Part of Many Surfactants and Polymers

For ionic surfactants, the electrostatic interactions are, as seen in Chapter 6, decisive for the properties of simple and complex systems. Nonionic surfactants are controlled by very different hydrophilic interactions. The most important type of nonionic surfactant (Figure 1.7) is that with an oligo(oxyethylene) group as the polar head. Denoting an oxyethylene group by E, simple nonionics can be abbreviated as C_mE_n if we have an alkyl chain as the lipophilic part. We can also have a more complex hydrophobic part with a branched and/or unsaturated group; many nonionics contain aromatic groups.

For typical ionic surfactants, as well as many other surfactants, the volume of the polar group is much smaller than that of the nonpolar part. For the oxyethylene surfactants, the situation is different in that the volumes of the two parts are of similar size; typically the polar part is larger than the nonpolar one. It is, therefore, appropriate and fruitful to consider a nonionic surfactant as a short AB block copolymer.

One conspicuous feature of a nonionic surfactant is the temperature dependence of physicochemical properties. This may be problematic in applications but can also be turned into an advantage, since temperature-triggered systems can be designed. To master and understand the special temperature-dependent interactions between the polar solvent and the oxyethylene chains proves to be essential. These interactions are obviously not unique for surfactant systems but have a general bearing also for polymers containing oxyethylene groups, some of which are pictured in Figure 7.1.

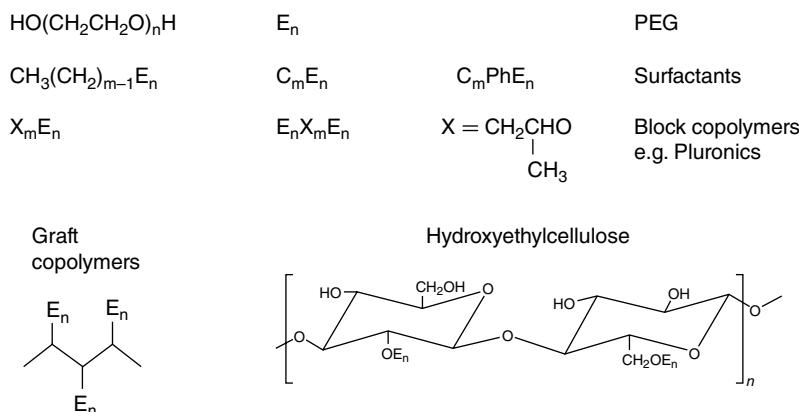


Figure 7.1 Chemical structure of some oxyethylene (EO)-based polymers and surfactants

It is thus logical to treat oxyethylene-based surfactants and polymers, homo, graft, and block copolymers, in a single context. In this chapter we firstly review the general properties of nonionic surfactants and, in comparison with other types of surfactants, identify their particular behavior. We then consider the unusual temperature effects in a broader context and review our present understanding of mechanisms in terms of intermolecular interactions. For the polymer solutions, we focus here on the special temperature-dependent properties and treat the more general polymer aspects in Chapters 9 and 10.

Surfactants in applications are rarely chemically homogeneous. For all types of surfactants there may be a considerable distribution in the nonpolar part, different alkyl chain length, partial unsaturation, and so on, resulting from the fatty raw material used. This has normally only minor consequences for our analysis of physicochemical observations and our modeling. For nonionics, we have typically, in addition, a marked heterogeneity in the polar head group, as discussed in Chapter 1. It is, therefore, necessary to treat the nonionic surfactants used in commercial applications as mixed surfactant systems. However, well-defined homogeneous nonionics are available. The significance of these for scientific work and for our improved understanding cannot be overestimated. In this chapter we will mainly refer to results obtained in work on well-defined surfactants.

CMC and Micellar Size of Oxyethylene-Based Surfactants are Strongly Temperature Dependent

The critical micelle concentration (CMC) of nonionic oxyethylene surfactants, C_mE_n , varies strongly with m , while the variation with n is quite weak, with a slight increase as the EO chain becomes longer (Table 4.3). A plot of the logarithm of the CMC as a function of the number of carbons in the alkyl chain (Figure 4.4) gives, as noted above, a straight line with a slope that is considerably larger than for ionics. Lengthening of the alkyl chain by one methylene lowers the CMC by a factor of three rather than two. As noted above, nonionics show a CMC variation paralleling the solubility of hydrocarbons in water, while the

variation is weaker for ionics because of an opposing electrostatic effect, which becomes more important the lower the CMC.

The temperature dependence of the CMC (Figure 4.5 and Figure 7.2) differs from that of ionics in two respects: it is markedly stronger and there is typically a monotonic decrease with increasing temperature rather than an increase at higher temperatures. A nonionic micelle (Figure 7.3) has a thick interfacial layer of polar head groups rather than the quite sharp transition from the hydrophobic micellar interior to the aqueous bulk of ionics. We

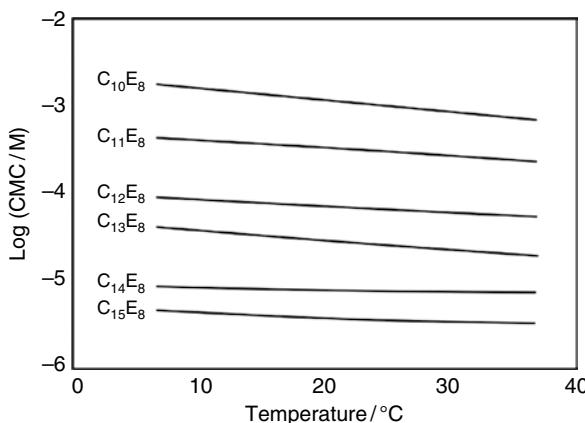


Figure 7.2 The logarithm of the CMC plotted against the temperature for C_mE_8 surfactants. (Data from Meguro, K., Takasawa, Y., Kawahashi, N., et al. (1981) Micellar properties of a series of octa(ethylene glycol)-n-alkyl ethers with homogeneous ethylene oxide chain and their temperature dependence. Journal of Colloid and Interface Science, **83**, 50–56. With permission from Elsevier.)

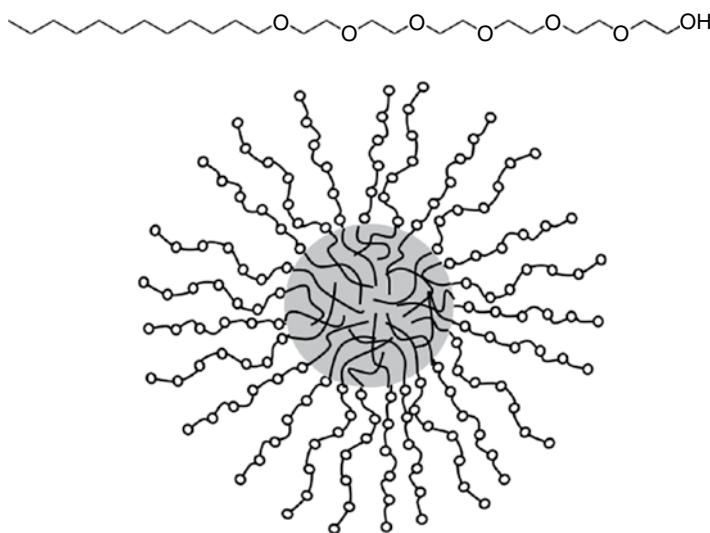


Figure 7.3 A schematic picture of a nonionic micelle

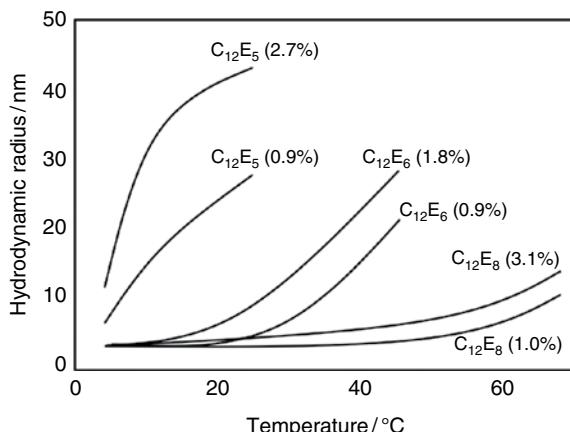


Figure 7.4 Nonionic micelles grow with increasing temperature for surfactants with short polar heads, while growth is weak or insignificant for larger head groups. The size is characterized by the hydrodynamic radius (R_h). (Adapted with permission from Lindman, B. and Jonströmer, M. (1987) Nonionic micelles, in Physics of Amphiphilic Layers, Proceedings in Physics (eds J. Meunier, D. Langevin and N. Boccara), Volume 21, Springer, Berlin, pp. 235–240.)

will see that changes in the intermolecular interactions in the polar layer account for the special temperature-dependent behavior of nonionics.

The spherical micelle, pictured in Figure 7.3, is typical for surfactants with long polyoxyethylene chains, in particular at low temperatures and concentrations. As for ionics, micellar growth to elongated micelles may occur but the conditions are different for nonionics. In particular, the temperature dependence of micelle size is opposite to that of ionics.

The most significant features are illustrated in Figure 7.4, where the hydrodynamic radii of the micelles are given as a function of temperature for three relatively dilute surfactants. For a surfactant such as $C_{12}E_8$ there is insignificant or moderate growth up to high temperatures; a longer polyoxyethylene chain would give even less growth. For a short oxyethylene chain, illustrated by $C_{12}E_5$, there is a dramatic growth with increasing temperature.

In general, we can summarize micellar size effects for nonionics as follows:

1. The polyoxyethylene chain length is the prime factor in determining growth. The shorter the chain, the larger is the tendency to grow both with temperature and with concentration.
2. As for all types of surfactants, micellar growth is promoted by an increased alkyl chain length. For example, C_{16} surfactants give much stronger growth than C_{12} ones.
3. Cosolutes influence growth differently than for ionics. Salting-out (see below) electrolytes tend to promote growth and salting-in ones to inhibit growth. Ionic surfactants have a strong tendency to reduce growth and even quite small amounts may inhibit growth.

Phase Diagrams are Very Different at Different Temperatures

Phase diagrams of nonionic surfactant–water systems show many resemblances to those of ionics, with those of longer oxyethylene chains being similar to single-chain ionics and those of short oxyethylene chains being more similar to double-chain ionics. However,

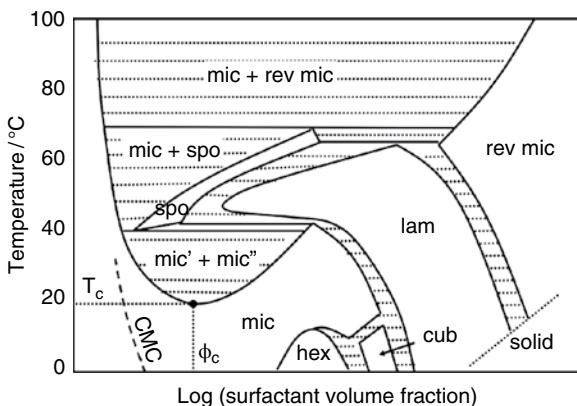


Figure 7.5 Phase diagram of the $C_{12}E_5$ -water system given as a function of the volume fraction of surfactant on a logarithmic scale; *mic*, *rev mic*, and *spo* denote isotropic solution phases and *hex*, *lam*, and *cub* denote hexagonal, lamellar, and cubic liquid crystalline phases, respectively. On heating a micellar solution, there is a phase separation into two isotropic solutions. The boundary of the two-phase region is a so-called lower consolute curve. The minimum of the lower consolute curve is a critical point, defined by a critical temperature (T_c) and composition (ϕ_c or c_c). (Adapted with permission from Strey, R., Schomäcker, R., Roux, D., et al. (1990) Dilute lamellar and L_3 phases in the binary water- $C_{12}E_5$ system. Journal of the Chemical Society, Faraday Transactions, **86**, 2253–2261. Copyright 1990, The Royal Society of Chemistry.)

there are also significant differences. This can be highlighted by using the phase diagram of $C_{12}E_5$ (Figure 7.5). At low temperatures we have the previously encountered sequence of micellar solution phase, normal hexagonal, bicontinuous cubic, lamellar, and solid surfactant, with an increasing percentage of surfactant. In the micellar region, there is a very strong micellar growth both with increasing temperature and with increasing concentration. A major difference when compared to typical ionics is the splitting of the water-rich solution phase into two liquid phases at higher temperature and also the appearance of the sponge phase, a new solution phase, at still higher temperatures. We also note that the lamellar phase and the reversed micellar phase, the liquid surfactant with solubilized water, gain in importance at higher temperatures at the expense of the micellar, hexagonal, and cubic phases.

Comparing the phase behavior of a sequence of surfactants with the same alkyl chain but different oxyethylene chain lengths (Figure 7.6), we note a dramatic variation. With a long polyoxyethylene chain, the micellar phase (with a strong preference for small, roughly spherical, micelles), a cubic phase of discrete micelles and the normal hexagonal phase dominate. Shortening the oxyethylene chain is accompanied by a larger tendency for micellar growth and by the progressive disappearance of the phases mentioned. Instead, in particular, the regions of the lamellar phase and the surfactant-rich solution phase, and at higher temperatures also the sponge phase, increase in size. For a surfactant like $C_{12}E_3$ no micelles form on addition of surfactant to water, but there is directly a two-phase region of the lamellar phase and a very dilute solution, a situation reminding us of that for lecithin. Besides the lamellar phase, the dominating phase is the reversed micellar, which has a narrow channel extending into the water-rich part of the diagram.

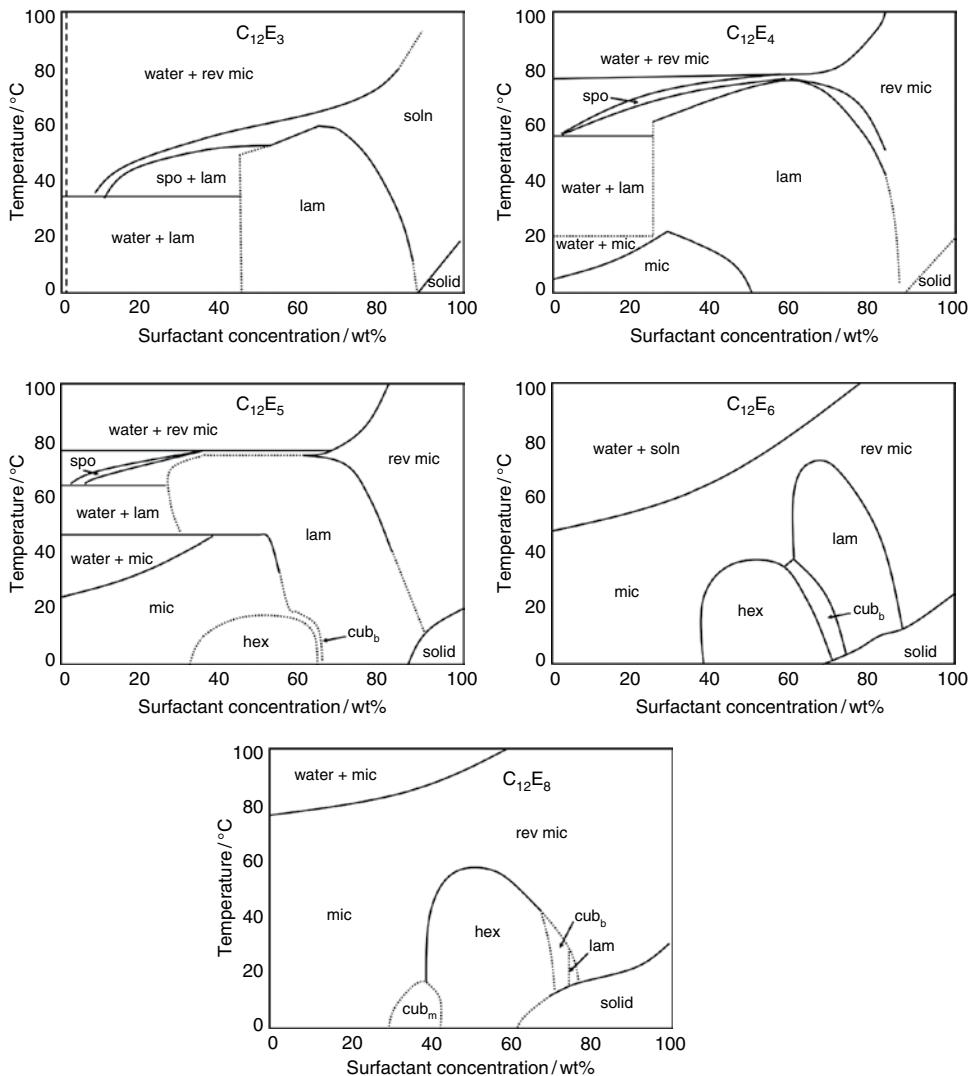


Figure 7.6 Phase diagrams (somewhat simplified) of nonionic surfactant–water systems for C₁₂ surfactants with 3, 4, 5, 6, or 8 oxyethylenes in the polar head; water, mic, rev mic, and spo denote isotropic solution phases and hex, lam, cub_m, and cub_b denote hexagonal, lamellar, and discrete (micellar) and bicontinuous cubic liquid crystalline phases, respectively. (Adapted with permission from Mitchell, D.J., Tiddy, G.J.T., Waring, L., et al. (1983) Phase behavior of polyoxyethylene surfactants with water. Mesophase structures and partial miscibility (cloud points). Journal of the Chemical Society, Faraday Transactions 1, **79**, 975–1000. Copyright 1983, The Royal Society of Chemistry.)

The L₃ or “Sponge” Phase

This phase was originally discovered in phase diagram studies of the system C₁₀E₆ and was denoted “anomalous”, since encountering a second micellar solution region at higher temperatures was unexpected. Now we know that it is of the bicontinuous type, with surfactant bilayer films connected over macroscopic distances. The surfactant bilayers form zero or low mean curvature surfaces separating different water channels. We encountered the structure previously in Chapters 4 and 6.

The L₃ or sponge phase is common for nonionic surfactants and has been mainly studied for those. In recent years, we have also learnt that it occurs for all classes of surfactants, provided there is a suitable balance between the hydrophilic and the lipophilic parts. For ionics, the formation of the sponge phase can be induced by the addition of electrolyte.

Sequence of Self-Assembly Structures as a Function of Temperature

If we summarize a large number of observations of phase diagrams, we may obtain a quite general sequence of phase structures as a function of temperature, which is spherical micelles, discrete cubic phase, elongated micelles, hexagonal phase, lamellar phase, bicontinuous cubic phase, sponge phase, and reversed micellar solution. Selected structures are illustrated in Figure 7.7. We should note that temperature and oxyethylene chain length have opposing effects and that for a given surfactant only a few of the structures are formed within the accessible range of temperatures.

The Critical Packing Parameter and the Spontaneous Curvature Concepts are Useful Tools

These results can now be examined in the light of the principles of surfactant self-assembly described in Chapter 6. Recall that the dimensionless critical packing parameter (CPP) or surfactant number is given by the volume of the surfactant hydrophobe divided by the

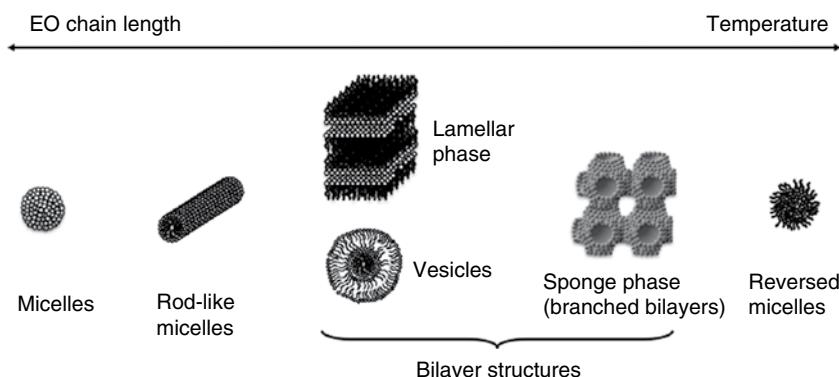


Figure 7.7 The surfactant self-assembly structures of nonionic surfactants are mainly governed by temperature and the number of oxyethylene groups. Only selected structures are represented

product of the area of the polar head group and the extended length of the surfactant molecule, and that the spontaneous curvature of a surfactant film is taken to be positive if it is curved towards the hydrophobic part.

The effect of the head group size, that is, the EO chain length, is obvious: as the number of EO groups increases the area per head group increases and the CPP decreases.

The sequence of self-assembly structures that we have described also indicates that the CPP of nonionics increases progressively with increasing temperature. The only way in which we can understand this is in terms of a decreasing area per polar head group as the temperature increases. Therefore, it appears that there is a closer packing of polar head groups at the aggregate surface at higher temperatures. This is consistent with observations of a decreased hydration number—or a decreased concentration of water in the head group area—at higher temperatures, as observed by spectroscopy and by water self-diffusion. The spontaneous curvature is similarly inferred to decrease and become negative at higher temperatures (Figure 7.8).

Since unusual temperature dependences are ubiquitous for oxyethylene-containing systems we are looking for some general underlying mechanism. As indicated, there is a weakened interaction between the oxyethylene groups and the water with increasing temperature. There is a smoothly decaying hydration with increasing temperature, which is strikingly similar for quite dissimilar systems. In fact, the apparent number of water molecules per oxyethylene group is sensitive to temperature but closely the same for different systems.

The lower consolute curve (cf. Figure 5.2b) is typical of phase diagrams of oxyethylene-based surfactants and polymers. This implies that the effective solute–solute interactions have significant temperature dependence and changes from repulsive to attractive with increasing temperature. In turn, this can reflect changes in either solute–solute, solute–solvent, or solvent–solvent interactions or a combination of those. All alternatives have been suggested and there is, as yet, no consensus about the dominating effect. However, a

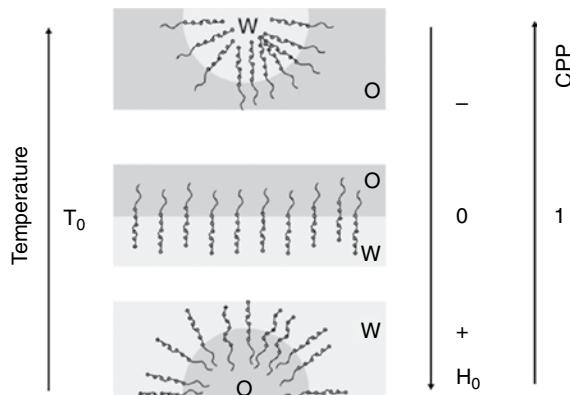


Figure 7.8 For nonionic surfactants, best considered as short AB block copolymers, the CPP changes from a low value to a high value with increasing temperature, and the spontaneous curvature (H) changes from positive at low temperatures to negative at high temperatures. At some intermediate temperature (T_0), $\text{CPP} = 1$ and the spontaneous curvature is zero and the surfactant is “balanced.” The inferred change in spontaneous curvature with temperature suggests that while water is a good solvent for the head groups at low temperature, the oxyethylene–water interactions become less favorable at higher temperatures

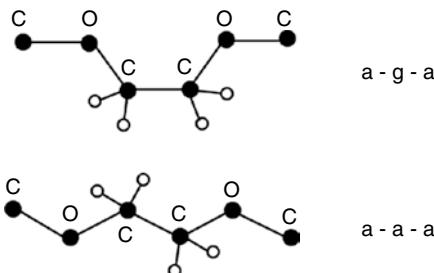


Figure 7.9 Different conformations of a chain of oxyethylene groups have different stabilities and polarities. The upper anti-gauche-anti conformation has a lower energy and is more polar than the lower anti-anti-anti conformation

water–water interaction mechanism, relating to a temperature-dependent structuring of water around oxyethylene groups, is less likely in view of analogous observations in solvents other than water. Hydrogen bonding between water molecules and ether oxygen is another model that has been analyzed. Described here is a model based on temperature-dependent solute conformational effects, which has a strong predictive power.

A polyoxyethylene chain may exist in a large number of conformations, which have different energies. The conformation of an oxyethylene group, which is *gauche* around the C–C bond and *anti* around the C–O bond (Figure 7.9, top) has the lowest energy of all conformers. This low-energy conformation, which will dominate at low temperatures, has a large dipole moment. On the other hand, it has a low statistical weight. With increasing temperature, other conformations of higher statistical weight will become increasingly more important. These have smaller or no dipole moments, like the *anti-anti-anti* conformation (Figure 7.9, bottom).

The conformational changes will consequently make the polyoxyethylene chains progressively less polar as the temperature is increased. Becoming less polar they will interact less favorably with water, leading to reduced hydration, and more favorably among themselves, leading to a closer packing of head groups in surfactant self-assemblies, as well as to an increased tendency to separate into a more concentrated phase. The succession of self-assembly structures with increasing temperature also follows logically from the decreased polarity. The same applies to many other observations, given below, such as the increased adsorption of oxyethylene-containing homopolymers, copolymers, and surfactants at higher temperatures, resulting from the worsened solvency conditions. Irrespective of the model adopted, temperature effects of nonionic polymers and surfactants are best analyzed in terms of water being a good solvent for the oxyethylene groups at low temperatures, while at high temperatures it is a poor solvent. We can thus effectively tune the solute–solvent interaction with temperature.

Clouding is a Characteristic Feature of Polyoxyethylene-Based Surfactants and many Nonionic Polymers

A common observation for a solution of a nonionic surfactant is that on heating the solution may start to scatter light strongly in a well-defined temperature range. It becomes “cloudy.” This is a consequence of one feature of the phase diagram. The isotropic solution region is bordered towards higher temperatures by a lower consolute curve, above which there is a

phase separation into one surfactant-rich and one surfactant-poor solution. The onset of phase separation manifests itself by a cloudiness of the solutions. The minimum in the lower consolute curve is a critical point. Approaching this is accompanied by strong scattering of light due to critical fluctuations.

The clouding temperature or the cloud point depends strongly on the polyoxyethylene chain length but is less influenced by the hydrophobe size. The cloud point is recorded for a certain fixed solute concentration (normally 1% by weight). We infer from the phase diagrams (Figure 7.6) that the cloud point of $C_{12}E_8$ is around 80°C, while it is around 50 and 10°C for $C_{12}E_6$ and $C_{12}E_4$, respectively. For still shorter polyoxyethylene chains, the surfactant is insoluble, even at the freezing temperature of water, so the cloud point is

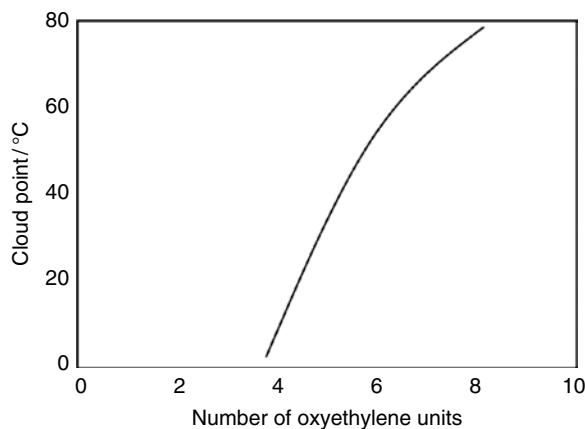


Figure 7.10 The cloud point (at 1% by weight) as a function of the oxyethylene chain length for C_{12} surfactants

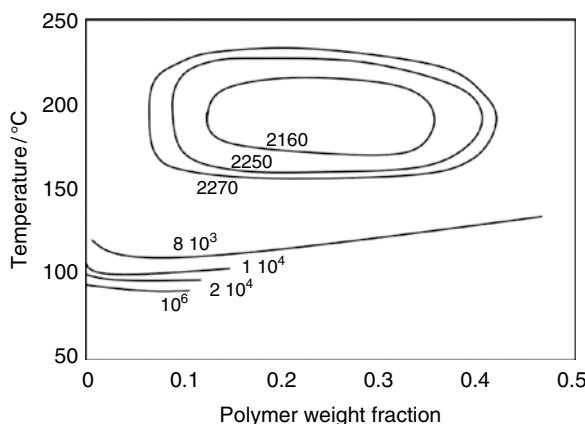


Figure 7.11 Phase diagrams for poly(ethylene glycol)-water for different polymer molecular weights. (Adapted from Saeki, S., Kuwahara, N., Nakata, M. and Kaneko, M. (1976) Upper and lower critical solution temperature in poly(ethylene glycol) solutions. *Polymer*, **17**, 685–689. With permission from Elsevier.)

below 0°C. In Figure 7.10, the cloud point at a fixed surfactant weight concentration is plotted as a function of the number of oxyethylene units for C₁₂ surfactants.

The clouding phenomenon occurs for many systems and is a common feature for a large class of solutions with solutes containing oxyethylene groups. For poly(ethylene glycol) (PEG) or poly(ethylene oxide) (PEO) there is a simple closed-loop two-phase region. As can be seen in Figure 7.11, the two-phase region grows strongly in all directions as the molecular weight of the polymer is increased. The basic features of the closed-loop appearance of the phase diagram are the same for the surfactant systems but these are more complex due to self-assembly leading to additional phases. Furthermore, the cloud point is strongly dependent on micelle size, which is very different for different surfactants. A high micellar aggregation number will have an effect analogous to a high degree of polymerization of a polymer, and thus give a low cloud point and a critical point at a low concentration.

Clouding is Strongly Dependent on Cosolutes

The clouding of nonionic surfactants and polymers can be enhanced or decreased by cosolutes but both classes are affected in similar ways. Electrolytes may either increase or decrease the cloud point (as illustrated in Figure 7.12) and may be termed salting-in or salting-out, respectively. The sequence of ions follows the so-called lyotropic or Hofmeister series. The effect may be understood from the interaction between the polymer or surfactant and the cosolute. The effect is dominated by the anions. Some anions, like I⁻ or SCN⁻, behaving in a similar way, show a preference for the polymer or surfactant relative to the bulk solvent and are enriched in the vicinity of the oxyethylene groups. Others, like Cl⁻ or SO₄²⁻, do not show such a preference and are depleted in the vicinity of the oxyethylene groups. In the former case, increased solubility and an increased cloud point results, while the opposite is observed in the latter case. The effects can be related to the polarizability,

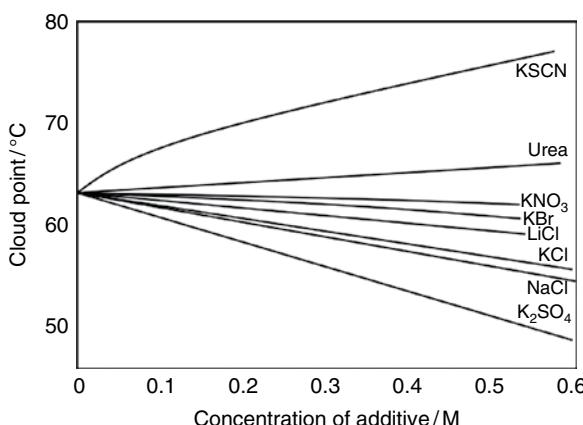


Figure 7.12 Effect of additives on the cloud point of 5 mM C₁₂E₇. (Adapted with permission from Meguro, K., Muto, K. and Ueno, M. (1980) The effects of inorganic salts and urea on the micellar structure of nonionic surfactant using keto-enol tautomerism of benzoylacetanilide. Nippon Kagaku Kaishi, 3, 394–399. Copyright © 1980, The Chemical Society of Japan.)

and thus the size of the ion. A large and polarizable ion like SCN^- or I^- can be considered to be less polar, and thus partition into the vicinity of the polymer or the surfactant aggregate rather than into the bulk water.

Very low concentrations of an ionic surfactant strongly increase solubility and thus also the cloud point. This is due to the formation of mixed micelles in the case of a clouding surfactant and to an association of the surfactant to the polymer (Chapter 14) in the case of a clouding polymer. This results in charged aggregates that are much more difficult to concentrate in one of the phases due to the unfavorable electrostatic interactions arising from the entropy of the counterion distribution.

Physicochemical Properties of Block Copolymers Containing Polyoxyethylene Segments Resemble those of Polyoxyethylene-Based Surfactants

A related behavior to that of nonionic surfactants and poly(ethylene glycol) is shown by random and block copolymers containing oxyethylene groups. (Examples are given in Figure 7.13.) Random copolymers, containing in addition to oxyethylene less polar groups, such as oxypropylene (PO) mainly show a behavior similar to that of poly(ethylene glycol) but with lower solubility and lower cloud points.

Many polyoxyethylene-based block copolymers are known and have found important applications. They range from poly(ethylene glycol) “end-capped” by alkyl chains to complex structures of a star type geometry. Triblock systems with poly(propylene glycol) (PPO) or poly (butylene glycol) (PBO) as the central segment have attracted special interest. They show many analogies with surfactant systems, since they are also characterized by a considerable self-assembly. However, because of the higher molecular weight, temperature-dependent effects become much more pronounced.

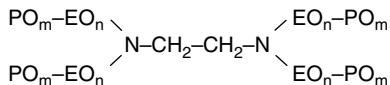
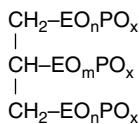


Figure 7.13 Structures of some oxyethylene–oxypropylene copolymers. “Pluronic” is the BASF trade name of EO–PO block copolymers and has become widely used as a general product name

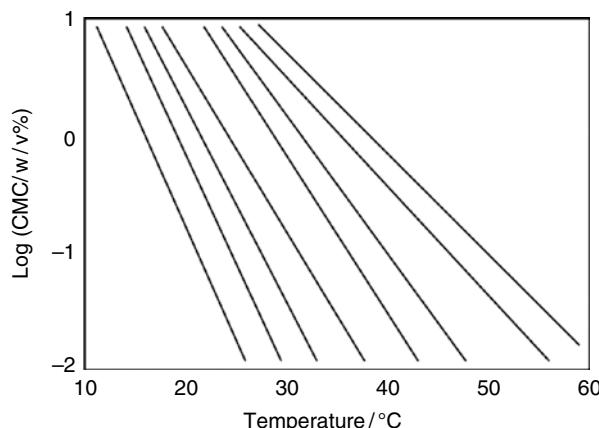


Figure 7.14 The transition from free polymer to micelles in EO–PO block copolymer solutions takes place at much lower concentrations as the temperature is increased. This feature is illustrated for EO–PO block copolymers of different polarities and molecular weights from the Pluronics family. (With permission from Alexandridis, P. and Hatton, T.A. (1995) Poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) block copolymer surfactants in aqueous solution and at interfaces: thermodynamics, structure, dynamics and modeling. *Colloids and Surfaces*, **96**, 1–46. Copyright Elsevier.)

A CMC, defining the onset of self-assembly, can be defined equally well for the block copolymers as for simple surfactants. For the block copolymers, there is a dramatic decrease in CMC with increasing temperature (Figure 7.14). Clouding is also observed for the block copolymers and, as expected, the cloud point increases with the proportion of oxyethylene groups and decreases with increasing molecular weight.

Another striking phenomenon is the transition of a low-viscous solution of a PEO–PPO–PEO polymer into a highly viscous clear “gel” at a moderate temperature increase (Figure 7.15). This gelation is, in fact, the result of the formation of a cubic liquid crystalline phase.

The phase diagram of a typical two-component system of such a triblock copolymer has an analogous sequence of phases as for a rather polar nonionic surfactant (cf. C12E6 in Figure 7.6). However, there are often a larger number of liquid crystalline phases for the block copolymer systems and the extension is more sensitive to temperature. The phases appearing can be controlled by varying the ratio between the more polar oxyethylene groups and the less polar oxypropylene groups, so that with a high proportion of oxyethylene we find mainly the phases to the left in the Fontell scheme (Chapter 6) and conversely with a high proportion of oxypropylene the phases to the right dominate. In contrast to typical surfactants, these block copolymers can form structures with a wide range of spontaneous curvatures and surfactant numbers. This is even more striking for ternary systems, including an oil component as illustrated in Figure 5.9.

From Figure 7.16 we can infer that, for certain concentrations of block copolymer, a temperature increase can induce first micellization and then, at high enough micelle concentration, a crystallization of the micelles into a cubic liquid crystalline phase, thus explaining the “thermal gelation” (Figure 7.15).

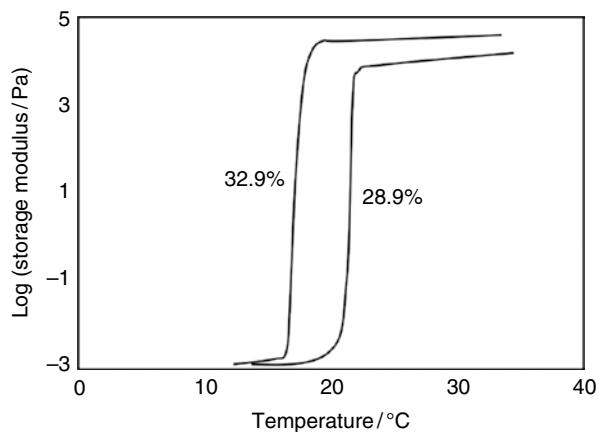


Figure 7.15 Aqueous solutions of EO-PO block copolymers may become very viscous over a narrow temperature range. Here the storage modulus, G' , which characterizes the solid-like or elastic properties of the system, is shown as a function of temperature for solutions of an EO-PO block copolymer at two different concentrations. (Adapted from Bahadur, P. and Pandya, K. (1992). Aggregation behavior of Pluronic P-94 in water. *Langmuir*, **8**, 2666–2670. Copyright 1992, American Chemical Society.)

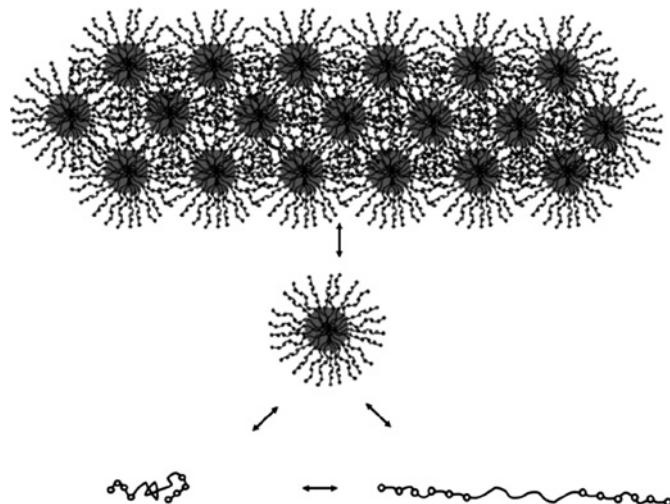


Figure 7.16 At a low temperature a hydrophilic EO-PO block copolymer is present in the unimeric state (bottom); at a higher temperature the CMC is reached (middle). With increasing temperature more micelles form, leading to the formation of a cubic phase (top)

Temperature Anomalies of Oxyethylene-Based Surfactants and Polymers are Ubiquitous

We have already encountered a number of novel temperature effects for the different types of oxyethylene-containing solutes, that is, surfactants, homopolymers and copolymers. In fact, these and other temperature “anomalies” have a much broader significance and are found for a wide range of systems.

Clouding and phase behavior are examples of such unusual temperature effects. We expect, in general, two substances to become more miscible at higher temperatures due to the more significant contribution from entropy to the free energy of mixing. For a few systems, there is an inverse effect of temperature on solubility, as we have noted for the oxyethylene-containing solutes. Then we have a lower consolute curve and a lower critical point. We expect, therefore, that if the temperature can be raised to sufficiently high values we will retrieve complete miscibility, so that we have a closed-loop type of phase behavior (cf. Figure 7.11).

Clouding is one temperature anomaly displayed by these systems, but there are numerous others. A closely related observation is that if we have a two-phase system of oil and water and add surfactant, the surfactant will mostly partition into the lower aqueous phase at low temperatures but into the upper oil phase at higher temperatures. The surfactant not only decreases its solubility in water with increasing temperature but also increases its solubility in oil. This behavior is opposite to that of other surfactants, like ionics. A related observation is the strong decrease of the CMC of a nonionic surfactant with an increase in temperature, again different from what is observed with other surfactants. The CMC in oil shows an opposite behavior to that in water. We can infer that a nonionic surfactant becomes more hydrophobic at higher temperature.

Micelle size and shape are strongly dependent on temperature, with a growth from spheres to rods and to bilayer structures. Again this is the opposite to what is seen for other surfactant classes.

As described in Chapter 17, the microstructure of nonionic microemulsions shows a dramatic variation with temperature. At low temperatures a structure of oil droplets is formed, while at higher temperatures water droplets form. Again this is opposite to what we are used to for other surfactants.

The interactions between aggregates of oxyethylene-based surfactants or between surfaces covered with such surfactants or oxyethylene-containing polymers change from being repulsive at lower temperatures to being attractive at higher temperatures. This observation applies to self-assembly structures like micelles, to droplets and particles, as is seen for emulsions and suspensions, and to macroscopic surfaces. In Chapter 24 it is shown that this behavior can be used for the transformation of an oil-in-water emulsion into a water-in-oil emulsion. The adsorption of oxyethylene-containing polymers and surfactants increases in magnitude with increasing temperature (Chapters 8 and 11). At higher temperatures the adsorbed layers become more compact.

In mixed systems (polymer–polymer or polymer–surfactant), a number of unusual temperature dependencies are noted; for example, with regard to incompatibility and association.

Temperature Anomalies are Present in Solvents Other than Water and for Other Polymers

It appears that these effects are not limited to water as a solvent. They are also found for some other polar solvents although the effects are weaker. As an example we may consider nonionic surfactants in formamide. Here there is also the formation of micelles and different liquid crystalline phases. However, the CMCs are much higher and the ranges of liquid crystal stability lower. The solubility is much higher than in water, which corresponds to a higher cloud point. The cloud point of $C_{12}E_3$ in formamide is a little higher than that of $C_{12}E_4$ in water and the cloud point decreases progressively as water is added.

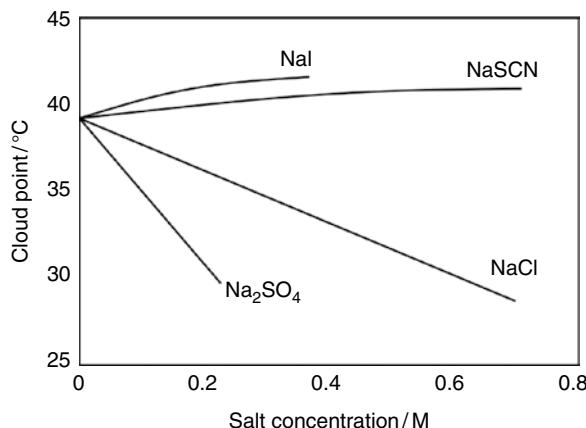


Figure 7.17 Cloud point variations of ethylhydroxyethylcellulose in some salt solutions. (With permission from Malmsten, M. and Lindman, B. (1990) Ellipsometry studies of the adsorption of cellulose ethers. *Langmuir*, **6**, 357–364. Copyright 1990, American Chemical Society.)

Also, other polymers show these “anomalous” temperature effects, such as the important class of nonionic cellulose derivatives (methylcellulose, hydroxyethylcellulose, etc.). Shown in Figure 7.17 are the effects of electrolyte addition in solutions of ethylhydroxyethylcellulose, giving the same sequence as for poly(ethylene glycol). These cellulose derivatives thus also become less polar at higher temperatures, again because of conformational changes with temperature. Such conformational effects also explain why cellulose becomes more soluble in water at low temperature.

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8

Surfactant Adsorption at Solid Surfaces

Adsorption of surfactants at solid surfaces is of great importance in many technical processes as well as products, for example, in the stabilization of suspensions, in detergency, and in lubrication. The surfactant adsorption from aqueous solutions is driven by two factors: (i) the energy gained on changing a surface–water contact into a surface–surfactant contact and (ii) the hydrophobic effect, that is, the escaping tendency of the surfactant hydrocarbon moiety from the aqueous environment.

One of the two requirements for a substance to be termed a surfactant is that it should adsorb at surfaces. The other requirement is that it should form aggregates in solution. We will in this chapter illustrate that aggregates may also be formed at surfaces, although at much lower bulk surfactant concentrations.

The simplest view of surfactant adsorption is to see it as a partitioning between a *surface phase* and the bulk *solution phase* (Figure 8.1a). Adsorption is normally described in terms of the adsorption isotherm, where the adsorbed amount of surfactant, that is, the amount in the surface phase, is determined as a function of the surfactant concentration in the bulk solution (Figure 8.1b and c). In many instances it is informative to plot the adsorption isotherm on a lin-log or log-log scale (Figure 8.1c). In this way more details are revealed at low surfactant concentrations.

Surfactant adsorption always reaches a limiting value, Γ_{\max} , when the solution concentration is above the critical micelle concentration (CMC) (Figure 8.1). Above the CMC the surfactant activity in the solution is constant and, therefore, the adsorbed amount should not increase. From this limiting adsorption we can calculate the area per

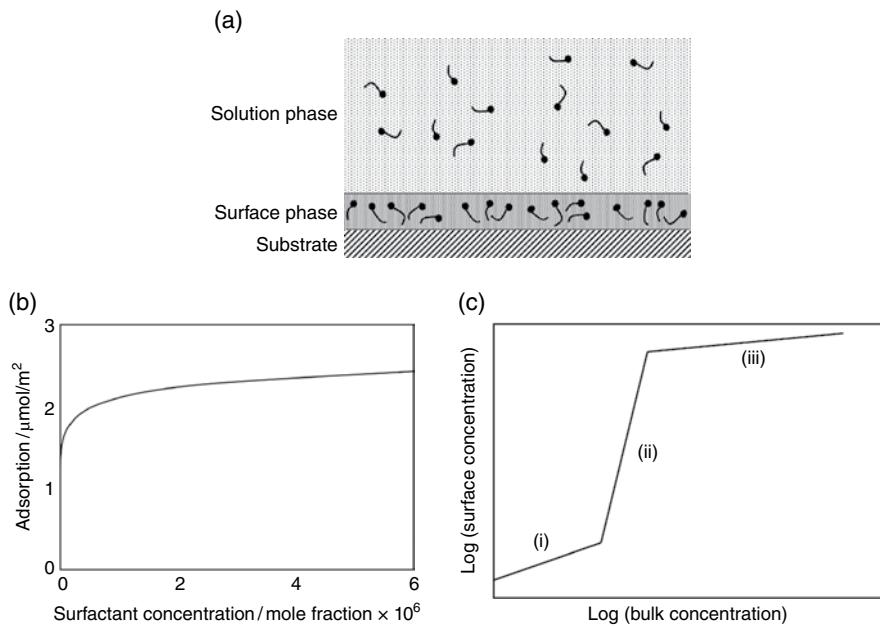


Figure 8.1 (a) In describing adsorption the surface is regarded as a separate phase in equilibrium with the solution. (b) The surfactant concentration in the surface phase versus the concentration in the solution phase is termed the adsorption isotherm. (c) Plotting the adsorption isotherm on a log-log scale reveals features at low surfactant concentrations

surfactant molecule (A), which expressed in $\text{\AA}^2/\text{molecule}$, is obtained from the following relationship:

$$A = \frac{M}{\Gamma_{\max} (\text{mg/m}^2) 6.02} = \frac{1000}{\Gamma_{\max} (\mu\text{mol}/\text{m}^2) 6.02} \quad (8.1)$$

Here M is the molecular weight of the surfactant. The steep increase in adsorption below the CMC is a reflection of the adsorption energy—the higher the adsorption energy, the larger the slope. A conclusion is, therefore, that surfactants with a low CMC display a strong adsorption and vice versa. Hence, the factors that affect the CMC also affect the adsorption. Increasing the surfactant alkyl chain length, for example, strongly increases the adsorption strength.

The adsorption differs depending on whether the surface is hydrophobic or hydrophilic. These cases are therefore treated separately.

Surfactant Adsorption at Hydrophobic Surfaces

At very low concentrations the surfactants adsorb with their hydrocarbon chain laying down at a hydrophobic surface, whereas at higher concentrations a monolayer is formed (Figure 8.2). The driving force for the adsorption is the hydrophobic effect, namely the tendency of the surfactant hydrocarbon moiety to escape from the aqueous environment.



Figure 8.2 Illustration of the adsorption of surfactant at a hydrophobic surface. (a) At low surfactant concentrations the surfactant molecules lie down at the surface whereas (b) at higher concentrations a monolayer is formed

On adsorbing at a hydrophobic surface some of the unfavorable water–hydrocarbon contacts are lost and this is the main driving force for adsorption. Discrete surfactant aggregates do not form at hydrophobic surfaces unless there is very strong surface–surfactant interaction, such as at a graphite surface.

Surfactant adsorption on hydrophobic surfaces can be modeled by the Langmuir equation (Equation 8.5). A derivation and description of this are given later in this chapter. From such an analysis one obtains (i) the surface area occupied per surfactant molecule when the adsorption reaches a limiting value, Γ_{\max} (Equation 8.1), and (ii) the adsorption free energy. This in turn is split up into two contributions (Equation 8.11): The first contribution is due to the exchange of surface–water contacts with surface–surfactant contacts. The second contribution equals the micellization free energy and stems from the transfer of a surfactant hydrocarbon moiety from the aqueous environment to the surface phase where the surfactant hydrocarbon moiety is less exposed to water. It is thus a measure of the tendency of the surfactant hydrocarbon moiety to escape from the aqueous environment. It will be shown later that this contribution is of the order of 30–40 KJ/mol, whereas the former contribution is constant and equal to about 5 kJ/mol. The tendency of the surfactant to escape from the aqueous environment is, therefore, the dominating driving force for surfactant adsorption.

Nonionic Surfactants at Hydrophobic Surfaces

Figure 8.3 shows the adsorption of three nonionics, namely, nonylphenol with 10, 20, and 50 polyoxyethylene units, on two polymer surfaces, that is, polystyrene and poly(methyl methacrylate) (PMMA). Firstly, we note that there is a considerable difference in adsorption between the three surfactants, with the one with the shortest polyoxyethylene chain adsorbing the most. Secondly, we note that there is only a slight difference in adsorption between the two polymer surfaces, with the polystyrene latex, which is the most hydrophobic, adsorbing the most. The adsorption reaches a limiting value at solution concentrations slightly above the CMC of the surfactants.

Analysis of the isotherms shows that it is the exchange of contacts between water and surfactant hydrocarbon moiety to contacts between surfactant hydrocarbon moieties at the surface that dominates the adsorption of nonionic surfactants at hydrophobic surfaces. Hence, the exchange of surface–water molecular contacts to surface–hydrocarbon moiety molecular contacts is of less importance.

Table 8.1 shows the results obtained from a Langmuir analysis of the isotherms, including sodium dodecyl sulfate (SDS) as a reference. The table reveals that the cross-sectional area per molecule (A) increases as the polyoxyethylene chain length is increased. The Gibbs free energy of adsorption (ΔG_{ads}) decreases with polyoxyethylene chain length,

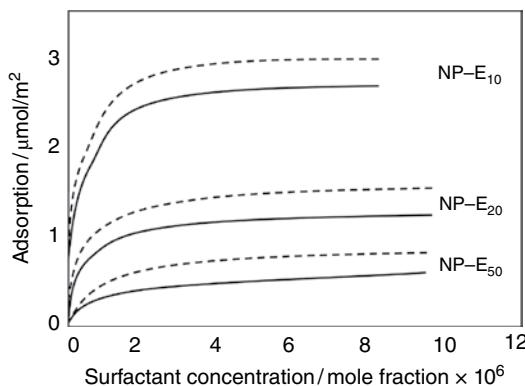


Figure 8.3 Adsorption of nonylphenol ethoxylates, $NP-E_n$, on polystyrene latex (dashed curves) or PMMA latex (full curves). (With permission from Kronberg, B., Stenius, P. and Igoborn, G. (1984) The effect of surface polarity on the adsorption of nonionic surfactants, II adsorption on poly(methyl methacrylate) latex. *Journal of Colloid and Interface Science*, **102**, 418–423. Copyright Elsevier.)

Table 8.1 Results obtained from Langmuir analysis for the adsorption on polystyrene, PMMA and poly(vinyl chloride) surfaces^a

Surface	Surfactant	ΔG_{ads} kJ/mol	ΔG_{mic} kJ/mol	$A N_A (\gamma_w^o - \gamma^{CMC})$ kJ/mol	$A \text{ Å}^2/\text{molec.}$
Polystyrene	SDS	-28.0	-22.6	-5.4	52
Polystyrene	NP-EO ₁₀	-38.2	-33.8	-4.4	54
Polystyrene	NP-EO ₂₀	-37.0	-31.9	-5.1	106
Polystyrene	NP-EO ₅₀	-34.7	-30.0	-4.7	200
PVC	NP-EO ₁₀	-39.4	-33.8	-5.6	60
PVC	NP-EO ₂₀	-37.5	-31.9	-5.6	119
PVC	NP-EO ₅₀	-35.3	-30.0	-5.3	244
PMMA	NP-EO ₁₀	-38.6	-33.8	-4.8	60
PMMA	NP-EO ₂₀	-37.3	-31.9	-5.4	134
PMMA	NP-EO ₅₀	-34.3	-30.0	-4.3	280

^aSDS values taken from Kronberg, B., Lindström, M. and Stenius, P. (1986) Competitive adsorption of an anionic and a nonionic surfactant on polystyrene latex, in *Phenomena in Mixed Surfactant Systems* (ed. J.F. Scamehorn), ACS Symposium Series **311**. Values of NP-EO_n on PS and PVC taken from Kronberg, B., Käll, L. and Stenius, P. (1981) Adsorption of nonionic surfactants on latexes. *J. Disp. Sci. Technol.*, **2**, 215–232. Values on PMMA taken from Kronberg, B., Stenius, P. and Igoborn, G. (1984) The effect of surface polarity on the adsorption of nonionic surfactants II: Adsorption on poly (methyl methacrylate) latex. *Journal of Colloid and Interface Science*, **102**, 418–423.)

although all the nonionic surfactants show higher values (more negative ΔG_{ads}) than that of SDS. This table also includes the Gibbs free energy of micellization (ΔG_{mic}) as a comparison. The Gibbs free energy of micellization is obtained from the relationship:

$$\Delta G_{mic} = RT \ln X_{mic} \quad (8.2)$$

Here X_{mic} is the critical micelle concentration expressed in terms of mole fractions. The difference between ΔG_{ads} and ΔG_{mic} is equal to $A N_A (\gamma_w^o - \gamma^{CMC})$, which is the energy gained on changing a surface–water contact into a surface–surfactant contact (Equation 8.11).

The small ΔG_{ads} of SDS is due to the counterions that hamper adsorption by their electrostatic attraction to the surface, which in turn lowers the entropy (Figure 3.2). As a comparison, the CMCs of nonionic surfactants are, in general, of the order of 10–100 times smaller than those of ionic surfactants with the same hydrocarbon chain length. In Chapter 13 the implications of this difference in adsorption free energy will be discussed in the simultaneous adsorption of SDS and NP-E₁₀.

There is also a large difference in Gibbs free energy of adsorption between NP-E_n surfactants with differing polyoxyethylene chain lengths. Thus, in surfactant mixtures, such as in technical grade surfactants, there will be a chromatographic effect in the sense that the surfactant homologues with short polyoxyethylene chains will be preferentially adsorbed on hydrophobic surfaces. Hence, when a technical surfactant batch is used, the long polyoxyethylene chain homologues will mainly stay in solution and the short ones will be enriched at the surfaces of the system (Figure 13.10).

The adsorption depends on the polarity of the hydrophobic surface, that is, the higher the polarity, the lower is the adsorption. Increasing the polarity of the surface will decrease the surface–surfactant contribution to the free energy of adsorption somewhat. However, since this contribution to the total free energy of adsorption is small, the effect of surface polarity on adsorption is only marginal. The major contribution comes from the transfer of a surfactant hydrocarbon moiety from water to the hydrocarbon environment of the surfactant layer at the surface.

Nonionic surfactants are known to have a strong temperature dependence with respect to their solution properties in aqueous systems (Chapter 7). Hence, a strong temperature dependence is also expected for the adsorption on solid surfaces. Figure 8.4 shows the temperature dependence of the adsorption of NP-E₂₀ on a PMMA surface. As can be seen, the adsorption increases strongly with temperature. As for the adsorption of polymers, the

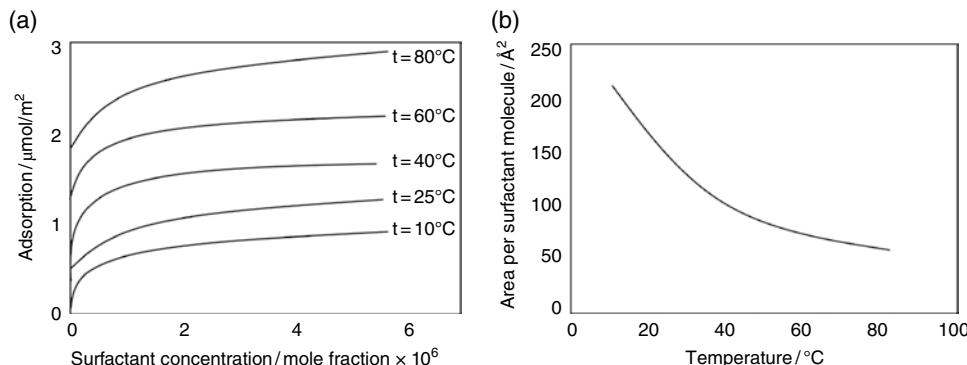


Figure 8.4 The temperature dependence of the adsorption of NP-E₂₀ on (a) a PMMA surface and (b) the cross-sectional area per surfactant molecule. (With permission from Steinby, K., Silveston, R. and Kronberg, B. (1993) The effect of temperature on the adsorption of a nonionic surfactant on a PMMA latex. Journal of Colloid and Interface Science, 155, 70–78. Copyright Elsevier.)

adsorption is a reflection of the solution properties, namely the poorer the affinity for the aqueous phase, the stronger is the adsorption. Figure 8.4b shows that the cross-sectional area per surfactant molecule decreases continuously with the temperature.

Ionic Surfactants at Hydrophobic Surfaces

Also, the adsorption of ionic surfactants reaches a limiting value at the CMC, since the unimer activity is constant above the CMC. This is exemplified in Figure 8.5 for the adsorption of SDS on polystyrene latex. The value of the limiting adsorption (Γ_{\max}) is the result of a balance between the adsorption energy of the surfactant and the entropy loss of the counterions. The transfer of a unimer surfactant from the bulk solution to a surface (i.e., the adsorption process) is accompanied with a partial binding of the counterions (Chapter 3) due to the charges originating from the surfactant at the surface. In the bulk solution the surfactant is totally dissociated. Hence, due to the counterion binding, the counterions lose entropy on adsorption of a surfactant molecule. This entropy loss is higher the larger the surface charge density, that is, the higher the adsorption (Figure 3.2). A limiting adsorption is reached when this loss in entropy balances the driving force for adsorption, which is based on the hydrophobic effect. Note that this limiting adsorption does not correspond to a close packing of the surfactant. A close packing of hydrocarbon chains standing perpendicular to the surface would be of the order of $20\text{--}25\text{ }\text{\AA}^2/\text{molecule}$, corresponding to $6.5\text{--}8.5\text{ }\mu\text{mol/m}^2$. The adsorption of SDS on polystyrene is only $3\text{--}4\text{ }\mu\text{mol/m}^2$.

Adding salt decreases the entropy loss on adsorption due to the binding of the counterions, with the result that the adsorption now reaches a limiting value at higher surface charge, that is, at a higher adsorption (Figure 8.5). A conventional, but not entirely correct,

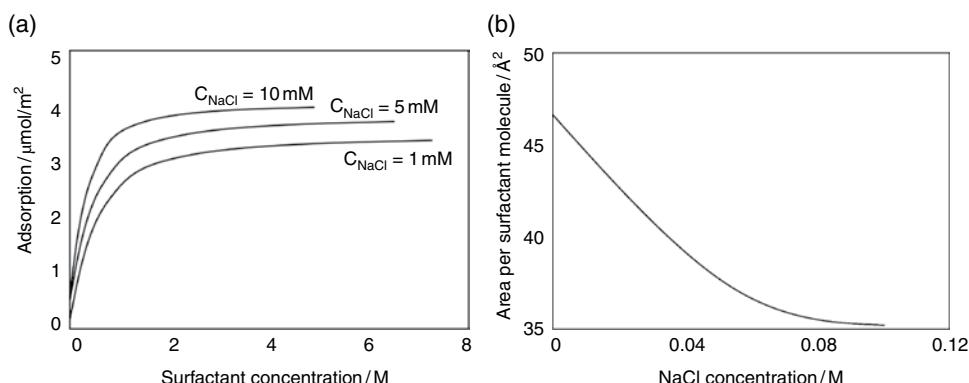


Figure 8.5 Adsorption of SDS at three different salt (NaCl) concentrations illustrating that (a) the adsorption increases with the salt concentration and (b) the cross-sectional area per surfactant head group decreases with the salt concentration. (With permission from Tajima, K. (1971) Radiotracer studies on adsorption of surface-active substance at, aqueous surface. III. The effects of salt on the adsorption of sodium dodecylsulfate. Bulletin of the Chemical Society of Japan, **44**, 1767–1771, copyright The Chemical Society of Japan, and Pirma, I. and Chen, S. (1980) Adsorption of ionic surfactants on latex particles. Journal of Colloid and Interface Science, **74**, 90–102, copyright Elsevier.)

way of expressing the phenomenon is that the addition of salt reduces the lateral electrostatic repulsion between the surfactant molecules at the surface, thus resulting in closer packing and, hence, a smaller effective cross-sectional area per surfactant head group. The cross-sectional area per surfactant (A) is shown as a function of salt concentration in Figure 8.5b.

Surfactant Adsorption at Hydrophilic Surfaces

Surfactants also adsorb at hydrophilic surfaces, such as silica or mica, but the adsorption mechanism is very different from that at hydrophobic surfaces. Firstly, there is no driving force where the surfactant minimizes the exposure of the surface to the aqueous solution as the surface is polar. Hence other factors must come into play.

The adsorption isotherms normally have the shape illustrated in Figure 8.1c, that is, (i) a weak adsorption at very low surfactant concentrations, (ii) a strong adsorption beyond a critical surfactant concentration, which is a surface-induced self-assembly of surfactant unimers, and (iii) a limiting value of the adsorption at higher surfactant concentrations. These three stages are illustrated in Figure 8.6a.

In the first region, there is typically little or no adsorption of individual surfactant molecules. Here the surfactant molecules adsorb individually, that is, as unimers, without interacting with each other. For *ionic surfactants* the driving force for this adsorption is ion exchange when the surfactant has opposite charge to that of the surface. Since the surfactant ions normally have a lower solubility than the original counterions at the surface there is a partitioning favoring surfactant ions at the surface. The break point to the next adsorption regime is termed the *critical surface association concentration* (CSAC), since at higher surfactant concentration the surfactant self-assembles at the surface. Hence, it is a surface induced self-assembly of surfactant unimers. It can be seen as the critical micelle concentration in the surface phase (Figure 8.6). This concentration is normally about one-tenth of the CMC. The steep rise in adsorption in region (ii) (Figure 8.1c) signifies a cooperative association at the surface and is similar in nature to the surfactant self-assembly at polymers in solution (Chapter 14). The structures of these self-assembled aggregates at surfaces is discussed in detail later in this chapter. The break point at which the adsorption reaches a limiting value is the CMC in the solution. Above the CMC the surfactant activity in solution is constant, hence there is no further adsorption.

Historically, before the advent of the AFM (atomic force microscopy) technique, there had been an alternative model of the surfactant adsorption at hydrophilic surfaces

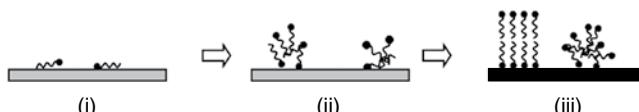


Figure 8.6 Illustration of the adsorption of a surfactant at a hydrophilic surface. (a) The surfactant molecules self-assemble at the CSAC and form a bilayer, or close packed structures of self-assemblies, at the CMC.

(Figure 8.6b). In this model the surfactant was thought to adsorb in hydrophobic patches, hemimicelles (i), where the surfactant hydrocarbon faces the aqueous solution. At higher surfactant concentration a surfactant monolayer was believed to form (ii), followed by a bilayer at the CMC (iii). This model, now abandoned, overemphasizes the importance of the interaction between the surfactant and the surface while it at the same time underestimates the importance of the hydrophobic effect.

The older view was supported by the fact that surfaces become hydrophobic when taken out of solutions. However, this could be understood from a reorientation of the surfactant when in contact with the liquid–air interface. A well-known example where this occurs is mineral ore flotation. The surfactant self-assemblies that are typically present on the mineral surface under the conditions used in the flotation process will rearrange into a monolayer when contacted with an air bubble. The polar head group of the surfactant will point down toward the mineral surface, often binding with a high degree of specificity to surface sites, and the hydrophobic tails will go into the air. The relatively large air bubbles will then lift the attached mineral particles into the froth region of the flotation cell.

Also, colloids are known to flocculate when a surfactant with a charge opposite to that of the particle surface is added. The reason for this behavior is not a hydrophobization, however, but rather a neutralization of the particle charge leaving no stabilization mechanism left (see further Chapter 18 on colloidal stability). Interestingly, both AFM and molecular dynamics calculations have shown that the surfactant molecules arrange in charged patches at the surface and the long-range attraction between such particles is due to electrostatic interaction between these patches and patches of naked particle surface, which have opposite charge.

Nonionic Surfactants at Hydrophilic Surfaces

Polyoxyethylene Chain Surfactants

The exact nature of the interaction between nonionic surfactants with polyoxyethylene chains and a polar surface has been disputed. However, it appears that the driving force is essentially a hydrophobic interaction between the (weakly polar) oxyethylene chains and the surface. Another contribution stems from the bound water at the surface and at the polyoxyethylene chains that are released on adsorption, hence increasing the entropy. Hydrogen bonding between the surface silanol groups and the oxygen in the polyoxyethylene cannot be the driving force for adsorption since both the surface silanol groups and the polyoxyethylene chains are already binding to hydration water before the adsorption.

Figure 8.7 illustrates the fact that the interaction between the surfactant and the surface is important in order for adsorption to take place. This figure shows that for the adsorption of two nonionic surfactants on silica the adsorption decreases to zero at pH levels of about 10 and above. Hence, the increased presence of counterions from the now highly charged silica surface hampers the adsorption, especially for the more hydrophobic surfactant, that is, $C_{12}E_5$. This indicates that only a small change in interaction between the surfactant and the surface is sufficient to prevent, or promote, the adsorption of nonionic surfactants. Figure 8.7b shows an AFM image of this surfactant at the silica surface. The figure shows the formation of aggregates at the surface (micelles).

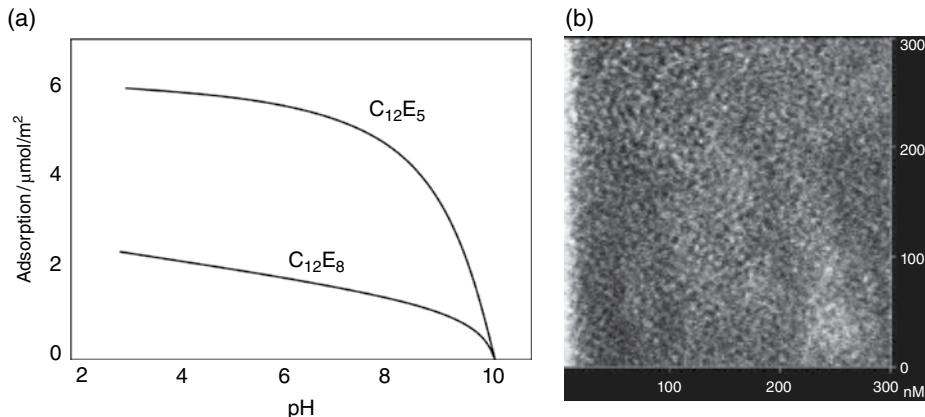


Figure 8.7 (a) Adsorption of two nonionic surfactants ($C_{12}E_5$ and $C_{12}E_8$) on silica as a function of pH; (b) an AFM image of $C_{12}E_8$ micelles at a silica surface where the light areas represent regions of high surfactant concentration (surface micelles). (Reproduced with permission from Tiberg, F. (1994) Self-assembly of nonionic amphiphiles at solid surfaces, PhD Thesis, Lund University, and Grant, L., Tiberg, F., and Ducker, W. (1998) Nanometer-scale organization of ethylene oxide surfactants on graphite, hydrophilic silica and hydrophobic silica. Journal of Physical Chemistry B, **102**, 4288–4294, Copyright 1998, American Chemical Society.)

Figure 8.8 shows the adsorption isotherms of some nonionic surfactants of type C_mE_n on silica. There is a CSAC of about one-tenth of the CMC. This implies that the number of surfactant aggregates at the surface grows in a concentration range of 0.1–1 times the CMC. The sharp growth of the adsorbed amount is attributed to the lack of counterions that

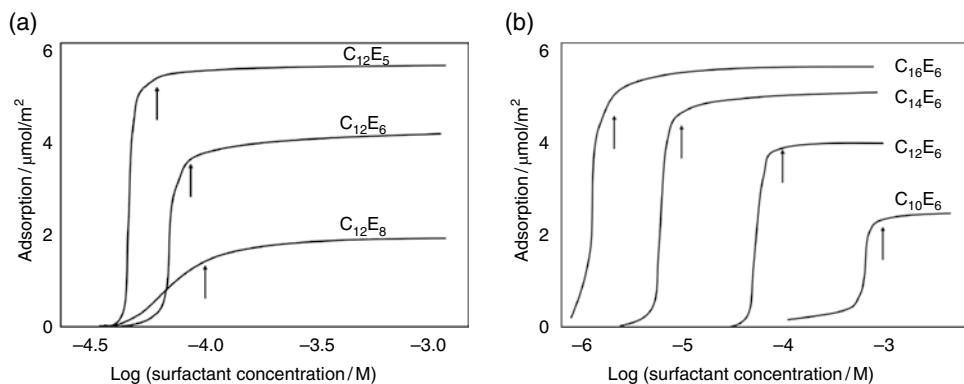


Figure 8.8 Adsorption isotherms of (a) $C_{12}E_n$ and (b) C_mE_6 on silica. The arrows indicate the CMC values of the surfactants. (With permission from Tiberg, F., Lindman, B. and Landgren, M. (1992) Interfacial behavior of nonionic surfactants at the silica-water interface revealed by ellipsometry. Thin Solid Films, **234**, 478–481. Copyright Elsevier.)

oppose the adsorption (Chapter 3). We also note that plateau adsorption is reached at concentrations of around the CMCs of the surfactants. Finally, the step-like isotherms are especially pronounced for those surfactants that have a low polyoxyethylene content, thus indicating a high degree of cooperativity. These results are indicative of self-assembled structures being formed at the surface, as shown in Figure 8.7b. The first evidence of surface-induced self-assemblies at surfaces came from studies of fluorescence quenching. The size of these surface aggregates increases with increasing hydrocarbon chain length of the surfactant. The thickness of the adsorbed layer jumps at the CSAC from zero to 40–55 Å, corresponding to twice the length of a surfactant molecule, thus the same dimensions as surfactant aggregates in general.

Alkylpolyglucoside (APG) Surfactants

The same dependency of the hydrocarbon chain length as illustrated for polyoxyethylene-based nonionics on silica is found for the adsorption of alkyl maltosides, C_mG_2 , on titanium dioxide (Figure 8.9).

Interestingly, alkyl maltosides do not adsorb at silica surfaces. In Chapter 13 it will be demonstrated, however, that these surfactants can be lured to adsorb at a silica surface by adding small amounts of some other surfactant that does adsorb (Figure 13.12a).

Ionic Surfactants at Hydrophilic Surfaces

The typical adsorption pattern of ionic surfactants at oppositely charged surfaces is shown in Figure 8.1c and illustrated by the adsorption of SDS and C_mTAB in Figure 8.10. At very low surfactant concentrations, region (i) in Figure 8.1c, the adsorption is

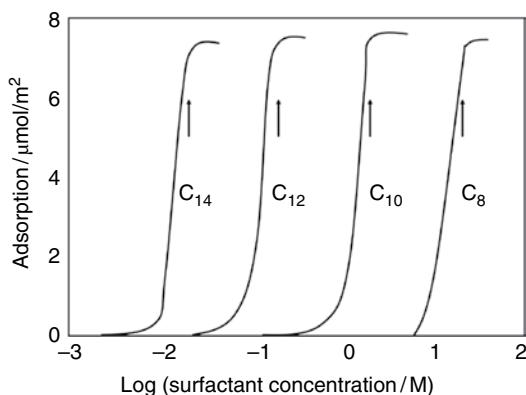


Figure 8.9 Adsorption isotherms of C_mG_2 surfactants on titanium dioxide, illustrating the effect of the surfactant hydrocarbon chain length on adsorption. The arrows indicate the CMC values of the surfactants. (With permission from Matsson, M., Kronberg, B. and Claesson, P. (2004) Adsorption of alkyl polyglucosides on the solid/water interface: equilibrium effects of alkyl chain length and head-group polymerization. *Langmuir*, **20**, 4051–4058. Copyright 2004, American Chemical Society.)

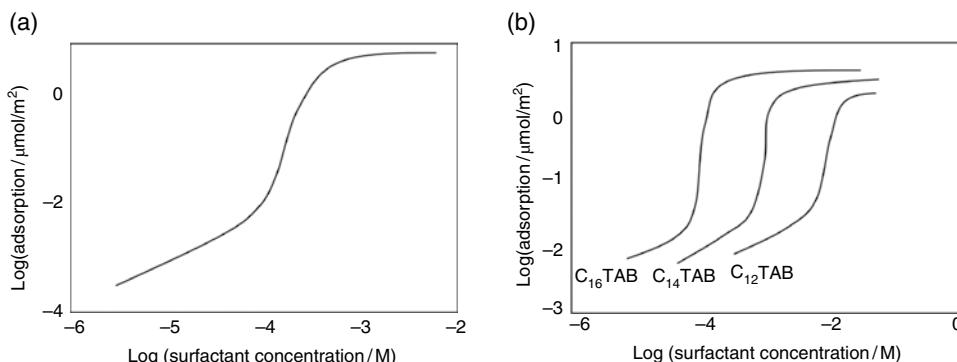


Figure 8.10 Adsorption of (a) SDS on alumina at pH = 6.5 and of (b) C_mTAB on alumina at pH = 10. (With permission from Chandar, P., Somasundaran P. and Turro, N.J. (1987) Fluorescence probe studies on the structure of the adsorbed layer of dodecyl-sulfate at the alumina-water interface. *Journal of Colloid and Interface Science*, **117**, 31–46, copyright Elsevier, and Fan, A., Somasundaran, P and Turro, N. (1997) Adsorption of alkyltrimethylammonium bromides on negatively charged alumina. *Langmuir*, **13**, 506–510, Copyright 1997, American Chemical Society.)

governed by an ion exchange mechanism, that is, the counterions of the surface are exchanged for the surfactant molecules, serving as counterions. This ion exchange at the surface gives rise to a higher surfactant concentration in the surface phase compared to the solution.

At higher surfactant concentrations, at the critical surface association concentration, the surfactant starts to form surface-induced self-assemblies. This occurs at the breakpoint between regions (i) and (ii) in Figure 8.1c. Figure 8.11 shows AFM pictures of how surface aggregates of cetyltrimethyl ammonium bromide (CTAB) on a mica surface grow in region (ii) with increasing surfactant concentration. The self-assembly is driven by the hydrophobic effect, that is, the gain in free energy in transferring the hydrophobic moiety of the surfactant from water to a hydrophobic environment. Regions (i) and (ii) in Figure 8.1c are, therefore, two surfactant concentration regions where the driving forces for adsorption are fundamentally different.

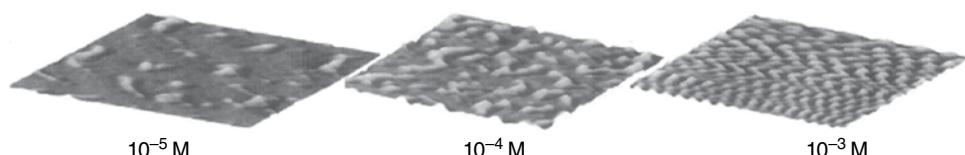


Figure 8.11 Adsorption of CTAB on mica at three different surfactant concentrations showing the formation and growth of surfactant aggregates at the surface. (With permission from Sharma, B.G., Basu, S. and Sharma, M.M. (1996) Characterization of adsorbed ionic surfactants on a mica substrate. *Langmuir*, **12**, 6506–6512. Copyright 1996, American Chemical Society.)

At higher surfactant concentrations (above the CMC), region (iii), the adsorption reaches a limiting value. The reason is that the unimer activity now is constant in the solution. The value of the limiting adsorption is governed by the charges originating from the surfactants at the surface. In the bulk solution the surfactant is totally dissociated; hence, due to the counterion binding, the counterions lose entropy on adsorption of a surfactant molecule. This entropy loss is higher the larger the surface charge density, that is, the higher the adsorption (Figure 3.2). A limiting adsorption is reached when this loss in entropy balances the driving force for adsorption, which is based on the hydrophobic effect.

Note that the CSAC is lower than the concentration when aggregates form in the solution, that is, the CMC, since the surfactant concentration at the surface is higher due to the ion exchange. Note also that the CSAC does not coincide with the surfactant concentration where the surface charge is neutralized by surfactant adsorption. The charge neutralization occurs at higher concentrations, as will be shown later in this chapter.

Since the association structures at surfaces are akin to the association structures in solution it would be expected that the adsorption would be very dependent on the surfactant alkyl chain length. This is indeed the case, as shown in Figure 8.10; the electrophoretic mobility curves, shown in Figure 18.26, confirm this. Here, those compounds with the longest alkyl chain adsorb at lower surfactant concentrations. They also show the greatest cooperativity, as revealed by the steeper increase in adsorption in the region between the CSAC and the CMC. This is again an example of the fact that surfactant adsorption depends primarily on the surfactant structure and only secondarily on the interaction with the surface. The only requirement for adsorption is that the surfactant should have some affinity for the surface, such that the surfactant concentration at the surface is enhanced compared to the concentration in solution. This will further promote the self-assembly at the surface at the critical surface association concentration. Increasing the surfactant hydrocarbon chain length increases the intermolecular interaction, which, in turn, also increases the stability of the surface aggregates. Figure 18.26 shows the zeta potential of quartz in solutions of alkyl ammonium acetates, clearly showing that these surfactants reverse the charge of the surface and that their effectiveness increases by a factor of about ten as the surfactant alkyl chain length increases by two carbon atoms.

Adding electrolyte has two effects. Figure 8.12 shows adsorption of the cationic surfactant dodecylpyridinium chloride (DPC) on silica and kaolin as a function of surfactant concentration at three different salt concentrations. In the figure there is a common intersecting point (CIP) where the three adsorption isotherms meet. This point corresponds to the isoelectric point, where there is no net charge at the surface. At concentrations below the CIP, the adsorption decreases with increasing salt concentration, whereas at concentrations above charge reversal the adsorption increases with salt concentration.

The origin of the decrease in adsorption below the CIP and the increase in adsorption above the CIP as salt is added is described in Chapter 3. Below the CIP the surface and surfactant have opposite charge. Hence, on adsorption there is a gain in entropy from the release of counterions from the surface. Adding salt will hamper this gain in entropy, thus adsorption is lowered. Adding salt above the CIP gives an opposite effect. Here, further adsorption increases the surface charge, hence the counterion binding increases. This lowers the entropy (Figure 3.2), which, in turn, hampers the adsorption. Adding salt will lower this effect, that is, the loss in entropy is not as large as without salt, hence the adsorption increases.

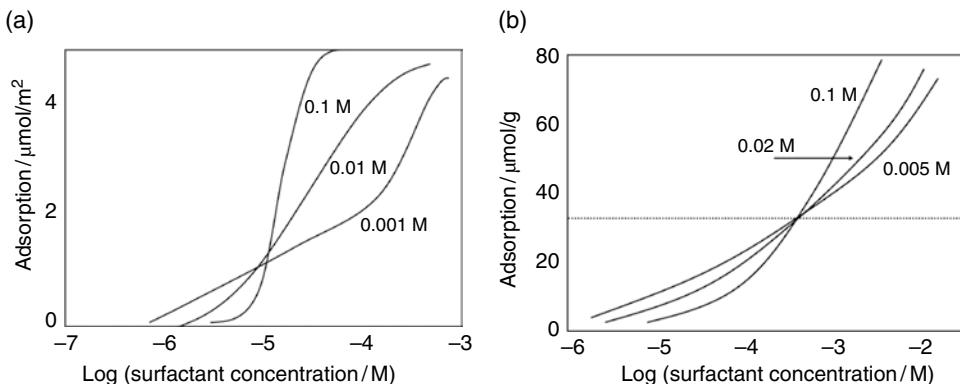


Figure 8.12 Adsorption of DPC on (a) silica and (b) kaolin at three different NaCl concentrations. (With permission from Goloub, T. and Koopal, L. (1997) Adsorption of cationic surfactants on silica: comparison of experiment and theory. *Langmuir*, **13**, 673–681, Copyright 1997, American Chemical Society, and Mehrian, T., de Keizer, A. and Lyklema, J. (1991) Effect of temperature on the adsorption of organic cations on charged surfaces. *Langmuir*, **7**, 3094–3098, Copyright 1991, American Chemical Society.)

One point of observation is that there is no apparent change in the isotherm when passing the CIP in Figure 8.12. If there were two different mechanisms, one above and one below the CIP, there would likely be different slopes of the isotherm. This supports the view that in this concentration range ($\text{CSAC} < \text{C} < \text{CMC}$) the adsorption is driven by the hydrophobic effect, irrespective of the net charge of the surface and this hydrophobic driving force is much larger than the ion exchange driving force.

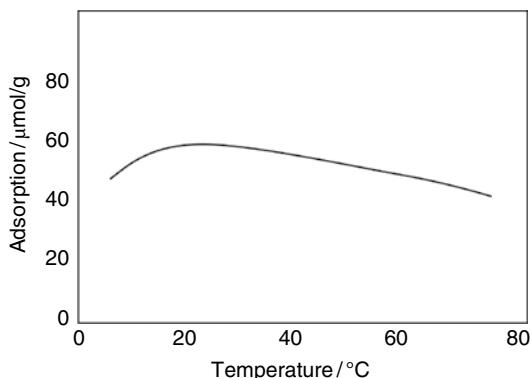


Figure 8.13 Adsorption of DPC on kaolin at a constant surfactant concentration (5.5 mM) as a function of temperature. (With permission from Mehrian, T., de Keizer, A. and Lyklema, J. (1991) Effect of temperature on the adsorption of organic cations on charged surfaces. *Langmuir*, **7**, 3094–3098. Copyright 1991, American Chemical Society.)

The adsorption of ionic surfactants is only weakly dependent on the temperature. The adsorption changes only by 10–20% over a temperature range of 50 °C (Figure 8.13). The maximum in adsorption at around 25 °C coincides with a minimum in the CMC of the

surfactant at this temperature. Comparing nonionic and ionic surfactants in this respect, the former have a strong temperature dependence and a weak dependence on ionic strength while the latter have a small temperature dependence and a strong dependence on ionic strength.

Surfactant Self-Assemblies at Surfaces Have Various Shapes

The type of surface aggregates that forms on the surface depends on the molecular geometry of the surfactant, that is, the CPP. This is illustrated in Figure 8.14, showing the adsorption of three surfactants on a mica surface. Depending on the molecular geometry there are micelles, cylinders, or a feature-less double layer formed at the surface. Since the shape of the surface aggregates depends on the packing of the surfactant molecules, it is pertinent to list the parameters that affect the surfactant packing parameter (CPP). An increase of the critical packing parameter, hence also an increase in the adsorbed amount, can be accomplished by the following alterations of the surfactant: (i) change to a surfactant with a longer hydrocarbon chain (this is known as Traube's rule, which states that "the adsorption of organic substances from aqueous solutions increases strongly and regularly as we ascend the homologous series"); (ii) change to a surfactant with a branched hydrocarbon chain; (iii) use of surfactants with two hydrocarbon chains; (iv) change of the surfactant counterion to a counterion with high affinity to the micellar surface (or with poor solubility).

The shape of the surfactant aggregates at a surface can also be manipulated by adding a second amphiphile, such as a second surfactant or a medium-chain alcohol. One important difference between aggregates at surfaces and in bulk solution is that the aggregates at

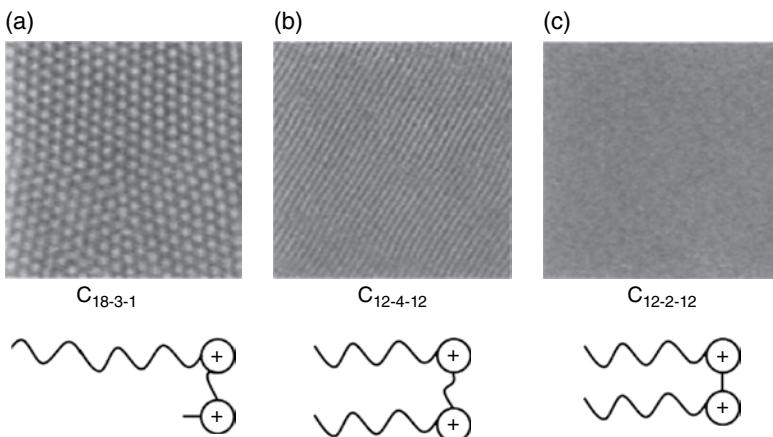


Figure 8.14 Adsorption of three different surfactants on mica, illustrating how the surface aggregate structure depends on the molecular geometry of the surfactant. (a) For low CPP values globular micelles are formed; (b) for intermediate values there are cylinders; (c) while for high CPP values featureless double layers are found. (With permission from Manne, S., Schaffer, T.E., Huo, Q., et al. (1997) Gemini surfactants at solid–liquid interfaces: control of interfacial aggregate geometry. *Langmuir*, **13**, 6382–6387. Copyright 1997, American Chemical Society.)

surfaces are in equilibrium with low bulk surfactant concentrations. Hence, in adding a second surfactant it is necessary to be aware that surfactants do not adsorb in the same ratio as they are present in the solution. There is always an enrichment of the more hydrophobic surfactant at the surface. Also, adding a surfactant of opposite charge to the surfactant already at the surface will give large effects. The addition of surfactant molecules of opposite charge will release bound counterions, so increasing the entropy. Hence, the driving force for mixing at the surface is large. This mismatch between the surface and solution composition is dealt with further in Chapter 16.

Changing the counterion could have large effects on the adsorption. Counterions with poor solubility display a high affinity towards the surface layer. This effect increases the CPP of the surfactant in question, which, in turn, can have large effects on the adsorption of ionic surfactants, as is illustrated in Figure 8.15. Here the adsorption of the surfactant CTAB on silica is shown in the presence of sodium bromide and sodium salicylate. The figure shows that not only the total adsorbed amount but also the concentration at which the surface is covered differ tremendously between the two salt solutions. These trends are valid, too, for the binding of counterions to micelles in solution; for example, the more hydrophobic counterions bind to the micellar surface and are more effective in lowering the CMC.

Figure 8.15b shows AFM images corresponding to these systems. In the presence of salicylate the aggregates are elongated, which is attributed to the strong partitioning of the salicylate ion to the surface of the aggregates; this, in turn, reduces the surfactant head group area, hence raising the CPP.

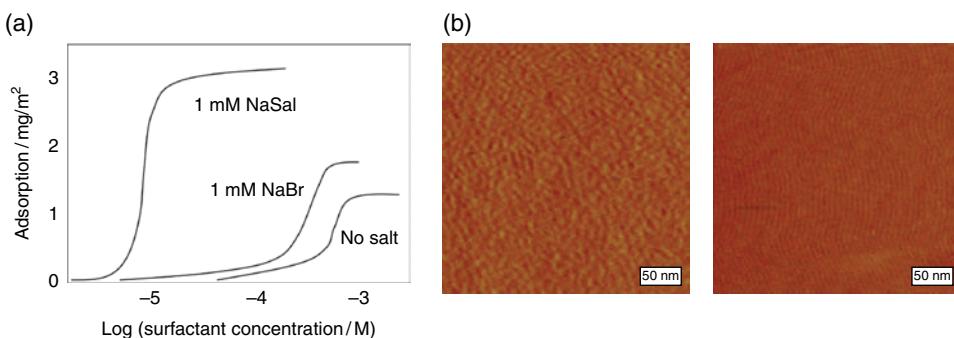


Figure 8.15 (a) Adsorption of CTAB on silica in the presence of sodium bromide and sodium salicylate; (b) AFM images of CTAB on silica without (left) and with (right) the addition of salicylate. (With permission from Howard, S.C. and Craig, V.S.J. (2009) Adsorption of the cationic surfactant cetyltrimethylammonium bromide to silica in the presence of sodium salicylate: surface excess and kinetics. *Langmuir*, **25**, 13015–13024. Copyright 2007, American Chemical Society.)

Strong Interaction with the Surface Can Give Epitaxial Effects

Surfactant aggregate structures at surfaces are not a direct copy of the structures in the solution. One reason for this stems from the surface charges and the fact that the surface charge density varies depending on the type of surface. Comparing, for example, silica and mica

surfaces there is a lower charge density on silica. This results in a larger spacing of the hexagonal packing at silica, greater axial curvature, and a greater sensitivity of the aggregates towards the counterion binding affinity. Also, the charge density of the basal plane of kaolin particles is less than that of mica, rendering it very susceptible to changes in the environment concerning the surface aggregate size and shape.

At a graphite surface the hydrophobic interaction between graphite and the hydrocarbon tails is much stronger than the electrostatic interaction between the surfactant head groups. Hence, the aggregates are determined by the atomic layers in the graphite. Similarly, surfactant structures formed at a gold surface reveal that the aggregate shapes are controlled by the gold lattice. Here, as in graphite and also molybdenum disulfide (MoS_2), the surfactants adsorb with their tails parallel to the symmetry axis of the solid.

Adsolublization is the Solubilization of Substrates in the Surface Aggregates

Adsolublization is the coadsorption of an external component in the surfactant aggregates at the surface. Normally the phenomenon is referred to when a hydrophobic substance with no, or low, solubility in the aqueous phase partitions into the surfactant aggregates at the surface. Figure 8.16 shows the adsolublization of 2-naphtol into adsorbed aggregates of PEO–PPO–PEO block copolymers on hydrophobic silica particles as a function of the surfactant concentration in the equilibrium solution. Maximum adsolublization is obtained just below the CMC of the surfactant in the solution. At higher surfactant concentrations the 2-naphtol is solubilized in the micelles in the solution and the amount of adsolublized material decreases. For the more hydrophilic surfactant there is no solubilization in the solution micelles, hence the adsolublized amount stays constant and independent of the

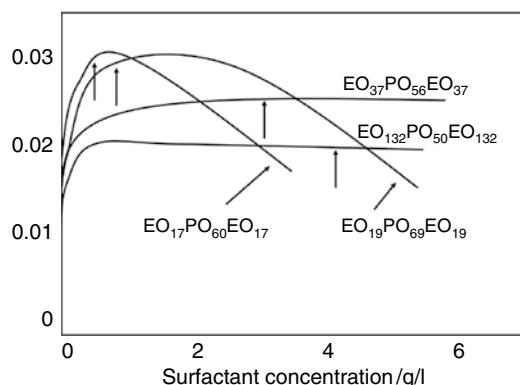


Figure 8.16 Adsolublization of 2-naphtol into adsorbed aggregates of PEO–PPO–PEO copolymers on hydrophobic silica particles. The arrows indicate the CMC values of the surfactants. (With permission from Tsurumi, D., Sakai, K., Yoshimura, T. and Esumi, K. (2006) Adsolublization of 2-naphtol into adsorbed layers of triblock PEO-PPO-PEO copolymers on hydrophobic silica particles. *Journal of Colloid and Interface Science*, **302**, 82–86. Copyright Elsevier.)

surfactant concentration. In order to prevent desorption of material from the surface a surfactant that is unable to solubilize the substance in solution should be used. Note that the surfactant concentration at which the adsolublized amount peaks is lower than the CMC of the pure surfactant system. This is because a hydrophobic solublizate decreases the CMC of the surfactant.

There is no clear distinction between adsolubilization and coadsorption. Coadsorption is the term used where the second component is amphiphilic, such as hexanol, whereas for adsolubilization the second component is nonamphiphilic. The solubilization into the surface aggregates could increase or decrease the CPP and, hence, induce a change in shape of the surfactant aggregates. Factors influencing adsolubilization are the solubility characteristics of the adsolubilizate, the surfactant structure, and the surface.

Analysis of Surfactant Adsorption Isotherms

It is often desirable to analyze surfactant adsorption in terms of a theoretical model in order to obtain a molecular interpretation. The parameters from such an analysis can be used to understand the adsorption behavior of different surfactants and also to predict the adsorption in new systems. An overwhelming majority of the analyses of surfactant adsorption at hydrophobic surfaces are based on the Langmuir equation. The Langmuir equation is derived under the assumptions that (i) the surface is homogeneous, (ii) the surfactant adsorbs in only one layer, such as shown in Figure 8.2, (iii) there are no surfactant–water or surfactant–surfactant interactions, and (iv) the surfactant and water molecules have equal sizes and hence equal cross-sectional surface areas.

The first two assumptions are quite reasonable but the last two are not. It has been shown that taking both the interaction and the molecular size difference into account gives deviations from the Langmuir equation that are opposite to each other. Thus, the good fit usually obtained when using the Langmuir equation for the adsorption isotherms of surfactants is fortuitous.

The Langmuir equation can be derived in the following simple way. Let the adsorption rate be proportional to the surfactant concentration (C) and also the fraction of the surface free for adsorption. We then have:

$$\text{Rate of adsorption} = k_a C(1 - \Theta) \quad (8.3a)$$

Here Θ is the fraction of the surface that is covered with surfactant and k_a is a rate constant. Similarly, the desorption rate is assumed to be proportional to the fraction of the surface covered with surfactant, that is:

$$\text{Rate of desorption} = k_d \Theta \quad (8.3b)$$

where k_d is a rate constant. At equilibrium, the adsorption and the desorption rates are the same, hence we have:

$$k_a C(1 - \Theta) = k_d \Theta \quad (8.4)$$

Recognizing that the equilibrium constant is the ratio between the rate constants, that is, $K = k_a/k_d$ we get:

$$\frac{\Theta}{1-\Theta} = KC \text{ or } \Theta = \frac{KC}{1+KC} \quad (8.5)$$

Equation 8.5 is termed the Langmuir equation. The equilibrium constant (K) describes the partitioning of the surfactant between the surface phase and the solution phase. This is realized if the Langmuir equation is applied at the limit of infinitely low solution concentrations where:

$$K = \left(\frac{\Theta}{C} \right)_{C \rightarrow 0} \quad (8.6)$$

Hence, a low K value indicates weak adsorption, whereas a large K value indicates strong adsorption. The adsorption free energy (ΔG_{ads}) is related to the K -value through:

$$\Delta G_{ads} = -RT \ln(K) \quad (8.7)$$

The fraction of the surface that is covered with surfactant (Θ) is obtained by assuming that a full coverage is obtained at high equilibrium concentrations (at and above the CMC) in the bulk liquid. Thus, the fraction of covered surface can be written as:

$$\Theta = \frac{\Gamma}{\Gamma_{max}} \quad (8.8)$$

Γ is the adsorbed amount and Γ_{max} is the adsorption at full coverage. This equation can be combined with the Langmuir Equation 8.5 to give:

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_{max}} + \left(\frac{1}{K \Gamma_{max}} \right) \frac{1}{C} \quad (8.9)$$

Therefore, a plot of $1/\Gamma$ versus $1/C$ gives us both the Γ_{max} and the K -value from the intercept and the slope, respectively. Thus, both the Γ_{max} -value and the K -value, and hence an adsorption free energy (ΔG_{ads}), can easily be obtained from an adsorption isotherm. An alternative to this procedure is to plot C/Γ versus C according to:

$$\frac{C}{\Gamma} = \frac{1}{K \Gamma_{max}} + \frac{C}{\Gamma_{max}} \quad (8.10)$$

Here also the parameters are obtained from the intercept and the slope. The former procedure is sensitive to values at low concentrations while the latter is sensitive to values at higher surfactant concentrations.

A more thorough thermodynamic treatment of adsorption reveals that there are two contributions to the free energy of adsorption, namely:

$$\Delta G_{ads} = -RT \ln K = -RT \ln CMC + AN_A (\gamma_w^o - \gamma^{CMC}) \quad (8.11)$$

N_A is the Avogadro number. The first term on the right-hand side stems from the hydrophobic effect and equals the free energy of micellization, whereas the second term stems from changing a surface–water contact into a surface–surfactant contact at its CMC. The free energy of micellization is a reflection of the process where the surfactant hydrocarbon moiety is transferred from the aqueous environment to a hydrocarbon environment inside the micelle core. It is, therefore, a measure of the hydrophobic effect. Table 8.1 shows the two contributions to the free energy of adsorption for the adsorption of some surfactants at different polymer surfaces. The table illustrates that the largest contribution to the adsorption free energy comes from the hydrophobic effect, that is, from the free energy of micellization. The other contribution is constant and, within experimental error, independent on both surfactant and surface. This is in line with the picture that the surfactant molecules adsorb with their hydrocarbon moiety in contact with the surface.

Model Surfaces and Methods to Determine Adsorption

Dispersed Systems

Latex particles are very common as model surfaces for studying surfactant adsorption. Most often latices of polystyrene are used but other polymers, such as PMMA, have been used as well. The latices are synthesized without any surfactant and the colloidal stability is achieved by the presence of charged initiator residues located at the surface of the particles. In Chapter 18 a presentation of the stabilization mechanisms is given. The charges give sufficient colloidal stability provided that the solids content is kept low, preferably in the range 5–10%. Under certain conditions, monodisperse latices are obtained. The size of such latex particles is normally in the range 0.1–0.4 µm, giving a specific surface area of 15–60 m²/g. The monodispersity and the large specific surface area make these latex dispersions ideal for adsorption studies.

Particles of amorphous silica are also very common in model studies of adsorption. The silanol groups on the silica surface are easily deprotonated leaving a negative surface charge at pH ≥ 2. The silica surface is easily chemically modified. The particles can be synthesized to give a fairly monodisperse size distribution.

For dispersed systems, the method of determining surfactant adsorption is almost exclusively by adding surfactant, leaving time for the system to come to equilibrium, separating the solids and, finally, determining the residual surfactant concentration in the solution. The concentration depletion gives the adsorption, Γ (mg/m²), from:

$$\Gamma = \frac{(C_o - C)V}{ma_{sp}} \quad (8.12)$$

C and C_o are the surfactant equilibrium concentration (mg/ml) and the concentration before adsorption, respectively. V is the solution volume (ml), m is the particle amount (g) and a_{sp} is the particle specific surface area (m²/g). The concentration determination can be accomplished by, for example, ion-selective electrodes, UV/vis spectroscopy, refractive index, titration, chromatography, or surface tension measurements. In fact, if the latter is used the solids need not be separated, as the particles do not contribute to the surface tension provided they are completely wetted by the liquid. Hence, the dispersed system can be

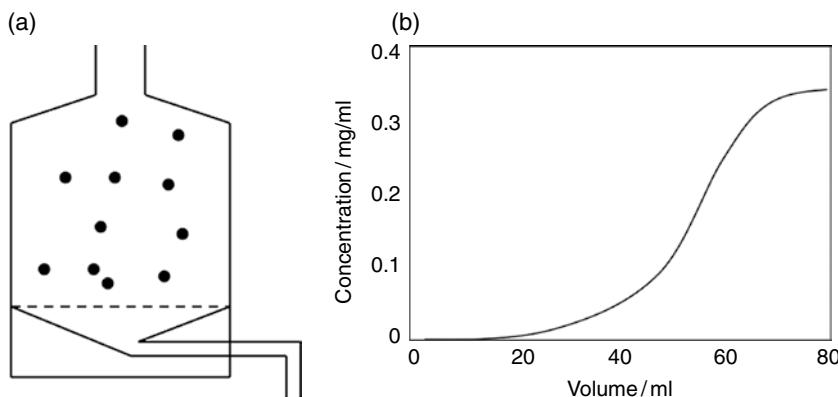


Figure 8.17 (a) Schematic of the use of the serum replacement cell for determination of the surfactant adsorption isotherm on suspended particles and (b) the concentration of the surfactant solution in the effluent stream versus the elution volume from the serum replacement cell. (With permission from Steinby, K., Silveston, R. and Kronberg, B. (1993) The effect of temperature on the adsorption of a nonionic surfactant on a PMMA latex. Journal of Colloid and Interface Science, **155**, 70–78. Copyright Elsevier.)

titrated with the surfactant to be investigated. This method is termed soap titration. The accuracy in adsorption isotherm determination depends on the method of surfactant analysis. Low accuracy is, for example, obtained using ion-selective electrodes, since the determined potential is proportional to the logarithm of the surfactant concentration, that is, small changes in the potential correspond to large changes in the surfactant concentration.

Some systems are suitable for the serum replacement technique. Here, the dispersion is confined in a flow cell with stirring. The confinement is achieved by a filter. The surfactant solution is allowed to flow slowly through the cell and its concentration is determined at the outlet. A schematic of such a cell is shown in Figure 8.17a. Figure 8.17b shows a surfactant concentration profile. Important parameters for such a set-up are the flow-through speed and the stirring rate (too high a stirring rate might cause coagulation, while too low a stirring rate will cause the filter to clog). The residence time of a surfactant in the cell should be of the order of at least one hour in order to ensure that equilibrium is attained. The adsorption isotherm is calculated from a mass balance from knowledge of what has entered and exited the cell.

Measuring the electrophoretic mobility of particles in the presence of surfactant is also a method to detect adsorption, although the adsorbed amount cannot be obtained other than through indirect calculations. This method is further discussed in Chapter 18.

Macroscopic Surfaces

A great advantage of measuring at macroscopic surfaces is that detection can be performed *in situ*, that is, when the surface is in contact with the solution, allowing the adsorption/desorption kinetics to be determined. A disadvantage is that the surface-to-volume ratio is very low. This implies that even minute amounts of surface active impurities may dominate the adsorption measurement.

Ellipsometry has proven to be a very powerful method to determine the adsorption of surfactants from solution on macroscopic surfaces. In brief, elliptically polarized light is reflected on a surface and the change in polarization is measured. This change is dependent on the presence of adsorbed molecules at the surface and, hence, the presence of these is detected and quantified. The detection limit is about 0.1 mg/m^2 , which implies that adsorption well below monolayer coverage can be detected. The method also allows the determination of the adsorbed layer thickness, as well as the refractive index of the adsorbed layer. The typical model surface for ellipsometry studies is silica. Mica cannot be used since it is birefringent. A drawback of the method is that the solution needs to be transparent.

Another method is the *Dual Polarization Interferometry* (DPI). Here, a light beam, which travels within the solid and is bounced at the boundaries, determines the refractive index of the adsorbed layer. Changes in the refractive index, before and after adsorption, alter the speed of propagation within the solid. High sensitivity is achieved through directly measuring the signal from an identical set-up, but without surfactant, giving an interference pattern from the two. A drawback of the method is that the solution needs to be transparent.

An alternative method, where turbid samples can be used, is the *Quartz Crystal Microbalance with Dissipation* (QCM-D). By measuring the resonance frequency of a quartz crystal, information of its mass is obtained (higher mass renders lower resonance frequency). Hence, measurements in solutions with and without surfactant will reveal the amount of surfactant adsorbed at the crystal surface. As the driving voltage of the crystal shuts off, the energy of the crystal dissipates into the solution. Depending on the rigidity of the adsorbed layer, the energy will dissipate slowly (rigid layer) or rapidly (soft layer).

We have already seen in this chapter the power of AFM where images of the surfactant aggregates on a surface can be obtained. Here a tip scans the surface and its deflection from the surface is recorded. The resolution depends on the sharpness of the tip, as well as on a high force gradient normal to the surface. This method is under rapid development.

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9

Polymers in Solution

A polymer is a large molecule, a macromolecule, built up of smaller chemical units, monomers. A natural division of the science of polymers is into biological and nonbiological macromolecules. Biological macromolecules are, for example, proteins, nucleic acids, and polysaccharides while nonbiological macromolecules include the common plastics and adhesives. This chapter deals mainly with water-soluble polymers.

Polymer Properties are Governed by the Choice of Monomers

Synthetic polymers are synthesized by the polymerization of monomers. The monomers in the polymerization constitute the repeat units, for example, acrylic acid is polymerized into poly(acrylic acid). A polymer can either be linear, branched, or cross-linked, as depicted in Figure 9.1a. It is important to characterize the category a certain polymer belongs to in order to understand its solution behavior, since it differs considerably between the three categories. When only one type of monomer is used the polymer is termed homopolymer. If the polymer is synthesized with more than one kind of monomer, it is termed a copolymer. The monomer units in a copolymer can be (i) randomly distributed, (ii) distributed in blocks, or (iii) distributed such that one of the monomers is grafted in chains onto the backbone of the other monomer chain (Figure 9.1b). Also, the solution properties and the surface chemical properties are very sensitive to which category a copolymer belongs. Some of the structures shown in Figure 9.1b are strikingly surface active. Surface active polymers are dealt with specifically in Chapter 10.

The polarity of the monomer units forms a convenient basis to categorize nonbiological polymers: (i) nonpolar polymers, such as polystyrene and polyethylene; (ii) polar, but water-insoluble, polymers, such as poly(methyl methacrylate) and poly(vinyl acetate);

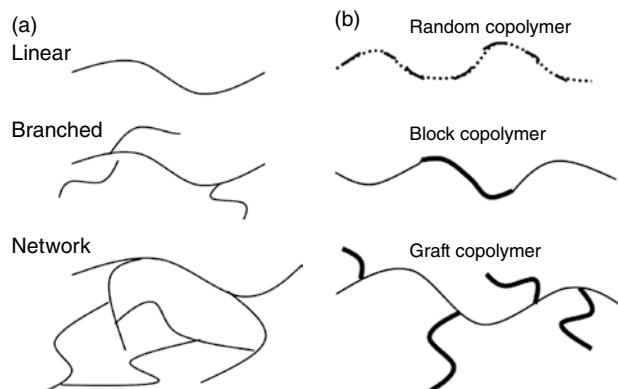


Figure 9.1 Polymers are differentiated with respect to their (a) structure or (b) chemical composition

(iii) water-soluble uncharged polymers, such as polyoxyethylene (POE) and poly(vinyl alcohol) (PVA); and (iv) ionizable polymers, or polyelectrolytes, such as poly(acrylic acid) and sodium poly(acrylate).

Molecular Weight is an Important Parameter

With the exception of proteins it is impossible to find a polymer batch where all macromolecules have exactly the same molecular weight. Synthetic polymers, as well as polysaccharides, have a molecular weight distribution that differs depending on the method of synthesis and on the fractionation procedure. A schematic of a molecular weight distribution is shown in Figure 9.2. It is important to realize that some physical properties are sensitive mainly to the low molecular weight fraction while others are more sensitive to the high molecular weight species. A molecular weight distribution such as that shown in Figure 9.2 is conveniently determined by size exclusion chromatography. Another way to obtain a measure of the polydispersity in molecular weight is to determine the average molecular weight by two methods that give different averages. Conceptually, the number average molecular weight (M_n) is the simplest and is defined as:

$$M_n = \frac{\sum N_i M_i}{\sum N_i} \quad (9.1)$$

where N_i is the number of molecules with molecular weight M_i . M_n may be determined by freezing point depression, osmosis, or chemical analysis of end groups.

Another molecular weight average is the weight average molecular weight (M_w), where the weight (w) is the weighting factor for each molecular weight species, and is thus defined as:

$$M_w = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum N_i M_i^2}{\sum N_i M_i} \quad (9.2)$$

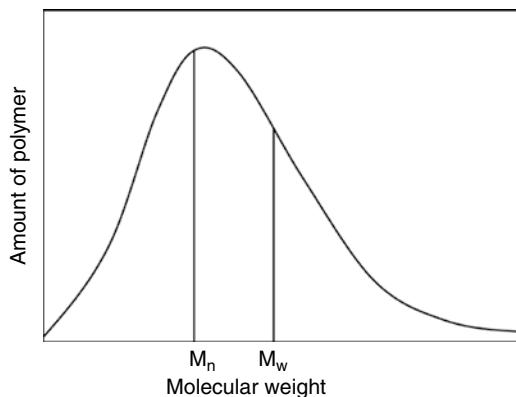


Figure 9.2 Molecular weight distribution of a polymer

M_w can be determined by light scattering, either quasi-elastic or classic. This molecular weight value is sensitive to high molecular weight species and is, hence, always larger than M_n . An illustrative example is the following calculation. If we have 100 molecules with a molecular weight of 100 and 1 molecule with a molecular weight of 10 000, the M_n is about 200 and the M_w is about 5000. In light scattering experiments, it is, therefore, very important to control the conditions such that no high molecular weight contamination (dust for example) affects the results. The ratio of the weight average to the number average molecular weight is a measure of the polydispersity of a sample. A sample is considered to be monodisperse if this ratio is less than 1.1.

A convenient way to characterize a polymer in solution at low concentrations is to measure the viscosity. This can be achieved by measuring the efflux time (t) of a polymer solution for the flow through a capillary in an Ubbelohde viscometer and comparing with the corresponding time for the solvent (t_0). The viscosity is then proportional to the efflux time multiplied by the density of the liquid. Since dilute solutions can be approximated to have the same density as the pure solvent, we then have the relative viscosity as $\eta_{\text{rel}} = \eta/\eta_0 = t/t_0$. Table 19.3 gives the common nomenclature used in dilute solution viscosity. The specific viscosity is a measure of the thickening effect of the polymer solution as compared to the solvent. This quantity is naturally very dependent on the polymer concentration, hence the reduced viscosity is a property that tells us more about the specifics of a polymer system. If the reduced viscosity, or the inherent viscosity, is plotted versus the polymer concentration a straight line is normally obtained. The extrapolation of this line to zero polymer concentration gives us the intrinsic viscosity $[\eta]$, which is also called the limiting viscosity number. The intrinsic viscosity is independent of polymer concentration but dependent on the solvent that is chosen. It is also dependent on the polymer molecular weight and can be used to obtain a viscosity average molecular weight (M_v) from the Mark–Houwink equation:

$$[\eta] = K M_\eta^\alpha \quad (9.3)$$

K and α are constants that conveniently can be found for common polymer/solvent combinations in the literature, for example, the *Polymer Handbook* by Brandrup and Immergut

(see the Bibliography at the end of this chapter). The viscosity average molecular weight is an intermediate between the number average and the weight average molecular weights.

Dissolving a Polymer can be a Problem

Dissolution of a polymer can sometimes be a problem, not only in the laboratory but also on an industrial scale. The dissolution process starts with the solvent, which is more mobile than the polymer chains, penetrating into, and hence swelling, the polymer. The polymer then becomes highly viscous and sticky with the result that the material will be found somewhere on the container walls. The next step in the dissolution process is that the polymer chains disentangle from the gel and diffuse into the solvent. This is a slow process since the polymer chain dynamics, which is dependent on the polymer molecular weight, is rate determining. Furthermore, a polymer that is swollen by a solvent and sticking to the container walls is hard to detect. This is because the polymer gel has almost the same refractive index as the solvent. One can, therefore, make the hasty and false conclusion that the entire polymer has dissolved. The polymer sticking to the container walls will have a rather small exposure area to the solvent, hence the dissolution will indeed be time consuming. Dissolving poly(vinyl pyridine) into water at neutral pH, for example, takes at least 24 hours.

There are, however, some tricks that are handy. Technically, the problem of dissolving a polymer can be circumvented by handling polymers that are already dissolved at some high concentration in a solvent. Another way is used when the pure polymer is in the form of a powder. Let us take the poly(vinyl pyridine) example as an illustration. At high pH the polymer is not soluble in water and, therefore, the polymer powder can easily be dispersed into water at high pH values and high stirring rates. The pH is then quickly lowered to about 3–4 under vigorous stirring. The polymer particles will then not agglomerate but rather start to dissolve. Now the dissolution process will be orders of magnitude faster (about 30 min for the system above) since the total area of the polymer particles is much larger than that of a polymer adhering to the container walls.

The Solubility Parameter is Used to Find the Right Solvent

In the search for a solvent for a certain polymer the solubility parameter concept can be conveniently used. The solubility parameter is based on the assumption that “like dissolves like.” A polymer is not soluble in certain liquids due to a large difference in the interaction energy between segments of the polymer and solvent molecules when compared to the interaction energy between segment–segment and solvent–solvent molecules. Thus, in order to achieve some solubility the segment–solvent interaction energy should be as close as possible to the interaction energy between the segments and between the solvent molecules. The enthalpy of vaporization, which is a reflection of the cohesive forces in the liquid, is used as a measure of these molecular interaction energies of the solvent. However, since the enthalpy of vaporization (ΔH_{vap}) depends on the molar volume (V) it should be normalized, thus giving the cohesive energy density as:

$$\delta^2 = \frac{\Delta H_{\text{vap}}}{V} \quad (9.4)$$

where δ is called the solubility parameter. The units for the solubility parameter are $\text{cal}^{1/2} \text{cm}^{-3/2} \text{mol}^{-1}$, or in SI units, $\text{J}^{1/2} \text{cm}^{-3/2} \text{mol}^{-1}$ ($=\text{MPa}^{1/2}$). These parameters can be found from tables for solvents as well as those for polymers, for example, the *Polymer Handbook* (Brandrup and Immergut) or the *Handbook of Solubility Parameters and Other Cohesion Parameters* (Barton) (see the Bibliography at the end of this chapter). In order to find a suitable solvent for a polymer it is first necessary to find the solubility parameter for the polymer and then select solvents that have solubility parameters which are close to that of the polymer. Polystyrene, for example, has a solubility parameter of $9.1 \text{ cal}^{1/2} \text{cm}^{-3/2} \text{mol}^{-1}$ and suitable solvents are cyclohexane ($\delta = 8.2$), benzene ($\delta = 9.2$), and methyl ethyl ketone ($\delta = 9.3$), while n-hexane ($\delta = 7.3$) and ethanol ($\delta = 12.7$) are nonsolvents, that is, they do not dissolve the polymer.

In a more elaborate analysis, the solubility parameter is split up into contributions originating from dispersion forces, polar forces, and hydrogen bonding. Hence, the total solubility parameter can be written as:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (9.5)$$

where the subscripts d, p, and h represent the dispersion, polar, and hydrogen bonding contributions to the total solubility parameter. Another approach is to split the solubility parameter into van der Waals and acid-base contributions.

Polyelectrolytes are Polymers with Charges

Polyelectrolytes in solution have many applications and are used technically as thickeners, dispersants, flocculation aids, and so on. The word polyelectrolyte is sometimes used for all types of aggregates that carry a high net charge. Some of the literature reserves it for charged polymers and it is the latter type we will consider now. A polymer often obtains a net charge from carboxylate or sulfate groups ($-\text{COO}^-$, $-\text{OSO}_3^-$) or from ammonium groups ($-\text{NH}_3^+$). Polyelectrolytes can be classified as strong or weak; the net charge of the latter varies with pH. Thus, a carboxylate-based polymer is a weak polyelectrolyte whereas a sulfate-based polymer is a strong polyelectrolyte.

Compared to dissolving two liquids with similar molecular sizes there is a very small entropy effect associated with the dissolution of a nonionic polymer in water (see further below) leading to poor solubility. Polyelectrolytes, however, are very soluble in water, which is due to the counterions contributing to the entropy of solution. The resulting effect is that the solubility of polyelectrolytes is much larger than that of nonionic polymers of related structure and similar molecular weight. Polystyrene sulfonate, for example, is water-soluble whereas polystyrene is insoluble in water. Note, however, that the counterions are partially associated with the polyelectrolyte and, hence, have lower entropy compared to, for example, a dissolved salt. This effect was noted in the discussion of ionic surfactant micellization and is termed *counterion condensation* (Chapter 3). Hence, the entropy of solution is lower than in dissolving a salt.

Adding salt to a polyelectrolyte solution lowers the entropy gain from the counterions, making the polymer more vulnerable to phase separation. This is termed *salting out* of the

polyelectrolyte. Only if the polyelectrolyte is highly polar will it be soluble in the presence of appreciable amounts of electrolyte.

If a polyelectrolyte carries only one type of ionizable monomer unit, for example, acrylic acid, the degree of ionization (α) is defined as the fraction of ionizable groups that are ionized. This property is dependent on the pH and the relationship can be written as:

$$\text{pH} = \text{pK}_{\text{app}} + \log \frac{\alpha}{1-\alpha} \quad (9.6)$$

where pK_{app} is the apparent acidity (or basicity) constant of the monomer unit. This “constant” is not a constant in a strict sense, since it depends on the degree of ionization. This is accounted for in more elaborate descriptions of polyelectrolyte behavior in aqueous solution of which the simplest is:

$$\text{pK}_{\text{app}} = \text{pK}_o + \alpha\psi(\alpha) \quad (9.7)$$

Here $\psi(\alpha)$ is the difference in electrostatic potential between an ion associated with the polymer and an ion at infinite distance from the polymer and pK_o is the pK of the neutral polymer, that is, when $\alpha=0$. Figure 9.3 shows that the pK_o for chitosan is 9.0 whereas the pK_{app} at half neutralization is 6.5.

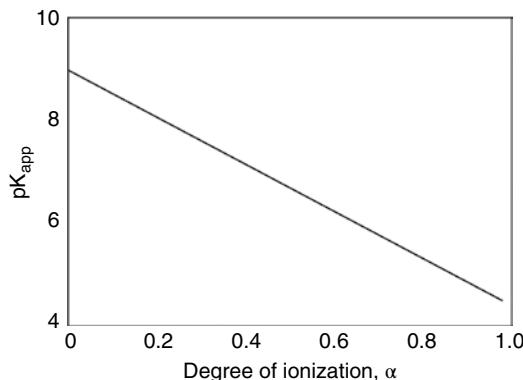


Figure 9.3 Katchalsky plot, that is, pK_{app} versus the degree of ionization (α) for chitosan showing that pK_{app} decreases linearly with α . (With permission from Anthosen, M.W. and Smidsrød, O. (1985) Hydrogen ion titration of chitosans with varying degrees of N-acetylation by monitoring induced H-NMR chemical shifts. Carbohydrate Polymers, **26**, 303–305. Copyright Elsevier.)

Polymer Size and Shape are Important Characteristics

A polymer in aqueous solution can take various forms. The globule is the most compact form and is a common form for proteins, for example. The driving force of forming a globule is normally hydrophobic interaction of constituents of the polymer. Another form is the random coil, where all the polymer segments have contact with the water molecules

to some degree. The random coil can be compact or expanded, depending on the interaction strength with the water. A third shape is the rod, which could be a helix formed from the polymer. Proteins and polysaccharides commonly form helices; some synthetic polymers, such as poly(methacrylic acid) (PMAA), also occur in this form. A polymer dimension is normally characterized by the radius of gyration (R_G). For compact globules the R_G is proportional to $M^{1/3}$, for random coils it is proportional to $M^{0.5-0.6}$ whereas for rods it is proportional to M .

The theta (Θ) temperature is one particularly important parameter that describes a polymer–solvent system. At this temperature a polymer segment has the same interaction with a water molecule as with another polymer segment. Hence, from a contact energy point of view, a polymer segment is not able to tell whether it is in contact with another segment or a solvent molecule. The polymer will have the same conformation as it would have in its own liquid. The polymer is said to be in its *unperturbed dimension*.

The solvent quality normally increases as the temperature is raised (due to the higher thermal energy), hence each polymer segment will have a tendency to prefer to be in contact with the water molecules rather than in contact with the polymer's own segments. Thus, the polymer molecule will expand its conformation as the temperature is increased. On the other hand, at temperatures below the theta temperature the polymer segments will prefer to be in contact with other polymer segments rather than with the solvent molecules. Therefore, the polymer will contract. The theta temperature is also called the Flory temperature and the solvent, or solvent mixture, used at this temperature is called a theta solvent. Some polymers, such as oxyethylene containing polymers in water, have a reverse behavior in that the solvent quality decreases as the temperature is raised. This is discussed in Chapter 7.

The degree of expansion (α) of a polymer coil is related to the radius of gyration at the theta temperature (R_G^Θ) through:

$$\alpha = \frac{R_G}{R_G^\Theta} \quad (9.8)$$

Hence, in normal cases, when the solubility increases with temperature, $\alpha < 1$ below (and $\alpha > 1$ above) the theta temperature. As shown in Chapter 7, the opposite occurs for poly-oxyethylene containing polymers, i.e. the solubility decreases with temperature and hence then $\alpha < 1$ above (and $\alpha > 1$ below) the theta temperature.

Compared to polyelectrolytes, nonionic polymers are less sensitive to electrolyte addition. For nonionic polymers the effect of salts normally follows the Hofmeister series (page 25), where *salting-out* ions decrease the solubility and, hence, decrease the polymer molecule extension, that is, the R_G decreases. *Salting-in* ions have a tendency to associate with the polymer, rendering it a polyelectrolyte character. Hence, these ions increase the solubility and also increase the expansion of the polymer coil in solution, namely R_G increases.

The degree of expansion of a polyelectrolyte increases with the degree of ionization. The conventional view of the expansion of a polyelectrolyte is that the polymer expands upon increasing the degree of ionization due to the repulsion between the ionized groups. A more correct view, however, is in terms of the entropy of the counterions and the effect of the charge density of the polymer. This is illustrated in Figure 3.2, where the charge

density at the surface is replaced with the charge density of the polymer. Hence, if the polymer at a certain degree of ionization expands (going to the left in the diagram) we have a lower degree of counterion binding and, thus, a higher entropy. This expansion is counteracted by a lowering in entropy of the polymer itself (due to a lower number of available conformations) and a balance between the two contributions is obtained. This is the reason why a polyelectrolyte does not become a stiff rod on increasing the degree of ionization. This is illustrated in Figure 9.4 showing the radius of gyration of a polyelectrolyte, PMAA, as a function of the degree of ionization. This figure shows that, to a first approximation, the expansion, as revealed by the radius of gyration, reaches a limiting value at a degree of ionization of about 0.3. Thus, if elongated polyelectrolyte molecules (“polyions”) are required there is no point in charging the polyelectrolyte beyond this value, as the dimensions will not change much once about 30% of the ionizable groups have become charged. This corresponds to only about half a unit from the pK_a value of the polymer.

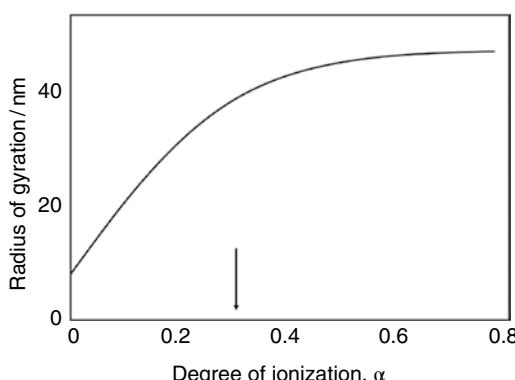


Figure 9.4 The radius of gyration of poly(methacrylic acid) (PMAA) as a function of the degree of ionization

There are Various Classes of Water-Soluble Polymers

Some examples of water-soluble polymers, together with their properties and uses, are given here. We consider first nonionic water-soluble polymers with an oxygen or nitrogen in the backbone of the polymer. Of the polyoxyalkylenes only POE is water-soluble. Polyoxymethylene is not water soluble despite the fact that it contains a higher portion of oxygen than POE. The reason for the aqueous solubility of POE is discussed in Chapter 7. These polymers can be synthesized with molecular weights up to the millions. POEs are used in various applications, such as cosmetic and pharmaceutical formulations, ceramic binders, and so on. Polyoxypolypropylene (POP) is insoluble in water; only quite short oligomers are soluble in water. Longer polymer sequences serve as efficient hydrophobic segments in surface active block copolymers. If one changes the oxygen atom in POE for nitrogen, we then obtain poly(ethylene imine) (PEI). Commercial samples of PEI are

normally branched and the ratio between the secondary, tertiary, and quaternary amino groups is typically 1:2:1.

Secondly, there are synthetic nonionic polymers. The first example is PVA, which is obtained by a base-induced hydrolysis of poly(vinyl acetate). Polymers with a degree of hydrolysis over about 86% are soluble in water. If the degree of hydrolysis is higher than 90%, the system needs to be heated in order to fully go into solution. Once dissolved in hot water, the polymer remains in solution even when cooled. This apparent irreversibility is due to the formation of internal hydrogen bonds in the solid polymer rendering a higher packing density in the solid state. Another example is poly(vinyl pyrrolidone) (PVP), which is highly soluble in water. This polymer has a weak basic character and associates with anionic surfactants, such as sodium dodecyl sulfate (SDS), in aqueous solution. Aqueous solutions of PVP are used in pharmaceuticals, cosmetics, and medicine due to the low toxicity and high water solubility of the polymer. PVP is also used in detergent formulations, where its role is to prevent re-deposition of soil on fibers. Another example is polyacrylamide (PAAm). This is a very hydrophilic polymer and it is fairly insensitive to the addition of salts. This polymer is used as a flocculent because it has a high affinity to surfaces due to its cationic nature at low pH values.

Thirdly, we have synthetic polyelectrolytes. The first examples are poly(acrylic acid) (PAA) and PMAA. These polymers, or their sodium salts, are used in the cross-linked form in disposable diapers due to their high swelling capacity. They are also used as thickeners and dispersing agents. Polystyrene sulfonate is derived from sulfonation of polystyrene. It is a polyelectrolyte that is charged over a wide pH range. Industrially important cationic polyelectrolytes are polyacrylamide (PAAm) and poly(ethylene imine), whereas polyMAPTAC (poly(3-(2-methylpropionamide)propyl)-trimethylammonium chloride) is popular as model polymer.

In the fourth and final group, the polymers have a natural origin, such as polysaccharides or proteins. Many polysaccharides are used in the food industry as gelants. Examples are gum arabic, guar gum, agar, carrageenan, and dextran. Inulin is a polysaccharide that is increasingly used in processed foods, in particular as a protective colloid for stabilizing emulsions. Finally, chitosan is a glucosamine derived from deacetylation of chitin. It has a pK_a of 6.5 and is, therefore, cationic at low pH values (Figure 9.3).

Many water-soluble polymers are derived from cellulose. Cellulose can be made water-soluble by chemical derivatization. Most commonly, the three hydroxyl groups on the β -anhydroglucoside unit, which constitutes the cellulose building block, are used as starting points in the derivatization. The extent of the reaction of these cellulose hydroxyls is called the degree of substitution (DS) and is defined as the average number of hydroxyls that have reacted; the DS is thus a number between 0 and 3.

Carboxymethylcellulose (CMC) is manufactured by reacting cellulose with sodium monochloroacetate, giving a sodium salt of the carboxylic acid with a DS varying between 0.4 and 1.4. CMC is normally sold in the salt form. The pK_a of the polymer is normally around 4.4, and depends slightly on the DS. Thus, at neutral pH values most of the carboxyl groups are in the dissociated form and, therefore, it displays almost no surface activity (Figure 12.12). An important use of CMC is in detergents, where the role is to prevent soil re-deposition after such soil has been removed from the fabrics (anti-redeposition agent). CMC is also used as a dispersant in waterborne paints and paper coatings. CMC, as well as

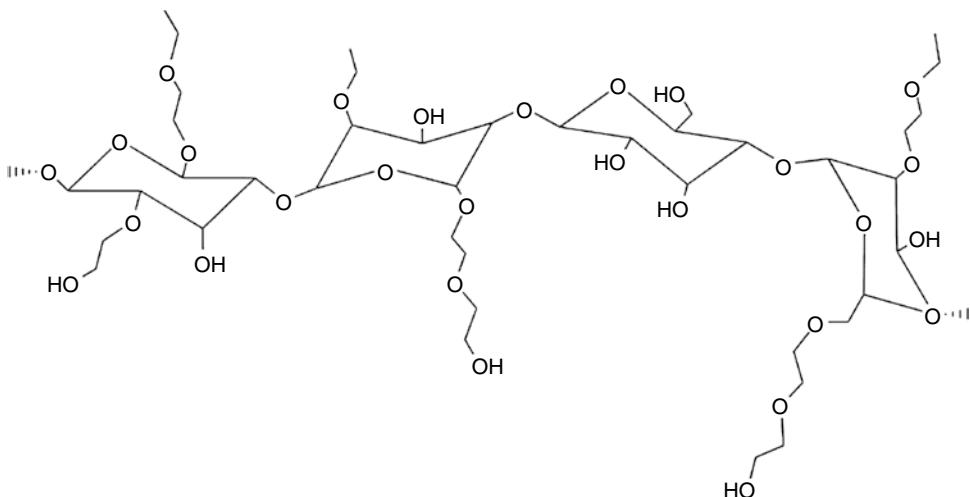


Figure 9.5 Cellulose can be modified by a relative random substitution of hydroxyethyl and ethyl groups to give ethylhydroxyethylcellulose (EHEC)

nonionic cellulose derivatives, are also used in pharmaceutical formulations as constituents in tablets.

Hydroxyethylcellulose (HEC) is manufactured by reaction of alkali-swollen cellulose with ethylene oxide. The product is a versatile water-soluble polymer that is used in numerous applications as thickener, protective colloid, binder, and so on. The molar substitution (MS) is the molar ratio of ethylene oxide to cellulose hydroxyl groups. The aqueous solution properties depend both on the DS and the MS in that a minimum in both DS (about 0.65) and MS (about 1.0) is required for water solubility. In aqueous solutions the polymer phase separates on heating.

Ethylhydroxyethylcellulose (EHEC) is produced by first reacting cellulose with ethylene oxide and then adding ethyl chloride. The polymer structure is shown in Figure 9.5 and the solution properties of this polymer are described in Chapter 7.

Methylcellulose (MC) is produced by treating alkali-swollen cellulose with methyl chloride. The DS is typically 1.3–2.6 and the polymer is soluble in cold water. It has a cloud point on heating of 40–50 °C, depending on the DS. Commercial MC is known for its uneven distribution of methyl groups, which creates soluble and insoluble blocks, which means that it can be considered as a block copolymer and not a random copolymer. MC is often used in toothpaste, hair shampoos, and foodstuff, for example, in ice cream.

Cellulose itself is the most abundant organic polymer on earth and is mainly used to produce paper and paperboard. Cellulose is insoluble in water, which has been considered to be a result of internal hydrogen bonding in the molecule. This idea has been challenged, since water itself is a solvent with high hydrogen bonding capacity; thus, the insolubility in water must be due to hydrophobic interactions and, therefore, cellulose is amphiphilic. Furthermore, the insolubility of cellulose is affected by efficient packing in the solid state. Perturbing this packing by derivatization leads to a higher solubility; a striking example is MC, which is highly soluble even if it is less polar than cellulose.

Polymers are Used as Thickeners

Polymers are frequently used as thickeners in technical applications. One thickening mechanism is the entangling of polymer coils as the polymer concentration is increased. This causes the viscosity to dramatically increase with polymer concentration (Figure 9.6). This effect increases with the molecular weight of the polymer. The polymer concentration at which the viscosity starts to increase rapidly is denoted C^* , the *overlap concentration*.

Thickening can also be achieved by increasing the solubility in water, by, for example, a change in temperature. The thickening effect is especially sensitive to temperature changes around the theta temperature. This is exemplified by the polymer poly(N-isopropyl-acrylamide) (poly(NIPAM)), which goes from poor solubility and low viscosity at high temperatures to good solubility and high viscosity at low temperatures, the theta temperature being about 33 °C.

Polyelectrolytes are more efficient as thickeners than nonionic polymers since they are more extended (see above) and there is, thus, more polymer–polymer entanglement; because of the extension they are characterized by a low C^* . The effect is, however, decreased considerably in the presence of added electrolyte, because of contraction of the polymer chains.

Another class of polymers used as thickeners is the associative thickeners. These polymers have a small fraction of hydrophobic chains attached to a hydrophilic backbone and these chains associate in solution, forming a physical network (Figures 10.2, 10.3 and 10.4). The formation of a network can be strengthened by the presence of surfactant. Interactions of surfactants with such hydrophobically modified water-soluble polymers are described in detail in Chapter 14.

Thickening can also be achieved by linking polymer backbones together with multivalent ions, such as Ca^{2+} . This is especially common with polysaccharides (Figure 9.7a), for example, in the formation of calcium alginate, which forms a gel. Polysaccharides also exhibit a thickening effect from helix formation. A polysaccharide can form helices in parts of the molecules and these helices may associate with helices from other molecules, thus forming a network (Figure 9.7b).

Bonding polymers together into a network can also be achieved by nanoparticles, such as silica. Here, each polymer adsorbs at the surface of more than one particle and the particles function as nodes in the network.

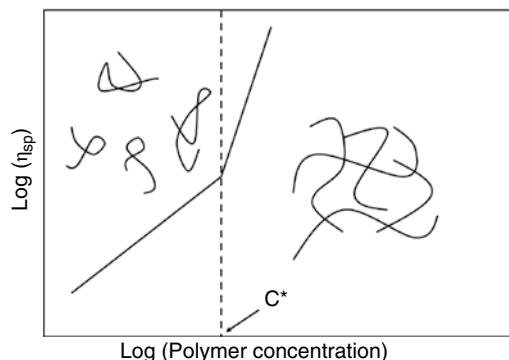


Figure 9.6 Polymer coils start to entangle at higher polymer concentrations, resulting in thickening of the solution

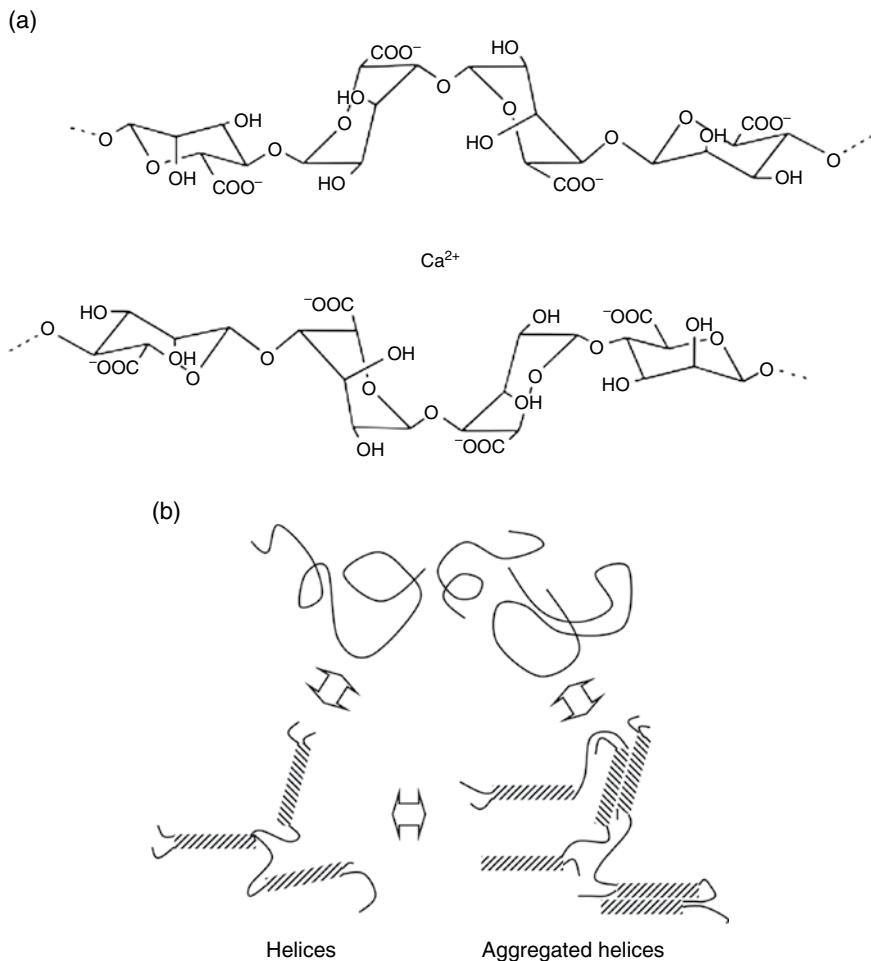


Figure 9.7 Adding Ca^{2+} to a solution of a polysaccharide increases the viscosity. The mechanism is either (a) through bridging by the Ca^{2+} ions or (b) by inducing helix formation

Polymers in Solution Differ from Ordinary Mixtures

There is a fundamental difference between polymers in solution and ordinary binary mixtures. This difference stems from the size difference between a polymer molecule and a solvent molecule, such as water. When mixing two liquids, the molecules can freely move around, hence the entropy is large. In a polymer solution, however, the polymer segments are tied to each other. Hence, in comparing a single polymer segment with a free solvent molecule, the entropy is considerably less for the polymer segment. Polymer solutions, therefore, have lower total entropy and are less stable with respect to phase separation when compared to mixtures of ordinary liquids. Flory and Huggins first quantified this in the late 1940s in what has later became known as the Flory–Huggins

theory for polymer solutions. The free energy of mixing a polymer with a solvent (ΔG_M) is given by:

$$\frac{\Delta G_M}{RT(r_1n_1 + r_2n_2)} = \left\{ \frac{\varphi_1}{r_1} \ln \varphi_1 + \frac{\varphi_2}{r_2} \ln \varphi_2 \right\} + \varphi_1 \varphi_2 \chi \quad (9.9)$$

Here the term in the brackets on the right-hand side represents the entropy of mixing and the second term the enthalpy of mixing. The equation is general and also holds for the mixing of two polymers, each with a degree of polymerization of r_1 and r_2 . For a polymer–solvent system we have $r_1=1$ and $r_2=r=V_2/V_1$, where the V_i 's are the molar volumes of the polymer or solvent. The polymer concentration is given in terms of the polymer volume fraction, $\varphi_2(=1-\varphi_1)$, and χ is the polymer–solvent interaction parameter. It is defined as:

$$\chi = \frac{z\Delta w}{kT} \quad (9.10)$$

where z is the number of nearest neighbors of a polymer segment and Δw is the energy exchange when changing solvent–solvent and polymer segment–polymer segment interactions for solvent–polymer segment interaction. Since this contribution is temperature independent we realize that the χ parameter decreases with temperature, thus giving a better solubility as the temperature is raised. The parameter is related to the enthalpy of mixing according to:

$$\frac{\Delta H_M}{(r_1n_1 + r_2n_2)} = z\Delta w \varphi_1 \varphi_2 = kT \chi \varphi_1 \varphi_2 \quad (9.11)$$

The terms within the bracket in Equation 9.9 represent the negative of the entropy of mixing according to:

$$\frac{\Delta S_M}{R(r_1n_1 + r_2n_2)} = \left\{ \frac{\varphi_1}{r_1} \ln \varphi_1 + \frac{\varphi_2}{r_2} \ln \varphi_2 \right\} \quad (9.12)$$

The question of whether or not a polymer will dissolve in a solvent is a matter of a balance between the two terms on the right-hand side of Equation 9.9. The first term, originating from the entropy of mixing, is always negative and acts in favor of mixing and the second term, representing the enthalpy of mixing, mostly disfavors mixing (Figure 9.8b).

Figure 9.8a shows the entropy of mixing of a solute and a solvent that have the same size ($r_1=r_2=r=1$) as well as for a polymer solution where the size differs by a factor of $r=100$. The figure also shows the entropy of mixing of two polymers, each with $r_1=r_2=100$, which is discussed later in this chapter. The figure shows that the entropy of mixing is less positive for the polymer solution than for ordinary mixtures where $r_1=r_2=1$. This poor entropy contribution often leads to a phase separation where a concentrated polymer solution is in equilibrium with a dilute solution (Figure 9.8b). The phase behavior of polymer–solvent systems can be modeled by Equation 9.9. We note from Figure 9.8a, in comparing the

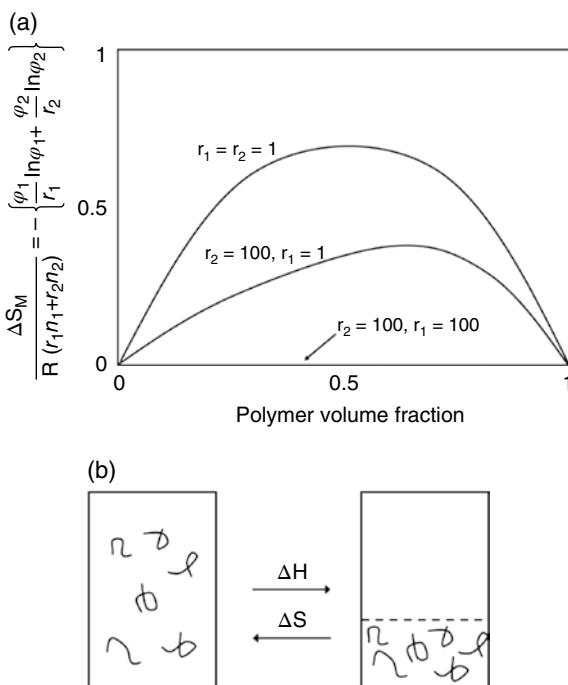


Figure 9.8 (a) The entropy of mixing of a polymer/polymer ($r_1 = r_2 = 100$) polymer/solvent system ($r_2 = 100, r_1 = 1$) and an ordinary solution ($r_1 = r_2 = 1$) as calculated from Equation 9.9. (b) An illustration of the two driving forces for mixing/demixing of polymer solutions

curve where $r_1=r_2=1$ with the curve where $r_1=1$ and $r_2=100$, that the entropy of mixing for a polymer solution is reduced in going from a monomer to a polymer, especially at low polymer concentrations. Hence, the system is most susceptible to phase separation at low polymer concentration, as will be seen next.

The enthalpy of mixing is a measure of the interaction energy between a polymer segment and a solvent molecule when compared to the interaction energy among segments and solvent molecules alone. The enthalpy of mixing is normally positive, hence opposing the mixing of the two components (Figure 9.8b). As the temperature increases this contribution becomes less important in ordinary liquids (Equation 9.10) and, hence, the propensity to phase separate decreases with temperature. At sufficiently high temperatures a homogeneous solution is obtained (Figure 9.9).

Figure 5.2 shows two schematic phase diagrams of polymer–solvent systems where the polymer phase separates on cooling or heating. Here, a polymer solution separates into a concentrated and a dilute solution. Being at a constant temperature and increasing the polymer concentration the system phase separates at the borderline of the two-phase region. This point represents the solubility of the polymer in the water. The second borderline, at higher polymer concentrations, represents solubility of the solvent in the polymer. The highest (Figure 5.2a), or lowest (Figure 5.2b), temperature where a phase separation occurs is called the *critical temperature* and the corresponding polymer

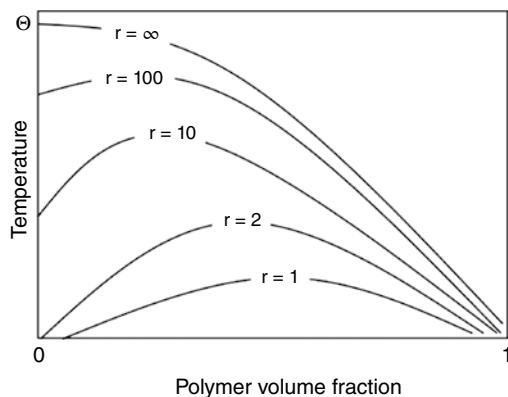


Figure 9.9 Calculated phase diagrams, using Equation 9.9, for the indicated values of r

concentration is called the *critical composition*. This temperature/composition is called the *critical point*. The cloud point is defined as the phase separation temperature at a certain polymer concentration, such as 1 or 0.1%.

From what has been outlined above concerning the entropy of mixing, it is obvious that a solution of a polymer with a high molecular weight is less stable and more prone to phase separation when compared with a solution of the same polymer but of lower molecular weight (Figure 9.9). Hence, for a polydisperse polymer sample that phase separates in solution, the high molecular weight species separate out first, leaving the lower molecular weight species in solution. This phenomenon is used in fractionation of polymer samples with respect to molecular weight. Figure 9.9 shows that, as the molecular weight increases, the critical temperature reaches a limiting value, termed the *theta (Θ) temperature* at zero polymer concentration. This temperature is of fundamental importance not only in terms of the polymer dimensions (Equation 9.8) and polymer–solvent interaction but also for the stability of steric stabilized dispersions, as will be seen next.

There is a Bridge to Colloidal Systems

The critical temperature for a polymer–solvent system asymptotically approaches a certain value as the molecular weight of the polymer is increased (Figure 9.9). The limiting value when the polymer molecular weight is infinitely large is identified as the theta temperature. According to the Flory–Huggins theory the critical temperature is related to the polymer molecular weight as:

$$\frac{1}{T_c} = \frac{1}{\Theta} \left(1 + \frac{C}{\sqrt{M}} \right) \quad (9.13)$$

Here C is a constant. Hence, the theta temperature can be found from a plot where the reciprocal of the critical temperature is plotted as a function of the reciprocal of the square root of the molecular weight (Figure 9.10).

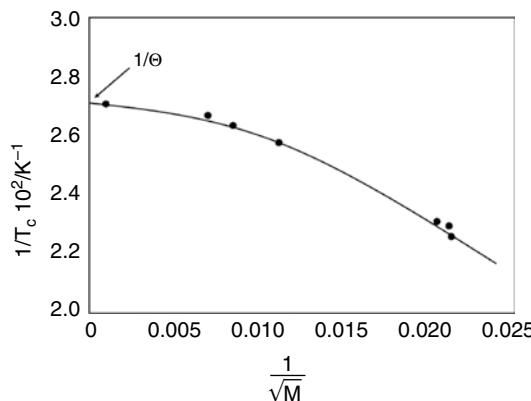


Figure 9.10 Determination of the theta temperature by plotting the reciprocal of the critical temperature versus the reciprocal of the square root of the molecular weight for the system poly(ethylene glycol) in water, with data taken from Figure 7.11

In colloidal chemistry, a particle, or emulsion droplet, can be stabilized against flocculation by adsorption of polymer on the particle surface, as illustrated in Figure 18.5b. If the particle is sufficiently covered with the polymer and if the polymer segments extend into the solution, as is shown in this figure, the particle will behave as if it were a polymer with an infinitely high molecular weight. *Thus, a colloidal system is expected to flocculate at the same conditions as those where a polymer–solvent system reaches the theta condition, that is, when a polymer with infinitely high molecular weight phase separates.* This has been proven true, without any exceptions, for numerous systems. Knowledge of the theta conditions is, therefore, of fundamental importance when designing a dispersed system stabilized with polymers (Chapter 18).

Phase Equilibrium Considerations

Some aqueous systems display the extraordinary behavior in that they phase separate on heating. Polymers containing oxyethylene groups belong to this category and are discussed in detail in Chapter 7. Figure 7.11 shows some phase diagrams of poly(ethylene glycol), with various molecular weights, in water (note that this phase diagram has been determined at elevated pressures in order to reach high temperatures for aqueous systems). It can be seen that at very high temperatures the two-phase region diminishes and, eventually, the system becomes homogeneous again.

Adding a second component, such as salt or a water-soluble solvent, to a polymer–water system sometimes induces phase separation. To a good approximation, the water–second component mixture can be considered as an average liquid giving an average of their interaction energies with the polymer segments. This philosophy is illustrated in Figure 7.17, where the cloud point of EHEC is plotted as a function of the concentration of salt. It is necessary to be aware, however, that such systems are indeed composed of three components, namely polymer, water, and salt. It is not obvious that the salt should be evenly distributed between the polymer-rich and the polymer-poor phases.

Whenever there is a phase separation of a polyelectrolyte solution there will be an uneven distribution of ions. Such a compartmentalization could be the swelling of polyelectrolyte gels, or the confinement of polyelectrolytes in vesicles or living cells. Of course, if no salt is added the counterions are in the same phase as the polyelectrolyte, in order to obey the requirement of electroneutrality. When salt is added it does not distribute evenly between the polyelectrolyte solution and the outside solution. This uneven equilibrium of salt is termed the *Donnan equilibrium*. Taking the condition of electroneutrality into consideration, the conclusion is that the concentration of co-ions is lower in the polyelectrolyte phase than in the outer phase and that the concentration of counterions is higher in the polyelectrolyte phase compared to the outer phase. Hence, the two phases will contain different concentrations of salt and the salt concentration is always higher in the polyelectrolyte-free compartment.

Mixtures of Two Polymers in Water

We have seen that the driving force for the mixing of two components is the entropy gain. In mixing two polymers the entropy gain is very small, as is realized from Equation 9.9 and illustrated in Figure 9.8a. The entropy of mixing decreases with increasing size of the two components; hence, the determining factor regarding phase behavior is the interaction between the two polymers, that is, the second term on the right-hand side of Equation 9.9.

Depending on the interaction between the polymers there are three types of phase behavior (Figure 9.11). When there is a net repulsive interaction between the polymers there is a *segregative phase separation*, where two phases, each rich in one of the polymers, are in equilibrium (Figure 9.11a). In this manner the two polymers have minimum molecular

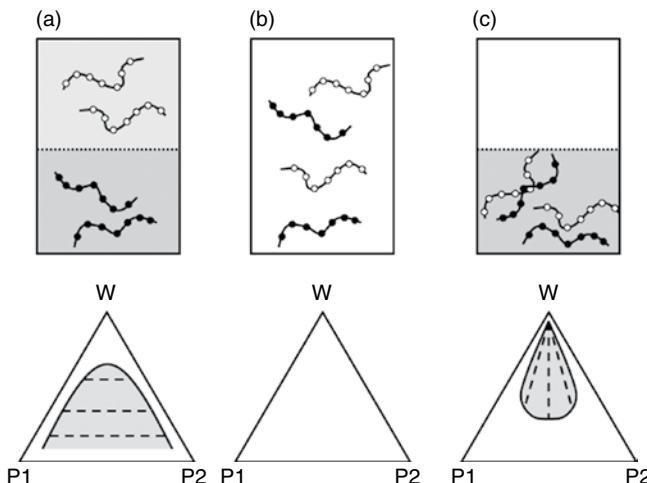


Figure 9.11 Phase separation of polymer–polymer–solvent systems: (a) segregative phase separation due to repulsive forces between the polymers; (b) complete miscibility due to weak attractive forces between the polymers; and (c) associative phase separation due to strong attractive forces between the polymers

contact. Segregative phase separation (“polymer incompatibility”) is the most common case for mixtures of polymers. The second case occurs when there is a very weak attraction between the two polymers. This leads to complete miscibility (Figure 9.11b). The third case occurs when there is a strong attraction between the polymers leading to an *associative phase separation* (Figure 9.11c). This is also termed *complex coacervation*.

Segregative phase separation is the most common case in nonaqueous solutions. This is the case also in aqueous solutions when the two polymers are nonionic. A well-known example is the mixture of poly(ethylene glycol) and dextran. This system has been used for partitioning of cell debris and biomacromolecules in biochemical research. Figure 9.12 shows a typical effect of molecular weight in such systems, that is, increasing the molecular weight increases the segregation, and thus the two-phase region.

Adding charges to one of the polymers results in interesting effects on the phase behavior. Now there is an entropic force originating from the counterions. If phase separation of the system should occur, there will be an entropic penalty, as the counterions, due to the condition of electroneutrality, must be confined to that phase. This entropic penalty hampers the tendency for phase separation compared to mixing of two nonionic polymers. Hence, the phase boundaries in phase diagrams, such as the ones in Figure 9.12, are lowered by introduction of charges in one of the polymers.

In mixing two polyelectrolytes of the same charge there is no effect of the counterions. Such mixtures behave in a similar manner as mixtures of two nonionic polymers, as shown by the example in Figure 9.13. An interesting feature of this particular phase diagram is that when the molecular weight of the sodium poly(styrene sulfonate) is increased, the water content in the sodium dextran sulfate phase is increased, despite the fact that nothing is altered in this particular phase. This is just a reminder of that the end points of a tie line, or the water

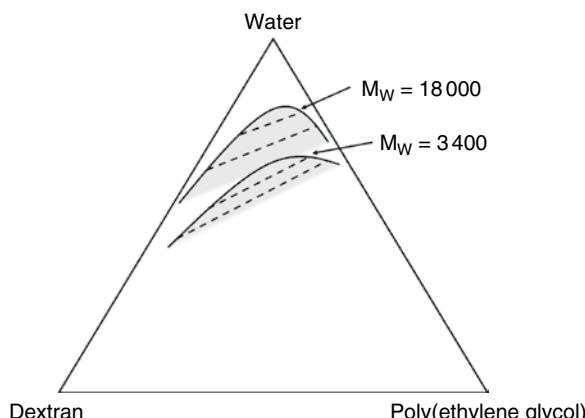


Figure 9.12 Segregative phase separation of dextran ($M_w = 23\,000$) and poly(ethylene glycol) with the indicated molecular weights, showing that the segregation becomes stronger with higher molecular weight. The dashed lines are tie-lines connecting the two equilibrium solutions. (With permission from Piculell, L. and Lindman, B. (1992) Association and segregation in aqueous polymer/polymer, polymer/surfactant, and surfactant/surfactant mixtures: similarities and differences. Advances in Colloid and Interface Science, **41**, 149–178. Copyright Elsevier.)

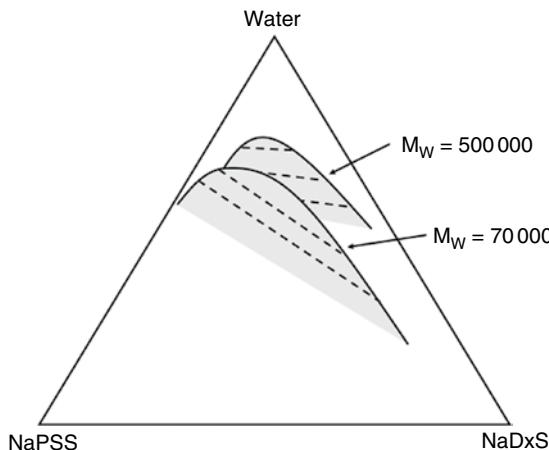


Figure 9.13 Segregative phase separation of mixtures of sodium poly(styrene sulfonate) (NaPSS) with the indicated molecular weights and sodium dextran sulfate (NaDxS) ($M_w = 500\,000$) in water. The dashed lines are tie-lines connecting the two equilibrium solutions. (With permission from Piculell, L. and Lindman, B. (1992) Association and segregation in aqueous polymer/polymer, polymer/surfactant, and surfactant/surfactant mixtures: similarities and differences. Advances in Colloid and Interface Science, **41**, 149–178. Copyright Elsevier.)

content in each phase, is a matter of balance of the water activity in each phase. Hence, one phase can be manipulated by altering the other phase. Decreasing the charge density of one of the polymers will gradually lead to the situation where one of the polymers is nonionic as described above, that is, it will increase the mutual solubility (i.e., disfavor phase separation).

In mixing two polyelectrolytes of opposite charge there will be an association, or polyelectrolyte complex formation, of the two polymers. The reason for the attraction is the release of the bound counterions, giving an entropy gain. This is the driving force for associative phase separation. The water content in the formed polyelectrolyte complex depends on the hydrophilicity of the backbone of the polymer. Polysaccharides with a very hydrophilic backbone have a high water content whereas polymers with a more hydrophobic backbone, such as sodium poly(styrene sulfonate), have a low water content (Figure 9.14).

Adding salt hampers the driving force of polymer association and, hence, disfavors associative phase separation. A polyelectrolyte complex can, therefore, be dissolved at higher ionic strengths (Figure 9.15a). Realizing that salt is produced on polyelectrolyte complex formation, we draw the conclusion that there is a critical polymer concentration where there is a sufficient amount of salt produced from the formation of polyelectrolyte complexes to dissolve the formed complexes. This is termed *self-screening*. Figure 9.15a illustrates that polyelectrolyte complexes are dissolved at higher ionic strengths and Figure 9.15b shows an example of self-screening, that is, when the total polymer concentration increases, the upper and lower phase boundaries approach each other more closely. Here, the upper and lower phase boundaries are determined at a specific total polymer concentration by measuring the amount of material in each phase and applying the lever rule (Equation 5.2). For higher polymer concentrations the phase boundaries are closer to each other. In fact,

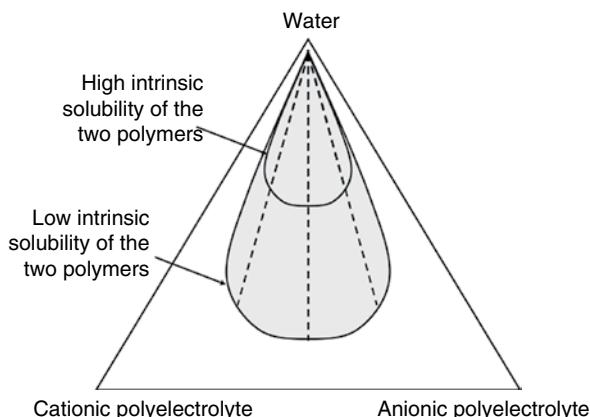


Figure 9.14 Two cases of associative phase separation of two oppositely charged polyelectrolytes. High solubility of the polymer backbones in water renders a polyelectrolyte complex with a high water content whereas low backbone solubility renders a complex with low water content

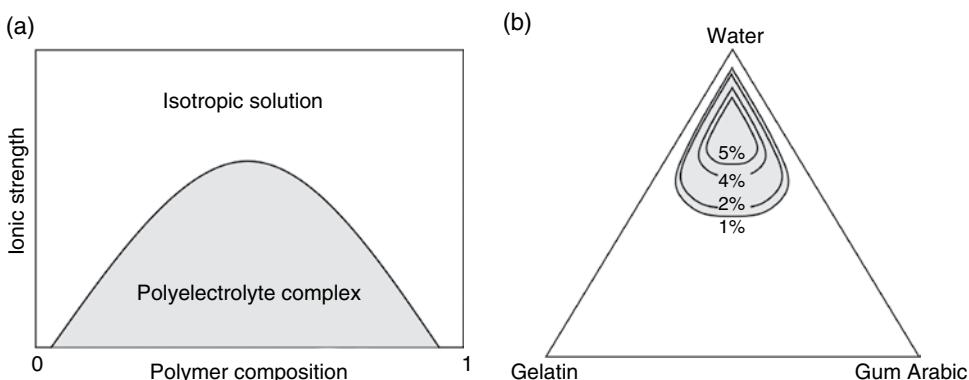


Figure 9.15 Schematic representation of the stability of a polyelectrolyte complex. (a) On the vertical axis is the ionic strength, or salt concentration, and on the horizontal axis is the composition of the mixture. (b) An illustration of self-screening, that is, the effect of polymer concentration on polyelectrolyte complex formation; the higher the polymer concentration for the determination of the phase boundaries, the smaller is the two-phase region (see text). (Data from Bungenberg de Jong, H.G. (1949) Complex colloid systems, in Colloid Science, Volume II (ed. H.R. Kruyt), Elsevier, Amsterdam, pp. 335–432.)

polyelectrolyte complexes cannot be formed at sufficiently high polymer concentrations. This phenomenon is important to take into consideration in formulation with polyelectrolyte complexes, such as microencapsulation.

It is more precise to describe these systems as composed of five components, namely (i) water, (ii) one polyelectrolyte, (iii) the other polyelectrolyte of opposite charge, (iv) the complex salt (the polyelectrolyte complex) and (v) the simple salt, that is, the salt formed from the counterions. This is further discussed in Chapter 5.

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10

Surface Active Polymers

Surface active polymers, or polymeric surfactants, have gained in popularity during the last decades. They are now used commercially in many different applications, either as the sole surface active agent or together with low molecular weight amphiphiles. As is discussed in this and several chapters to follow, surface active polymers and low molecular weight surfactants complement each other in many respects. This chapter reviews the most important classes of surface active polymers and also discusses typical properties and uses of the various types.

Surface Active Polymers can be Designed in Different Ways

A polymer with surface active properties can be built along three main routes: with hydrophobic chains grafted to a hydrophilic backbone polymer, with hydrophilic chains grafted to a hydrophobic backbone, and with alternating hydrophilic and hydrophobic segments. The first two types are called *graft copolymers* and the third type is named *block copolymer*. The three types are treated individually here.

Surface active polymers are plentiful in nature and the three principal types exist both in the plant and the animal kingdoms. The hydrophilic segment is often a polysaccharide, which may be charged or uncharged. For instance, antibodies contain carbohydrate residues attached as side chains far away from the antigen binding region and one important role of these side chains is to improve the water solubility of the otherwise relatively hydrophobic protein. Other proteins in the body, such as milk and saliva proteins, contain well-defined amino acid sequences very rich in phosphate groups. Such proteins exhibit considerable surface activity and are excellent stabilizers of fat droplets.

The classification of surface active polymers into the three types indicated should not be seen as a clear-cut division. In reality, two or more types may be combined into one product.

For example, a surface active macromolecule may have a backbone polymer consisting of alternating hydrophilic and hydrophobic segments and, in addition, contain hydrophilic or hydrophobic side chains, that is, the molecule may at the same time be a block and a graft copolymer. A graft copolymer may also contain both hydrophilic and hydrophobic grafts. The important feature from a physicochemical point of view is that the molecule is able to orient itself so as to expose hydrophilic regions into a polar environment and hydrophobic segments into an apolar phase. By doing so, the interfacial tension will be reduced, that is, the polymer is by definition an amphiphile.

Polymers with a Hydrophilic Backbone and Hydrophobic Side Chains

This type of graft copolymer, illustrated in Figure 10.1, is plentiful in nature with lipopolysaccharides being a prominent example. Lipopolysaccharides have a carbohydrate backbone onto which lipophilic chains are attached. Different types of lipopolysaccharides are produced in relatively high yields by microorganisms and many attempts have been made to use nature as a source of products for technical use.

An example of some historical interest is that of Emulsan. Emulsan is the trade name of a polyanionic lipopolysaccharide produced as an extracellular product by the bacterium *Acinetobacter calcoaceticus*. The heteropolysaccharide backbone contains a repeating tri-saccharide carrying a negative charge. Fatty acid chains are covalently linked to the polysaccharide through ester linkages.

Emulsan, or rather the action of it, was first observed stabilizing a crude oil–brine emulsion that had been formed on a sea shore by the mere action of the waves. The bacterium producing the emulsifying agent was isolated and later the surface active macromolecule was characterized. More in-depth studies revealed that the bacterium actually produced two components vital to the emulsion-forming process, a low molecular weight peptide, which is very surface active and which is an excellent emulsifier, and the lipopolysaccharide of molecular weight around 10^6 , which is remarkably effective in stabilizing the newly formed emulsion. This is a good illustration of how nature often uses surface active polymers—not to create emulsions but to stabilize emulsions formed by low molecular weight amphiphiles. In fact, polymeric surfactants are usually not suitable as emulsifying agents, as they are

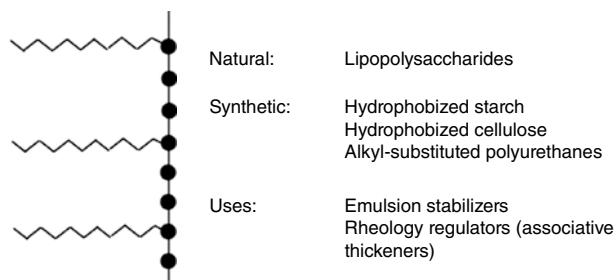


Figure 10.1 Some examples of polymers containing a hydrophilic backbone and hydrophobic side chains

unable to diffuse rapidly to newly created interfaces. This is further discussed in Chapter 24, which is devoted to emulsions and emulsifiers.

Some characteristic properties of Emulsan are as follows: (i) it gives only moderate reductions of surface and interfacial tensions; (ii) it has a very strong tendency to go to oil–water interfaces; (iii) it is, by itself, not an efficient emulsifying agent; (iv) it is an extremely good stabilizer for emulsions of specific oils in water (but not water in oil); and (v) it is very “substrate specific” and functions best in the presence of divalent cations.

It is interesting to note that the molecule is only moderately surface active. For instance, it reduces the water–hexadecane interfacial tension from 47 to around 30 mN/m, which is not a very low value. The combination of the lipopolysaccharide and the peptide reduces the same interfacial tension to 14 mN/m. Emulsan is very insoluble in both oil and water; hence its driving force for the interface is very strong, which is an important property of an emulsion stabilizer.

The “substrate specificity” of Emulsan is striking. Stable emulsions are only formed with specific oils, that is, with specific hydrocarbon combinations. The best results in terms of emulsion stability are obtained with an oil consisting of a mixture of aliphatic hydrocarbons and alkylaryl compounds, that is, the typical composition of heavy crude oil. This is the type of substrate which the bacterium that produces Emulsan has become adapted to. Excretion of Emulsan is the bacterium’s way of helping to increase the crude oil–water interface where it lives.

Great expectations were put on Emulsan as a crude oil emulsifier. The production of crude oil-in-water emulsions with a high ratio of dispersed to continuous phase (high internal phase ratio emulsions) were seen as a means to make extremely viscous heavy oils mobile enough to be pumped in pipelines. Of particular interest at the time when Emulsan was developed was the transport of Alaskan oil to mainland USA. Crude oil-in-water emulsions of around 75% oil content, which are feasible with Emulsan as the emulsion stabilizer, would enable direct burning without water evaporation, in analogy with the burning of concentrated coal slurries.

The efforts to use Emulsan as a crude oil emulsifier for transport in pipelines were thwarted by the observation that Emulsan could be enzymatically hydrolyzed. Breakdown of the emulsion stabilizer would lead to emulsion coalescence during transport, which would be very serious. The main use of Emulsan today is for cleaning oil tanks—an application of much smaller potential. The concept of using surface active polymers as stabilizer for crude oil-in-water emulsions with high concentration of the dispersed phase is not dead, however. It is, for instance, currently used for transport of heavy Venezuelan crude oil.

Emulsan is one well-known example of a biologically produced surface active polymer for industrial use. Considerable efforts are today directed towards development of applications and improved production methods for other lipopolysaccharides excreted by microorganisms, both bacteria and fungi. In later years applications in the cosmetic field have come in focus. The work-up process involved in the production of these biosurfactants is still a rather tedious matter, however, and the product prices are comparatively high. It is reasonable to assume that the price gap between biosurfactants and synthetic surfactants will decrease in the future.

Natural polysaccharides may also be chemically modified into the equivalent of lipopolysaccharides by attachment of long alkyl or alkylaryl chains. One example of an abundant and cheap polymer used for the purpose is starch. Native starch is typically a

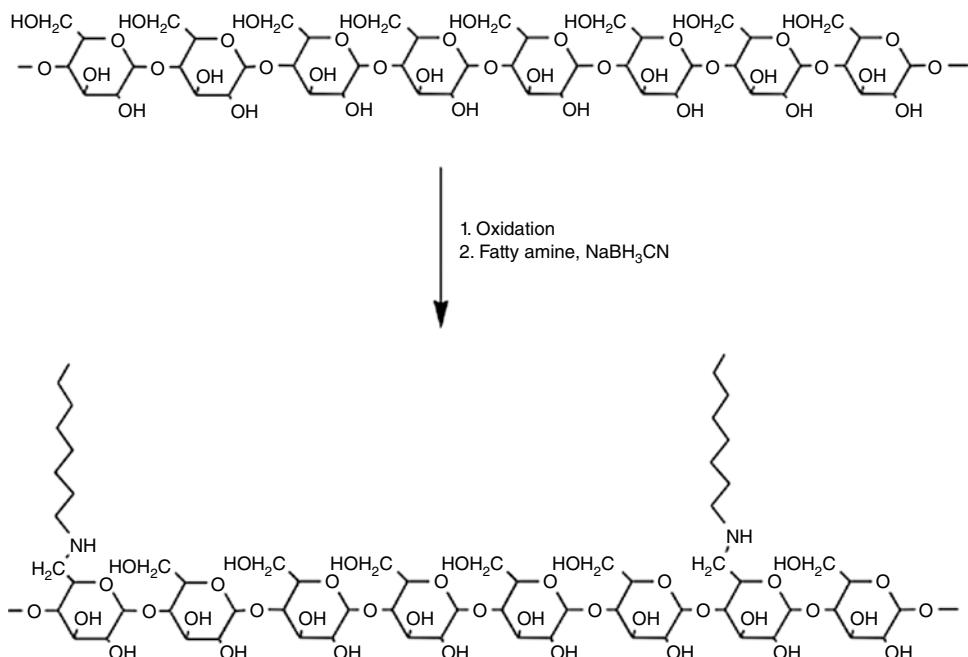


Figure 10.2 Derivatization of linear starch into a surface active polymer. In the scheme the oxidation and subsequent derivatization occurs only at the six-carbon of the anhydroglucose units. In reality, the oxidation may also lead to ring cleavage between carbon atoms 2 and 3, so generating aldehyde groups at these positions. These aldehydes may also undergo reductive amination with the fatty amine

mixture of linear amylose and highly branched amylopectin. The amylopectin component has too high a molecular weight to be suitable for controlled chemical modification. One option, therefore, is to start with so-called high amylose starch, which contains only a small amylopectin fraction. Alternatively, the amylopectin component may be selectively degraded at the cross-links by an enzyme acting only on 1,6-glucosidic linkages. The linear polysaccharide formed is oxidized to create aldehyde groups (and possibly ketones) and then reacted with a fatty amine, as is illustrated in Figure 10.2. The degree of substitution, which is the ratio of hydrophobic substituents to anhydroglucose rings, should be low, just a few percentage, otherwise solubility problems will arise.

A similar type of derivatization is made on cellulose in large scale. A common practice is to swell cellulose in strong alkali (mercerization) and then react the semi-dissolved material with ethylene oxide and a short alkyl chloride. A product with moderate surface activity is obtained. This nonionic cellulose derivative may then be treated with a reactive derivative of a fatty alcohol, giving long hydrophobic side chains on the molecule. A polymer with relatively high surface activity is then obtained. Figure 10.3 shows the structure of a typical product of this class, hydrophobically modified ethylhydroxyethylcellulose.

Such graft copolymers self-associate in solution via their hydrophobic side chains. This can lead to practically useful rheological effects. The network already formed in solution at

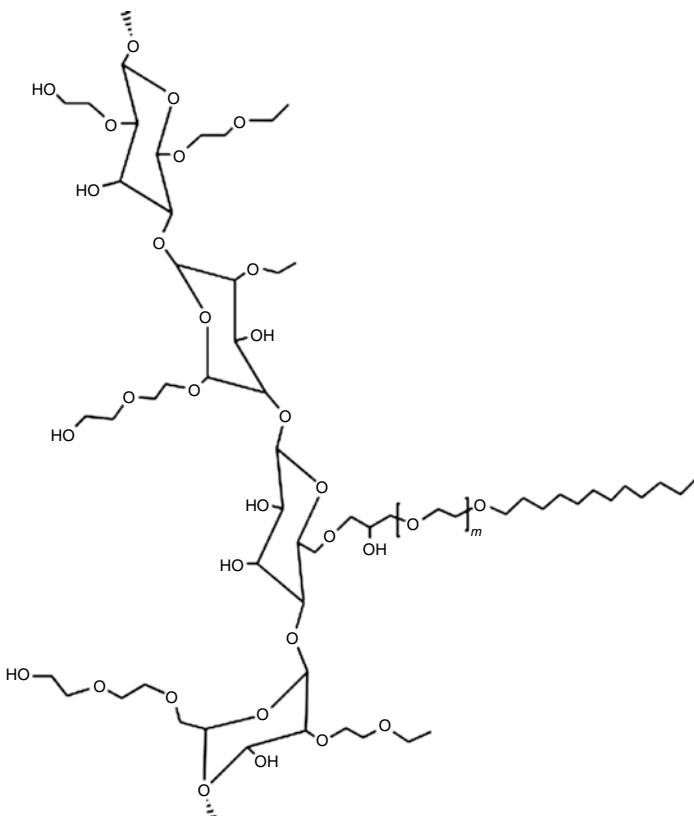


Figure 10.3 A hydrophobically modified ethylhydroxyethylcellulose. Only a small percentage of the anhydroglucoside rings carry a long-chain substituent. (Courtesy of Dr Leif Karlson, AkzoNobel, Stenungsund, Sweden)

very low polymer concentration (of the order of 1 wt%) can give a considerable increase in viscosity. However, the forces holding the network together are not very strong. The viscosity decreases rapidly on shearing the solution. Such a shear-induced decrease in viscosity is needed in, for instance, waterborne paints. The shear involved in the brush application of a coating is enough to give low viscosity to the formulation, which is needed in order to get good leveling of the paint. As soon as the shearing disappears, the transient network is re-formed in the paint film, creating the high viscosity needed for the film to remain at vertical substrates. Such graft copolymers are often referred to as “associative thickeners.” As with the starch-based product discussed above, only a few percent of the anhydroglucoside rings should carry a long-chain substituent, otherwise the product will become insoluble in water. Depending on reaction conditions, the hydrophobic substituents could be more or less randomly distributed along the polysaccharide backbone. The substitution pattern is of importance for the physicochemical properties. It seems that domains of highly substituted anhydroglucoside rings followed by domains of a low degree of substitution give a more

surface active polymer. However, it is not easy to govern the substitution pattern, particularly in large-scale synthesis. Figure 10.4 shows a schematic of a network created with this type of graft copolymer.

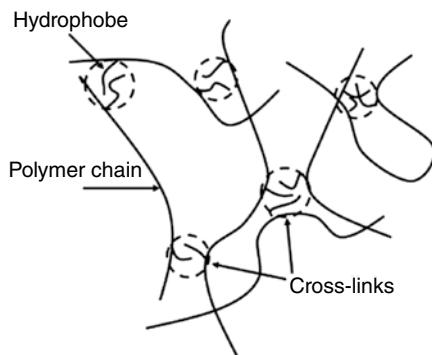


Figure 10.4 A network formed in solution by a hydrophobically modified water-soluble polymer

Linear, hydrophilic polymers end-grafted with long hydrophobic tails constitute a special example of hydrophobically modified water-soluble polymers. The hydrophilic base polymer is often poly(ethylene glycol) (PEG). Such polymers form micelles, sometimes called “flower micelles,” in which the long hydrophilic polymer chains form loops. At higher concentration such “end-capped” polymer molecules will bridge between flower micelles, in which case micelle clusters may form. At even higher concentration networks may be created by bridging between clusters. Such a series of events is illustrated in Figure 10.5.

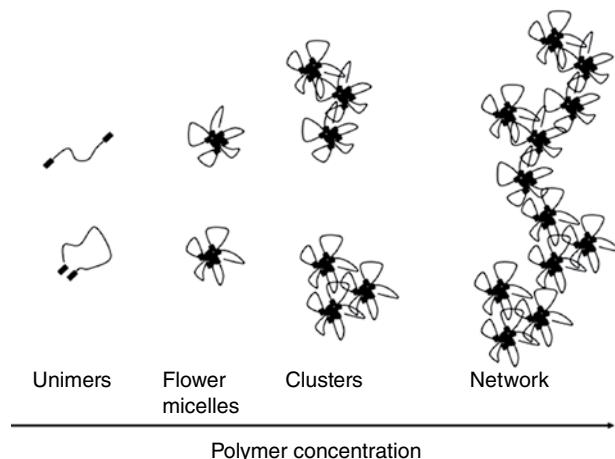


Figure 10.5 A hydrophilic polymer, for example, poly(ethylene glycol), end-modified with long, hydrophobic chains forms micelles at low concentration. At progressively higher concentration of clusters of micelles and networks are formed

Polymers with a Hydrophobic Backbone and Hydrophilic Side Chains

Glycoproteins can be said to represent a natural product class of this type although the polypeptide backbone is, of course, not entirely hydrophobic. In fact, many glycosylated proteins can be seen as a combination of graft and block copolymers, as the polypeptide chain often contains distinct hydrophobic and hydrophilic segments.

Several types of synthetic graft copolymers of this type are mentioned in Figure 10.6. There is considerable current interest in copolymers with PEG tails. These are effective steric stabilizers for various kinds of dispersions. Polymers with PEG chains can be prepared by ethoxylation, that is, reaction with ethylene oxide, which requires that there are hydroxyl groups or other nucleophilic groups on the backbone polymer. Polymers having PEG substituents may also be prepared by coupling a pre-prepared PEG segment to the backbone polymer. Both routes are used commercially.

The term *pegylation* is often used in connection to proteins with grafted PEG chains. Such grafting is usually performed by reaction of the protein with an electrophilic PEG derivative, often one with one reactive end and the other end capped by a methyl group. Figure 10.7 shows a schematic of a pegylated protein and, in addition, indicates possible benefits with pegylation of a protein. Also, other bioactive molecules than proteins are being pegylated, for instance in order to prolong the circulatory life of a drug. There also exist pegylated liposomes. In this case pegylation is made in order to avoid the liposomes to be detected by the body's immune system. Such liposomes are sometimes called *stealth liposomes*.

As already mentioned, this type of graft copolymer has found use as a steric stabilizer of dispersions, for instance in the paint field. Another interesting application of these surface active polymers is for modification of solid surfaces in order to prevent adsorption of proteins and other biomolecules. Polymers of this type can be made to adsorb in a monolayer at hydrophobic surfaces; the adsorption occurs via interaction between the hydrophobic backbone and the solid surface, that is, the PEG chains become oriented towards the

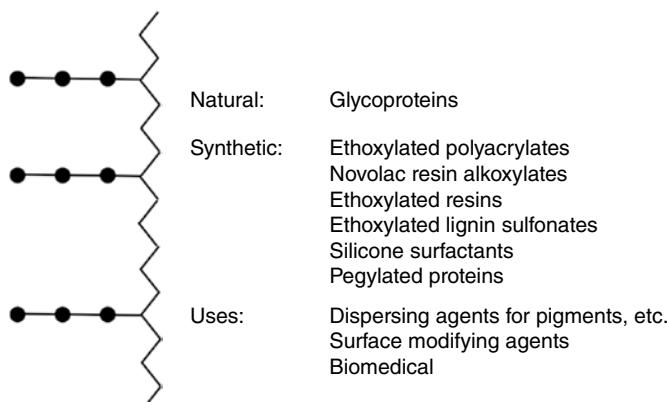


Figure 10.6 Some examples of polymers containing a hydrophobic backbone and hydrophilic side chains

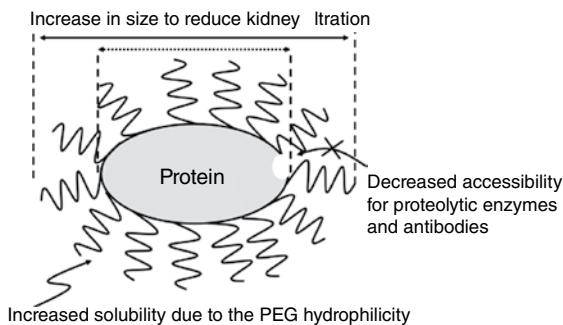


Figure 10.7 A pegylated protein

aqueous phase. This type of PEG coating has been found to be an efficient way of obtaining low protein adsorption and low cell adhesion characteristics. For instance, PEG coatings are reported to give a marked suppression of plasma protein adsorption and platelet adhesion, leading to reduced risk of thrombus formation, as demonstrated both *in vitro* and *in vivo*.

The inert character of PEG surfaces is believed to be due to the solution properties of the polymer and to the fact that it is completely uncharged. The polymer has a high dipole moment and is strongly solvated in water, as is discussed in some detail in Chapter 7. Interestingly, its homologues, polyoxymethylene and polyoxypropylene, as well as its isomer, polyacetaldehyde, are insoluble in water and, thus, not useful as hydrophilic polymer grafts.

The ability of PEG to prevent proteins and other biomolecules from approaching the surface can be considered a steric stabilization effect (Figure 10.8). As is discussed in more detail in Chapter 18, steric stabilization usually has two contributions, an elastic term and an osmotic term. The elastic, or volume restriction, component results from loss of conformational entropy when two surfaces approach each other, caused by a reduction in the available volume for each polymer segment (Figure 18.6a). However, the osmotic term is the dominating contribution. This term arises from the increase in polymer concentration when the adsorbed polymer layer is compressed, or when two layers interpenetrate. This causes

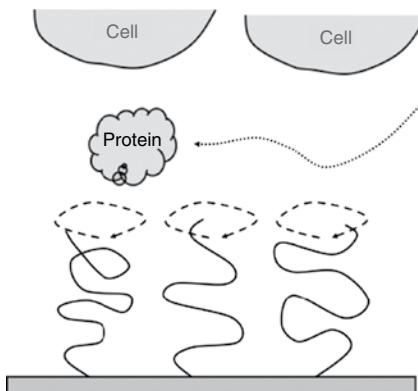


Figure 10.8 Protein rejection by PEG chains attached to a surface

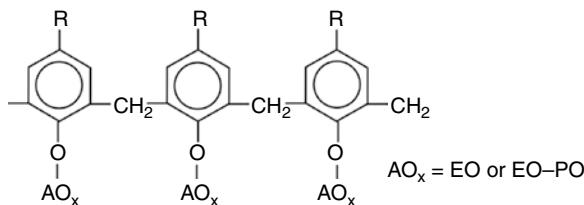


Figure 10.9 Phenol-formaldehyde resin alkoxylates. R is a lower alkyl, typically propyl or butyl

an osmotic force that gives a suction of water in order to dilute the polymer layer, resulting in repulsion. If the PEG grafting is dense, it is probable that compression is preferred to interpenetration, while if the grafting is less dense interpenetration is likely to dominate (Figure 18.6b). In both cases it is the temporarily increased polymer concentration, causing the osmotic flow of water, that is the dominating contribution.

Uncharged polysaccharides are also very efficient in preventing protein adsorption to solid surfaces. For instance, a dextran coating results in a very inert surface and the mechanism by which biomolecules are rejected is probably similar to that discussed above for PEG. The two types of polymers have very different temperature dependence, however. Whereas PEG and PEG derivatives are temperature sensitive, giving less efficient steric stabilization at higher temperatures, polysaccharides are relatively unaffected by the temperature.

Ethoxylated or ethoxylated and propoxylated phenol-formaldehyde resins, particularly of the novolac type, are a product class that has found use as a steric stabilizer in coatings. The EO-PO block copolymer products are also widely used as demulsifiers, for example, in oil production. The alkylaryl segment constitutes a strongly hydrophobic backbone that binds firmly to most hydrophobic surfaces and allows the hydrophilic chains to be long (often 50–100 oxyethylene units) without desorbing from the surface. The backbone, that is, the alkylphenol-formaldehyde condensate, is usually of relatively low molecular weight, typically 1000–3000. Figure 10.9 shows the product class.

Surface active silicone polymers constitute another type of comb polymer with polar side chains. There are different types of such silicones but they all contain polydimethylsiloxane as backbone. The most common type is shown on Figure 10.10.

The backbone polymer, polydimethylsiloxane, is highly hydrophobic and completely insoluble in water. Water-soluble substituents, charged or noncharged, will impart surface activity in aqueous systems. Poly(ethylene glycol) or poly(ethylene glycol)-poly(propylene glycol) block copolymers are by far the most common substituents. The linkages between

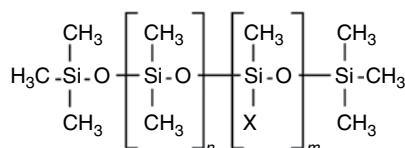


Figure 10.10 A surface active silicone polymer. X is an ionic or a nonionic polar group, most often an EO-PO copolymer. When m is 0, then polydimethylsiloxane is obtained. This is the very hydrophobic and nonsurface active silicone oil

Box 10.1 Properties of surface active silicone polymers

Very efficient in lowering the surface tension (down to around 20 mN/m)
 Excellent wetting on low-energy surfaces
 Powerful antifoamers
 Poorly biodegradable
 Relatively expensive. (However, due to high efficiency, cost performance may not be unfavorable when compared with conventional surfactants.)

silicon and the polyether chain may be either Si–O–C or Si–C. The Si–O–C link is made by esterification of chloropolysiloxanes with hydroxyl-functional organic compounds such as an EO–PO copolymer. The bond is not very stable to hydrolysis and such products are unsuitable for use under either acid or alkaline conditions. The Si–C linkage, where a carbon of the EO–PO copolymer is directly linked to the silicon atom, is stable. Such a linkage is usually made by a platinum-catalyzed addition of a Si–H bond across an olefinic bond introduced at the end of the block copolymer, a “hydrosilylation reaction”.

The substituent X of Figure 10.10 may also have a weakly polar character, in which case the product exhibits surface active properties in organic solvents. Some surface active silicone polymers, such as fluoro surfactants, are, therefore, suitable for use also in nonaqueous systems.

Surface active silicone polymers are typical specialty products used in niche areas in which they perform better than conventional surfactants. Box 10.1 lists some characteristic properties of such amphiphiles.

Surface active silicone polymers are used in a variety of applications, such as the following: (i) cell control additives in polyurethane foams, (ii) antifoams in many types of aqueous systems (EO–PO substituted products), (iii) additives in paints to prevent floating of pigments and film defects (cratering, orange peel, etc.), (iv) wetting agents on polyolefins and other hard-to-wet materials, and also as wetting agents in nonaqueous systems, for example, in lubrication, and (v) emulsifiers for silicone oil emulsions.

Comb copolymers based on poly(12-hydroxystearic acid) as grafts are frequently used as dispersants in nonaqueous formulations, for example, paints. The poly(12-hydroxystearic acid) chains, which are of low molecular weight, provide steric stabilization analogous to what PEG does in aqueous solution. The backbone polymer contains specific groups that function as anchoring sites for the polymer to the surface of the particles to be dispersed. Proper anchoring of the polymer, which usually is based on acid–base interactions, is often the critical issue, determining dispersion efficiency. Figure 10.11 shows the structure of poly(12-hydroxystearic acid).

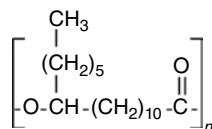


Figure 10.11 The repeating unit of poly(12-hydroxystearic acid), an important side chain of surface active graft copolymers. n is usually 5–10

Polymers with Alternating Hydrophilic and Hydrophobic Blocks

Many proteins contain regions with distinct hydrophilic and hydrophobic characters (Figure 10.12).

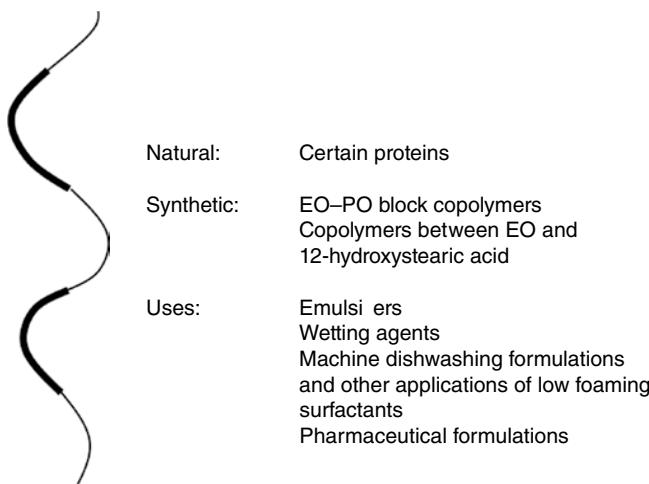


Figure 10.12 Some examples of polymers containing alternating hydrophilic and hydrophobic blocks

Casein, the milk protein, and many salivary proteins are examples of surface active proteins of this type; these contain polar segments with a high concentration of phosphate groups, along with regions dominated by hydrophobic amino acids. Membrane proteins are striking examples of well-ordered block copolymers. They are designed such that they have alternating segments of hydrophobic amino acids long enough to penetrate the lipid bilayer of a cell membrane and segments of hydrophilic amino acids that prefer to be exposed to the exterior, either inside or outside the cell. Figure 10.13 shows the structure of bacteriorhodopsin, a protein that penetrates the membrane no less than seven times.

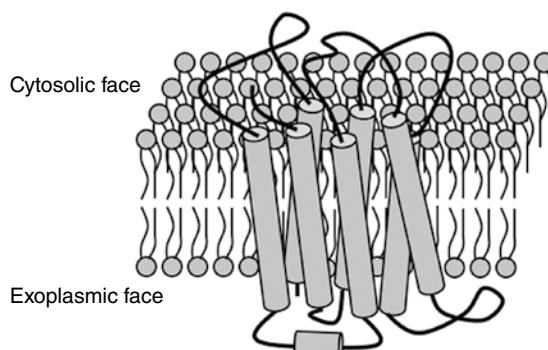
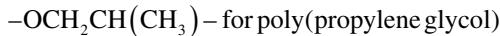
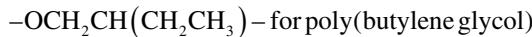


Figure 10.13 Bacteriorhodopsin, a membrane protein. Bacteriorhodopsin acts as a proton pump, capturing light which it uses to move protons across the membrane out of the cell. A lipid bilayer is 3–4 nm thick

There is a variety of man-made surface active block copolymers. By far the most common and well-known are poly(alkylene glycol) copolymers. The hydrophilic segment is almost invariably PEG, obtained by ethylene oxide (EO) polymerization. The hydrophobic segment is usually poly(propylene glycol) (PPG) but poly(butylene glycol)-based products also exist. Since propylene oxide (PO) and butylene oxide (BO) are the starting materials for the two latter polymer segments, all three poly(alkylene glycol)s will have the same –O–C–C– backbone structure, that is, the repeating units are



and



As mentioned before, the small difference in structure between the three types of repeating units makes a surprisingly large difference in physicochemical properties. Whereas PEG is water soluble regardless of molecular weight, the two other poly(alkylene glycol)s are water insoluble and, thus, act as hydrophobic segments in block copolymers.

In the literature the term poly(alkylene oxide) is sometimes used instead of poly(alkylene glycol), for example, poly(ethylene oxide) instead of PEG. PEGs are also sometimes referred to as polyoxyethylene (POE) or polyoxirane. In general usage, PEG refers to polymers of molecular weight below about 20 000, poly(ethylene oxide) to higher molecular weight polymers and POE and polyoxirane are not specific in this regard. The segments used in the block copolymers are always of relatively low molecular weight; PEG is, therefore, the appropriate term.

There are many possible variations of EO–PO block copolymers and the patent literature is rich in suggestions. However, the number of commercially available types is more limited and the most important ones are shown in Figure 7.13.

There are also EO–PO copolymers that are claimed to contain segments with random distribution of the monomers. These are made by copolymerization of EO and PO. However, EO is much more reactive than PO; therefore, such mixtures give products with considerable block character. Various methods are being used to affect the monomer distribution in these products, for example, specific procedures for monomer feeding. These procedures differ from one producer to another. Since the product properties are very dependent on the monomer distribution, random EO–PO copolymers with the same monomer ratio obtained from different sources may have large differences in properties.

Box 10.2 lists important properties of EO–PO block copolymers. In general, the products are versatile and inexpensive and their physicochemical properties can be tailor-made more easily than is the case for most other surfactant types since both the hydrophobic and the hydrophilic segments can be varied at will. In Chapter 7 some physicochemical properties of these block copolymers are discussed in some detail. Poor degradability is a negative characteristic that limits their use at the present time and which can be expected to do so even more in the future.

Some typical uses of EO–PO block copolymers include: (i) foam control agents in machine dishwashing powders, the textile industry (dyeing and finishing), oil production,

Box 10.2 Properties of EO–PO block copolymers

They show reversed solubility versus temperature dependence, that is, they are more soluble in cold than in warm water, and exhibit a cloud point

Products with low EO content give low foam. (The best antifoam is obtained for EO/PO ratios of 1:4–1:9.) Reverse products, that is, PO/EO/PO, usually give low foam

High molecular weight products with high PO contents have good wetting properties

Products with high EO contents have good dispersing properties

Biodegradability is slow, particularly for products with high PO contents

and emulsion paints; (ii) wetting agent in machine dishwashing (rinse aid) and lubricants; (iii) dispersing agents for pigments; (iv) emulsifiers or coemulsifiers for herbicides and insecticides; (v) demulsifiers, for example, in oil production (products with 20–50% EO are used for w/o emulsions and 5–20% EO products for o/w emulsions); (vi) personal care products; and (vii) pharmaceutical formulations.

Polymeric Surfactants have Attractive Properties

The growing interest in polymeric surfactants (or surface active polymers) can be said to emanate from two characteristic features:

1. They have a very strong driving force to go to interfaces and this tendency to collect at interfaces is not as dependent on physical variables as for normal, low molecular weight surfactants. This means that:
 - a. the products are effective at low total concentrations;
 - b. the products show little sensitivity to salts, temperature changes, and so on.
2. They can have very long POE (or polysaccharide) chains and still be retained at interfaces. (Low molecular weight surfactants with long hydrophilic chains tend to desorb from the interface and dissolve in the aqueous phase.) Thus, such products are very efficient steric stabilizers for dispersed systems and effective non-fouling agents on solid surfaces.

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11

Adsorption of Polymers at Solid Surfaces

Technically, the adsorption of polymers is utilized in many applications, such as in the dispersion of particles, flocculation processes, treatment of surfaces, and so on. In these processes, the purpose of polymer adsorption is to modify interactions between surfaces.

Adsorption of a polymer at a surface is a question about the partitioning of the polymer between the surface phase and the solution phase. Strong adsorption can be achieved by either a strong attraction between the polymer segments and the surface or alternatively a poor interaction between the polymer and the solvent. Adsorption is always accentuated in solvents of poor quality; the poorer the solvent–polymer interaction, then the better the adsorption and vice versa. Of course, strong adsorption is also obtained when both these forces are at work.

Characteristic of polymer adsorption isotherms is the sharp increase in adsorption at very low polymer concentrations, followed by a plateau that does not change significantly with polymer concentration (Figure 11.1). The very strong adsorption at low concentrations is a reflection of the “unhappiness” of the polymer in the solution. The constant adsorption at higher polymer concentrations is simply due to the fact that the surface is saturated with the polymer.

When a polymer coil adsorbs at a surface it loses some of its conformational entropy and this opposes adsorption. Hence, there needs to be some net favorable interaction between polymer segments and the surface for adsorption to occur. This interaction is normally given the symbol χ_s . As stated above, another reason could be poor solubility, that is, adverse interaction between polymer and solvent in the solution forcing the polymer to the surface.

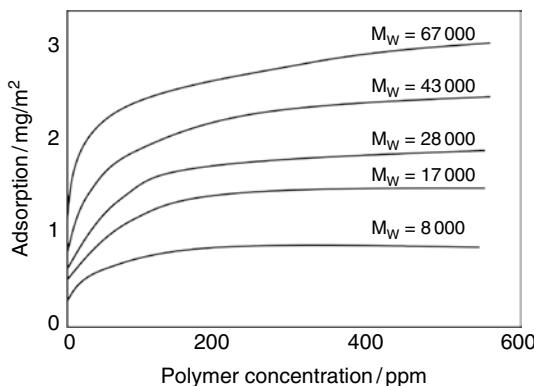


Figure 11.1 Adsorption of poly(vinyl alcohol) on polystyrene latex, showing the typical features of polymer adsorption, namely the steep rise in adsorption at low polymer concentrations and a plateau-like adsorption at high concentrations. The figure also illustrates that the adsorption increases with the polymer molecular weight. (With permission from Tadros, Th.F., Vandamme, A., Levecke, B., et al. (2004) Stabilization of emulsions using polymeric surfactants based on Inulin. Advances in Colloid and Interface Science, **108–109**, 207–226. Copyright Elsevier.)

The Adsorbed Amount Depends on Polymer Molecular Weight

High molecular weight (M_w) species are more prone to adsorb than low molecular weight polymers. This is understandable as we learned from Chapter 9 that high M_w species are less stable in solution than lower M_w analogs. Analyzing the molecular weight dependence of the adsorbed amount gives an idea of how the polymer is adsorbed on the surface. If the polymer molecules lie flat on the surface there will not be any molecular weight dependence. On the other hand, if the polymer adsorbs “head on,” that is, with only the polymer chain end at the surface, the adsorbed amount will be directly proportional to the molecular weight. Most polymer systems are found to adsorb in a coil conformation and the molecular weight dependence of the adsorbed amount is proportional to M according to:

$$\Gamma \propto M^\alpha \quad (11.1)$$

where M is the polymer molecular weight and α is a constant with a value in the range 0.3–0.5. Figure 11.1 shows a typical molecular weight dependence of adsorption, in this case adsorption of poly(vinyl alcohol) (PVA) in aqueous solution at a polystyrene latex surface. Notice that at low polymer concentrations the adsorption progressively becomes steeper as the polymer molecular weight increases. Analyzing these isotherms in terms of Equation 11.1 a value of $\alpha = 0.6$ is obtained, indicating that the polymer adsorbs in a coil conformation. Contrary to these results is the adsorption of poly(ethylene oxide) on a silica surface from water. In this system, there is no molecular weight dependence of the adsorption and α is zero indicating that the polymer adsorbs flat on the surface.

We have seen that a polymer with a high molecular weight shows a larger adsorption than polymers with lower molecular weights (Figure 11.1). Thus, in adsorbing a polydisperse

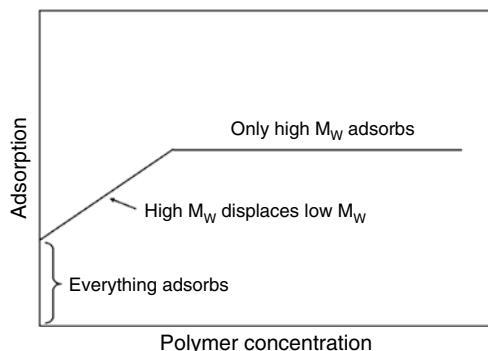


Figure 11.2 The principle of simultaneous adsorption of two polymers differing in molecular weight where the high M_w species displace the low M_w species at the surface

polymer sample the high molecular weight species will preferentially adsorb at the expense of the low molecular weight species. Figure 11.2 illustrates the adsorption of a mixture of two polymers with different molecular weights. The figure shows that the adsorption of a binary polymer mixture is divided into three different regions. In the first region, at very low polymer concentrations, there is sufficient surface available for all polymer molecules to adsorb, thus resulting in a strong increase in the adsorption. Eventually the binary polymer mixture covers the surface and an exchange process starts to take place where the high molecular weight polymer adsorbs at the expense of the low molecular weight species. Finally, at higher polymer concentrations, only the high molecular weight polymer covers the whole surface and a constant adsorption is found.

An illustrative example of the competitive adsorption between low and high molecular weight polymers is shown in Figure 11.3 for the simultaneous adsorption of poly(ethylene

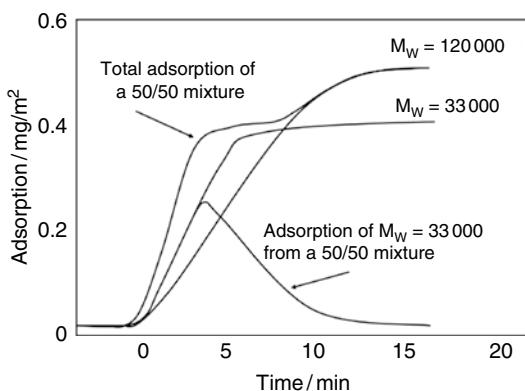


Figure 11.3 Simultaneous adsorption versus time from a 50:50 wt% mixture of two poly(ethylene oxide) polymers with molecular weights of 33 000 and 120 000 together with their individual adsorption. (With permission from Fu, Z. and Santore, M.M. (1998) Kinetics of competitive adsorption of PEO chains with different molecular weights. *Macromolecules*, **31**, 7014–7022. Copyright 1998, American Chemical Society.)

oxide) polymers with molecular weights of 33 000 and 120 000 on silica surface. Here it is seen that the lower M_w poly(ethylene oxide) adsorbs in the beginning of the experiment, that is, when there is sufficient surface available, but desorbs when the higher M_w polymer competes for the surface.

Since the adsorbed amount depends on the molecular weight, we will for a polydisperse sample monitor adsorption with respect to the ratio of the polymer solution volume to the available surface area. A small available surface area will adsorb only high molecular weight species, hence a large adsorption is detected. A high available surface area will adsorb also the lower molecular weight species, hence a lower total adsorption is detected. This problem is circumvented by normalizing the polymer concentration variable (C_p) according to:

$$\Gamma_b = C_p V/A \quad (11.2)$$

Here V is the total liquid volume and A is the total available surface area. Figure 11.4 illustrates that when plotting the adsorption versus the polymer concentration, according to Equation 11.2, data fall on a single curve.

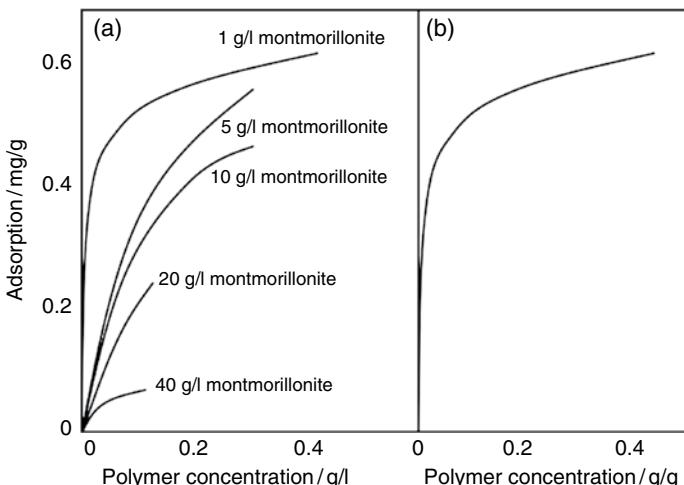


Figure 11.4 Effect of montmorillonite concentration on the adsorption isotherms of PVP (a) plotted against the equilibrium polymer concentration and (b) plotted against the ratio of equilibrium concentration relative to the montmorillonite concentration. (With permission from Séquaris, J.-M., Hild, A., Narres, H.D. and Schwuger, M.J. (2000) Polyvinylpyrrolidone adsorption on Na-montmorillonite. Effect of the polymer interfacial conformation on the colloidal behavior and binding of chemicals. Journal of Colloid and Interface Science, **230**, 73–83. Copyright Elsevier.)

There are three general conclusions concerning how adsorption of a polydisperse polymer sample differs from a monodisperse one. The first is that polydisperse samples take longer time to reach equilibrium, as shown in Figure 11.5a; this is due to the exchange of low M_w species for high M_w species at the surface. The second conclusion is that, for the same reason, the polydisperse sample does not reach a plateau in the adsorption isotherm, as when the polymer concentration increases so does the availability of the higher M_w species,

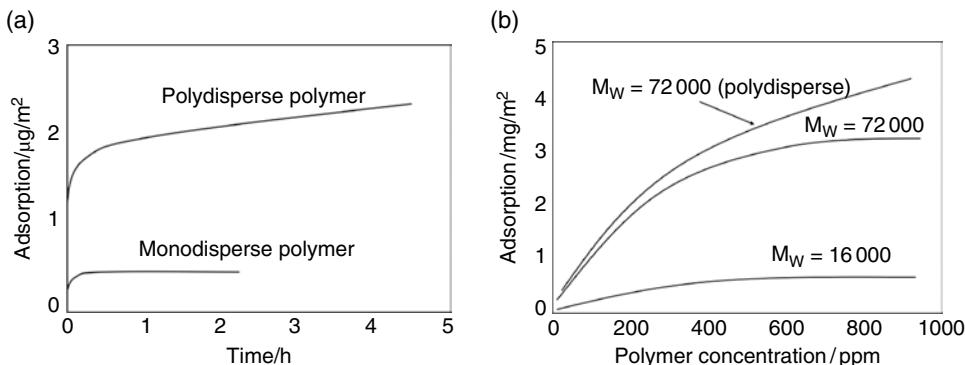


Figure 11.5 (a) Adsorption kinetics of a monodisperse and a polydisperse cationic polymer on silica and (b) adsorption of two monodisperse and one polydisperse PVA sample on TiO_2 . (With permission from Terada, E., Samoshina, Y., Nylander, T. and Lindman, B. (2004) Adsorption of cationic cellulose derivatives/anionic surfactant complexes onto solid surfaces. I Silica surfaces. *Langmuir*, **20**, 1753–1762. Copyright 2004, American Chemical Society and Chibowski, S. and Paszkiewicz, M. (2001) Studies of the influence of acetate groups from polyvinyl alcohol on adsorption and electrochemical properties of the TiO_2 -polymer solution interface. *Journal of Dispersion Science and Technology*, **22**, 281–289, Copyright Taylor & Francis Ltd, <http://www.tandf.co.uk/journals>.)

as shown in Figure 11.5b, hence there is an exchange of lower M_w species for higher M_w species. The third conclusion is that for a polydisperse sample the measured adsorbed amount depends on the surface to solution volume ratio, as discussed above and illustrated in Figure 11.4.

Solubility has a Profound Influence on the Adsorption

The solvent–polymer interaction, or the solvent quality, influences the polymer adsorption in two ways. Firstly, the solvent–polymer interaction influences the polymer conformation. As was discussed earlier in Chapter 9, polymers expand in good solvents and contract in poor ones. Thus, a polymer adsorbed at a surface occupies a larger surface area in a good solvent and a smaller surface area in a poor solvent, giving a larger adsorption from poor solvents. Secondly, a solvent influences the adsorption by the stability in solution, that is, if the polymer is not “happy” in the solution it will seek any opportunity to escape the solvent, for example, by adsorbing at a surface. The effect of solubility on the adsorption of polymers is illustrated below.

The adsorption of a polymer is a function of the solubility in solution, the poorer the solubility the larger is the adsorption. This is illustrated for the adsorption of ethylhydroxyethylcellulose (EHEC) on silica (Figure 11.6). In Figure 11.6a the change in cloud point on salt addition for various salts is shown, while in Figure 11.6b the corresponding adsorption at a silica surface is shown. It is clearly demonstrated that those salts that decrease the cloud point, that is, the salts that decrease the solubility, increase the adsorption of the

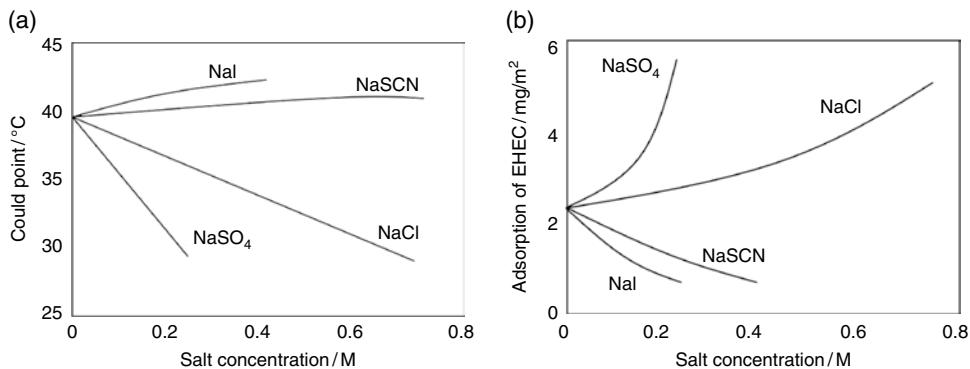


Figure 11.6 (a) Cloud point variation of aqueous EHEC salt solutions and (b) adsorption of EHEC from the same solutions on a silica surface, illustrating that the adsorption increases as the EHEC solubility decreases. (With permission from Malmsten, M. and Lindman, B. (1990) Ellipsometry studies of the adsorption of cellulose ethers. *Langmuir*, **6**, 357–364. Copyright 1990, American Chemical Society.)

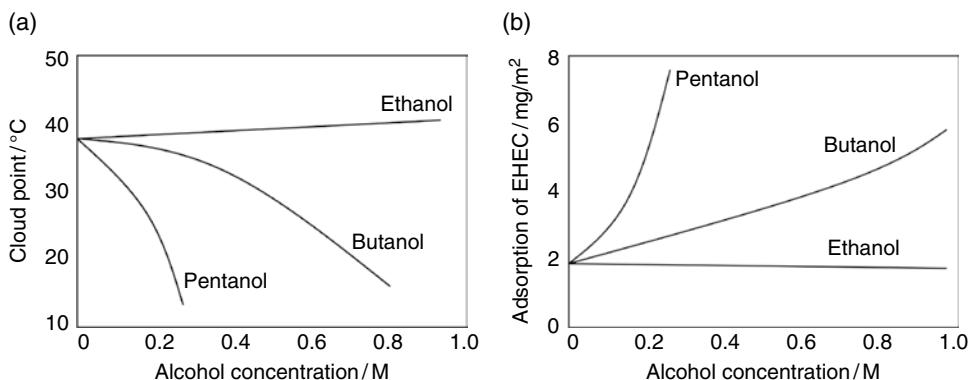


Figure 11.7 (a) Cloud point variation of aqueous EHEC + alcohol solutions and (b) adsorption of EHEC from the same solutions on a silica surface, illustrating that the adsorption increases as the EHEC solubility decreases. (With permission from Malmsten M. and Lindman, B. (1990) Ellipsometry studies of the adsorption of cellulose ethers. *Langmuir*, **6**, 357–364. Copyright 1990, American Chemical Society.)

polymer, thus illustrating the fact that adsorption is a measure of the escaping tendency of the polymer from the solution. Equivalently for those salts that increase the cloud point, that is, increase the solubility, the adsorption decreases, as illustrated for sodium iodide (NaI) and sodium thiocyanate (NaSCN). We stress that this is a general phenomenon and not specific to salt additions. Figure 11.7 shows the corresponding results for the adsorption of EHEC on silica when various alcohols are added. Also, here we conclude that those additives that decrease the solubility, that is, decrease the cloud point, also increase the adsorption, and vice versa.

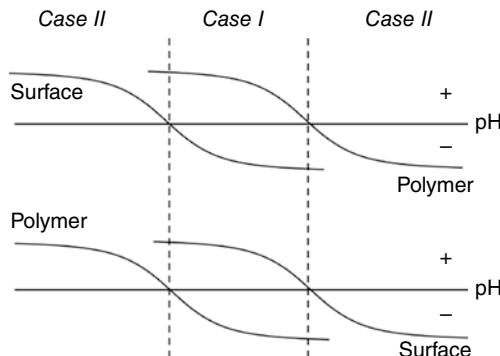


Figure 11.8 Schematic illustration of the variation of charge of a polyelectrolyte and a surface as a function of pH for the two cases when the pK_a of the polymer is larger and smaller than the pK_a of the surface. Case I and Case II stand for oppositely and similarly charged polyelectrolyte and surface, respectively

Adsorption of Polyelectrolytes

Adsorption of polyelectrolytes at a surface can be categorized as described in Figure 11.8. Here, the pH-dependent charges of both the surface and the polyelectrolyte are shown. The general trend is that the charge is positive at low pH values and negative at high pH values. Of course, the curves could also level off towards zero charge at either low or high pH values. In this figure, two different regions are identified where one has either opposite (case I) or similar (case II) charge on the polyelectrolyte and the surface.

Case I: Polyelectrolyte and the Surface Have Opposite Charge

In the first case, that is, when the polymer and the surface have opposite charges (Figure 11.9a), the driving force of adsorption could at first sight seem obvious, that is, the Coulombic attraction between the polyelectrolyte and the surface. However, in view of the fact that the counterions are also attracted to the surface and the polymer it might not be so obvious. The driving force indeed stems from the presence of the bound counterions. When a polyelectrolyte adsorbs at an oppositely charged surface, the counterions from both the polymer and the surface are released into the bulk solution. This increases the entropy in the system, which brings the system into a lower free energy state. This mechanism is the driving force for the adsorption of a polyelectrolyte at an oppositely charged surface (case I). From the above, we predict that the adsorption of a polyelectrolyte should decrease on addition of salt, since the entropy gain from the release of the counterions will become less when compared to the salt-free system. In the next sections examples are given on how such systems react to salt addition; discussed as well are the effect of the degree of ionization of the polymer and charge overcompensation, that is, when the surface charge changes sign due to polymer adsorption.

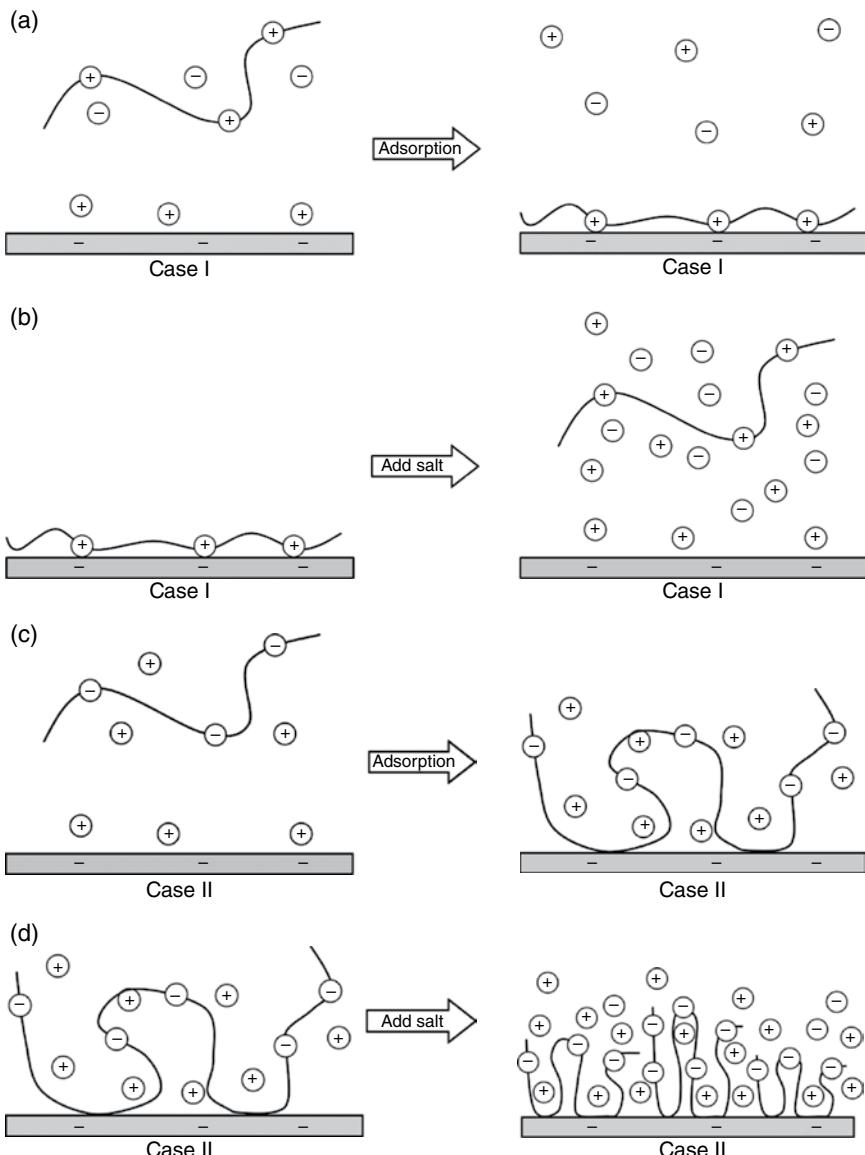


Figure 11.9 Schematics illustrating the two cases shown in Figure 11.8 and the effects of addition of salt

Effect of Polymer Charge Density

Adsorption of a polyelectrolyte at a surface of opposite charge is termed *pure electrosorption* if there are no other contributions to the adsorption, such as van der Waals forces. One example of adsorption of a cationic polymer at negatively charged surfaces is shown in Figure 11.10. Starting with zero charge density of the polymer there is no adsorption. As the

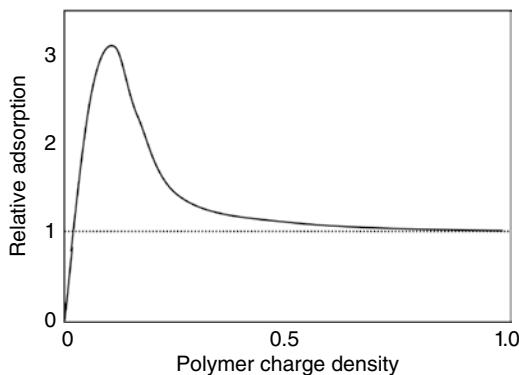


Figure 11.10 Relative adsorption of a cationic copolymer on a negatively charged latex as a function of the polymer charge density (the reference polymer is 100% charged). (With permission from Rakhnyanskaya, A.A., Pebalk, I.D., Orlov, V.N., et al. (2010) Controlled adsorption-desorption of cationic polymers on the surface of anionic latex particles. Polymer Science Part A, **52**, 483–489. Copyright Elsevier.)

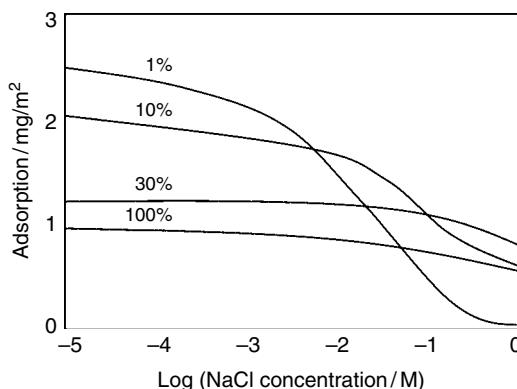


Figure 11.11 Effect of ionic strength on the desorption from mica of AM-MAPTAC (random copolymers of uncharged acrylamide (AM) and the positively charged [3-(2-methylpropionamido) propyl]trimethylammonium chloride (MAPTAC)) with the indicated polymer charge densities. (With permission from Rojas, O., Ernstsson, M., Neuman, R. and Claesson, P. (2002) Effect of polyelectrolyte charge density on the adsorption and desorption behavior on mica. Langmuir, **18**, 1604–1612. Copyright 2002, American Chemical Society.)

polymer attains charges there is attachment of the polymer, hence increased adsorption. However, with further increase in polymer charge density the polymer gradually changes conformation from an adsorbed coil to lying flat at the surface, giving a lower adsorption. Therefore, there is a maximum in adsorption as a function of polymer charge density.

Effect of Ionic Strength

Figure 11.11 shows an increased desorption of a pre-adsorbed polyelectrolyte as a function of ionic strength for a system where there is pure electrosorption of a charged polymer and

an oppositely charged surface. The reason for the desorption is that the driving force from the release of counterions is swamped by the excess ions in the solution. Hence, the net attraction between the oppositely charged polymer and surface is reduced with ionic strength due to lack of entropy gain from the released counterions. Note that for higher charge densities of the polymer there is hardly any effect of the ionic strength.

Charge Overcompensation

It is possible to obtain a charge reversal when a polyelectrolyte adsorbs on an oppositely charged surface. This is termed *charge overcompensation*. Charge overcompensation occurs for two reasons. The first is that there is an extra contribution to the adsorption free energy besides that of the freeing of counterions. Such contributions could be van der Waals forces or hydrophobic forces. The second reason is that there is a mismatch in surface charge densities, that is, the charge density of the surface is smaller than that of the polyelectrolyte. Thus, charge overcompensation occurs when the distance between the surface charges is larger than that between the charges of the polymer. This inevitably leads to a recharging of the surface when the polymer adsorbs.

The phenomenon of charge overcompensation is used in the technology of layer-by-layer (LbL) deposition. Here a first polyelectrolyte is adsorbed followed by rinsing. Then a second polyelectrolyte, with opposite charge, is added, which leads to charge reversal of the surface. After rinsing, the first polyelectrolyte is added, again giving charge reversal, and so on. In this manner multilayers of cationic and anionic polymers can be created (Figure 11.12). Note that it is necessary to wash with water between the steps. This is to remove excess polymer and to remove salt, since salt will dissolve the complexes (Chapter 9). The LbL technique is simple and cheap and has found applications in corrosion control and in the biomedical field among others.

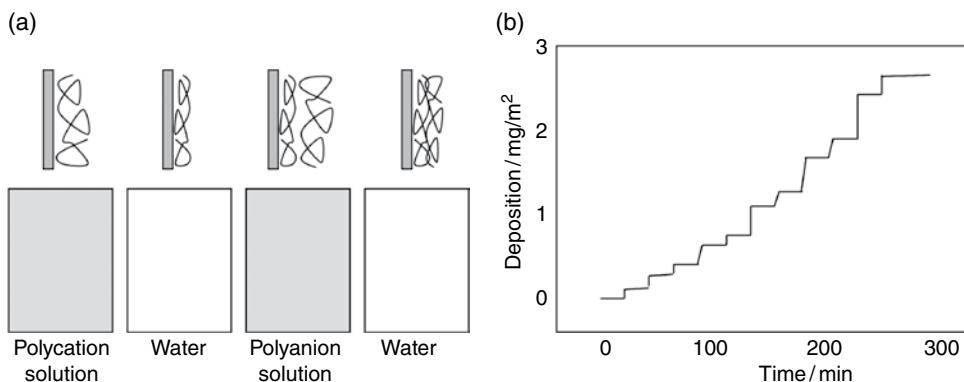


Figure 11.12 (a) The principle of the LbL technique and (b) the build-up of layers of the cationic poly(dimethylaminoethyl methacrylate) and the anionic polyacrylate. The polymer was switched every 20 min. (With permission from Kovacevic, D., van der Burgh, S., de Keizer, A. and Cohen Stuart, M.A. (2002) Kinetics of formation and dissolution of weak polyelectrolytes multilayers: role of salt and free polyions. *Langmuir*, **18**, 5607–5612. Copyright 2002, American Chemical Society.)

Case II: Polyelectrolyte and the Surface have the Same Charge

In the second case, that is, when the polymer and the surface have the same charge (Figure 11.9c), the driving force for the adsorption originates from attractive van der Waals forces, or hydrophobic forces, between the polymer and the surface. Here the addition of salt has the opposite effect to that the first case, that is, it increases the adsorption (Figure 11.9d). Because both the surface and the polyelectrolyte have bound counterions there will be a higher concentrations of counterions between the polyelectrolyte and the surface when the polymer approaches the surface. This causes an osmotic force for water molecules to enter the zone and keep the polymer away from the surface. At low ionic strengths there is, therefore, a depletion zone of polymer molecules close to the surface due to the counterions. Note that this is the same mechanism that keeps two colloidal particles of the same charge apart, which is depicted in Figure 18.5a.

For adsorption to take place there is therefore a need for a nonelectrostatic force between the polyelectrolyte and the surface. When a polyelectrolyte adsorbs at a surface with the same charge, the total charge of the surface increases, leading to an enhanced counterion binding. Hence, there will be a lowering of the entropy (Figure 3.2), which hampers the adsorption. Adding salt to the system reduces this effect and increases the adsorption. As mentioned previously, we also have the effect of polymer conformation, that is, at higher ionic strengths the polymer is more compact and the surface will be able to accommodate more polymer. This is exemplified in Figure 11.13 for the system poly(styrene sulfonate) on a negatively charged surface.

The valency of the counterions is of importance for the adsorption of polyelectrolytes on surfaces with the same charge. For example, salts with a divalent cation, such as calcium chloride (CaCl_2), are more effective in increasing the adsorption than sodium chloride (NaCl). Adding a divalent salt has the effect that the divalent ions replace the monovalent ions as counterions. The reason is purely entropic: on replacing two monovalent ions with one divalent there is a gain in entropy due to an increase in the number of entities in solution. With trivalent or other forms of multivalent ions, this effect will be even larger and

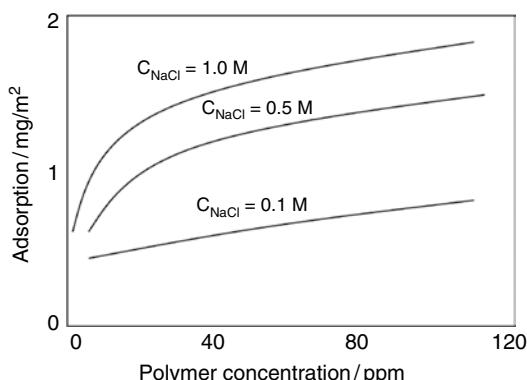


Figure 11.13 Adsorption isotherms for poly(styrene sulfonate) on negatively charged surfaces. (With permission from Cosgrove, T., Obey, T.M. and Vincent, B. (1986) The configuration of sodium poly (styrene sulfonate) at polystyrene/solution interfaces. Journal of Colloid and Interface Science, **111**, 409–418. Copyright Elsevier.)

the adsorption will increase. Also, the valency has an effect on the polymer conformation. Multivalent counterions decrease the polymer extension, which means that the surface will be able to accommodate more polymer.

Polymer Adsorption is Practically Irreversible

The question of whether or not a polymer is reversibly adsorbed has been the subject of many studies. The conclusion is that although polymer adsorption strictly is a reversible process, the polymer can practically be considered as irreversibly adsorbed. This apparent contradiction is explained by the slow dynamics in polymer systems. In order for a polymer to desorb from a surface, all polymer segments that are attached to the surface must detach at approximately the same time. If only a few segments detach, there is a high probability that other segments will adsorb before the whole polymer desorbs. Thus, the polymer chain is grounded on the surface by its own inertia. In analogy, this is the same inertia that causes a “busload of people to move more slowly than a single person.” Thus, over a limited timescale, polymers can be considered to be irreversibly adsorbed, while on very long timescales the adsorption is indeed reversible.

The fact that polymers adsorb almost irreversibly at surfaces can be used for surface modification. Hydrophilization of surfaces with surface active polymers was discussed in Chapter 10. An example where a polyelectrolyte is used to change the charge of a surface is shown in Figure 11.14. Here, poly(ethylene imine), which is a cationic polymer, is used to recharge an anionic surface. The cationic polymer is fully charged at pH 4, hence will adsorb strongly to the anionic surface (Figure 11.14a), giving a perfectly matched system. This conformation in the adsorbed state does not lead to a positively charged surface, however. If the polymer is adsorbed at a higher pH, such as pH 8, where only a fraction of the cationic sites are charged, the polymer will adsorb in a more coiled conformation (Figure 11.14b). If the pH of the system is subsequently reduced to pH 4 the already adsorbed polymer will be fully ionized, thus resulting in a charged cationic surface, that is, giving an overcompensated system (Figure 11.14c). Here, the inertia of a polymer is used since sufficient time is not given for the polymer to desorb and reach the equilibrium state at pH 4, as depicted in Figure 11.14a. Given sufficient time, however, the system will relax into the conformation shown in Figure 11.14a.

Figure 11.15 shows the adsorption of a cationic polyacrylamide at a silica surface. When pH is changed from 4 to 9 the polymer adsorption increases. The polymer layer thickness decreases, however. This is because the silica is highly charged at pH 9 and there is a strong

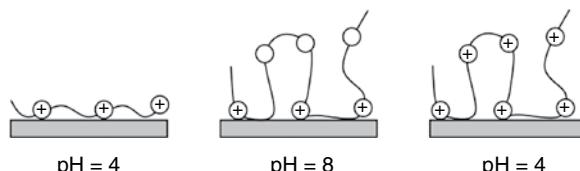


Figure 11.14 Schematics for the adsorption of poly(ethylene imine) on an anionic surface, illustrating that the apparent irreversibility can be utilized to reverse the charge in order to obtain a cationic surface. See text for discussion

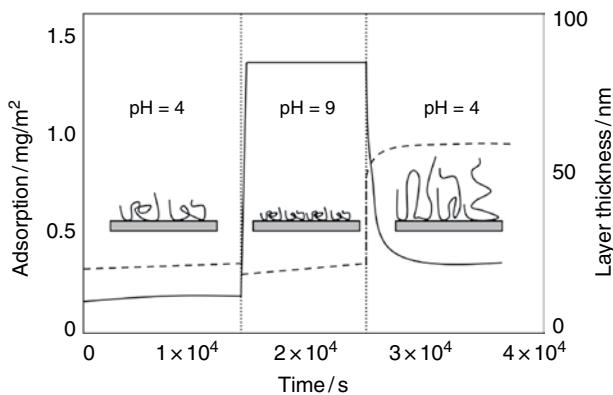


Figure 11.15 Adsorbed amount (full drawn line) and adsorbed layer thickness (dashed line) of a cationic polyacrylamide on silica as a function of time as pH is changed at two instances, showing that a thick layer can temporarily be obtained by altering the pH such that a high adsorption is obtained and then switching the pH back to the original value. (With permission from Samoshina, Y., Nylander, T., Shubin, V., et al. (2005) Equilibrium aspects of polycation adsorption on silica surface: how the adsorbed layer responds to changes in bulk solution. *Langmuir*, **21**, 5872–5881. Copyright 2005, American Chemical Society.)

polymer–surface interaction. When the pH is subsequently brought back to pH 4 the adsorbed amount slowly reaches the original value, but the thickness stays much larger. Of course, the system will eventually reach the original state. However, the larger thickness can meanwhile be used in surface engineering, such as building a second layer with an anionic polymer (layer-by-layer), or adding surfactants of opposite charge in order to create a surface boundary layer. It can also be used to attach oppositely charged particles to the surface.

Polymers can be Desorbed

Polymers can be forced to desorb from a surface in three different manners. One is to add a second component that has a strong affinity for the surface and displaces the polymer from the surface. The second way is to reduce the driving force for adsorption, for example, by manipulating the counterions. The third way is to alter the solubility of the polymer, which can be achieved, for example, by a pH change or by the addition of a surfactant that associates with the polymer.

The competition between a polymer and any other molecules for the surface can be measured accurately in the following type of experiment. Firstly, the polymer is allowed to adsorb to the surface from water. Then a second water-soluble additive is added. This additive has a certain affinity for the surface and competes with the polymer for the surface sites. At higher concentrations of this additive, the polymer will completely desorb; therefore, this additive is termed a *displacer*.

Figure 11.16a shows that poly(vinyl pyrrolidone) (PVP) continuously desorbs from a silica surface in water as displacers are added in increasing concentration until the critical displacer concentration (at which all polymer is desorbed) is reached. The figure shows

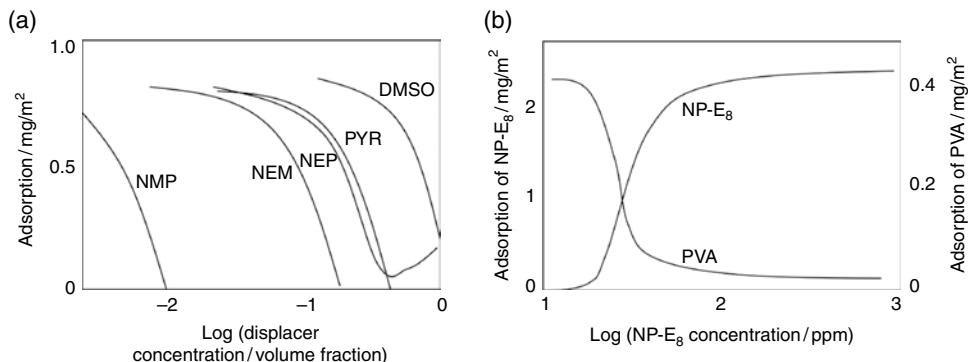


Figure 11.16 Two examples of desorption of a polymer by displacement: (a) desorption of PVP from silica in aqueous solutions with varying concentration of displacer, showing that total polymer desorption is obtained at a critical displacer concentration; and (b) displacement of the polymer PVA from silica by addition of octa(ethylene glycol) monononylphenyl ether (NP-E₈). (With permission from Cohen Stuart, M., Fleer, G. and Scheutjens, J. (1984) Displacement of polymers: II experiment. Determination of segmental adsorption energy of poly(vinylpyrrolidone) on silica. Journal of Colloid and Interface Science, **97**, 526–535, and Rachas, I., Tadros, T.F. and Taylor, P. (2000) The displacement of adsorbed polymer from silica surfaces by the addition of a nonionic surfactant. Colloids and Surfaces A **161**, 307–319. Copyright Elsevier.)

that N-methylpyrrolidone (NMP) is the most efficient displacer, being able to completely desorb the polymer at a volume fraction in water of about 1%, whereas dimethyl sulfoxide (DMSO) does not completely desorb the polymer even if present as a neat solvent.

These results correlate perfectly with the adsorption strength of the displacers at silica as determined from their adsorption isotherms. Thus, the stronger the adsorption of the displacer, then the less displacer is needed to totally remove a polymer from the surface. We conclude that a polymer can be “washed out” from a surface by adding a displacer that has a stronger affinity for the surface than the polymer segments have.

Not only organic solvent molecules are able to displace polymers from the surface, surfactants also show this ability. Figure 11.16b shows the displacement of PVA from a silica surface by addition of the nonionic surfactant octa(ethylene glycol)monononylphenyl ether (NP-E₈). The figure shows that the surfactant adsorbs in place of the polymer. Hydrophobic surfaces provide a special case since they give a very strong surfactant adsorption. Therefore, a polymer adsorbed onto a hydrophobic surface will be displaced on addition of surfactant.

Desorption of polymer by manipulating with the driving force is illustrated in Figure 11.11. Here the pre-adsorbed polymer is dipped into a salt solution at various concentrations. The weakly charged polyelectrolyte desorbs at higher salt concentrations since the driving force for adsorption is reduced. Hence, at high salt concentrations there is no appreciable entropy gain in adsorbing the polymer and, therefore, the polymer desorbs, despite the poor solubility in the solutions of high salt concentration. Polyelectrolytes with a high charge density cannot be made to desorb from a surface of opposite charge in this manner.

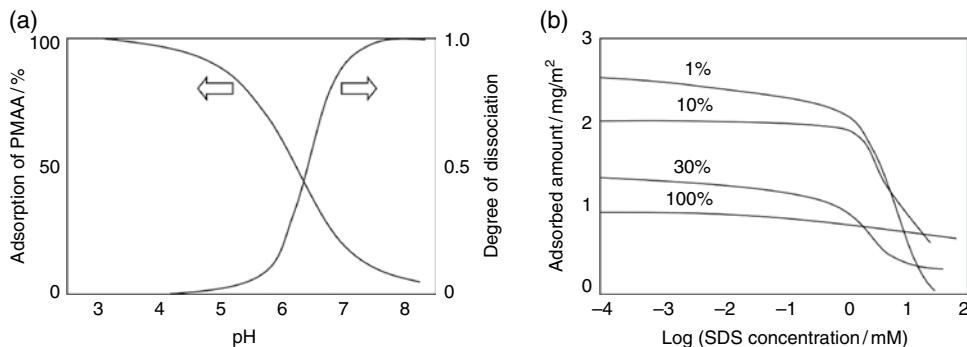


Figure 11.17 Two examples of desorption by increasing the solubility: (a) desorption of poly(methacrylic acid) from a poly(methyl methacrylate) surface with increasing pH; and (b) desorption of AM-MAPTAC from mica by immersion in SDS solutions with the indicated polymer charge densities (AM-MAPTAC is a random copolymer of uncharged acrylamide (AM) and the positively charged [3-(2-methylpropionamido)propyl]trimethylammonium chloride (MAPTAC)). (With permission from Andersson-Trojer, M., Wendel, A., Holmberg, K. and Nydén, M. (2012) The effect of pH on charge, swelling and desorption of the dispersant poly (methacrylic acid) from poly(methyl methacrylate) microcapsules. Journal of Colloid and Interface Science, **375**, 213–215, and Rojas, O., Ernstsson, M., Neuman, R. and Claesson, P. (2002) Effect of polyelectrolyte charge density on the adsorption and desorption behavior on mica. Langmuir, **18**, 1604–1612, Copyright 2002, American Chemical Society.)

Desorption of a polymer by increasing the solubility is illustrated in Figure 11.17a, showing the relative adsorbed amount of poly(methacrylic acid) as a function of pH. At higher pH the polymer is charged and has a high solubility in the aqueous phase. Since in this case there are no other driving forces for adsorption than the solubility of the polymer, it desorbs as the charge density increases.

Desorption of a cationic polymer by immersion in sodium dodecyl sulfate (SDS) solution is illustrated in Figure 11.17b. Here it is seen that the weakly charged polyelectrolyte can easily be desorbed from the surface. There is an association between the polymer and the surfactant giving the complex a negative charge and a high solubility in the bulk water. The higher charged polymers, however, have a lower hydrophobicity and are less prone to associate with the surfactant. This is further discussed in Chapters 15 and 16.

The Kinetics of Polymer Adsorption is Limited by Rearrangement

Polymer adsorption is generally regarded as a three-step process (Figure 11.18). The first step involves polymer transport from the bulk to the surface. The second step involves the attachment of the polymer to the surface and depends on electrostatic and steric barriers built up by previously adsorbed polymers. The third step is a rearrangement, or relaxation, of the polymer at the surface where an optimization of polymer segments at the surface sites takes place. This third step takes a longer time compared to the first two steps and is the rate-determining step.

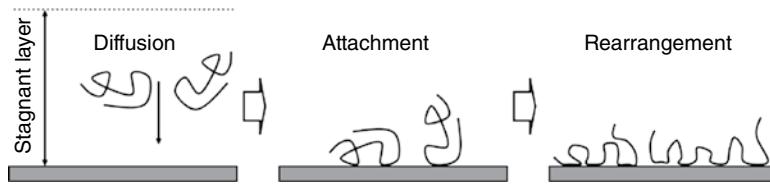


Figure 11.18 Polymer adsorption occurs in three steps: (i) transport to the surface, (ii) attachment, and (iii) rearrangement at the surface

It is interesting to get a feel for the diffusion of the polymer to the surface. This process can be modeled as:

$$\frac{d\Gamma}{dt} = \frac{D}{\delta} c_p \quad (11.3)$$

where D is the diffusion coefficient of the polymer (typically $D = 10^{-11} \text{ m}^2/\text{s}$), δ the thickness of the stagnant layer just above the surface (typically $\delta = 100 \mu\text{m}$), and c_p the polymer concentration (typically 50 ppm). These values give an adsorption rate of about $0.005 \text{ mg/m}^2 \cdot \text{s}$. Hence, it should not take more than about five minutes to reach saturation at the surface, far less than is normally observed. The reason for this discrepancy lies in the time for rearrangements of the polymer at the surface. A 24 h equilibrium period is normally recommended in the measurement of polymer adsorption.

As mentioned in the introductory part there is also a time effect due to the exchange at the surface, where the low molecular weight species are replaced by higher molecular weight species. For a polydisperse sample the kinetics to attain equilibrium is slow due to this exchange (Figure 11.5a).

Measurement of Polymer Adsorption

Polymer adsorption is most commonly measured through the concentration depletion of a solution after being in contact with the particle surface. Thus, to a solution of known volume and polymer concentration, the particles, for example, latex or pigment, are added. After equilibration, the particles are separated and the polymer concentration in the solution is determined. Problems often occur in the selection of a suitable and accurate analysis method for the polymer. If only qualitative results are sufficient, there is an alternative method through the determination of the electrophoretic mobility of the particles. In electrophoresis, the mobility of the particles in an electric field is determined. This mobility is a measure of the potential at the slipping plane just outside the particle surface. The potential depends on the distance from the particle surface (Figure 11.19a). When a nonionic polymer is adsorbed at a particle surface, the slipping plane will be extended further out from the surface (Figure 11.19a). Thus, a lower absolute electrophoretic mobility, or zeta potential, will be detected (Figure 11.19b). Such measurements are rapidly performed and can serve as a guideline for the interaction between the polymer and the particle surface. The electrophoretic mobility can also be used

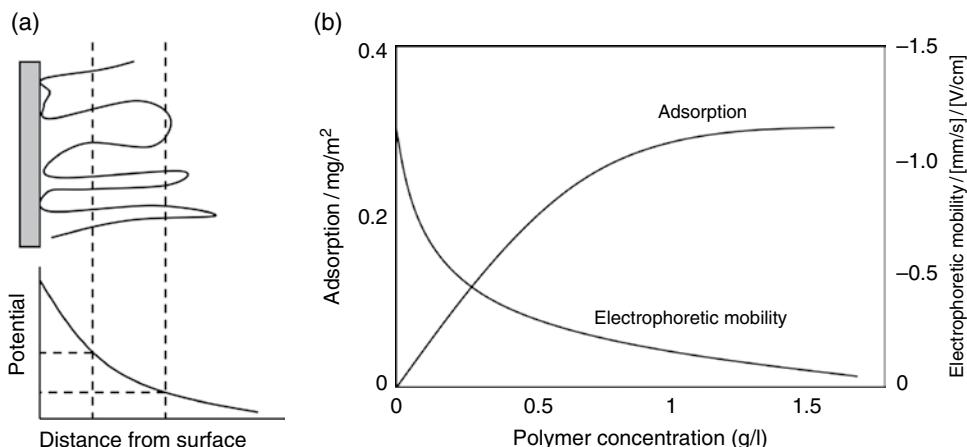


Figure 11.19 (a) Illustrations of how the electrophoretic mobility changes upon addition of a neutral polymer. (b) The adsorbed polymer EHEC shifts the slipping plane out from the surface, thus resulting in a lower electrophoretic mobility. (With permission from Hulden, M. and Sjöblom, E. (1990) Adsorption of some common surfactants and polymers on TiO_2 -pigments. Progress in Colloid & Polymer Science, **82**, 28–37. Copyright Springer Science+Business Media.)

to detect the adsorption of ionic polymers on particle surfaces but care should be taken since the results might not always be unambiguous.

Measurements of polymer adsorption on macroscopic surfaces have the advantage that the adsorption dynamics can be followed (e.g., Figure 11.5a). A major drawback is that the surface-to-volume ratio is low and, consequently, only the adsorption of the higher molecular weight species is measured, as these are preferentially adsorbed. It is necessary, therefore, to have good control of the molecular weight distribution of the sample (Figure 9.2). Polymer adsorption on macroscopic surfaces is conveniently measured by ellipsometry. Here, elliptically polarized light is reflected at the surface at which the polymer adsorbs. The polarization of the reflected light is sensitive to the polymer layer and the method allows both the adsorbed amount and the adsorbed layer thickness to be determined.

Other methods are the Quartz Crystal Microbalance (QCM) and Dual Polarization Interferometry (DPI); these are briefly described in Chapter 8. The surface force apparatus and the atomic force microscope (AFM) have both become powerful tools in determining the polymer extension and lateral distribution at surfaces.

We will here briefly just caution the experimentalist when designing an experiment where the adsorption of polyelectrolytes in salt solution is determined. In these systems, it is important to control the surface-to-volume ratio. The reason is that the counterions in the system are associated with the adsorbed polymer because of the requirement of electro-neutrality. If a salt with a multivalent ion of the same sign as the counterions is added, then multivalent ions will replace the counterions for entropic reasons. For simplicity we call this coadsorption, even though there is no adsorption *per se* of the multivalent counterion. If the adsorption is determined in a system where there is a small surface area available, such as in QCM or DPI measurements, there will be plenty of salt that can coadsorb with

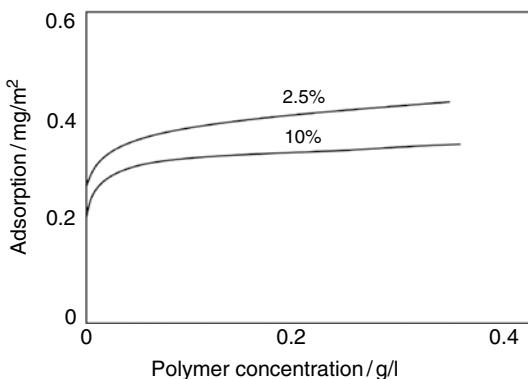


Figure 11.20 Adsorption isotherms of carboxymethylcellulose on kaolin from aqueous solutions containing 0.0033 M CaCl_2 at two different contents of kaolin. (With permission from Järnström, L., Ström, G. and Stenius, P. (1987) The adsorption of dispersing and thickening polymers and their effect on the rheology of coating colors. Tappi Journal, **70**, 101–107. Copyright TAPPI, 1987.)

the polymer. If, however, the adsorption is determined in a system where there is a large surface area available, such as in a dispersion, there is a risk that all the salt in the system is used up in the coadsorption with the polymer and the availability of salt in the system may become a limiting factor for the adsorption. This is illustrated in Figure 11.20 for adsorption of carboxymethylcellulose on kaolin from aqueous solutions containing 0.0033 M CaCl_2 at two different kaolin contents. Here, one finds a lower adsorption at a higher kaolin content, which is due to the fact that the Ca^{2+} ions are used up in the adsorption process, thus leaving a low Ca^{2+} ion concentration in solution.

Concerning the polymer conformation on a surface, the following values for the adsorbed amounts are useful as guidelines. At surface concentrations below 1 mg/m^2 the polymer molecules lie flat on the surface, at concentrations around 3 mg/m^2 the polymers adsorb in a monolayer in a coil conformation, and, finally, at surface concentrations above 5 mg/m^2 the polymer adsorbs as aggregates or multilayers at the surface. These values are, of course, only approximate and it is assumed that the entire surface is available for polymer adsorption.

We conclude this chapter by giving a checklist of relevant parameters in polymer adsorption:

- the molecular weight and molecular weight distribution of the polymer;
- pH;
- polymer charge density;
- ionic strength;
- presence of multivalent ions;
- presence of additives;
- surface-to-volume ratio;
- temperature.

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12

Surface and Interfacial Tension

The surface tension of liquids causes the formation of drops and is related to the attractive forces between the molecules (Figure 12.1a). These attractive forces are the source of condensation of vapors into liquids and they originate from dispersion, dipole–dipole, dipole-induced dipole forces, and hydrogen bonding among others. In the bulk liquid, a molecule senses the same attractive forces in all directions, whereas for a molecule at the surface this attraction is lacking in one direction. This asymmetry is the origin of the surface energy and is manifested in the surface tension. Hence, the surface tension is a reflection of the cohesive forces in a liquid.

A second, and a physically more correct, molecular explanation for the surface tension is depicted in Figure 12.1b. Close to the surface the molecules are at larger separations and, hence, they have a larger energy, as depicted in the energy versus distance diagram in Figure 12.1c. Also in this molecular picture, the surface tension correlates with the cohesive energy of the liquid.

Examples of the surface tension for some neat liquids are shown in Table 12.1. The surface tension is expressed in units of dyn/cm or mN/m. Fortunately, the conversion factor is unity in going from one unit to the other, so they can be used interchangeably. Since the surface tension is equivalent to a surface energy, or to be more correct, a surface free energy, the surface tension can also be expressed in energy units, erg/cm² or mJ/m², again also with a conversion factor of unity. From Table 12.1, we note that the surface tension correlates with the cohesion energy in the liquid as reflected in the solubility parameter (Chapter 9), where diethyl ether has the smallest and mercury the largest cohesion energy.

The cohesion energy is, in turn, a function of the strength of the dispersion forces in the liquid, as exemplified by comparing the surface tension of chloroform and bromoform; the latter is a more polarizable molecule and shows a higher surface tension. The cohesion

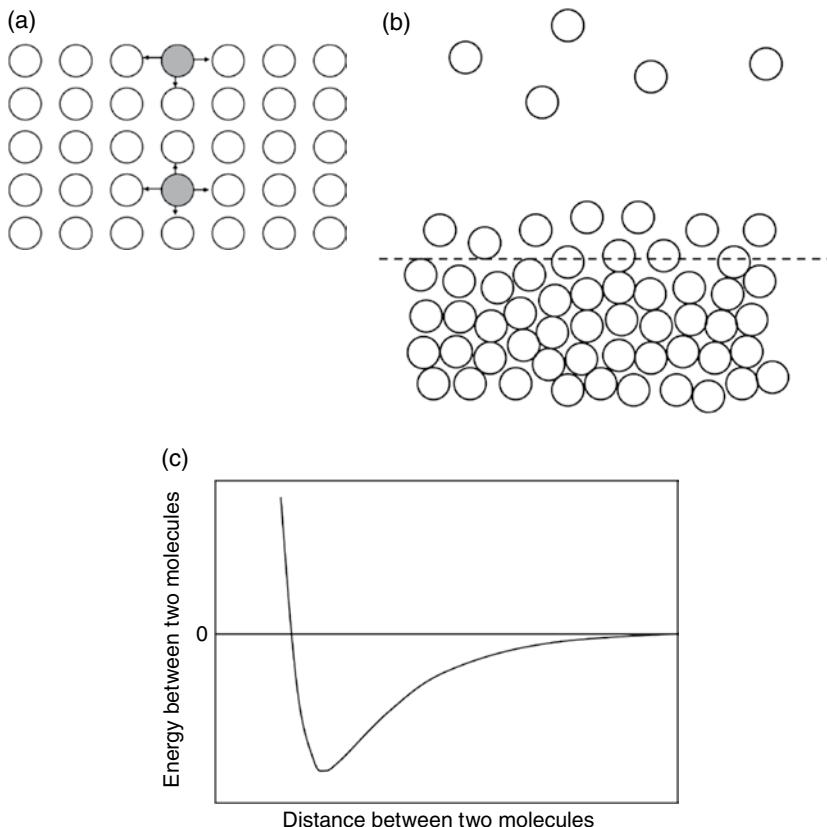


Figure 12.1 (a) The origin of the surface tension is found in the imbalance of the attractive forces on a molecule at the surface. (b) Close to the surface the molecules are at larger separations and hence they have a higher energy, (c) as depicted in the energy versus distance diagram

Table 12.1 Surface tension (in mN/m) of some neat liquids at 25°C

Water	72
Ethanol	22
Chloroform	27
Bromoform	45
<i>n</i> -Hexane	18
<i>n</i> -Octane	22
<i>n</i> -Dodecane	25
<i>n</i> -Hexadecane	27
Diethyl ether	17
Mercury	480

energy is also correlated with the free volume in the liquid, which is realized when comparing the surface tension of the series of normal alkanes. The higher the free volume, then the lower the cohesion energy and, hence, the lower the surface tension. The relationship between the surface tension and the cohesive forces in the liquid, as described by the solubility parameter, (δ) (Chapter 9) is:

$$\gamma = C \delta^2 V^{1/3} \quad (12.1)$$

where V is the molar volume of the liquid and C is a constant.

The Surface Tension of Droplets Increases their Pressure

Thomas Young and Pierre-Simon Laplace first formulated a very important effect of the surface tension in 1806. The surface tension of a drop tends to shape the drop into a sphere, as this is the form of lowest surface energy. In fact, the surface tension pushes the fluid inwards such that the pressure inside the drop increases. The energies emerging from the two opposing forces are:

Surface energy:

$$E = \gamma 4\pi r^2 \quad (12.2a)$$

Pressure–volume energy:

$$E = \Delta p \frac{4\pi}{3} r^3 \quad (12.2b)$$

An incremental change of the drop radius affects both these quantities to the same extent, leading to the Young–Laplace equation:

$$\Delta p = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right). \quad (12.3)$$

where r_1 and r_2 are the two radii of the drop (for a spherical drop $r_1=r_2$). The Laplace equation reveals that the pressure increases as the drop size decreases. Hence, whenever there is a distribution of drops the pressure is largest for the smallest drops, implying that these will evaporate first. Equation 12.3 forms the basis of Ostwald ripening (p. 353), which has implications on the stability of both emulsions and foams as well as in particle formation, as will be discussed in Chapters 24, 23 and 21, respectively.

Surface Tension is Related to Adsorption

In aqueous systems, an added component affects the surface tension in one of three different ways (Figure 12.2). Organic water-soluble materials, such as ethanol, normally decrease the surface tension monotonically with increasing concentration. This is due to a preferential

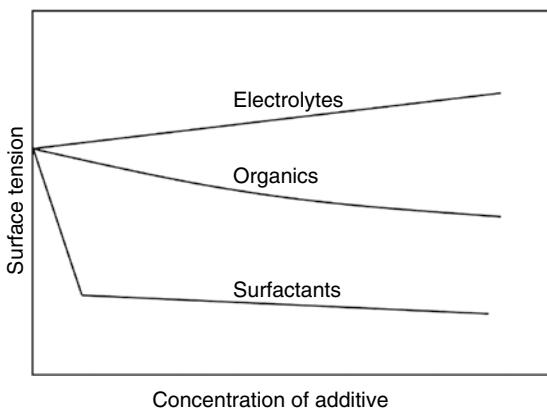


Figure 12.2 In aqueous systems, an added component affects the surface tension in one of three different ways

adsorption of the organic molecules at the liquid–air surface. The preferential adsorption of the component with the lower surface tension is the reason why the surface tension of a solution is always lower than the arithmetic mean of the surface tensions of the pure components (e.g., Figure 12.9a).

Electrolytes normally increase the surface tension. The reason is that the electrolytes are depleted from the surface, that is, there is a negative adsorption of the ions at the surface. Not only electrolytes are depleted from the surface. Very hydrated molecules, such as sucrose and glucose, also give a positive increment to the surface tension.

Surfactants show a large reduction in surface tension at very low concentrations up to the critical micelle concentration (CMC), above which the surface tension is practically constant. This large reduction in surface tension is due to a strong adsorption of the surfactants at the surface. At concentrations higher than the CMC, all additional surfactant forms new micelles, thus keeping the surfactant unimer activity constant. Therefore, the surface tension will not change with surfactant concentration above the CMC.

A thermodynamic treatment of surface tension (γ) leads to the following expressions for the surface tension:

$$\gamma = \gamma_w^o + \frac{kT}{A_w} \ln \frac{a_w^s}{a_w^b} \text{ or } \gamma = \gamma_s^o + \frac{kT}{A_s} \ln \frac{a_s^s}{a_s^b} \quad (12.4)$$

Here a_w^s and a_w^b are the activities of water and a_s^s and a_s^b are the activities of the surfactant in the surface and bulk phases. The constant A_i represents the molecular cross-sectional area and can be estimated from:

$$A_i = \left(\frac{V_i}{N} \right)^{2/3} \quad (12.5)$$

V_i is the molar volume and N is the Avogadro number. Inspection of Equations 12.4 reveals that a change in the surface tension does not necessarily imply that the surface has

changed. It could also be a reflection of a change in the bulk solution. Aqueous mixtures of inorganic electrolytes are examples of this. Here, the electrolyte has no affinity for the surface and, hence, is accumulated in the bulk solution, thus decreasing the activity of the water, causing the surface tension to increase according to Equations 12.4. Likewise, if the surface tension is not changed upon the addition of a second component, it cannot be concluded that the solute does not adsorb at the surface. Equations 12.4 reveal that the addition of a second component might well lead to a situation where the surface tension is not changed when the solute partitions equally between the surface and the bulk, that is, $a_i^s / a_i^b = 1$.

Eliminating the solution surface tension in Equations 12.4, we find an expression for the adsorption isotherm, that is, a relationship between the surface composition and the solution composition:

$$\ln\left(\frac{a_s^s}{1-a_s^s}\right) - \ln\left(\frac{a_s}{1-a_s}\right) = \left(\frac{a(\gamma_w^o - \gamma_s^o)}{kT}\right) \quad (12.6)$$

At low surfactant concentrations, this is identified as the Langmuir equation (Equation 8.5), with the Langmuir constant as:

$$K = \exp\left(\frac{a(\gamma_w^o - \gamma_s^o)}{kT}\right). \quad (12.7)$$

As we have seen in Chapter 8, the adsorption of surfactants can be described in terms of the Langmuir equation, Equation 8.5.

In discussing the adsorption of a surfactant it is first necessary to define the surface. This was first done by Gibbs, who identified the surface to be the position where the solvent concentration is half between that in the solvent and in the vapor. The adsorption of a surfactant is normally written as $\Gamma^{(1)}$, where (1) indicates that the surface, and hence the adsorption is defined by the solvent. We will here, however, use the symbol Γ .

The adsorption is related to the surface tension through the Gibbs equation:

$$\Gamma = -\frac{1}{nRT} \frac{d\gamma}{d \ln a} \quad (12.8)$$

Here a is the activity of the surfactant in the bulk solution and n is a constant. Since the surfactant concentration in bulk solutions below the CMC is normally very low, the surfactant activity can be replaced by the surfactant concentration (C). Hence, the surfactant adsorption is obtained from the slope of a plot of the surface tension versus the logarithm of the concentration. The factor n in the denominator has a value of one for a surfactant that does not dissociate, that is, nonionic surfactants. For ionic surfactants it has a larger value. This is discussed further below. Assuming monolayer adsorption, we realize that the adsorbed amount is inversely proportional to the cross-sectional area per adsorbed molecule (A). The relationship is given in Equation 8.1.

The Surface Tension of Surfactant Solutions

The surface tension decreases with surfactant concentration as is shown in Figure 12.3. The figure reveals two interesting features. The first is that the surface tension is constant above the CMC. The reason for this is that the unimer activity of the surfactant is constant above the CMC. Hence, the break in surface tension is not a reflection of something happening at the surface but rather in the solution. Secondly, the slope of the curve is constant just below the CMC. Therefore, according to Equation 12.8, the adsorption is constant. We would like to emphasize that it is sometimes wrongly suggested that the surface tension after the CMC is constant due to a saturation of the surface with surfactant. The saturation of the surface occurs below the CMC according to Equation 12.8 when the graphs have the look as in Figure 12.3. As stated above, the constant surface tension after the CMC is due to a constant unimer activity.

Conventionally there are two terms to describe the curve in Figure 12.3. The first term is the *efficiency* of the surfactant, that is, how much surfactant is needed to achieve a certain surface tension reduction. By convention this is set to 20 mN/m and the surfactant concentration for this surface tension is denoted by C_{20} . The second term is the *effectiveness* of the surfactant and is defined as the surface tension reduction at the CMC, that is, $\gamma_w^o - \gamma_{CMC}$.

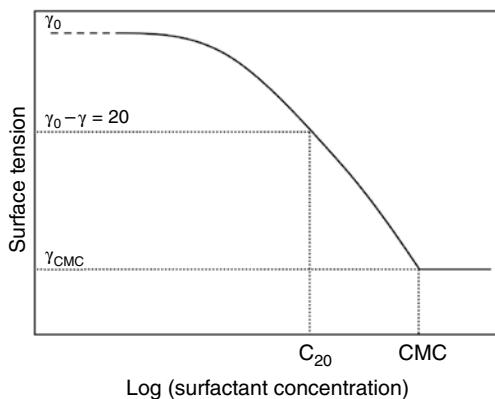


Figure 12.3 Surface tension versus the logarithm of surfactant concentration

Nonionic Surfactants

Figure 12.4 shows the surface tension of aqueous solutions of a series of medium-chain alcohols. The curves have the same slope, indicating that the adsorption, or surface excess, is the same irrespective of the chain length of the alcohol according to Equation 12.8. Note the asymptotic linearity of the curves at high concentrations, that is, the lower part of the curves, indicating a constant adsorption according to Equation 12.8. The identical slopes of the curves in Figure 12.4 therefore imply that the alcohols have the same surface area per molecule, irrespective of their chain length. This is in accordance with a molecular ordering at the interface, where the polar part is directed towards the water and the nonpolar hydrocarbon chain is directed towards the air.

The value of A obtained from Figure 12.4 is $27\text{--}28\text{\AA}^2/\text{molecule}$ (corresponding to $\Gamma=5.9\text{--}6.1\text{ }\mu\text{mol/m}^2$), independent of the chain length of the alcohol. This corresponds to a limiting value due to close packing at a steep angle to the surface. Hence, adsorption reaches a limiting value due to *steric restriction*.

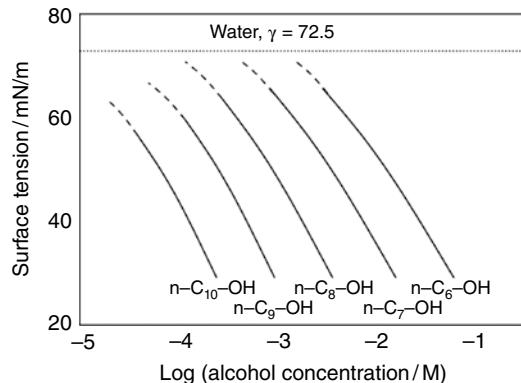


Figure 12.4 Surface tension versus concentration for aqueous solutions of a series of medium-chain alcohols

Like the medium-chain alcohols, surfactants adsorb at the surface with their polar parts directed towards the aqueous solution and the hydrocarbon parts directed towards the air. Figure 12.5 shows the surface tension versus surfactant concentration of four n-alkyl- β -D-maltosides, that is, nonionic surfactants with two glucose rings. The figure clearly demonstrates that both the efficiency and the effectiveness increase with the alkyl chain length. As for micellization, an increase with two carbon atoms in the alkyl chain increases the efficiency by an order of magnitude. Note also how the slope approaches a constant value at concentrations up to the CMC, indicative of a constant adsorbed amount.

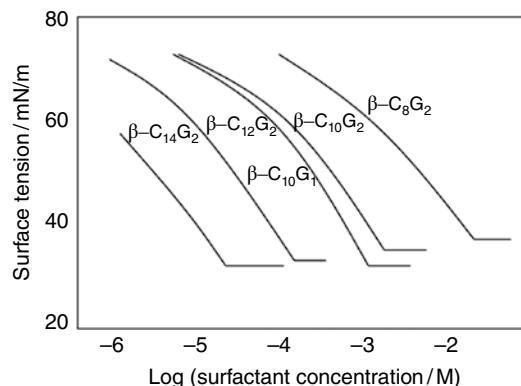


Figure 12.5 Surface tension versus surfactant concentration for four n-alkyl- β -D-maltosides. (With permission from Varga, I., Mészáros, R., Stubenrauch, C. and Gilányi, T. (2012) Adsorption of sugar surfactants at the air/water interface. Journal of Colloid and Interface Science, **379**, 78–83. Copyright Elsevier.)

Figure 12.6 shows some surface tension data obtained for the nonionic series $C_{16}E_n$. The surfactants with shorter polyoxyethylene chains pack better at the liquid–air interface, as seen by their steeper slopes at concentrations just below the CMC. We also note that the effectiveness is higher, that is, the surface tension at and above the CMC is lowered, as the polyoxyethylene chains are shortened. The effect on the CMC is rather small, however.

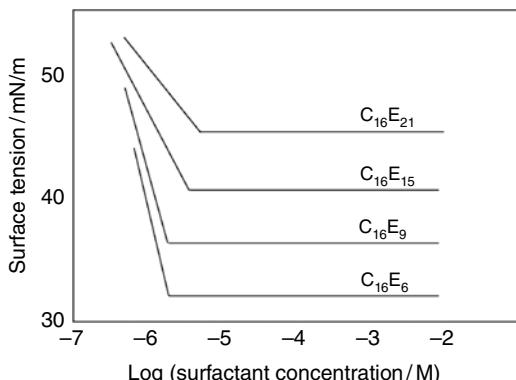


Figure 12.6 Surface tension data for the nonionic series $C_{16}E_n$ with the indicated values of n . (With permission from Elworthy, P.H. and MacFarlane, C.B. (1962) Surface activity of a series of synthetic nonionic detergents. *Journal of Pharmacology and Pharmacotherapeutics*, **14**, 100T–102T. Copyright 2011, John Wiley & Sons.)

Figure 12.7 shows the temperature dependence of the surface tension for $C_{12}E_6$. As the temperature is increased, the polyoxyethylene chain compresses. The figure shows that this results in a higher effectiveness, that is, a lowering of the surface tension, as well as of the CMC. Careful analysis also shows that the adsorption at concentrations below the CMC increases with temperature, that is, the surface area per molecule decreases with temperature.

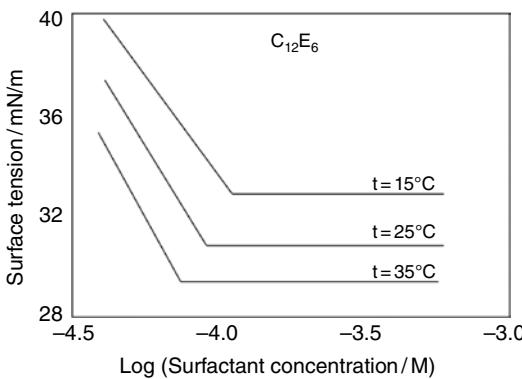


Figure 12.7 Temperature dependence of the surface tension from solutions of $C_{12}E_6$. (Reproduced from Corkhill, J.M., Goodman, J.F. and Ottewill, R.H. (1961) Micellization of homogeneous nonionic detergents. *Transactions of the Faraday Society*, **57**, 1627–1636 with permission of The Royal Society of Chemistry.)

Ionic Surfactants

Also for ionic surfactants the surface tension becomes constant at the CMC. This is due to a constant unimer concentration at higher concentrations. However, ionic surfactants differ from nonionic surfactants in that the limiting value of the adsorption just below the CMC is not limited by steric restriction but rather *electrostatic restriction* due to the entropy of the counterions. In the bulk solution the surfactant is totally dissociated, hence the counterions lose entropy when the unimers adsorb at the surface (counterion binding). This entropy loss is higher the larger the surface charge density, that is, the higher the adsorption (Figure 3.2). A limiting adsorption is reached when this loss in entropy balances the driving force for adsorption. This limiting adsorption does not correspond to a close packing of the surfactant as for nonionic surfactants, that is, as in steric restriction, but is determined by the entropy loss of the counterions.

For monovalent ionic surfactants the constant n in Equation 12.8 ideally has a value of two, since the surfactant contains two species, namely the surfactant ion and the counterion. However, due to the constriction of electroneutrality, the counterion is not free to move around in the bulk solution, which means that this value is in reality less than two. If the counterion is bound to the amphiphile, as in a zwitterionic surfactant, the value of n would be one. Therefore n could have any value between one and two for a 1:1 surfactant. For a divalent surfactant with two monovalent counterions the maximum value of n is three. As electrolyte is added the effect of counterion binding diminishes and the value of n approaches one. In reality it is, therefore, difficult to assign a reliable value of n of Equation 12.8, which means that there are considerable ambiguities in the use of Gibbs equation for assessing the value of area per molecule at the air–water interface for ionic surfactants.

In addition to the problem of ascribing a correct value of n in Gibbs equation, several other factors contribute to uncertainties in calculating area per molecule from the slope of the surface tension versus log surfactant concentration curve for ionic surfactants. First of all, the surface tension measurements are strongly affected by traces of divalent ions and it is often difficult to obtain surfactant solutions totally free of multivalent ions. Secondly, the adsorption does not generally reach saturation at the CMC. Thirdly, the surface tension curve is often not linear below the CMC and the break on the curve is often not sharp. Taken together, the values reported in the literature for area per molecule for ionic surfactants, based on surface tension data, should be treated with caution. More recent calculations based on neutron reflection data are probably more accurate. Based on such data it has been reported that the adsorption of sodium dodecyl sulfate (SDS) at the air–water interface increases far beyond the CMC. At $10 \times \text{CMC}$ the adsorbed amount at the surface is 25% greater than at the CMC and about the same as at the CMC in a 0.1 M NaCl solution.

Figure 12.8 shows the surface tension of an alkyl ether sulfate at various salt concentrations. This figure shows that with increasing salt content, (i) the CMC decreases and hence the efficiency increases, (ii) the effectiveness increases, and (iii) the slope of the curves just below the CMC increases, indicating that the adsorption increases, according to Equation 12.8. Adding salt will decrease the entropy loss on adsorption due to the binding of the counterions. This will result in an adsorption with a limiting value at higher surface charge, that is, at a higher adsorption as well as a lower CMC (Chapter 3). Hence, there is a smaller effective cross-sectional area per surfactant head group as salt is added.

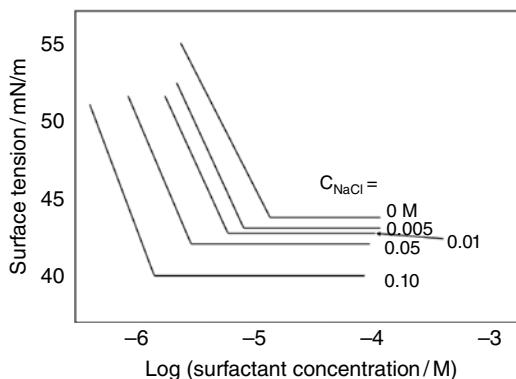


Figure 12.8 Surface tension of $C_{16}E_5SO_4^- Na^+$ at various salt concentrations. (With permission from Attwood, D. (1969) The effect of electrolyte on the micellar properties of an anionic-nonionic detergent in aqueous solution. *Kolloid-Zeitschrift & Zeitschrift für Polymere*, **232**, 788–792. Copyright 2011, John Wiley & Sons.)

Divalent ions have large effects on the surface tension of monovalent surfactants. As discussed previously, when a divalent ion replaces two monovalent counterions, there is a decrease in entropy. Hence, for example, Ca^{2+} ions have strong effects on the surface tension measurement of anionic surfactants. It is, therefore, necessary to make sure that the solutions are free of multivalent ions before measuring surface tension.

Dynamic Surface Tension

Dynamic surface tension is the change in surface tension before equilibrium conditions are attained. Dynamic surface tension is important in many technical processes, such as detergency, foaming, emulsification, wetting, and printing. Here, the equilibrium surface tension will never be attained, so characterization of such systems using equilibrium surface tension is not meaningful. Therefore, it is pertinent to take a closer look at the development of surface tension with time for aqueous surfactant solutions.

At the instant when a new liquid/air surface is formed, the surface composition is the same as the bulk composition and the surface tension is equal to the arithmetic mean of the surface tensions of the neat components. For a surfactant solution this is almost pure water, since surfactant solutions are normally very dilute. At equilibrium, the component with the lower surface tension preferentially adsorbs at the surface and, therefore, the surface tension of the solution is lowered. This process is time dependent and depends on the diffusion of the components as well as the adsorption process.

An example is shown in Figure 12.9a for the water–ethanol system. If a new surface suddenly is created in this system at a solution composition of 40% alcohol, for example, the surface tension will be equal to the arithmetic mean between the two pure component surface tensions. Due to the preferential adsorption of the alcohol, the surface tension is lowered to the equilibrium value, as shown by the arrow in the figure.

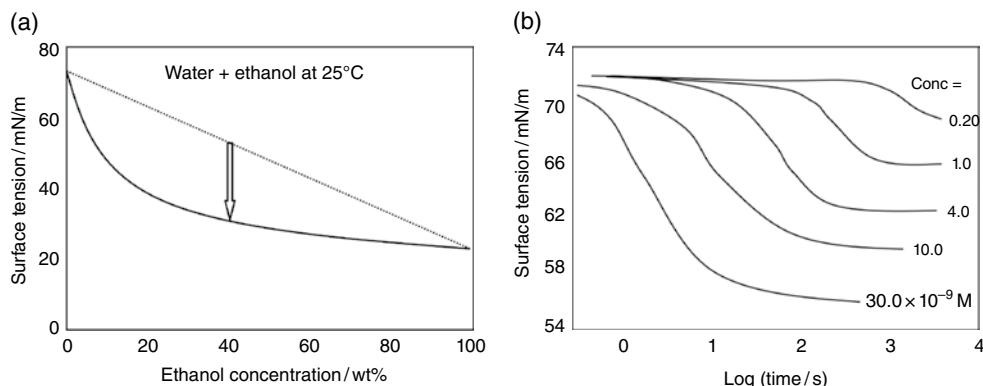


Figure 12.9 The dynamic surface tension is the change from the arithmetic mean of the surface tensions of the pure components to the equilibrium surface tension, shown here for (a) the system water–ethanol. After the formation of a new surface, the system relaxes to the equilibrium surface tension due to adsorption of the more surface active species as illustrated (b) by the dynamic surface tension of $C_{10}E_8$ in water at various concentrations, illustrating that the equilibrium surface tension is attained faster for higher concentrations. (With permission from Adamson, A.W. and Gast, A.P. (eds) (1997) *The surface tension of solutions*, in *Physical Chemistry of Surfaces*, 6th edn, John Wiley & Sons, Inc, New York, pp. 65–71. Copyright 1997, John Wiley & Sons, and Chang, H.C., Hsu, C.T. and Lin, S.Y. (1998) Adsorption kinetics of $C_{10}E_8$ at the air–water interface. *Langmuir*, **14**, 2476–2484, Copyright 1998, American Chemical Society.)

The time dependence of the surface tension of a surfactant solution normally follows a path depicted in Figure 12.9b, showing the dynamic surface tension of $C_{10}E_8$ at various concentrations. Here, the surface tension at the limit of infinitely short times is close to that of pure water. Note that the required time to approach equilibrium drastically decreases with surfactant concentration.

When a fresh surface is created two processes are initiated. One is a transport of surfactant to the surface, which is driven by the concentration gradient of the surfactant. The other is the adsorption at the interface and includes the transfer of surfactant from the subsurface to the surface. It could also include reorientation of surfactant molecules at the surface. In surfactant solutions this second step, that is, the adsorption, is generally much faster than the first, hence the dynamic surface tension is diffusion limited. In polymer solutions, however, this second step is rate determining. Polymers might take a very long time (of the order of hours) to reach equilibrium at any surface.

A very important side effect in using surfactant mixtures is the behavior of the dynamic surface tension. In those cases where the two surfactants differ in their CMC, such as in mixing an anionic and a nonionic surfactant, the more hydrophobic surfactant is normally present in lower concentrations. Hence, it will take a longer time to diffuse to the surface. On the other hand, it is more surface active and will, therefore, displace the other surfactant from the surface. With time the composition at the surface will consequently change from being dominated by the more hydrophilic surfactant to being dominated by the more hydrophobic surfactant.

The diffusion of the surfactant to the surface is not the only reason for the surface tension to change with time. Another very common reason is the presence of surface active impurities and the fact that technical surfactants are not single species but rather a mixture of homologues. For example, nonionic surfactants, which have a very wide distribution in polyoxyethylene chain length, show long equilibrium times due to the presence of hydrophobic homologues that are more surface active and present in low concentrations.

Impurities in Surfactant Samples can Play a Major Role

Hydrophobic Impurities

Figure 12.10 shows a schematic plot of surface tension versus the logarithm of the surfactant concentration of an ionic surfactant containing a hydrophobic impurity. A classic example is SDS in water, where dodecyl alcohol is formed by hydrolysis of the SDS molecules. The minimum in surface tension is due to the presence of a hydrophobic impurity, more surface active than the ionic surfactant. It is, therefore, preferentially adsorbed at the surface, lowering the surface tension. When micelles form in the solution, however, the hydrophobic molecules solubilize in the micelles and desorb from the surface, which leads to an increase in the surface tension. Therefore, whenever a minimum in surface tension versus surfactant concentration is found, the conclusion is that the surfactant sample contains an impurity that is more surface active than the surfactant itself.

Two important observations are made for such systems. The first is that the surface tension will usually decrease slowly over a very long period (hours) before equilibrium is attained. This is because the impurity is normally present in very low concentrations and the diffusion from the bulk to the surface is the rate determining factor. The other observation is that the equilibrium surface tension depends on the surface-to-volume ratio of the sample. The larger the bulk volume, then the more impurity is available for the adsorption at the liquid-air interface, and hence the lower the surface tension.

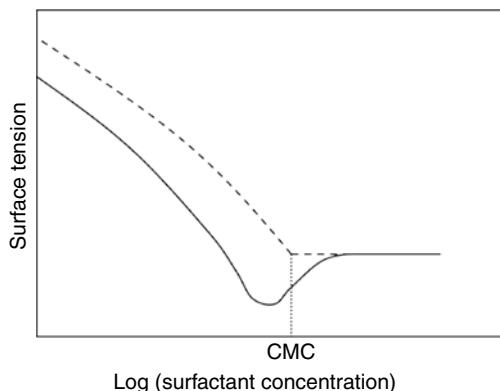


Figure 12.10 Surface active impurities in a surfactant sample cause a minimum in the surface tension versus surfactant concentration curve

Determining the CMC of surfactants with a surface active impurity, or mixtures of surfactants with a large difference in their CMCs, using the equilibrium surface tension is, therefore, not recommended. Such samples are better characterized by measurements of the CMC using bulk properties, such as the conductivity or light scattering.

Hydrophilic Impurities

Technical nonionic surfactants of the polyoxyethylene type usually contain a non-negligible amount of poly(ethylene glycol) (PEG), a byproduct from the ethoxylation when the starting fatty alcohol is not completely dry. PEG has very weak surface activity, however, and does not much affect the physicochemical behavior of the surfactant. The same is true for other very water-soluble organic compounds, such as glucose and other sugars.

Surface Tension of Polymer Solutions

The surface tension of polymer solutions can be regulated in two ways. The first is through variation in the molecular weight (M_w). We have seen in Chapter 11 that the tendency to adsorb at surfaces increases with molecular weight. The reasons behind this phenomenon are discussed in Chapter 11. The second parameter that influences the surface tension is the solution properties. These two parameters are exemplified below.

The surface tension of PEG solutions is shown in Figure 12.11, showing that higher M_w PEGs lower the surface tension more efficiently than lower M_w PEGs. The reason for this phenomenon is found in a lower solubility due to entropy effects (Chapter 9) of the higher M_w samples. The figure shows that for the higher M_w samples, the solution surface tension drops very quickly at low polymer concentrations. This is due to the poor interaction between the polymer and the solvent. As discussed in Chapter 9, the solubility of a polymer

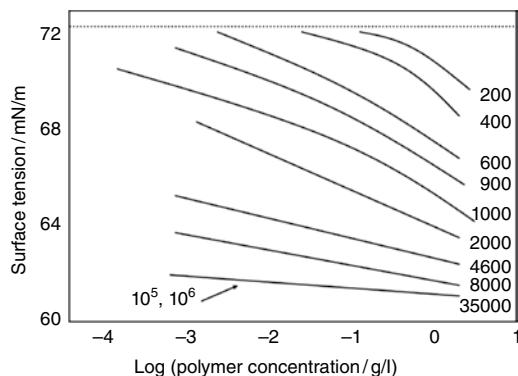


Figure 12.11 Surface tension of solutions of poly(ethylene glycol) of various molecular weights, showing that the higher M_w polymers lower the surface tension to a larger degree. (With permission from Gilányi, T., Varga, I., Gilányi, M. and Mészáros, R. (2006) Adsorption of poly(ethylene oxide) at the air/water interface: a dynamic and static surface tension study. Journal of Colloid and Interface Science, 301, 428–435. Copyright Elsevier.)

decreases as the molecular weight increases. Thus, the higher molecular weight polymers are “pushed out” towards the surface where the number of solvent–polymer segment contacts are less than in the solution. Due to the low solubility of the higher molecular weight species, much of the polymer is found at the surface, hence the surface tension is drastically lowered. This general phenomenon has, in the literature, sometimes been mistaken for a micellization of the polymer, since the surface tension curves somewhat resemble those of micellar solutions.

A second illustration of how the surface tension is influenced by solution properties combined with the macromolecular nature is taken from the adsorption of poly(methacrylic acid) from aqueous solution (Figure 12.12). As a model for the monomer unit, isobutyric acid is used. Firstly, we stipulate that it is the nonionized species that are surface active, that is, which adsorb at the liquid–air interface. Thus, at zero degree of ionization the surface tension, which is a reflection of the degree of adsorption, has the lowest possible value for both the polymer and the monomer systems. The surface tension has its highest possible value at very high degrees of ionization.

Figure 12.12a shows that the surface tension of isobutyric acid solutions increases linearly with the degree of ionization. However, for the polymer system the surface tension makes a jump at a degree of ionization of about 0.1. The reason for this jump is found in the polymeric nature of the system. When the degree of ionization is increased, some segments of the adsorbed polymer are ionized. However, the nonionized segments are still in sufficient amounts to keep the polymer at the surface. At a critical degree of ionization the whole polymer will leave the surface, thus causing the jump in surface tension seen in Figure 12.12a. An analogy is shown in Figure 12.12b where corks (nondissociated monomers or segments) float on water and where weights are hung on to the corks (dissociation process), pulling them down into the liquid. However, when the corks are connected by a

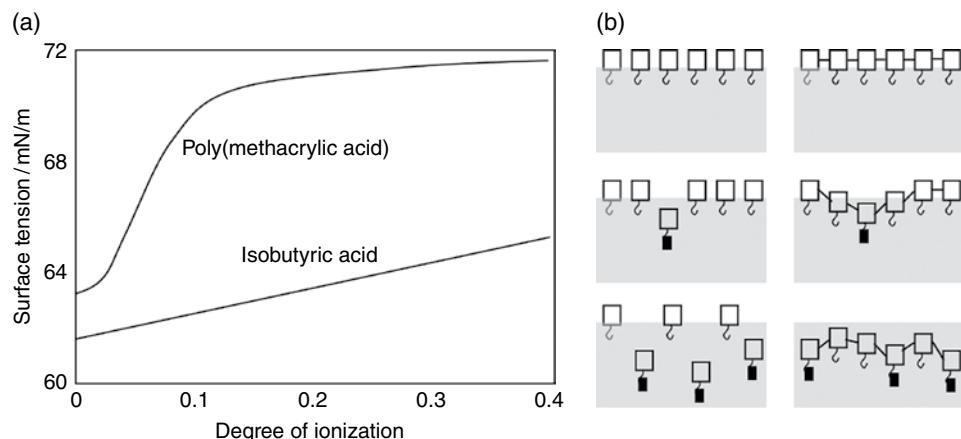


Figure 12.12 (a) Surface tension of poly(methacrylic acid) and isobutyric acid as a function of the degree of ionization. (b) An analogy using corks and weights, illustrating the adsorption of monomers and polymers at an interface. (With permission from Katchalsky, A. and Miller, P. (1951) The surface activity of polymeric acids in aqueous solutions. *Journal of Physical Chemistry*, **55**, 1182–1194. Copyright 1951, American Chemical Society.)

string (a polymer) all corks will float until a critical weight (critical degree of dissociation) is reached, whereupon the surface will be free of corks.

Interfacial Tension

The interfacial tension is the surface free energy of the interface between two immiscible, or poorly miscible liquids. The reason for immiscibility is the large difference in cohesion forces between the molecules in the two liquids. Thus, at the interface there will be a net force, as depicted in Figure 12.13. The larger the difference in cohesion forces, the larger the interfacial tension. If this difference is small enough, however, the two liquids will mix.

The units of interfacial tension are the same as for surface tension. Besides being dependent on the difference in cohesion forces, the interfacial tension also depends on the specific interactions between the molecules in the two liquids. Water/octane, for example, has an interfacial tension of 51 mN/m, whereas water/octanol has an interfacial tension of only 8 mN/m. Clearly, the hydroxyl group of octanol faces the aqueous phase and thus reduces the interfacial tension considerably. It is this phenomenon that is utilized in surfactant molecules, having one very polar part and one nonpolar part, thus reducing the interfacial tension between organic liquids and water.

Numerous attempts have been made to predict the interfacial tension from knowledge of the surface tensions of the two liquids. Using solution thermodynamics it can be shown that the interfacial tension is directly proportional to the χ parameter, which is a measure of the antipathy between the two types of molecules. Thus, for liquid pairs with a large antipathy the interfacial tension is large, as, for example, in the water–alkane system. If the liquid pairs are made more compatible, then the interfacial tension will decrease and eventually become zero. This occurs at the critical miscibility point. Addition of a surfactant drastically reduces the interfacial tension. However, the situation is more complicated than at the air–water interface because the surfactant now partitions, not only between the bulk aqueous

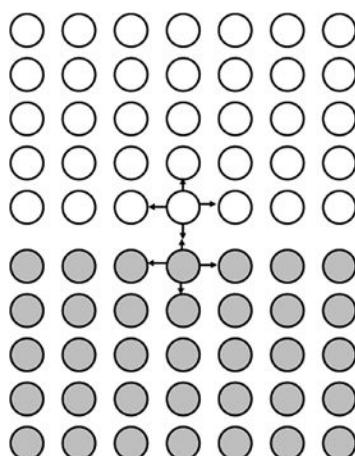


Figure 12.13 As for the surface tension, the interfacial tension originates from an imbalance of the attractive forces on molecules at the interface

phase and the interface but also between the aqueous and the organic phases. The latter partitioning is one of the most fundamental issues in the formulation of emulsions and microemulsions. Figure 12.14 shows the effect of adding Triton-X100 (octylphenol with 9.5 oxyethylene units) on the interfacial tension between water and hexane. The similarity with the situation at the air–water interface is obvious. This surfactant is almost insoluble in hexane, hence there are no complications with surfactant partitioning into the oil phase. The Gibbs adsorption equation (Equation 12.8) can be applied also to the interfacial tension.

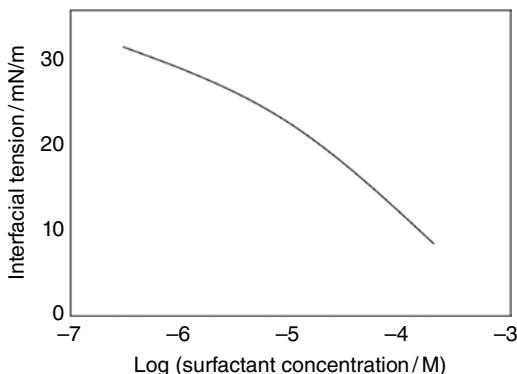


Figure 12.14 Interfacial tension of the water–hexane interface as a function of surfactant concentration (octylphenol- $E_{9.5}$). (With permission from Liggieri, L., Ravera, F. and Passerone, A. (1995) Equilibrium interfacial tension of hexane/water plus Triton X-100. *Journal of Colloid and Interface Science*, **169**, 238–240. Copyright Elsevier.)

In the case that the surfactant is soluble in both phases, we need to care about the partitioning coefficient, that is, the relative affinity of the surfactant for the two phases. This is illustrated in Figure 12.15, where the interfacial tensions for a number of water–*n*-octane– C_mE_n systems are plotted versus temperature.

At lower temperatures the surfactants have a higher affinity for the aqueous phase. As discussed in Chapter 7, the affinity for the aqueous phase is reduced with temperature. At the same time the affinity for the organic phase increases with temperature. Hence, the surfactant shifts from preferentially being in the aqueous phase at low temperatures to preferentially being in the organic phase at high temperatures. At one point the surfactant is equally partitioned between the two phases and this is where the interfacial tension is at minimum.

Besides the issue of relative affinity, the surfactant can be pushed to the interface by reducing its affinity, or solubility, in both phases. This will cause a drastic lowering of the interfacial tension, as is illustrated in Figure 12.15. As both the hydrocarbon length and the polyoxyethylene chain increase the surfactant becomes less soluble in both phases, resulting in a dramatic lowering of the interfacial tension (note the logarithmic scale of the surface tension).

We therefore conclude that the art of attaining a low interfacial tension with a surfactant system is to assure that (i) the surfactant partitions equally between the aqueous and organic phases, and (ii) the surfactant has a low affinity for both phases. These two criteria are required for the formation of microemulsions, which are formed around the point of minimum surface tension but at high surfactant concentrations, as will be discussed in

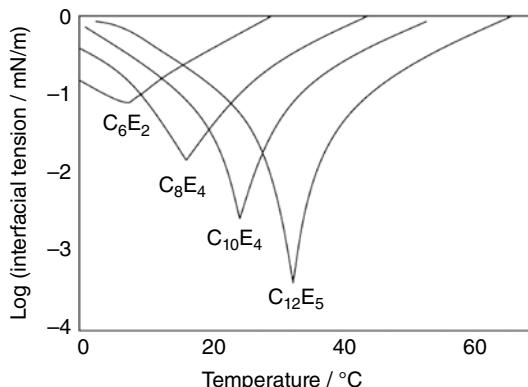


Figure 12.15 Interfacial tension of some water–n-octane–C_mE_n systems versus temperature. (With permission from Sottmann, T. and Strey, R. (1997) Ultralow interfacial tensions in water–n-alkane–surfactant systems. Journal of Chemical Physics, **106**, 8606–8615. Copyright 1997, AIP Publishing LLC.)

Chapter 17. For the formation of microemulsions there is also a third criterion, which is to assure a flexibility of the interfacial film in order to prevent the formation of liquid crystalline phases.

Measurement of Surface Tension

Equilibrium Surface Tension

A simple method to measure surface tension is by using the du Noüy ring. Here, a platinum ring is submerged in the liquid and the force that is required to pull the ring through the surface is measured (Figure 12.16a). Instead of a ring, a platinum plate can be used. The downward pull depends on the contact angle of the liquid towards the plate (Figure 12.16b). A very simple method to estimate the surface tension is to measure the capillary rise (Figure 12.16c). The height of the capillary rise (h) is directly proportional to the surface tension (γ) according to the equation $\gamma = r\rho\text{g}/2$, where r is the capillary radius, ρ the density of the liquid, and g the gravitation constant. This equation is only valid for liquids that perfectly wet the capillary surface, that is, the contact angle of the liquid towards the capillary surface should be zero.

Some systems have a very long relaxation towards equilibrium, hence surface tension measurements take a very long time to complete. This is, for example, the case with polymers in solution. Here the pendant drop (Figure 12.16d) is a suitable method to use. The shape of the drop is a measure of the surface tension; drops that are close to spheres are formed from liquids with a high surface tension whereas elongated drops are formed from liquids with a low surface tension. This method is also suitable for measurements of the interfacial tension between two mutually insoluble liquids.

Very low interfacial tensions are measured by the spinning drop method where a rotating tube contains the densest fluid. A drop of the less dense fluid is immersed and the shape of the drop is assessed as a function of the spinning speed. This method is frequently used to

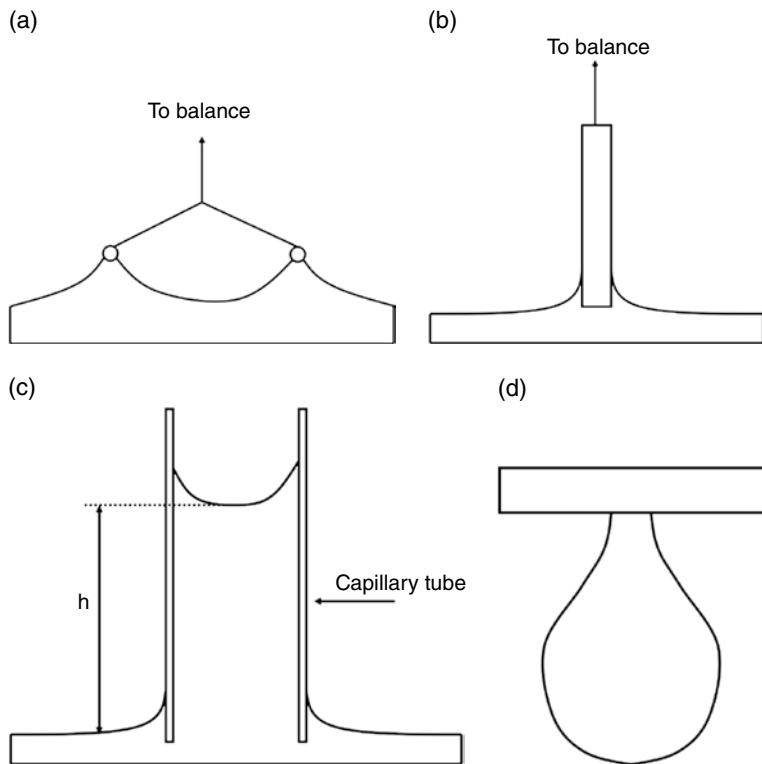


Figure 12.16 Surface tension can be measured by (a) the du Noüy method, (b) the Wilhelmy plate method, (c) the capillary rise method, or (d) the pendant drop method

measure the extremely low interfacial tensions that may be obtained between the phases in microemulsion systems of Winsor III type (page 316).

Dynamic Surface Tension

The dynamic surface tension can be measured by different means, for example, by using the maximum bubble pressure method. Air is continuously blown through two capillaries, of different diameters, which are dipped into the solution. The pressure required to form a bubble is inversely proportional to the capillary diameter and directly proportional to the surface tension of the liquid. The use of two capillaries makes measurements of the immersion depth unnecessary. The methods measure dynamic surface tensions at times down to about 1–10 ms. If the dynamic surface tension at even shorter times is to be measured, then the oscillating jet method is applicable. Here, a liquid jet emerges from an elliptically formed orifice. Since a noncircular cross-section of the jet is mechanically unstable, the liquid in the jet tries to attain the circular cross-section and, in doing so will, oscillate between extreme values. The frequency of these oscillations is related to the dynamic surface tension.

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13

Mixed Surfactant Systems

Technical uses of surfactants mostly involve more than one surfactant species in order to obtain synergistic effects with respect to both efficiency and effectiveness. Surfactant mixtures form micelles that almost invariably include all the surfactant species present. In many applications mixtures of an ionic and a nonionic surfactant are common. The first part of this chapter deals with mixed micelles in solution and how to understand and predict the critical micelle concentration (CMC) of surfactant mixtures, as well as the molecular composition of the micelles formed in bulk and of the assemblies formed at surfaces.

The Behavior of Surfactant Mixtures Depends on the Relative Surface Activities and on Interactions

The properties of a mixed surfactant system, in bulk or at an interface, depend on two factors:

1. The relative surface activity of the two surfactants, generally expressed by the ratios of the CMC values.
2. The interactions between the different surfactant molecules.

The interactions can be net attractive or net repulsive. This is characterized by an interaction parameter (β), which is negative for attractive interactions and positive for repulsive interactions. In the case that there is no net interaction, then $\beta=0$ and we have an *ideal solution*. In such a case, the interactions between two molecules of the same kind are the same as between two different molecules.

A simple case of an ideal solution is a mixture of two surfactants with the same head group. Also, when we mix two surfactants of the same class (nonionic–nonionic, anionic–anionic, etc.) we expect β values close to 0.

A clear case of strong attractive interaction, and a β value that is markedly negative, is a mixture of two oppositely charged surfactants. Another generally attractive system is a mixture of an ionic surfactant with a nonionic one. We recall that an ionic surfactant has a high CMC value because of the entropic penalty due to the high concentration of counterions in the vicinity of the micelle. Adding a nonionic surfactant reduces the charge density of the micelle, and thus stabilizes it as a result of reduced entropy penalty of surface-bound counterions (Figure 3.2). The attractive interaction in this case is weaker, which means that the β value is less negative than for the cationic-anionic mixture.

Repulsive interactions, and thus positive β values, are rare. The prime example is mixtures of surfactants with hydrocarbon and fluorocarbon tails.

We will here first discuss micelle formation in mixed surfactant solutions, then discuss other surfactant self-assemblies and phase diagrams, and finally the interfacial behavior. In discussing micelle formation and the CMCs of surfactant mixtures, we first consider the case of an ideal mixture and then introduce interactions.

The CMC of an Ideal Mixture has a Simple Relationship to the Individual CMC Values

If we mix two surfactants with the same CMC and with no net interaction ($\beta=0$), we observe, as expected, the same CMC for all mixing ratios. For an ideal case with different CMC values, we obviously expect some intermediate value between the two. However, the resulting CMC is not a simple mean value determined by the amounts of surfactant present in the solution; instead, the more surface active surfactant has a stronger influence on the CMC. It is also enriched in the micelles.

It can be shown that in the case of two surfactants without a net interaction the CMC is given by:

$$\frac{1}{CMC} = \frac{x_1}{CMC_1} + \frac{x_2}{CMC_2} \quad (13.1)$$

CMC and CMC_i are the CMC values of the mixture and of surfactant i , respectively; x_i is the molar fraction of added surfactant i . (By additional terms Equation 13.1 can be extended to apply for a mixture of more than two surfactants.) Thus, the CMC of the mixture can be calculated from the individual CMC values when the molar fractions of the two surfactants added are known. For such a system the molar fraction of surfactant 1 in the micelle is obtained from:

$$x_1^m = \frac{x_1 CMC_2}{x_1 CMC_2 + x_2 CMC_1} \quad (13.2)$$

It can be shown that the resulting CMC in a mixture is determined by the amounts of the surfactant in the micelles rather than in the solution. In terms of the micellar composition, x_1^m and x_2^m , the CMC is thus given by:

$$CMC = x_1^m CMC_1 + x_2^m CMC_2 \quad (13.3)$$

Systems of Surfactants with Similar Head Groups Require No Net Interaction

We will exemplify the case of $\beta=0$ with mixtures of two surfactants with the same head group but with different chain lengths. There is, of course, an interaction between the head groups of the surfactants in the mixed micelle, but since the head groups are of the same kind this interaction is the same for the different surfactant species, hence the net interaction is zero.

Figure 13.1 shows the calculated CMC and the micelle composition as a function of the solution composition using Equations 13.1 and 13.2 for three cases where $CMC_2/CMC_1 = 1, 0.1$, or 0.01 . As can be seen from these figures, the CMC and the micellar composition change dramatically with solution composition when the CMCs of the surfactants differ considerably, that is, when the ratio of the CMCs is far from one. Thus, a small amount of a very hydrophobic surfactant will change the solution properties of a system dramatically. This fact is taken advantage of in formulation work. Addition of a long-chain alcohol is, for instance, a way to increase the efficiency of many cleaning formulations. (Naturally, long-chain alcohols are not surfactants since they do not form micelles, but as will be shown later (Figure 13.7) the solubility limit of long-chain alcohols can successfully be used as a value of a fictitious CMC.)

If we assume that component 2 represents a very surface active species (i.e., CMC_2/CMC_1 is a small number, e.g., of the order of 0.01) and that it is present in low concentrations (x_2/x_1 is of the order of 0.01), we find from Equation 13.2 that $x_1^m \approx x_2^m \approx 0.5$, that is, at the CMC of the system the micelles are up to 50% composed of component 2. It is, therefore, not surprising that surface active contaminants may play an important role. An example of such a contaminant is dodecyl alcohol in sodium dodecyl sulfate (SDS), which is formed from hydrolysis of the surfactant and usually present in $1\text{--}2\%$. A measured CMC that is lower than expected is, therefore, an indication of a hydrophobic impurity.

Figure 13.2 shows examples with mixtures of potassium soaps with 8, 10, and 14 carbons (C_7COOK , C_9COOK , and $C_{13}COOK$). The resemblance with Figure 13.1 is obvious, thus confirming the dominant role of the more hydrophobic surfactant.

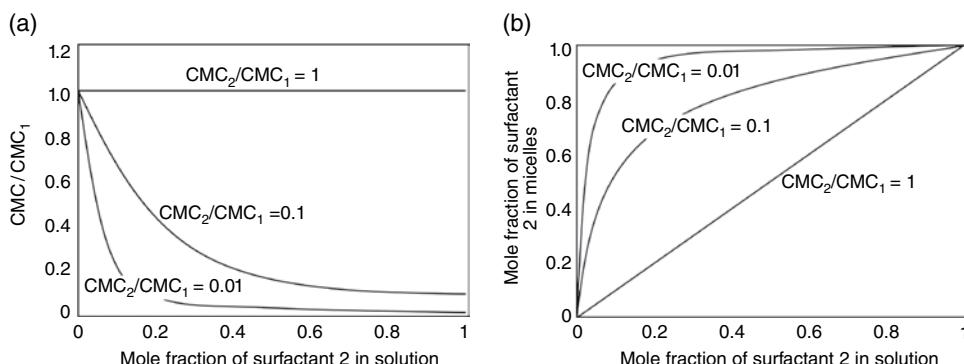


Figure 13.1 (a) The calculated CMC and (b) the micellar composition as a function of the surfactant composition in the solution for three systems where $CMC_2/CMC_1 = 1, 0.1$, or 0.01 and where there is no net interaction

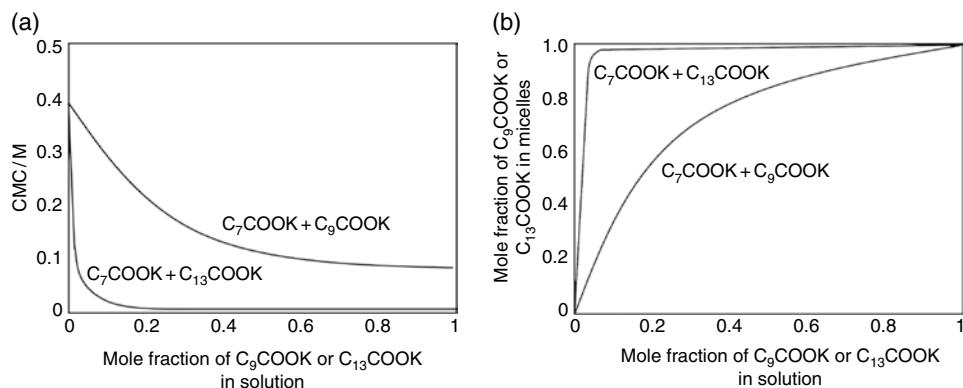


Figure 13.2 (a) The CMC and (b) micellar composition of mixtures of $C_7COOK + C_9COOK$ and $C_7COOK + C_{13}COOK$. (With permission from Nagarajan, R. (1992) *Micellization of binary surfactant mixtures*, in *Mixed Surfactant Systems* (eds P.M. Holland and D.N. Rubingh), ACS Symposium Series No. 501, American Chemical Society, Washington, DC, pp. 54–95. Copyright 1992, American Chemical Society.)

Many Other Surfactant Systems Require a Net Interaction

It can easily be understood that if we mix two attractive surfactants self-assembly is facilitated, corresponding *inter alia* to a lower CMC. Thus, attraction brings different surfactant molecules together and in the aggregates they are closer together than in the bulk solution. For the case of a repulsive interaction the opposite situation applies, that is, self-assembly is disfavored.

To take into account interactions we need to modify Equations 13.1 and 13.3. This is typically achieved by characterizing the deviations from an ideal behavior by activity coefficients f_i^m according to:

$$\frac{1}{CMC} = \frac{x_1}{f_1^m CMC_1} + \frac{x_2}{f_2^m CMC_2} \quad (13.4)$$

and

$$CMC = f_1^m x_1^m CMC_1 + f_2^m x_2^m CMC_2 \quad (13.5)$$

The activity coefficients in the mixed micelle are related to the interaction parameter (β) according to:

$$\ln f_1^m = (x_1^m)^2 \beta \quad (13.6a)$$

and

$$\ln f_2^m = (x_2^m)^2 \beta \quad (13.6b)$$

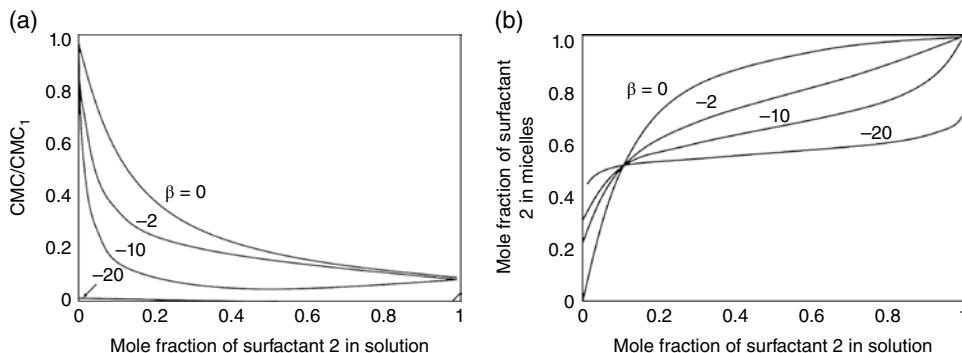


Figure 13.3 (a) Calculated CMC and (b) micellar composition for the indicated values of the β parameter for systems where $CMC_2/CMC_1 = 0.1$

Figure 13.3 shows the effects of the values of the β parameters on the CMC and the micellar composition. A ratio of the two CMCs of 0.1 has been used. Figure 13.3a shows that when the attraction between the surfactants increases, that is, when the β parameter becomes increasingly more negative, the CMC of the mixture decreases. β values of around -2 are typical for mixtures of anionic and nonionic surfactants. Values in the -10 to -20 range are characteristic for mixtures of anionic and cationic surfactants. (Note that in the $\beta = -20$ case the CMC curve is difficult to distinguish from the x -axis). Figure 13.3b shows that with an increasingly negative value of the β parameter the mixed micelles approach a molar ratio of the two surfactants of 50:50. The driving force is the decrease in surface charge of the micelle, which in turn increases the counterion entropy (Figure 3.2).

Mixtures of Anionic and Nonionic Surfactants

One example where there is a negative β parameter is when mixing anionic and nonionic surfactants. Figure 13.4a shows the CMC as a function of the molar composition for a mixture of SDS and nonylphenol with 10 oxyethylene ($NP-E_{10}$) units. The CMC of the mixture shows a dramatic decrease at low fractions of $NP-E_{10}$. This decrease is due to preferential incorporation of $NP-E_{10}$ in the micelle. This is illustrated further in Figure 13.4b, which shows the mole fraction of nonionic surfactant in the micelles as a function of the mole fraction of nonionic surfactant in the solution. This figure clearly illustrates that the nonionic surfactant is preferentially incorporated in the micelle, which is related to its lower CMC when compared to the anionic SDS.

Mixtures of Anionic and Cationic Surfactants

A system with a large net attraction between the surfactants is shown in Figure 13.5 for a mixture of sodium decylsulfate (SDeS) and decyltrimethylammonium bromide (DeTAB). The dashed line in Figure 13.5a is calculated with $\beta=0$, while the continuous curve corresponds to $\beta=-13.2$. We note that a very large synergistic effect is obtained when there is a large net attraction between the surfactants. This figure is also an illustration of the fact that it is indeed possible to lower the CMC of an anionic surfactant by adding a cationic surfactant

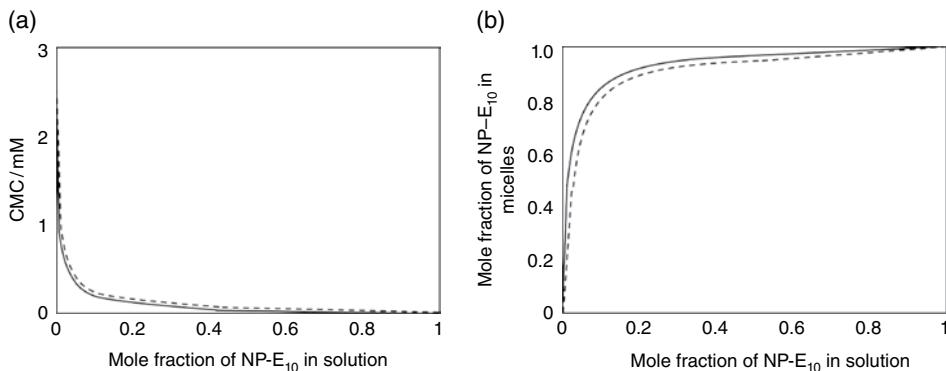


Figure 13.4 (a) The CMC and the surfactant composition in the micelles as a function of surfactant composition for the system SDS + NP-E₁₀. (With permission from Kronberg, B., Lindström, M. and Stenius, P. (1986) Competitive adsorption of an anionic and a nonionic surfactant on polystyrene latex, in Phenomena in Mixed Surfactant Systems (ed. J.F. Scamehorn), ACS Symposium Series No. 311, American Chemical Society, Washington, DC, pp. 225–240. Copyright 1986, American Chemical Society.)

without causing precipitation. A requirement is that the hydrocarbon chains of the surfactants are relatively short; in this example, each surfactant contains only 10 carbon atoms. Figure 13.5b shows that the micellar composition is relatively constant over a broad molar ratio of the two surfactants in the solution. The fact that the plateau is somewhat below 0.5 is due to the anionic surfactant having a somewhat stronger tendency for self-association in solution, as is evident from its lower CMC value (Figure 13.5a). The reason for a net attraction between an anionic and a cationic surfactant in a micelle is that neutral micelles are the most stable since for those there is no entropic penalty due to the counterions (Figure 3.2).

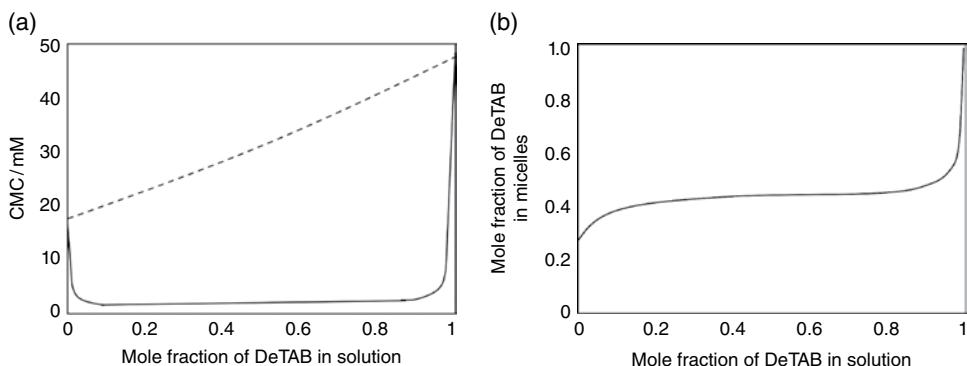


Figure 13.5 (a) The CMC and (b) micellar composition for mixtures of SDeS and DeTAB, illustrating that an anionic and a cationic surfactant can be used in combination to obtain a very high surface activity. (With permission from Nagarajan, R. (1992) Micellization of binary surfactant mixtures, in Mixed Surfactant Systems (eds P.M. Holland and D.N. Rubingh), ACS Symposium Series No. 501, American Chemical Society, Washington, DC, pp. 54–95. Copyright 1992, American Chemical Society.)

Effect of the β Parameter for Different Ratios between the CMCs

Both the CMC of a surfactant mixture and the micellar composition are thus sensitive to the value of the β parameter and the sensitivity is more pronounced when the CMC values for the two surfactants are similar. In contrast, when the ratio between the CMCs of the individual surfactants is large, the value of the mixed CMC, as well as the micellar composition, is more insensitive to variations in the β parameter. These aspects are illustrated when comparing the results shown in Figures 13.4 (SDS + NP-E₁₀) and 13.6 (SDS + C₈E₄). The dashed line given in Figure 13.4 is calculated with $\beta=0$, while the continuous line is calculated with $\beta=-2$. We note that there is only a small difference between the two curves. Figure 13.6, on the other hand, shows the CMC of a mixture of two surfactants with similar CMCs. Here the dashed line, corresponding to $\beta=0$, differs considerably from the continuous curve, which corresponds to experimental results and is calculated with $\beta=-3.1$.

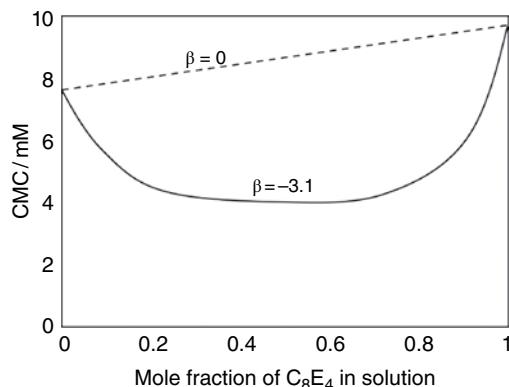


Figure 13.6 Variation in CMC for SDS and C₈E₄ mixtures. The dashed line is the case when $\beta = 0$, and the continuous line is when $\beta = -3.1$, illustrating that when the CMCs of the two individual surfactants are close to each other the predicted CMC is very sensitive to the value of the β parameter. (With permission from Nagarajan, R. (1992) *Micellization of binary surfactant mixtures*, in *Mixed Surfactant Systems* (eds P.M. Holland and D.N. Rubingh), ACS Symposium Series No. 501, American Chemical Society, Washington, DC, pp. 31–44. Copyright 1992, American Chemical Society.)

In Table 13.1 β values for selected surfactant mixtures are given. Note the following trends: (i) for a mixture of a nonionic and an ionic surfactant (using a cationic surfactant as example) the β value becomes less negative with increasing salt concentration; (ii) for a mixture of a nonionic and an ionic surfactant (using an anionic surfactant as example) the β parameter becomes less negative, that is, the net attraction decreases, with increasing temperature; (iii) for a mixtures of an anionic and a cationic surfactant the β parameter becomes less negative with increasing ionic strength; (iv) increasing the alkyl chain length for anionic–cationic mixtures will increase the attraction, that is, the β parameter increases in magnitude; and (v) in a mixture of an anionic surfactant and a surfactant that can be transformed from net neutral to positively charged the β parameter can be of the same magnitude as for mixtures of an anionic and a cationic surfactant. Amine oxide and betaine surfactants are examples of such amphiphiles. When mixed with an anionic surfactant,

Table 13.1 Values of the β parameter for selected surfactant binary mixtures

Mixture	Medium	Temperature (°C)	β
C ₁₂ PyrCl/C ₁₂ E ₈	Water	25	-2.7
C ₁₂ PyrCl/C ₁₂ E ₈	0.1 M NaCl	25	-1.4
C ₁₂ PyrCl/C ₁₂ E ₈	0.5 M NaCl	25	-1.0
C ₁₂ ΦSO ₃ Na/NP-E ₁₀	0.15 M NaCl	30	-3.2
C ₁₂ ΦSO ₃ Na/NP-E ₁₀	0.15 M NaCl	38	-2.8
C ₁₂ ΦSO ₃ Na/NP-E ₁₀	0.15 M NaCl	46	-2.1
C ₁₂ ΦSO ₃ Na/NP-E ₁₀	0.15 M NaCl	54	-1.8
C ₁₀ SO ₄ Na/C ₁₀ TAB	Water	25	-18.5
C ₁₀ SO ₄ Na/C ₁₀ TAB	0.05 M NaBr	25	-13.2
C ₁₂ SO ₄ Na/C ₁₂ TAB	Water	25	-25.5
C ₁₂ SO ₄ K/C ₁₂ AO	Water	25	-16.5
C ₁₂ SO ₄ Na/C ₁₂ N ⁺ (CH ₃) ₂ CH ₂ COO ⁻	Water	30	-14.1

Values taken from Holland, P.M. (1992) Modeling mixed surfactant systems, in *Mixed Surfactant Systems* (eds P.M. Holland and D.N. Rubingh, ACS Symposium Series No. 501, American Chemical Society, Washington, DC, pp. 31–44). Pyr, ϕ and AO stand for pyridinium, a phenyl ring, and amine oxide, respectively.

such as SDS or an ether sulfate, they spontaneously take up a proton from the surrounding water in order to form mixed micelles consisting of an anionic and a cationic amphiphile. The driving force is to lower the charge density of the mixed micelle.

The Concept of Mixed Micelles can also be Applied to Amphiphiles not Forming Micelles

There are amphiphilic molecules that are unable to form micelles and which instead phase separate at higher concentrations. A well-known example is the class of medium-chain alcohols. The concentration at which phase separation occurs is analogous to the CMC of micelle-forming surfactants. Hence, the solubility limit of a medium-chain alcohol can be used as a “CMC” of the alcohol in water and this value can be used in order to predict the CMC of a mixed system where the medium-chain alcohol is mixed with an ordinary surfactant. Figure 13.7 shows results for mixtures of an anionic surfactant and different alcohols.

Mixed Surfactant Systems at Surfaces

At a hydrophobic surface, as well as at the liquid–air interphase, mixtures of surfactants form mixed monolayers. (Only on rare occasions, such as in mixtures of a fluorinated and an ordinary surfactant, does the monolayer separate into domains, each with an excess of one of the surfactant species.) Furthermore, technical surfactants are never single species but mixtures, usually of molecules with widely different physicochemical properties. The parameter of interest is often the surfactant composition at the surface, not the composition in the bulk.

In Chapter 8 it was demonstrated that on both hydrophilic and hydrophobic surfaces the surfactants adsorb according to their solubility, that is, the lower the CMC the stronger the

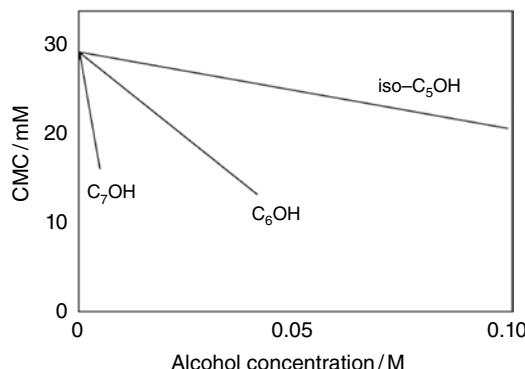


Figure 13.7 The mixed micelle concept can be applied to mixtures of surfactants and medium-chain alcohols that do not form micelles by themselves. The lines are calculated from Equation 13.1 with $f_1 = f_2 = 1$ and with the solubility limit of the alcohol being used as the CMC. The surfactant used is potassium dodecanoate

adsorption. This is the case also for surfactant mixtures, that is, the composition at the surface strongly depends on the relative hydrophobicity of the surfactants present in the system. The surfactant composition at a hydrophobic surface, or at the air–water interface, as a function of the surfactant composition in the solution follows the same curve as for surfactant composition in mixed micelles (figures b in Figures 13.1–13.5). Hence, the more hydrophobic surfactant will be most abundant at the surface. This has been verified experimentally for many systems.

Anionic and a Cationic Surfactant

Adsorption of a mixture of an anionic and a cationic surfactant has much in common with formation of mixed micelles in such systems. The examples below illustrate that the relative hydrophobicity of the surfactants is of great importance and more dominant than the electrostatic forces.

Figure 13.8 shows the zeta potential (zeta potential and electrophoretic mobility is discussed in Chapter 18, Figure 18.24) of a latex in the presence of mixtures of anionic, C_n^- , and cationic, C_n^+ , surfactants, differing in their chain length, n . The zeta potentials are determined at the CMC of the surfactant mixture, thus ensuring that the surface is saturated with surfactant. The mixture of C_8^- and C_8^+ surfactants shows the expected behavior, that is, a zeta potential of zero at a surfactant ratio of 50:50. Excess of one of the surfactants gives a net charge, hence a net zeta potential.

The mixtures of C_8^- and C_{12}^+ as well as C_{12}^- and C_8^+ surfactants show a different behavior. Here, the surfactant composition in the solution leading to a zero zeta potential is around 90:10, where the more hydrophilic surfactant is in excess. Hence one needs about 10 times the concentration of the hydrophilic surfactant in order to attain a 50:50 ratio at the surface. This is an illustration of the fact that the hydrophobicity is a very strong driving force for surfactant adsorption, irrespective of the fact that there is an electrostatic attraction between the head groups of the surfactants, trying to pull the surface composition into a 50:50 situation. Hence, the hydrophobicity dominates over the electrostatic forces and this example

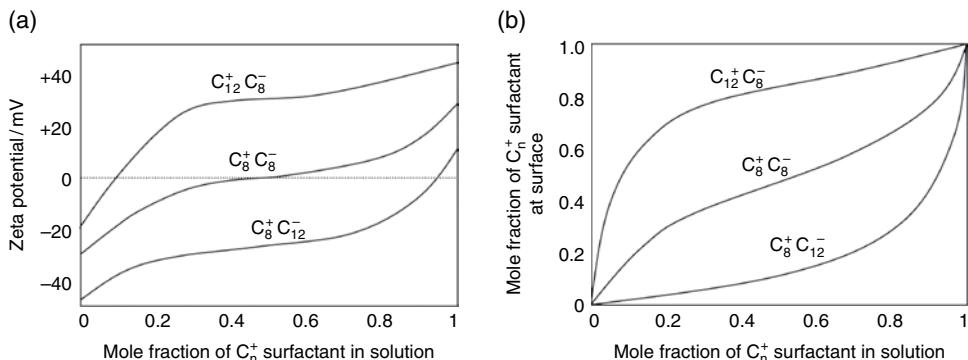


Figure 13.8 (a) The zeta potential and (b) the calculated surface composition of a latex in the presence of mixtures of anionic, C_n^- , and cationic, C_n^+ , surfactants, differing in chain length, n

illustrates that the solution properties, namely, the hydrophobicity, of the surfactants is a determining factor for surfactant adsorption.

Anionic and Nonionic Surfactants

Mixtures of anionic and nonionic surfactants are very common in technical applications; such systems provide both electrostatic repulsion and steric repulsion between particles where the surfactants are adsorbed (Chapter 18). The composition at a surface depends on the solution properties of the single surfactants, that is, their CMCs, as illustrated below.

Figure 13.9 illustrates competitive adsorption for such a surfactant combination. A solution of a mixture of a nonionic surfactant, NP-E₁₀, and an anionic surfactant, SDS, is

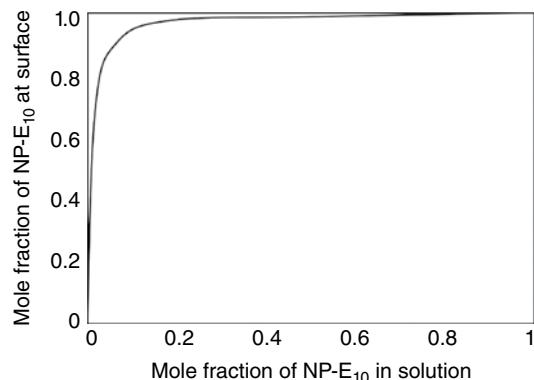


Figure 13.9 Simultaneous adsorption of a mixture of a nonionic surfactant, NP-E₁₀, and an anionic surfactant, SDS, on a polystyrene latex surface leads to a strong preferential adsorption of the former. (With permission from Kronberg, B., Lindström, M. and Stenius, P. (1986) Competitive adsorption of an anionic and a nonionic surfactant on polystyrene latex, in Phenomena in Mixed Surfactant Systems (ed. J.F. Scamehorn), ACS Symposium Series No. 311, American Chemical Society, Washington, DC, pp. 225–240. Copyright 1986, American Chemical Society.)

exposed to a hydrophobic surface, polystyrene. The CMCs of the surfactants differ by a factor of about 100, the nonionic having the lower CMC.

The figure shows the surfactant composition at the surface as a function of the surfactant composition in the bulk solution, at the CMC of the solution, that is, when the surface is saturated with the surfactant mixture. The nonionic surfactant adsorbs preferentially at the surface at all solution compositions. For example, a solution with a NP-E₁₀-to-SDS ratio of 10:90 is in equilibrium with a surface with a NP-E₁₀-to-SDS ratio of 90:10. Hence, the surfactant composition at a surface cannot easily be predicted by analyzing the bulk composition.

Two Nonionic Surfactants

We now turn to the case where two nonionic surfactants compete for the surface. Of course, here also the more hydrophobic surfactant dominates at the surface because of its lower affinity for the aqueous phase. In Table 8.1, the adsorption free energy of some nonionic surfactants at a polystyrene surface is presented. From the table we draw the conclusion that there is a large difference in free energy of adsorption between NP-E_n surfactants differing in their polyoxyethylene chain lengths. Thus, in surfactant mixtures there is a chromatographic effect in the sense that the surfactants with short polyoxyethylene chains are preferentially adsorbed on hydrophobic surfaces (assuming the same length of the hydrophobic tails). Hence, when a technical surfactant batch is used, the long polyoxyethylene chain homologues will stay in solution and the short ones will be enriched at the surfaces. Figure 13.10a shows a calculated example for a 50:50 (on a weight basis, corresponding to a 63:37 mixture on a molar basis) mixture of NP-E₁₀ and NP-E₂₀ where both surfactant batches follow a Poisson distribution. This figure shows that the surface is enriched in the short-chain polyoxyethylene species whereas the solution is enriched in the long-chain species. In Figure 13.10b we show the calculated surfactant composition at the surface versus the composition in solution for the two nonionic pairs NP-E₁₀ + NP-E₂₀ and NP-E₁₀ + NP-E₅₀.

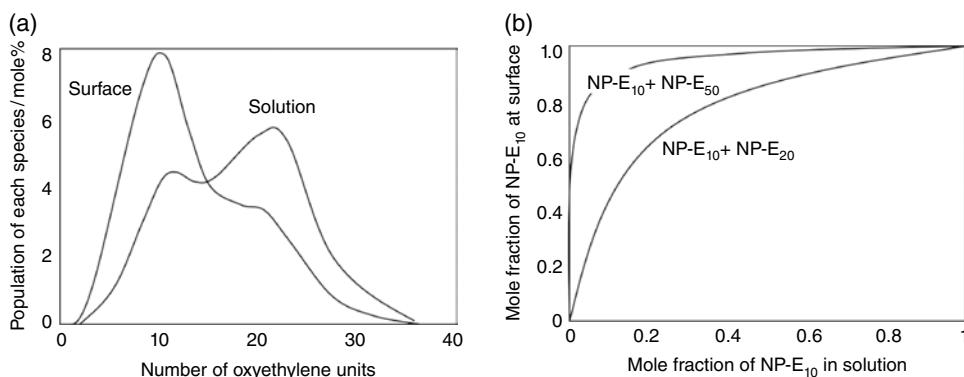


Figure 13.10 (a) Calculated normalized distribution curves of a surfactant mixture (50 wt% NP-E₁₀ + 50 wt% NP-E₂₀, corresponding to 63 mol% NP-E₁₀ + 37 mol% NP-E₂₀) adsorbed on a latex and in the equilibrium solution assuming a Poisson distribution of the polyoxyethylene chains; (b) calculated surface composition of the two nonionic pairs NP-E₁₀ + NP-E₂₀ and NP-E₁₀ + NP-E₅₀ versus the composition in solution

NP-E₁₀ + NP-E₅₀, illustrating the preference for the surface of the more hydrophobic surfactant, that is, NP-E₁₀.

Another example is the simultaneous adsorption of a 50:50 molar mixture of C₁₄E₆ and C₁₀E₆ at a silica surface (Figure 13.11). This figure shows that the single surfactants, C₁₀E₆ and C₁₄E₆, give an adsorption of about 3 and 5 μmol/m², respectively, while for the 50:50 mixture an adsorption of 4.5 μmol/m² is obtained. This indicates that the surface has an excess of C₁₄E₆ at the cost of C₁₀E₆. More interesting, though, is the behavior when the system is diluted. (In the figure the dilution starts at t=3000 s.)

On dilution the hydrophilic surfactant, C₁₀E₆, desorbs from the surface to be present as unimers in the aqueous solution. Before the dilution the surface is in equilibrium with mixed micelles in solution. Since the unimeric solubility (indicated by the CMC) of C₁₀E₆ is much larger than of C₁₄E₆, the dilution will cause removal of this surfactant from the surface and from the micelles. Eventually this leaves the surface in equilibrium with micelles of only the hydrophobic surfactant, C₁₄E₆. We now have the same situation as for the single hydrophobic surfactant, hence a higher adsorption is obtained. On further dilution the hydrophobic surfactant desorbs from the surface. This molecular picture is strengthened by experiments on single surfactants (Figure 13.11b), showing desorption with time for three nonionic surfactants (alkylhexaoxyethylenes) differing in the length of the alkyl chain. The greater the hydrophilicity, the more readily the surfactant leaves the surface. This is an important and general phenomenon in cleaning where rinsing may cause re-deposition of the more hydrophobic species (dirt) on the surface. One example of this is given in Figure 8.16 showing the adsolubilization of a hydrophobic substance. As the surfactant concentration is lowered, the adsolubilization increases, for the reason just outlined above.

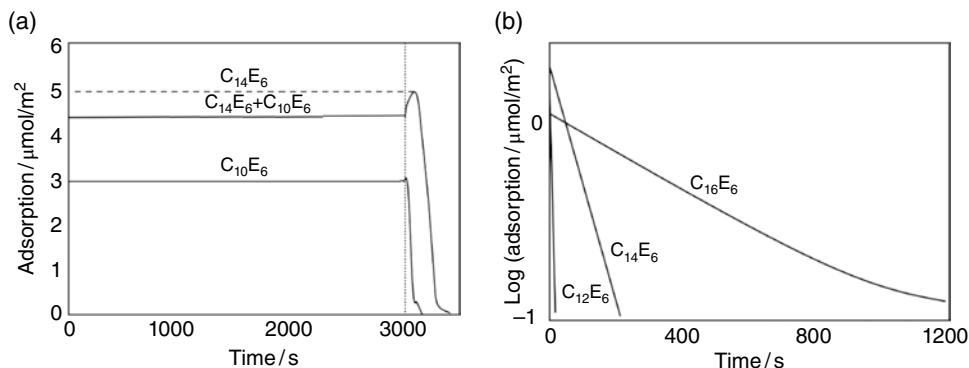


Figure 13.11 (a) Simultaneous adsorption of a 50:50 mixture (on a molar basis) of C₁₄E₆ and C₁₀E₆ at a silica surface, illustrating competitive adsorption, as well as deposition of the hydrophobic surfactant on dilution (see text for details); (b) desorption of single surfactants from a silica surface versus time in a rinsing experiment. (With permission from Brinck, J., Jönsson, B. and Tiberg, F. (1998) Kinetics of nonionic surfactant adsorption and desorption at the silica-water interface: binary systems. *Langmuir*, **14**, 5863–5876, Copyright 1998, American Chemical Society, and Tiberg, F., Jönsson, B. and Lindman, B. (1994) Ellipsometry studies of the self-assembly of nonionic surfactants at the silica-water interface: kinetic aspects. *Langmuir*, **10**, 3714–3722, Copyright 1994, American Chemical Society.)

Competitive Adsorption can be Understood from Thermodynamic Considerations

From a thermodynamic analysis it can be shown that the mole fraction of surfactant 1 at a hydrophobic surface (Θ) can be estimated if the CMCs of the single surfactants, CMC_1 and CMC_2 , and the β parameter are known:

$$\ln \frac{x_1}{1-x_1} = \ln \frac{\Theta_1}{1-\Theta_1} + (1-2\Theta_1)\beta + \ln \frac{\text{CMC}_1}{\text{CMC}_2} \quad (13.7)$$

Here x_1 is the mole fraction of surfactant 1 in the solution. This is an expression of the surfactant composition (i.e., the mole fraction of the surfactants) at the surface as a function of the surfactant composition (i.e., the mole fraction of the surfactants) in the solution. If $\beta=0$ we find that the mole fraction of surfactant 1 at a hydrophobic surface is related to the surfactant composition in the solution through:

$$\Theta_1 = \frac{x_1 \text{CMC}_2}{x_1 \text{CMC}_2 + x_2 \text{CMC}_1} \quad (13.8)$$

We note that the surface is not a parameter in this equation, hence it is a reasonable estimation for any hydrophobic surface, including the liquid–air interface. Equation 13.8 is identical to the expression for the surfactant composition in a mixed micelle (Equation 13.2).

To summarize, the simultaneous adsorption of surfactants at a surface is determined by the CMCs of the individual surfactants, that is, their hydrophobicity, and by the interaction between the surfactants, that is, the β parameter.

Surfactant Mediated Surfactant Adsorption

In Chapter 8 we learned that only a small attraction between the surfactant and the surface is needed in order for surfactant aggregates to form at the surface. In some instances there is no attraction between the surface and the surfactant, hence no adsorption. However, nonadsorbing surfactants can be made to adsorb if some other surfactant species is present in the solution. Figure 13.12 shows two examples of this phenomenon. The first is adsorption of dodecyl maltoside, C_{12}G_2 , (i.e., a nonionic surfactant with two glucose rings as polar head group) on silica. This surfactant, when alone, does not adsorb appreciably at the silica surface. However, in the presence of dodecyldimethylamine oxide (DDAO), there is a strong adsorption. This phenomenon is not specific for DDAO. Other cationic surfactants do the same. The proposed mechanism is that DDAO adsorbs because of its cationic character and that C_{12}G_2 adsorbs due to favorable interaction with DDAO.

The second example is the situation where the anionic surfactant, SDS, hardly adsorbs alone at a concentration of 0.5 mM, but only in the presence of C_{12}G_2 at a negatively charged alumina surface (Figure 13.12b). Hence, the presence of C_{12}G_2 triggers the adsorption of the negatively charged SDS on the likewise negatively charged alumina surface. C_{12}G_2 adsorbs because of its hydrophobic character and SDS adsorbs due to favorable interaction with C_{12}G_2 .

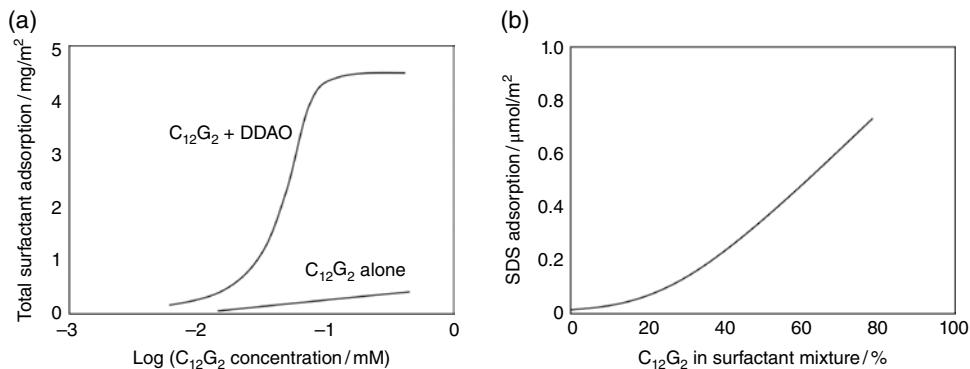


Figure 13.12 Adsorption of $C_{12}G_2$ on silica, in the absence and presence of DDAO, at a constant concentration of 0.1 mM (a) and adsorption of SDS on an alumina surface (at pH = 11) as a function of $C_{12}G_2$ content in the surfactant mixture, obtained at a constant SDS concentration of 0.5 mM. (From Matsson, M.K., Kronberg, B. and Claesson, P.M. (2004) Adsorption of alkyl polyglucoside on the solid-water interface: equilibrium effects of alkyl chain length and head-group polymerization. *Langmuir*, **20**, 4051–4058, Copyright 2004, American Chemical Society, and Zhang, L. and Somasundaran, P. (2006) Adsorption of mixtures of nonionic sugar-based surfactants with other surfactants at solid-liquid interfaces. I. Adsorption on n-dodecyl- β -D-maltoside with anionic sodium dodecyl sulfate on alumina. *Journal of Colloid and Interface Science*, **302**, 20–24. With permission from Elsevier.)

Surfactant Mixtures at the Air–Water Interface

DDAO is an amphoteric surfactant and may be present either as a nonionic or as a cationic species at neutral pH. In mixtures with SDS DDAO picks up a proton from the surrounding water. As seen in Figure 13.13 the mixtures display a lower CMC, as well as a higher effectiveness, compared to the individual surfactants. Formation of self-assemblies (micelles in bulk and a monolayer at the air–water interface) from the mixture of SDS and the amine oxide surfactant in protonated form is so favorable because of no or little entropy loss due to counterion binding. The protonation of DDAO may occur well above the pK_a of the protonated form because of the strong driving force exerted by the mixed aggregate formation. The same phenomenon occurs with other surfactants that may switch between a zwitterionic and a cationic form, for instance betaine surfactants. Mixtures of an anionic surfactant, for example, lauryl ether sulfate, and a betaine surfactant, such as cocamidopropyl betaine, are popular in personal care and also in hand dishwashing formulations. Such mixtures have very good dermatological characteristics.

Mixed Surfactant Systems at Higher Concentrations Show Interesting Features

The phase behavior of mixtures of surfactants is not always easy to predict from their physicochemical behavior in the dilute regime. Mixtures of surfactants of the same class, that is, anionic, nonionic, and so on, generally behave as one would expect from a weighted

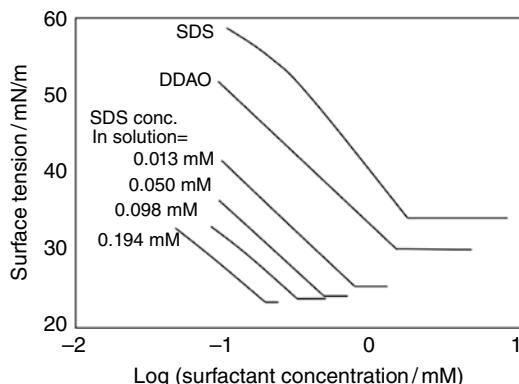


Figure 13.13 Surface tension as a function of total surfactant concentration for solutions of SDS, DDAO, and mixtures of the two. Four series of mixtures were investigated, each with a constant concentration of SDS (given on the figure) and varying concentration of DDAO, illustrating the synergistic effect of their mixtures. (With permission from Coloumb, T.P., Pugh, R.J. and Zhamud, B.V. (2000) *Micellar interactions in nonionic/ionic mixed surfactant systems*. Journal of Colloid and Interface Science, **229**, 72–81. Copyright Elsevier.)

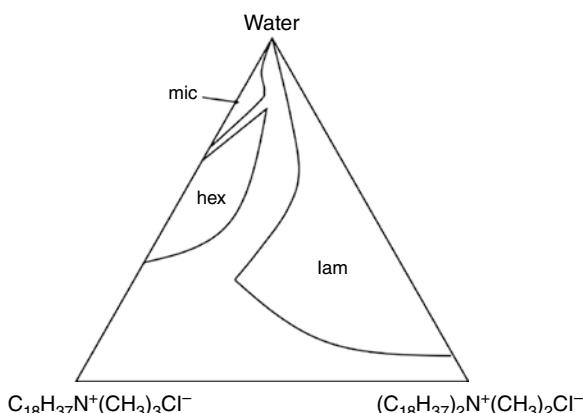


Figure 13.14 Phase diagram for a mixture of two cationic surfactants, the single-chained octadecyltrimethylammonium chloride ($(C_{18}H_{37})N^+(CH_3)_3Cl^-$) and the double-chained dioctadecyldimethylammonium chloride ($(C_{18}H_{37})_2N^+(CH_3)_2Cl^-$). Two- and three-phase regions are omitted. (With permission from Kunieda, H. and Shinoda, K. (1978) *Solution behavior of dialkyldimethylammonium chloride in water. Basic properties of antistatic fabric softeners*. Journal of Physical Chemistry, **82**, 1710–1714. Copyright 1978, American Chemical Society.)

average of the two amphiphiles but mixtures of different classes of surfactants may give a more complex pattern, as is illustrated below.

Figure 13.14 shows the phase diagram of a mixture of two cationic amphiphiles, one single-chained surfactant, octadecyltrimethylammonium chloride, which is micelle-forming, and one double-chained surfactant, dioctadecyldimethylammonium chloride, which forms

bilayers at low concentrations. The phase diagram is roughly according to expectations based on the average critical packing parameter (page 132) of the surfactant mixture. For example, going along a line representing 50:50 water to amphiphile and starting at 100% of the single-chained surfactant as the amphiphile component will take us from a hexagonal phase (which is the expected liquid crystalline phase for a single-chained surfactant at higher concentration), via a mixed region into a lamellar phase at high content of the double-chained surfactant. Thus, such surfactant mixtures will form liquid crystals with a packing arrangement representing the mean of the two surfactants.

A mixture of two oppositely charged surfactants, sometimes called a *catanionic surfactant*, on the other hand, does not behave as some kind of weighted average of the two amphiphiles. While self-assembly of a single ionic surfactant is counteracted by the loss of entropy arising from the accumulation of counterions around the aggregate, formation of aggregates comprising both anionic and cationic surfactants does not suffer from this entropy penalty. A micelle or a liquid crystal made of equimolar amounts of one anionic and one cationic amphiphile does not carry any counterions. This is the main reason why such mixed self-assemblies are so favored. For such systems it is meaningless to discuss in terms of an average critical packing parameter. Thus, the effective head group area in the mixture is small compared to that of the individual surfactants, which cannot pack closely because of the electrostatic penalty.

Compared to mixtures of surfactants of the same class, the catanionic systems often show a much richer phase behavior, unless they form a precipitate, which they usually do if the alkyl chains are long. The threshold for precipitation for single-chained surfactants is usually of the order of 12 carbons in the hydrophobic tail, but the tendency for precipitation also depends on the molar ratio of the two surfactants, as shown below. A scientifically interesting, and practically important, feature of such mixtures is that they form what seem to be thermodynamically stable single-walled vesicles. These vesicle dispersions often appear in two distinct regions in the phase diagram, one being rich in the cationic surfactant and one being rich in the anionic surfactant. At low surfactant concentrations the vesicle phase is in equilibrium with a micellar phase and at higher concentration it is in equilibrium with a liquid crystalline phase, often a lamellar phase. Figure 13.15 shows a schematic example of such a phase diagram. (As described in Chapter 5, a complete representation for such mixtures requires three dimensions.)

As can be seen in Figure 13.15, mixing equimolar amounts of the two surfactants leads to precipitation. However, increasing the amount of one of the surfactants makes the precipitate dissolve and on further increase of that amphiphile one enters the stable vesicle phase. The diagram is schematic, however, and the phase diagrams of real systems are usually not fully symmetric. The chain lengths, the type of substituents on the nitrogen atom, the type of anionic group, and possible branching of the long alkyl chains are parameters that all influence the phase diagram.

The unilamellar vesicles that can be created by mixing an anionic and a cationic amphiphile are interesting because they form spontaneously and they are stable for periods as long as several years, which means that they appear to be the equilibrium form of aggregation. This is in contrast to the vesicles that are generated from shearing a dispersion of a lamellar phase, which is the most common method of vesicle preparation. Such vesicles are not thermodynamically stable but revert to the equilibrium, multilamellar phase over time. From a compositional point of view the vesicles based on catanionic systems are akin to

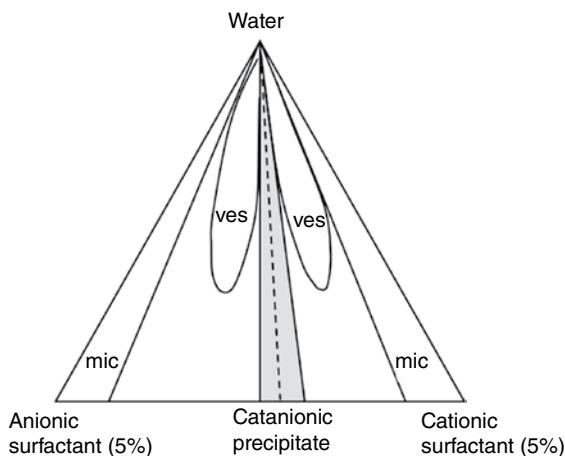


Figure 13.15 A schematic phase diagram for a mixture of an anionic and a cationic single-tailed surfactant. The diagram contains two vesicular regions. The one to the left of the narrow precipitation region contains vesicles with a negative net charge and the one to the right of the precipitation region contains positively charged vesicles. (With permission from Khan, A. (1996) Phase science of surfactants. Current Opinion in Colloid & Interface Science, **1**, 614–623. Copyright Elsevier.)

vesicles created by double-tailed zwitterionic surfactants. The catanionic vesicles are of interest for instance for delivery of active substances.

The vast majority of surfactant-based formulations comprise more than a single amphiphile. Mixtures of one or more anionic surfactants with one or more nonionic surfactants are particularly common and such mixtures constitute the basis for detergents, hand-dishwashing formulations, many personal care products, latex dispersions, paints, and so on. In such systems the surfactants always form mixed aggregates—micelles at low concentrations and liquid crystals at higher concentrations. A very common approach, for instance for cleaning formulations, is to mix a hydrophobic nonionic surfactant with a hydrophilic anionic surfactant. When the anionic component is very hydrophilic and without pronounced surface activity it is referred to as a hydrotrope; the use of hydrotropes is discussed in some detail on pages 23–26. Here it is also discussed how an alkyl glucoside can be used to raise the cloud point of a hydrophobic nonionic surfactant. Hydrophobic nonionics are generally very efficient for soil removal and for several other purposes but they suffer from poor water solubility and low cloud point. Raising the cloud point of a formulation to around or above the temperature at which the formulation will be used is one important reason why an anionic surfactant is often combined with a hydrophobic nonionic surfactant. Many properties exhibit a maximum at a specific ratio of the two surfactants. This is illustrated in Figure 13.16, which shows solubilization capacity, foam height, emulsifying ability, and wetting power for the system SDS-C₁₆E₃ at varying ratios of the two surfactants. As can be seen, the tests all display an optimum at a certain ratio of the surfactants and the performance at that composition is considerably better than that obtained with the individual surfactants. This is an example of synergism and applies to a broad range of physicochemical properties, such as CMC, surface tension,

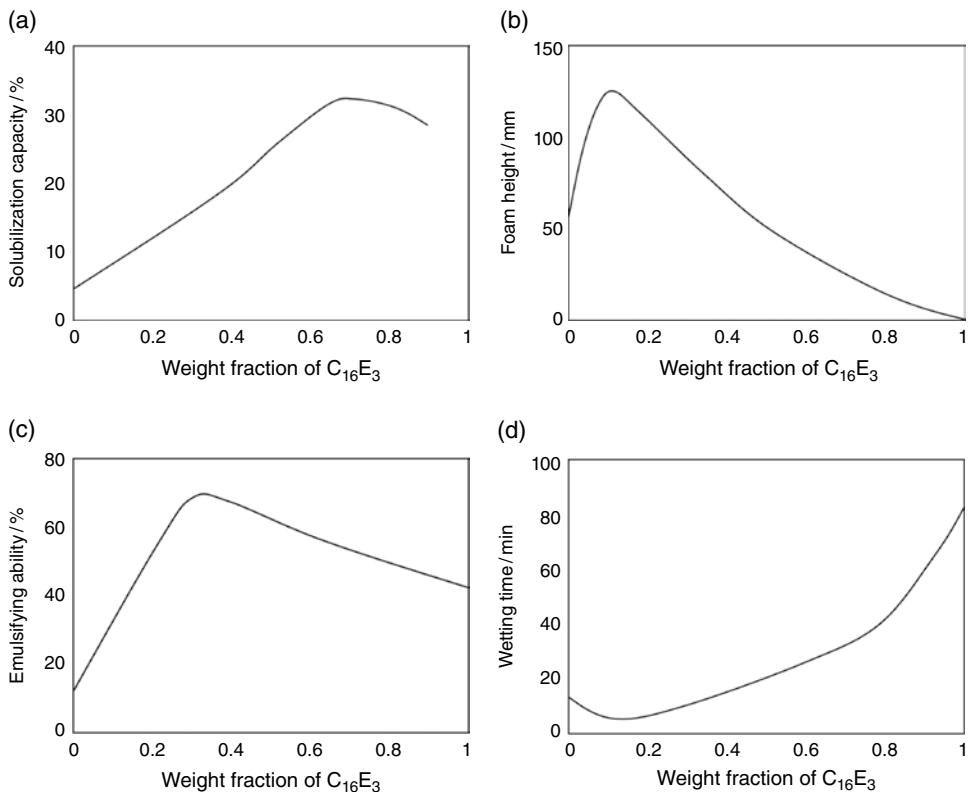


Figure 13.16 (a) Solubilization capacity (% of adsorption of a hydrophobic dye), (b) foam height, (c) emulsifying ability (% of toluene adsorption), and (d) wetting time of cotton swatches for a mixture of SDS and $C_{16}E_3$, all as a function of percentage of $C_{16}E_3$. (With permission from Jost, F., Leiter, H. and Schwuger, M.J. (1988) Synergism in binary surfactant mixtures. Colloid and Polymer Science, **266**, 554–561. Copyright 2011, John Wiley & Sons.)

and interfacial tension, as well as to performance criteria, such as the ones shown in Figure 13.16 and several others.

Another reason to use a surfactant mixture is to improve the action at a specific surface. Nonionic surfactants are, for instance, very efficient in removing oily soil from solid surfaces. To obtain good performance the surfactant needs to interact both with the surface (wetting) and with the soil (solubilization). However, the driving force for nonionics to adsorb at a polar surface is not so high and, since the majority of such surfaces carry a net negative charge, cationic surfactants adsorb more readily. Cationic surfactants are not very efficient in removing oily soil, however. The way this is handled in many commercial formulations is to mix in a small amount of a cationic surfactant into a nonionic surfactant-based formulation. A mixed double layer, dominated by the nonionic surfactant, will be formed at the surface. The role of the cationic surfactant can be said to be to trigger adsorption of the nonionic amphiphile.

Yet another reason for using a mixture of surfactants is to lower the Krafft point (or Krafft temperature, page 83) of the main surfactant in a formulation. The Krafft point

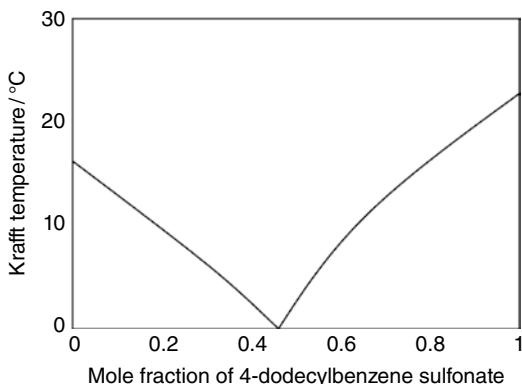


Figure 13.17 Kraft temperature for a mixture of 3-decyldbenzene sulfonate and 4-dodecylbenzene sulfonate as a function of percentage of 4-dodecylbenzene sulfonate. (With permission from Scamehorn, J.F. (1992) *Precipitation of mixtures of anionic surfactants*, in *Mixed Surfactant Systems* (eds P.M. Holland and D.N. Rubingh), ACS Symposium Series No. 501, American Chemical Society, Washington, DC, pp. 392–401. Copyright 1992, American Chemical Society.)

should always be lower than the temperature at which the formulation is used. Many systems show an eutectic with respect to the Kraft temperature, as illustrated in Figure 13.17 for a mixture of two alkylbenzene sulfonates. As can be seen, the reduction in Kraft point is substantial. This behavior is typical for mixtures of surfactants of the same class and explains the well-known fact that a technical surfactant, which is almost always a mixture of many different species, has a lower Kraft temperature than the pure substance with the same general formula.

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14

Surfactant–Polymer Systems

There are many Technical Applications of Polymer–Surfactant Mixtures

Surfactants and water-soluble polymers have very broad ranges of applications. This has been described in different chapters of this book, together with the underlying physico-chemical mechanisms. Reviewing the compositions of various products, we learn that in very many cases one or more polymers are present together with one or more surfactants. In a typical situation, they are employed to achieve different effects—colloidal stability, emulsification, flocculation, structuring and suspending properties, rheology control—but in some cases a synergistic effect is addressed. The combination of polymers and surfactants is found in such diverse products as cosmetics, paints, detergents, foods, personal care formulations, polymer synthesis, and formulations of drugs and pesticides.

The use of a polymer and a surfactant in combination may be based on different effects, such as controlling phase behavior, controlling the interfacial properties, or controlling the formation of networks due to association. The most important and well-understood use of polymers and surfactants together is to achieve a suitable rheology, that is, thickening and gelation effects. Phase behavior effects include the solubilization of water-insoluble polymers. One example is the depression of clouding (increase of the cloud point) of a polymer solution achieved by the addition of an ionic surfactant. The polymer-induced micellization leads to a lowering of the surfactant unimer concentration and activity. This can be significant for the elimination of irritation caused by the surfactant. Phase separation phenomena are the basis for the deposition of conditioning polymers in hair care formulations.

Broadly discussed in this chapter are the interactions between different types of polymers, in particular water-soluble homopolymers and graft copolymers, with the different classes of surfactants. Important starting points are other mixed solute systems, in particular surfactant–surfactant and polymer–polymer mixed solutions.

Polymers can Induce Surfactant Aggregation

One of the most significant aspects of a surfactant is its ability to lower the interfacial tension between an aqueous solution and some other phase. For an ionic surfactant, in particular, this is modified by the presence of a polymer in the solution. As illustrated in Figure 14.1, the effect of a polymer on the surface tension of an aqueous solution is different for different surfactant concentrations. At low concentrations, there may or may not be, depending on the surface activity of the polymer, a lowering of the surface tension. However, at some concentration there is a break in the surface tension curve and a more or less constant value is attained. There is then a concentration region, roughly proportional in extension to the polymer concentration, with a constant γ value. Finally, there is a decrease toward the value obtained in the absence of polymer.

We note that in a wide range of surfactant concentrations the polymer addition has the effect of increasing γ . The fact that the surfactant has a lower tendency to go to the air–water interface means that there is an association to the polymer. This association apparently starts at the concentration of the first break, often termed the critical association concentration (CAC). After that there is no further increase in surfactant activity and, thus, no further lowering of γ . As the polymer is saturated with surfactant (with the saturation concentration increasing with the polymer concentration), the surfactant unimer concentration and the activity start to increase again. Then there is a lowering of γ until the unimer concentration reaches the critical micelle concentration (CMC), after which γ is constant and normal surfactant micelles start to form.

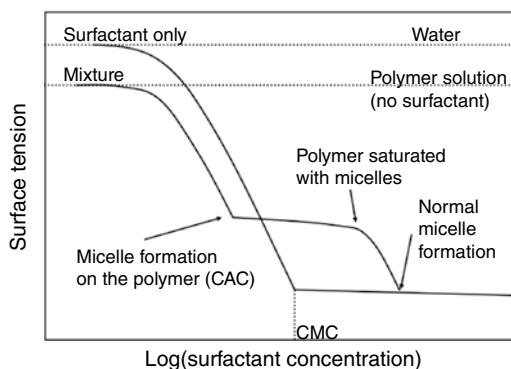


Figure 14.1 A schematic plot of the concentration dependence of the surface tension for mixed polymer–surfactant solutions. The corresponding curve for the system with only surfactant is also shown. For the case of surfactant alone there is a single-step decrease before the CMC, whereas for the mixed system there is a decrease until the onset of polymer–surfactant association (CAC), then a plateau before a second-step decrease

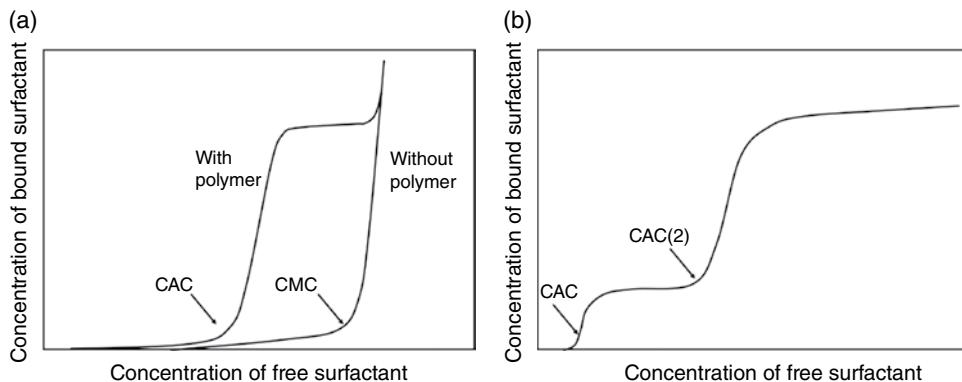


Figure 14.2 The binding isotherm of a surfactant to a polymer without distinct hydrophobic moieties, giving the concentration of bound surfactant as a function of the free surfactant concentration, can be interpreted as a lowering of the surfactant CMC by the polymer, or a strongly cooperative binding. For comparison the concentration of micellized surfactant in the absence of polymer is given (a). For polyelectrolytes with a significant hydrophobicity the binding isotherm is more complex. There can be one low concentration binding step to approximate charge neutrality (CAC) followed by a second step at higher concentrations (CAC(2)). A larger degree of hydrophobicity shifts the curve to the left (b). (With permission from Svensson, A.V., Huang, L., Johnson, E.S., et al. (2009) Surface deposition and phase behavior of oppositely charged polyion/surfactant ion complexes. 1. Cationic guar versus cationic hydroxyethylcellulose in mixtures with anionic surfactants. ACS Applied Materials & Interfaces, **1**, 2431–2442. Copyright 2009, American Chemical Society.)

This picture is confirmed if the association of the surfactant is monitored directly (e.g., by surfactant selective electrodes, by equilibrium dialysis, by self-diffusion, or by some spectroscopic technique). As illustrated by the binding isotherm shown in Figure 14.2, there is, at low surfactant concentrations, no significant interaction. At the CAC, a strongly cooperative binding is indicated. At higher concentrations, we see a plateau level, and then a further increase of the free surfactant concentration until the unimer concentration joins the curve obtained in the absence of polymer. We note from Figure 14.2 the strong analogy with micelle formation and the interpretation of the binding isotherm in terms of a depression of the CMC. As also illustrated in Figure 14.2, for the case of both hydrophobic and electrostatic attraction there may be a two-step binding process.

Such a description is supported by solubilization studies, as illustrated in Figure 14.3. We note that the solubilization curves in the presence of polymer are shifted to lower surfactant concentrations but are otherwise essentially the same as those without polymer. From the break-points, we can deduce CMC/CAC values, which decrease by the same factor as those without polymer as the alkyl chain is lengthened.

Experimental binding studies of mixed polymer-surfactant solutions can be summarized as follows (Figure 14.4):

1. CAC is only weakly dependent on the polymer concentration over wide ranges.
2. CAC is, to a good approximation, independent of the polymer molecular weight down to low values. For very low molecular weights, the interaction is weakened.

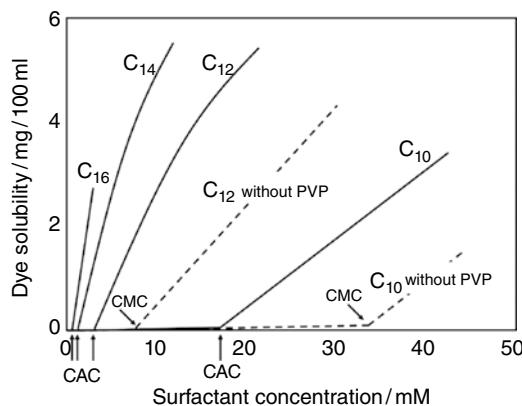


Figure 14.3 Solubilization experiments support the concept of a polymer-induced micellization. The amount of a dye, Orange OT, solubilized in mixtures of sodium alkyl sulfates of different chain lengths (C_{10} – C_{16}) and a constant concentration of poly(vinyl pyrrolidone) (PVP) is given as a function of the surfactant concentration. (Redrawn with permission from Lange, H. (1971) Interaction between sodium alkyl sulfates and polyvinyl pyrrolidone in aqueous solutions. Kolloid-Zeitschrift und Zeitschrift für Polymere, **243**, 101–109. Copyright © 1971, Springer.)

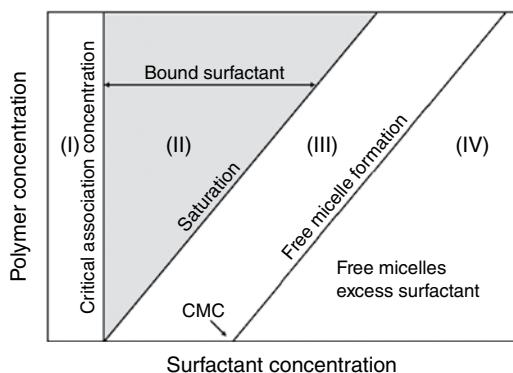


Figure 14.4 Association between a homopolymer and a surfactant in different concentration domains. (I) At low surfactant concentrations, there is no significant association at any polymer concentration. (II) Above the CAC, association increases up to a surfactant concentration, which increases linearly with the polymer concentration. (III) Association is saturated and the surfactant unimer concentration increases. (IV) There is a coexistence of surfactant aggregates at the polymer chains and free micelles

3. The plateau binding increases linearly with the polymer concentration.
4. Anionic surfactants show a marked interaction with most nonionic homopolymers while cationic surfactants show a weaker but still significant interaction. Nonionic and zwitterionic surfactants only rarely show a distinct interaction with homopolymers.
5. The association between ionic surfactants and oppositely charged polymers is strong and CAC decreases considerably with polymer charge density.

Attractive Polymer–Surfactant Interactions Depend on both Polymer and Surfactant

There are, thus, two alternative pictures of mixed polymer–surfactant solutions, one describing the interaction in terms of a (strongly cooperative) association or binding of the surfactant to the polymer and one in terms of a micellization of surfactant on or in the vicinity of the polymer chain. Both descriptions are useful and are largely overlapping. However, we will see that for polymers with hydrophobic groups the binding approach is preferred, while for hydrophilic (nonionic or ionic) homopolymers the micelle formation picture has distinct advantages.

As regards aggregate structure in these systems, the “pearl-necklace model” (Figure 14.5), with the surfactant forming discrete micellar-like clusters along the polymer chain, has received wide acceptance for the case of mixed solutions of ionic surfactants and homopolymers. The aggregation numbers are typically similar or slightly lower than those of micelles formed in the absence of a polymer.

In the presence of a polymer, the surfactant chemical potential may be lowered with respect to the situation without polymer (Figure 14.6). There are several interactions that can be responsible for surfactant binding or a polymer-induced micellization. We note that in many respects (effect of surfactant alkyl chain length, solubilization, micelle structure, and dynamics) there is a close similarity to the micellization of the surfactant alone. The normal hydrophobic interaction between the surfactant alkyl chains must, therefore, still be a dominating contribution to the free energy of association. However, it is modified by mainly one of the following two factors.

For polymers that have hydrophobic segments, there will be a hydrophobic attraction between the polymer molecules and the surfactant molecules. Such interactions will be particularly strong for block copolymers, with hydrophobic and hydrophilic blocks, and for graft copolymers, with hydrophobic groups grafted onto a hydrophilic polymer backbone. However, homopolymers can also have hydrophobic groups, strong as in poly(styrene sulfonate) or weak as in poly(ethylene glycol). Although weak individually, collectively they may have a very significant effect on surfactant self-assembly. The polarity of such groups (as we have seen in Chapter 7 for poly(ethylene glycol)) can decrease with increasing temperature and, thus, the association with surfactants becomes more important at higher temperatures.

Electrostatic interactions are obvious if both the surfactant and the polymer are charged; then in the case of opposite signs of the charges we can expect a quite strong association.

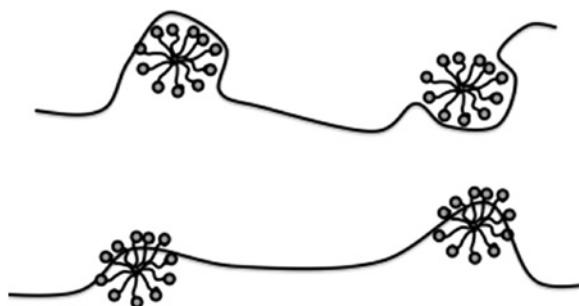


Figure 14.5 “Pearl-necklace model” of surfactant–polymer association

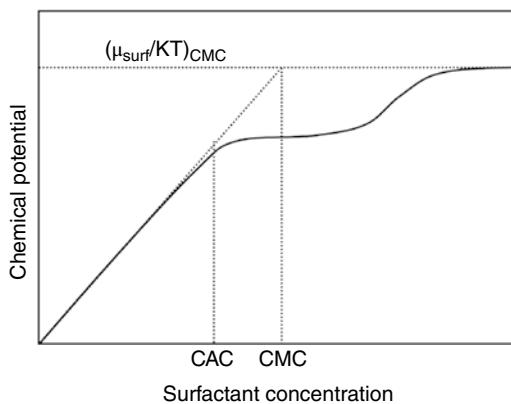


Figure 14.6 In the presence of a polymer, the chemical potential may be lowered, leading to micelle formation at a lower concentration. This figure gives the chemical potential (μ) of the surfactant divided by kT as a function of surfactant concentration on a logarithmic scale. In the presence of a polymer (solid curve), the chemical potential is lowered and micelle formation on the polymer starts at a lower concentration (CAC) than in the absence of polymer (CMC) (dashed lines). (With permission from Evans, D.F. and Wennerström, H. (1994) *The Colloidal Domain. Where Physics, Chemistry, Biology, and Technology Meet*, VCH, New York, p. 312. Copyright 1999, John Wiley & Sons.)

However, we must also take into account the repulsive interactions between charged polymer molecules or between charged surfactant molecules. In particular, we learnt in our discussion of ionic surfactant self-assembly that the entropy loss associated with the increased concentration of counterions at the aggregate surface compared to the bulk is highly unfavorable for self-assembly and explains, *inter alia*, why ionic surfactants have orders of magnitude higher CMCs than nonionics.

A polymer may modify this entropy contribution in a number of different ways. If it is ionic and has a similar charge, then we have a simple and relatively moderate electrolyte effect, whereas the polyion–surfactant interaction is repulsive. If its charge is opposite, and it acts as a multivalent electrolyte, then the interaction becomes very strong, as an association between the polymer and the micelle leads to a release of the counterions of both the micelles and the polymer molecules; a very similar effect will be obtained in mixtures of two oppositely charged polymers (Chapters 3, 5 and 9.). Indeed, for such a case there is a lowering of the CMC by orders of magnitude, as illustrated in Figure 14.7. As expected the effect becomes more important the larger the charge density of the polymer.

From the binding isotherms in Figure 14.8 it can be seen that, as expected, this polyion–surfactant association becomes weaker in the presence of electrolyte, as reflected in binding isotherms shifting to higher surfactant concentrations.

Nonionic cosolutes may decrease the CMC for ionics, as we learnt from the example of addition of different alcohols (Chapter 4). If the cosolute is slightly amphiphilic it will be located in the micelle surface. It will then lower the charge density and, hence, decrease the entropic penalty in forming micelles. This is believed to be the mechanism behind the moderate depression of the CMC for ionic surfactants by poly(ethylene glycol) and several nonionic polysaccharides.

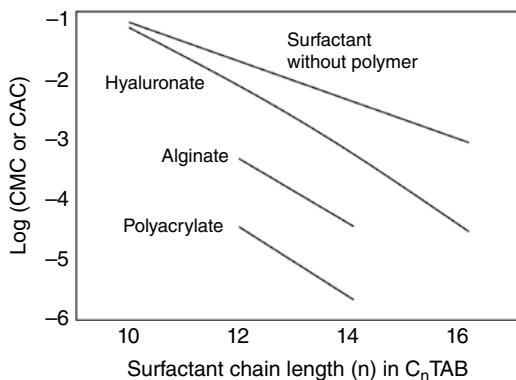


Figure 14.7 The CAC is typically orders of magnitude lower than the CMC for an ionic surfactant in the presence of an oppositely charged polymer. The logarithm of the CMC and the CAC of alkyltrimethylammonium bromides in the presence of two anionic polysaccharides, sodium hyaluronate and sodium alginate, and one synthetic anionic polymer, sodium polyacrylate, are plotted versus the number of carbons in the alkyl chain. (With permission from Per Linse. Based on data from Thalberg, K. and Lindman, B. (1989) Interaction between hyaluronan and cationic surfactants. *Journal of Physical Chemistry*, **93**, 1478–1483 and Hayakawa, K., Santerre, J.P. and Kwak, J.C.T. (1983) Study of surfactant-polyelectrolyte interactions. Binding of dodecyl- and tetradecyltrimethylammonium bromide by some carboxylic polyelectrolytes. *Macromolecules*, **16**, 1642–1645.)

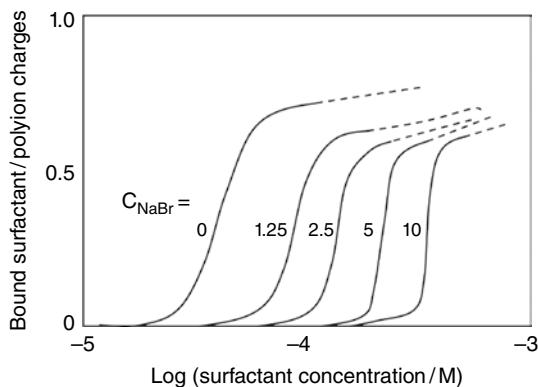


Figure 14.8 The binding isotherms of dodecyltrimethylammonium ions, expressed as the ratio of bound surfactant molecules and polyion charges, in solutions of sodium polyacrylate, as a function of the sodium bromide concentrations (in millimolar). (With permission from Hansson, P. and Almgren, M. (1995) Polyelectrolyte induced micelle formation of ionic surfactants and binary surfactant mixture studied by time-resolved fluorescence quenching. *Journal of Physical Chemistry*, **99**, 16684–16693. Copyright 1995, American Chemical Society.)

We note from these arguments that ionic surfactants would be expected to interact broadly with different types of water-soluble polymers. This is true, in particular, for anionics; the considerably weaker interaction of cationics is due to a higher degree of counterion binding. Nonionic surfactants, on the other hand, should have little tendency to interact

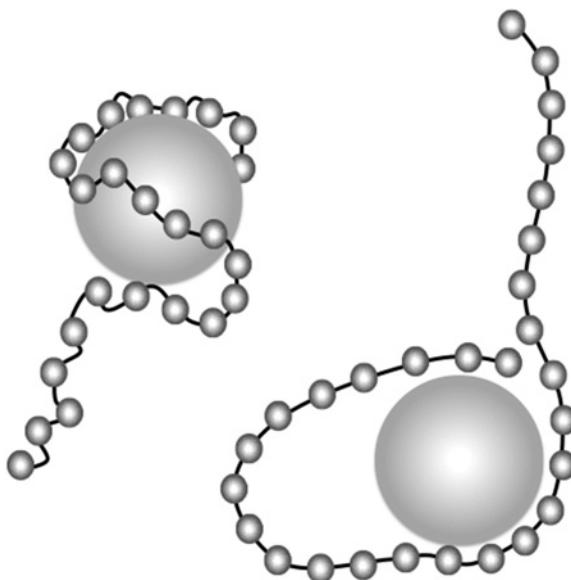


Figure 14.9 There is a stronger polymer–micelle association for flexible polymers than for rigid ones. (With permission from Wallin, T. and Linse, P. (1996) Monte Carlo simulations of polyelectrolytes at charged micelles. 1. Effects of chain flexibility. *Langmuir*, **12**, 305–314. Copyright 1996, American Chemical Society.)

with hydrophilic homopolymers, as no further stabilization of the micelles can be expected; we noted above that nonionic surfactants only rarely associate to homopolymers. The situation will, of course, be different for polymers with hydrophobic parts to which nonionics will associate by hydrophobic interaction.

Another factor that is important for polymer–surfactant association is the polymer stiffness. A polymer that is flexible and has a short persistence length is expected to adapt better to a surfactant micelle and, thus, give a lower CAC (Figure 14.9).

Surfactant Association to Surface Active Polymers can be Strong

The modification of water-soluble homopolymers with hydrophobic groups, such as alkyl chains, and using a low grafting density (of the order of 1% of the monomers reacted is a typical figure) leads to amphiphilic polymers, which have a tendency to self-associate by hydrophobic interaction. This weak aggregation (Figure 14.10) leads to an increase in viscosity and other rheological characteristics, hence the use of these “associative thickeners” as rheology modifiers in paints and other products.

An added surfactant will interact strongly with the hydrophobic groups of the polymer, leading to a strengthened association between the polymer chains, and thus to an increased viscosity. We exemplify this behavior with a hydrophobically modified (HM) nonionic cellulose ether (HM-EHEC, where EHEC is ethylhydroxyethylcellulose) (Figure 10.3). As can be seen in Figure 14.11, sodium dodecyl sulfate (SDS) increases the viscosity dramatically

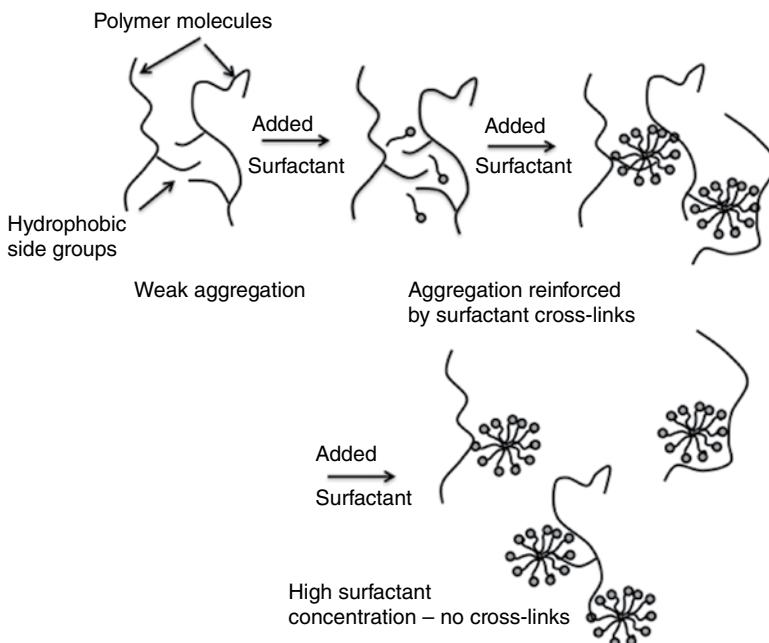


Figure 14.10 The self-association of a hydrophobically modified (HM) water-soluble polymer can be strengthened or weakened by a surfactant, depending on the stoichiometry

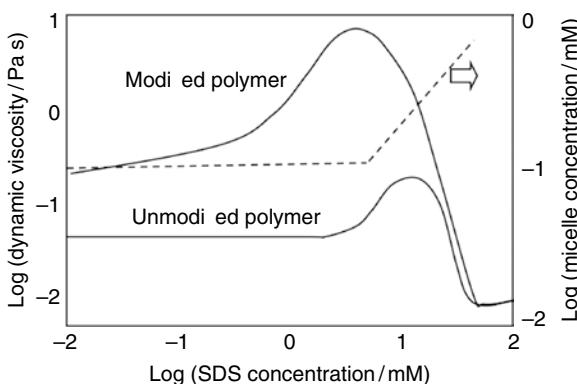


Figure 14.11 Addition of SDS to a solution of a HM polymer (EHEC) gives a strong increase in viscosity at first and then a decrease to a low value. For the unmodified polymer, changes in viscosity are small. Also shown is the concentration of micelles formed by the polymer hydrophobes and the surfactant. Addition of SDS leads to an increase in micelle aggregation number until the optimal aggregation of about 60 is reached. After this the micelle concentration increases leading to decreased cross-linking. (With permission from Thuresson, K., Lindman, B. and Nyström, B. (1997) Effect of hydrophobic modification of a nonionic cellulose derivative on the interaction with surfactants. *Rheology. Journal of Physical Chemistry B*, **101**, 6450–6459, Copyright 1997, American Chemical Society, and Nilsson, S., Thuresson, K., Hansson, P. and Lindman, B. (1998) Mixed solutions of surfactant and hydrophobically modified polymer. Controlling viscosity with micellar size. *Journal of Physical Chemistry B*, **102**, 7099–7105, Copyright 1998, American Chemical Society.)

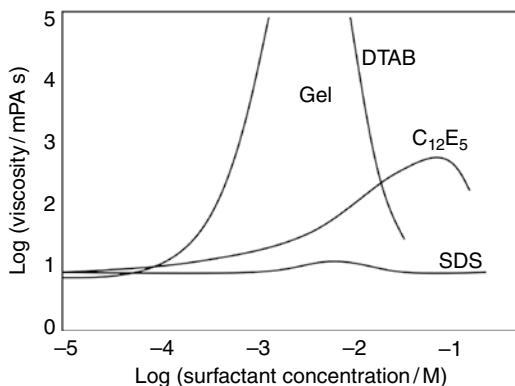


Figure 14.12 Addition of a surfactant to a solution of a HM polyelectrolyte (in this case, HM polyacrylate) gives very different viscosity effects for different types of surfactants. The effect is much larger for an oppositely charged surfactant (dodecyltrimethylammonium bromide) (DTAB) than for a nonionic ($C_{12}E_5$) or a similarly charged one (SDS). (With permission from Magny, B., Iliopoulos, I., Audebert, R., et al. (1992) *Interactions between hydrophobically modified polymers and surfactants*. Progress in Colloid and Polymer Science, **89**, 118–121. Copyright 1992, Springer.)

for HM-EHEC but only slightly for unmodified EHEC. At higher surfactant content, the viscosity effect is lost. As we will see, we can best understand these systems in terms of a mixed micelle formation between the surfactant and the amphiphilic polymer. In order to have cross-linking, and thus a viscosity effect, there must be a sufficiently high number of polymer hydrophobic groups per micelle. At higher surfactant concentrations, there will be only one polymer hydrophobic group in a micelle and all cross-linking effects are lost.

These viscosity effects of the addition of surfactant to a solution of a HM water-soluble polymer are general, but the effect will be modified by other interactions, such as electrostatic ones. As exemplified in Figure 14.12, addition of an oppositely charged surfactant to a solution of a HM polyelectrolyte gives much larger viscosity effects than for a nonionic or a similarly charged surfactant; however, even in the latter case, there are substantial effects, especially if the hydrophobic grafts are large.

In mixtures of surfactants and clouding polymers that become less polar at increasing temperatures, thermoreversible gels may be formed. On increasing the temperature, gelation is induced and on cooling the gel melts. Such an effect may also be obtained in mixtures of a nonionic surfactant and a HM water-soluble polymer, when there is an important temperature-induced micelle growth or a transition from micelles to vesicles or some other self-assembly structure.

The Interaction between a Surfactant and a Surface Active Polymer is Analogous to Mixed Micelle Formation

A HM water-soluble polymer (HM-polymer) is a strong amphiphile that can be viewed as a “polymer-modified surfactant.” It forms micelles, or hydrophobic microdomains, on its own at very low concentrations (Figure 14.10) and these micelles can solubilize hydrophobic

molecules. Furthermore, a HM-polymer and a surfactant in general have a strong tendency to form mixed micelles in a similar way as two surfactants. Two stoichiometries are important for HM-polymer–surfactant systems, namely the alkyl chain stoichiometry and the charge stoichiometry.

Since the mixed aggregates dominate, we have a low concentration of free surfactant and essentially no free micelles until the concentration of micelles exceeds the concentration of polymer hydrophobic groups. From this, we can understand the binding isotherm of a surfactant to a HM-polymer (Figure 14.13). The binding isotherm of an ionic surfactant to a nonionic HM-polymer will be very similar to its binding to nonionic surfactant micelles. We can distinguish between three concentration regions. In the first region, there is a high affinity non-cooperative binding of individual ionic surfactant molecules to micelles of the nonionic surfactant or the HM-polymer. As the number of ionic surfactant molecules per micelle exceeds one, the binding becomes anti-cooperative since the binding of surfactant to a similarly charged micelle is unfavorable. Finally, as the free surfactant concentration equals the CAC, that is, the CMC in the presence of the homopolymer, there is a self-association of the ionic surfactant to micelles at the polymer. This is seen as a cooperative binding region, which is the only binding seen for the corresponding homopolymer. At still higher surfactant concentrations, there is a coexistence of micelles at the polymer chains and free surfactant micelles (cf. Figure 14.4, not shown in Figure 14.13).

The peak in the plot of viscosity versus surfactant concentration in general occurs in the vicinity of the CAC. Here, the composition of the mixed HM-polymer–surfactant micelles changes strongly with concentration to become dominated by the surfactant; thus the cross-linking effect is lost.

The significance of the micelle–polymer hydrophobe stoichiometry is illustrated in Figure 14.11. The sensitivity of viscosity to surfactant concentration above the viscosity maximum is a major problem in many applications (especially when the surfactant concentration cannot be well controlled). However, playing with the micelle size can be an efficient

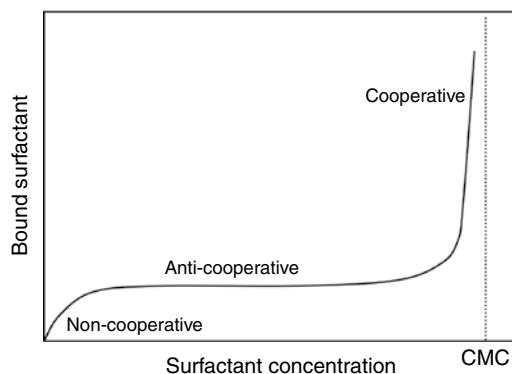


Figure 14.13 The binding isotherm (giving the concentration of bound surfactant as a function of the free surfactant concentration) for an ionic surfactant to a nonionic HM polymer is similar to the binding to a nonionic micelle, that is, with (a) one non-cooperative, (b) one anti-cooperative, and (c) one cooperative region. With the parent homopolymer, only the cooperative region is seen. (Courtesy of Lennart Piculell.)

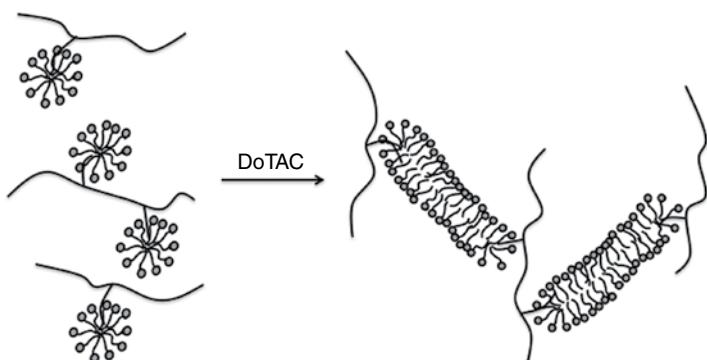


Figure 14.14 Inducing micellar growth in a system, where polymer chains are decoupled due to excess of micelles, leads to dramatic increases in viscosity. For the system of Figure 14.11, addition of small amounts of a cationic surfactant leads to a viscosity increase by more than three orders of magnitude. (With permission from Nilsson, S., Thuresson, K., Hansson, P. and Lindman, B. (1998) Mixed solutions of surfactant and hydrophobically modified polymer. Controlling viscosity with micellar size. *Journal of Physical Chemistry B*, **102**, 7099–7105. Copyright 1998, American Chemical Society.)

remedy for the problem. Thus reducing the number of micelles by inducing micellar growth (as illustrated in Figure 14.14) can lead to major increases in viscosity; growth of ionic micelles can, for example, be achieved by addition of small amounts of an oppositely charged surfactant or of an electrolyte.

Phase Behavior of Polymer–Surfactant Mixtures Resembles that of Mixed Polymer Solutions

General Aspects and Nonionic Systems

For the case of mixed solutions of a surfactant and a HM-polymer we can see a large tendency for association between the two cosolutes. Above we also learnt that many homopolymers facilitate micelle formation of an ionic surfactant. However, an associative interaction is by no means evident, as for many polymer–surfactant pairs there is no net attractive interaction.

For two polymers in a common solvent, the entropic driving force of mixing is weak and we typically encounter a segregation into two solutions, one rich in one polymer and one rich in the other (Figure 9.11); the tendency for phase separation increases strongly with the molecular weights of the polymers. Since a micelle is also characterized by a high molecular weight, we would expect segregative phase separation to be a common phenomenon (Figure 14.15).

For polymer solutions we can distinguish between two types of phase separation, that is, one segregative and one associative (Figure 9.11). For a mixed polymer–surfactant system the behavior is completely analogous. One difference is that the “degree of polymerization” of a micelle, unlike a polymer, is not fixed but may vary with the conditions (temperature, electrolyte concentration, etc.), as we learnt in our discussion of micellar growth (Chapters 6 and 7).

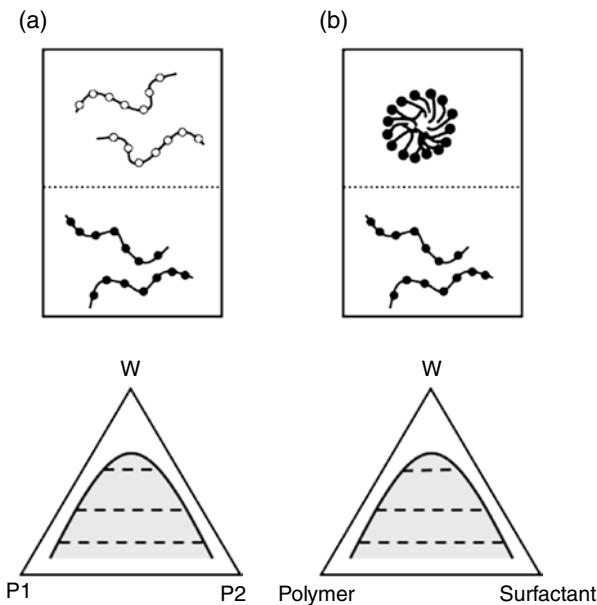


Figure 14.15 Because of the high molecular weight of a micelle we expect a mixed polymer–surfactant solution, in the absence of significant attractive interactions, to display the incompatibility typical of polymer mixtures (a), that is, segregation into one polymer-rich and one micelle-rich solution (b)

In Figure 14.16, we present the phase diagram of a surfactant–polymer mixture, a nonionic polyoxyethylene surfactant and dextran. Comparing with Figure 9.12 we can see that the two mixtures phase separate in qualitatively the same way. Since dextran is a quite polar polymer the attraction between the polymer and the micelles is insignificant.

Changing the surfactant produces major changes in the phase diagram. Thus, $C_{12}E_5$ gives a much stronger segregation than $C_{12}E_8$ and with $C_{12}E_5$ the segregation increases strongly with increasing temperature. We note that this is exactly what we would expect from our discussion of micelle sizes for these surfactants (Chapter 7): $C_{12}E_8$ forms small roughly spherical micelles at all temperatures; $C_{12}E_5$ forms large micelles, which grow strongly with temperature; and $C_{12}E_6$ exhibits an intermediate behavior.

The segregative phase separation is not the only one observed for mixtures of a non-ionic polymer and a nonionic surfactant. For the case of a less polar polymer, the phase separation can be associative, especially at higher temperatures, due to hydrophobic association.

Introduction of Charges

The introduction of charged groups in the solutes has a profound influence on phase separation phenomena. We have already learnt that polyelectrolytes are much more soluble than the corresponding uncharged polymers, which we attribute to the entropy of the counterions. Confining polymer molecules to part of the system costs little entropy due to the small number of entities. On the other hand, there is a large entropy loss on confining

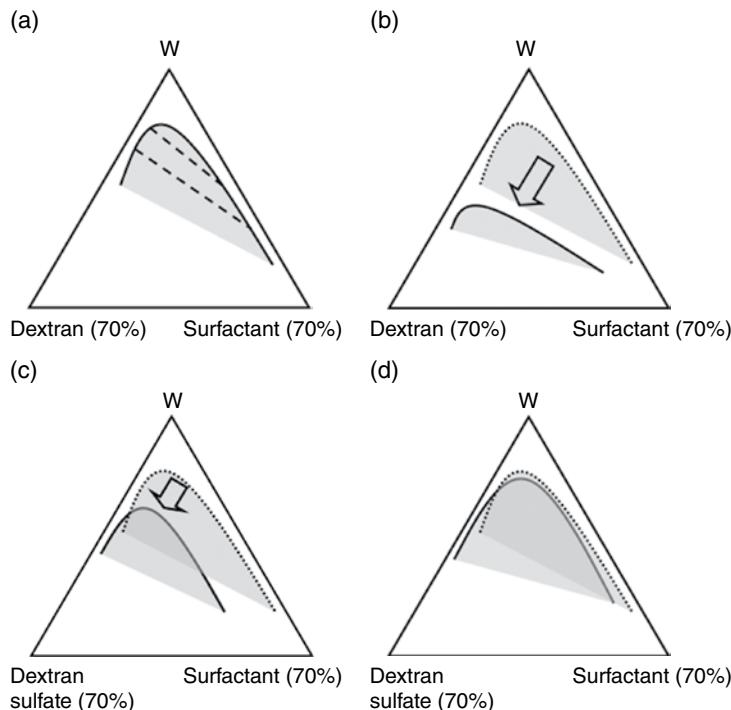


Figure 14.16 Phase diagrams of a mixture of dextran (M_w 40 000) with $C_{12}E_5$ (a). Both on introducing a low fraction of ionic surfactant in the micelles (b), or a low amount of sulfate groups in dextran (c), the mutual miscibility is strongly enhanced. This can be eliminated either if electrolyte is added or if both the polymer molecules and the micelles are charged up (d). Above the curves there is miscibility, while below there is phase separation into two solutions. The dotted curves give the miscibility limit for the reference system (a). (With permission from Bergfeldt, K. and Piculell, L. (1996) Phase behavior of weakly charged polymer/surfactant/water mixtures. *Journal of Physical Chemistry*, **100**, 5935–5940. Copyright 1996, American Chemical Society.)

the (much more numerous) counterions. Therefore, in mixed nonionic polymer–surfactant solutions even a slight charging up of either the polymer (by introducing ionic groups) or the micelles (by adding ionic surfactant) strongly enhances polymer–surfactant miscibility. This is illustrated in Figure 14.16, where we also see that addition of electrolyte tends to eliminate the effects of the charges. When the polymer molecules and the micelles are similarly charged, there is also a return toward the incompatibility of the parent nonionic mixture.

Ionic surfactants usually associate with nonionic polymers. The lower the polarity of the polymer, then the stronger the association. For clouding polymers, which are on the limit of being water soluble, the association is strong and leads (as we saw in Chapter 7) to a strong increase in the cloud point. This decreased tendency to phase separation is illustrated in Figure 14.17, where we also see that quite low concentrations of electrolyte change the

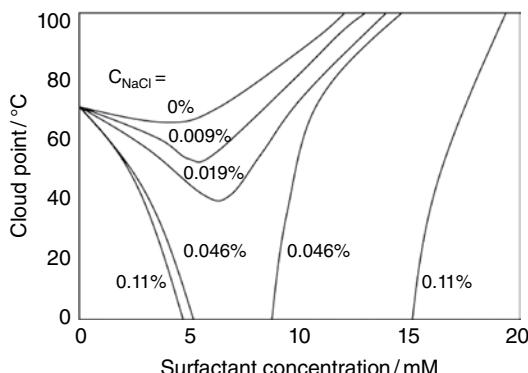


Figure 14.17 Addition of an ionic surfactant to a solution (0.9 wt%) of a clouding polymer (illustrated by EHEC) raises the cloud point in the absence of added electrolyte but decreases it in the presence of (low amounts of) electrolyte. The change in the cloud point on addition of SDS is given in the absence of added electrolyte and in the presence of different concentrations of added NaCl; from top to bottom the curves refer to 0, 0.009, 0.019, 0.046, and 0.11 wt% of salt. (With permission from Carlsson, A., Karlström, G. and Lindman, B. (1986) Synergistic surfactant-electrolyte effect in polymer solutions. *Langmuir*, **2**, 536–537. Copyright 1986, American Chemical Society.)

behavior completely. As we have seen above, there is polymer-induced micellization in these cases and, thus, a formation of polymer–surfactant complexes. Because of the charging up of the polymer, its solubility increases, again a result of the entropic penalty of confining the counterions. However, this increased solubility is eliminated on addition of low concentrations of electrolyte and there is a dramatic lowering of the cloud point. Thus, this system is intrinsically associative but associative phase separation is only possible in the presence of an electrolyte.

Mixed Ionic Systems

A mixture of two oppositely charged polyelectrolytes shows a strongly associative behavior, as demonstrated by a strong tendency to phase separation. A mixture of a polyelectrolyte and an oppositely charged surfactant will also associate strongly. This was exemplified in Figure 14.7 by a lowering of the CMC by orders of magnitude for long-chain surfactants. In addition, phase separation takes place in a broad range of concentrations. For example, if an ionic surfactant is progressively added to a solution of an oppositely charged polymer, turbidity is encountered for certain concentrations, as illustrated in the insert of Figure 14.18 for the case of a cationic cellulose derivative (cationically modified hydroxyethylcellulose (HEC)) and SDS. As SDS starts to bind to the polymer at the CAC, neutral insoluble complexes come out of solution. In this case there is a redissolution, as seen from the solutions becoming clear at higher SDS concentrations. This will occur if the polymer has a certain hydrophobicity and, thus, can bind the surfactant above charge stoichiometry; when the complexes become increasingly

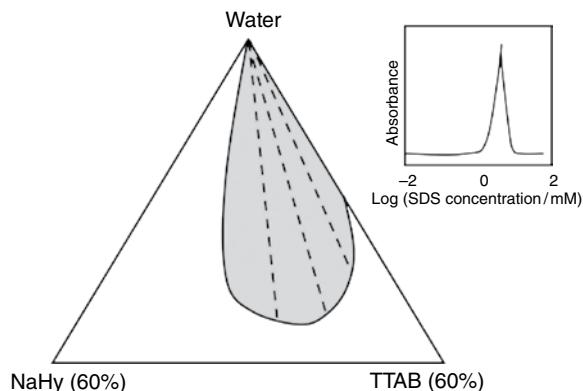


Figure 14.18 A mixture of an ionic surfactant and an oppositely charged polyelectrolyte typically gives an associative phase separation, as here exemplified by tetradecyltrimethylammonium bromide (TTAB) and sodium hyaluronate (NaHy). Inset: As measured from the absorbance of light, solutions of a polyelectrolyte normally become turbid on addition of an oppositely charged surfactant. If the polymer has some hydrophobicity, charge reversal of the complexes may occur, leading to redissolution and loss of turbidity at higher surfactant concentrations. The illustration concerns mixed solutions of cationic HEC and SDS. (With permission from Thalberg, K., Lindman, B. and Karlström, G. (1990) Phase diagram of a system of cationic surfactant and anionic polyelectrolyte: Tetradecyltrimethylammonium bromide-hyaluronan-water. *Journal of Physical Chemistry*, **94**, 4289–4295, Copyright 1990, American Chemical Society, and Svensson, A.V., Huang, L., Johnson, E.S., et al. (2009) Surface deposition and phase behavior of oppositely charged polyion/surfactant ion complexes 1. Cationic guar versus cationic hydroxyethylcellulose in mixtures with anionic surfactants. *ACS Applied Materials & Interfaces*, **1**, 2431–2442, Copyright 2009, American Chemical Society.)

negatively charged their solubility increases. This redissolution and charge reversal will not occur for entirely hydrophilic polymers.

The strong associative phase separation of such systems is better characterized in the conventional phase diagram for three-component systems as exemplified in Figure 14.18. As shown, an aqueous mixture of a polyelectrolyte and an oppositely charged surfactant phase separates into one dilute phase and one, typically highly viscous, phase concentrated in both polymer and surfactant.

The extent of phase separation in the system of Figure 14.18 increases strongly with the surfactant alkyl chain length and with the polymer molecular weight. On addition of an electrolyte, the phase separation is reduced and then eliminated, but at a higher electrolyte content there is a phase separation again. However, as we can see in Figure 14.19, this is of a different nature. This behavior, which is very similar to what we observe for mixtures of two oppositely charged polymers, can best be understood from a combination of polymer incompatibility and electrostatic effects. We note that the concentration of counterions is very high and, therefore, unlike for the nonionic polymers, phase separation with a polyelectrolyte in one phase leads to confinement of the counterions and a very significant

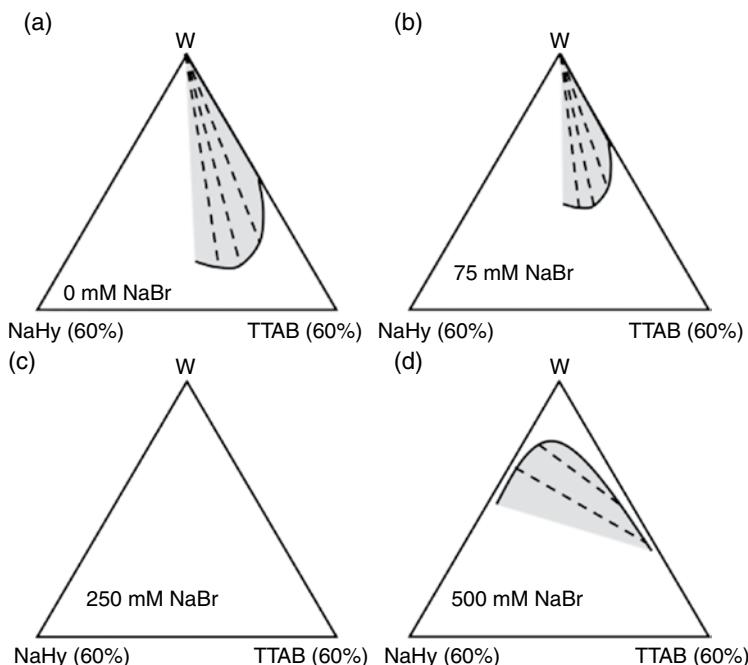


Figure 14.19 Phase separation in mixtures of a polyelectrolyte and an oppositely charged surfactant changes from associative to no phase separation and finally to segregative as electrolyte is added. The example shows mixtures of a cationic surfactant, tetradecyltrimethylammonium bromide, and an anionic polysaccharide, sodium hyaluronate. (With permission from Thalberg, K., Lindman, B. and Karlström, G. (1991) Phase behavior of systems of cationic surfactant and anionic polyelectrolyte: the effect of salt. *Journal of Physical Chemistry*, **95**, 6004–6011. Copyright 1991, American Chemical Society.)

entropy loss. At high electrolyte concentrations, this entropy contribution is eliminated and the phase separation will be similar to that of uncharged polymer systems. In the case of Figure 14.19, we have an intrinsically segregating system, as can be seen from the phase diagram at high electrolyte concentrations.

The associative phase separation, occurring for mixtures of both anionic and cationic polymers with oppositely charged surfactants, at low salt contents is thus understood from the entropy of the counterion distribution. The highly charged micelles and polyelectrolyte molecules are enriched with counterions at their surface due to the Coulombic attraction. On association, counterions of both cosolutes are transferred into the bulk with a concomitant entropy gain; therefore, there is a strong tendency to associative phase separation in the absence of added salt.

When the surfactant and the polymer have similar charges, the entropic loss is absent and a segregative phase separation is the rule (Figure 14.20). At high salt contents, phase separation is enhanced, which can be ascribed to the growth of SDS micelles.

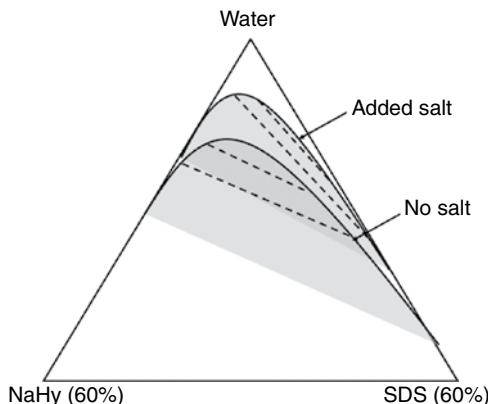


Figure 14.20 Phase separation in mixtures of a polyelectrolyte and a similarly charged surfactant is typically segregative and may be enhanced on salt addition if there is an electrolyte-induced micellar growth. The example refers to mixtures of SDS and the anionic polysaccharide sodium hyaluronate. (With permission from Thalberg, K. and Lindman, B. (1993) Segregation in aqueous systems of polyelectrolyte and ionic surfactant. *Colloids & Surfaces*, **76**, 283–288. Copyright Elsevier.)

Phase Behavior of Polymer–Surfactant Mixtures in Relation to Polymer–Polymer and Surfactant–Surfactant Mixtures

We may summarize the phase behavior of mixtures of polymer (P) and surfactant (S) depending on charge (superscript +, –, or 0) as follows:

P^+S^- , P^-S^+	Association without added electrolyte, miscibility at intermediate electrolyte, and segregation at high electrolyte concentration
P^-S^- , P^+S^+	Segregation
P^0S^0	Segregation; association may occur for less polar polymers, especially at higher temperatures
P^0S^+ , P^0S^- , P^+S^0 , P^-S^0	Phase separation inhibited; association or segregation may be induced by added salt

Polymer–surfactant systems are closely analogous to polymer–polymer systems. The molecular weights of both the polymer and the surfactant aggregate determine the extent of phase separation. Since the micelle size is not fixed but may vary with the conditions, the phase separation will be more difficult to predict than for polymer–polymer systems.

The phase behavior of polymer–surfactant systems is also affected by specific interactions between the two cosolutes, such as hydrophobic interactions for the case of the HM-polymer. This may enhance associative phase separation for nonionic systems but decrease it for ionics. For a mixture of oppositely charged polymer and surfactant, the formation of a concentrated phase with charge stoichiometric amounts of polymer and surfactant and a dilute phase containing an excess of either the polymer or the surfactant

becomes unfavorable if the polymer is hydrophobically modified. The reason is the tendency of the polymer to associate hydrophobically with the micelles in the concentrated phase. This phase will then lose the charge stoichiometry and have a tendency to swell. Therefore, associative phase separation will occur only over a restricted concentration region for a mixture of a HM polyelectrolyte and an oppositely charged surfactant.

Mixing two surfactants, on the other hand, does not give rise to segregative phase separation (Chapter 13). The reason is the strong tendency to form mixed aggregates, which gives an important additional contribution to the entropy of mixing. It is common, however, for a mixture of two oppositely charged surfactants to display an associative phase separation.

Oppositely Charged Systems are Complex: Phase Structures and Phase Diagrams

The associative phase separation occurring for systems of oppositely charged polymer and surfactant leads to one dilute and one concentrated phase. The concentrated phase can be solid or liquid in nature depending on the system but typically it has a liquid crystalline nature. Lamellar, hexagonal, and cubic structures have been identified (Figure 14.21).

The complexity of systems that contain water and two electrolytes without a common ion, like our case of a polyelectrolyte and an oppositely charged surfactant, was addressed in Chapter 5 (cf. Figure 5.17). There are four different electrolytes present; in

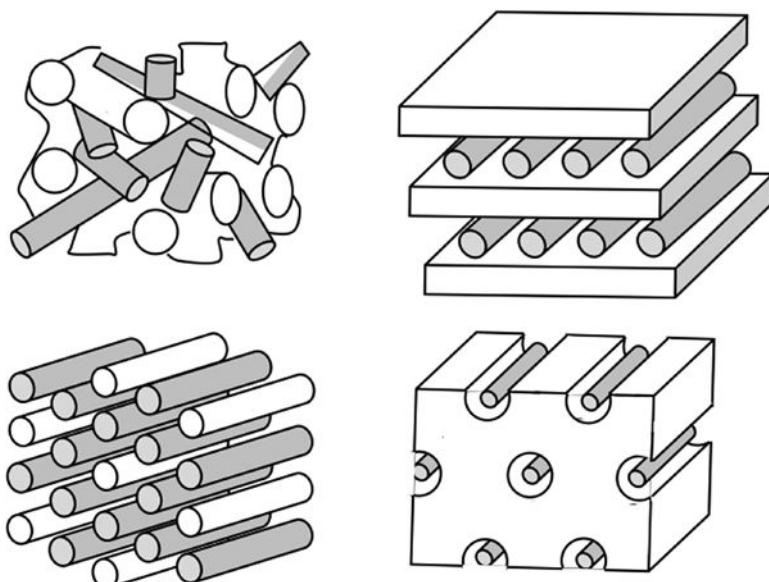


Figure 14.21 The most important liquid crystalline structures occurring in mixtures of a (rigid) polyelectrolyte (in gray) and an oppositely charged surfactant (in white). (Reproduced from Bilalov, A., Olsson, U. and Lindman, B. (2012) Complexation between DNA and surfactants and lipids: phase behavior and molecular organization. *Soft Matter*, **8**, 11022–11033 with permission of The Royal Society of Chemistry.)

addition to the surfactant and the polyelectrolyte, there is also the polyion with surfactant (the “complex salt”) and the two counterions (the “simple salt”). A representation of such a system thus requires a three-dimensional diagram as shown in Figure 5.17. The triangular phase diagrams given above represent two-dimensional cuts in such three-dimensional pyramids. A more appropriate simplification for many applications is the one represented in the right part of Figure 5.17c, in which is indicated the phase separation into dilute and concentrated phases induced on dilution with water. The more water that is added, the more concentrated will the concentrated phase be. The figure explains that the underlying mechanism is a dilution of the simple salt (present even if no salt is added to the formulation since it comes from the counterions). The salt decreases the attraction between the surfactant aggregates and the polyions. On dilution the attraction becomes stronger, inducing phase separation, an effect used for example in hair care formulations.

In view of the multicomponent character, these polyelectrolyte–surfactant systems are difficult to describe in phase diagrams without loss of important features. However, a remedy for this is to start from the complex salt. Thus, adding either surfactant or polyelectrolyte to a mixture of the complex salt and water leads to a genuine three-component system, which can be described in the two-dimensional triangular representation. Work along these lines has been instrumental in enlarging our understanding of formulations containing a polyelectrolyte and a surfactant.

Polymer–Surfactant Interactions are Significant for Gel Swelling and Gel Particles

Polymer gels and the effect of ions on the swelling capacity of cross-linked ionic gels were discussed in Chapter 3. Addition of ionic surfactants to polymer gels also dramatically changes the swelling of the gels, as illustrated in Figure 14.22. The nonionic polymer gel has a low swelling capacity in water by itself but when an ionic surfactant binds (from the CAC) a major increase in volume takes place. Thus, surfactant binding effectively transforms the polymer into a polyelectrolyte gel. The cationic polymer gel has, on the other hand, a large volume by itself. As an anionic surfactant starts to bind (again from the CAC) there is charge neutralization and deswelling to low volumes. In this case there is a reswelling at higher surfactant contents, which is due to surfactant binding in excess of charge neutralization (cf. Figure 14.2), leading to a charge reversal of the gel. We also note that such gel-swelling experiments provide a simple and accurate way of obtaining CAC values.

A corresponding behavior is seen for small cross-linked polymer gel particles or microgels. With ionizable groups, such as particles containing polyacrylate, the particle size will vary strongly with pH (Figure 14.23). This is very useful for many formulations, as in a wide range of volume fractions the changes in ionization will cause major changes in viscosity due to particle overlap. As can be seen, ionization by increasing the pH can induce a change in viscosity by seven orders of magnitude; this is due to particle swelling and overlap. Addition of an ionic surfactant to uncharged microgel particles gives a similar increase in viscosity; ionization by binding the surfactant causes a similar effect as ionization by deprotonation.

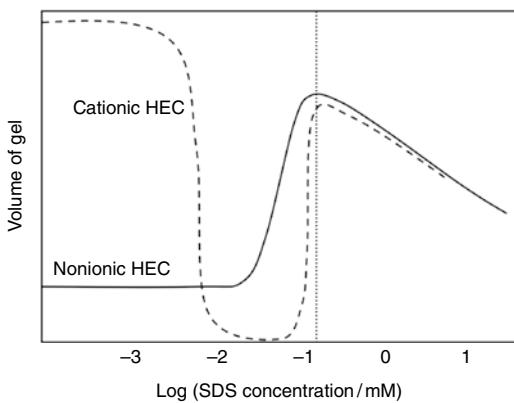


Figure 14.22 The effect of addition of an anionic surfactant (SDS) changes dramatically the volume of polymer gels as illustrated here for a nonionic polymer (HEC) and an oppositely charged polyelectrolyte (cationic HEC). (With permission from Sjöström, J. and Piculell, L. (2001) Simple gel swelling experiments distinguish between associating and nonassociating polymer–surfactant pairs. *Langmuir*, **17**, 3836–3843. Copyright 2001, American Chemical Society.)

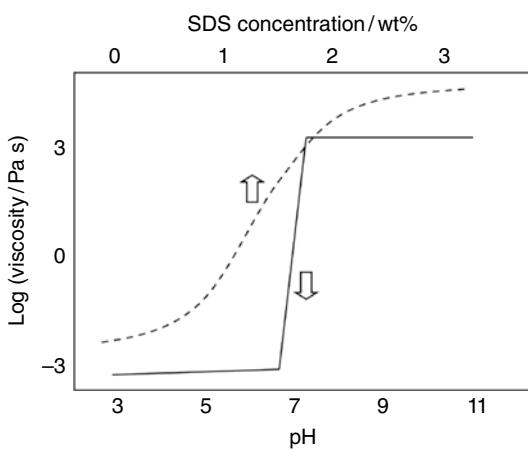


Figure 14.23 Ionization of microgel particles leads to swelling, which in turn produces major effects on viscosity. Ionization by deprotonation (solid curve) and binding of ionic surfactant (dashed curve) gives similar effects. (Adapted with permission from Antunes, F., Alves, L., Duarte, C., et al. (2012) Ionization by pH and anionic surfactant binding gives the same thickening effects of crosslinked polyacrylic acid derivatives. *Journal of Dispersion Science and Technology*, **33**, 1368–1372. Copyright Taylor and Francis Group LLC Books.)

Polymer gels can also be formed by physical cross-linking, for example, using the association between polyelectrolyte and oppositely charged surfactant. By adding small drops of a concentrated solution of a polyelectrolyte into a surfactant solution, gel particles in sizes ranging from hundreds of nanometers to millimeters can be formed; based on the associative phase separation either core-shell or homogeneous particles can be prepared.

Polymers may Change the Phase Behavior of Infinite Surfactant Self-Assemblies

The larger the surfactant self-assembly aggregate, then the larger will be the tendency for phase separation of any kind. For polymers mixed with infinite surfactant aggregates, as in a bicontinuous microemulsion or a lamellar phase, weak repulsive and attractive interactions will have a profound influence on the phase behavior. Polymer addition to microemulsions and the possibility to boost microemulsions formation are described in Chapter 17.

DNA is Compacted by Cationic Surfactants, which Gives Opportunities for Gene Therapy

Double-stranded DNA is a highly charged and stiff polyanion. Because of its high charge density, DNA interacts strongly with cationic surfactants. The surfactant binding isotherms show a strongly cooperative association, while the phase diagrams display a very strong associative phase separation. Since DNA has very high molecular weight, it is possible to directly monitor the interactions on a single molecular level by using microscopy. As a cationic surfactant is added to a DNA solution, the DNA molecules change their conformation from an extended “coil” state to compact “globules” (Figure 14.24). The DNA molecules are compacted individually, and over a wide concentration range there is a coexistence of coils and globules.

Native DNA is highly extended due to the electrostatic repulsions between different parts of the polymer molecule (driven by the entropy of the counterion distribution). DNA induces self-assembly of a cationic surfactant and DNA compaction by a surfactant can be viewed as an associative phase separation at the single molecular level.

Many diseases have a genetic origin and are cured by modifying the DNA sequence. However, in order to allow DNA to be transferred into cells, it needs to be compacted. Cationic cosolutes, such as surfactants and lipids, are efficient transfection agents of great interest for developments in gene therapy.

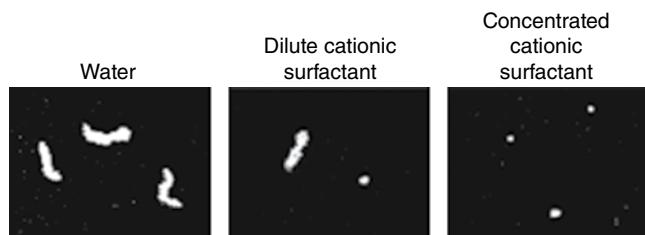


Figure 14.24 By adding a fluorescent probe molecule, DNA molecules can be directly visualized by fluorescence microscopy. Addition of a cationic surfactant leads to compaction of individual DNA molecules

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15

Surfactant–Protein Mixtures

Proteins are Amphiphilic

While our general treatise of surfactant–polymer interactions also applies to proteins, these have some features that are different from those of most other macromolecules. Proteins are copolymers built up of amino acids that contain polar and nonpolar groups; the polar groups may be ionic or nonionic, which may also vary with the pH of the solution. Thus, we can characterize a typical protein as an amphoteric polyelectrolyte with some hydrophobic groups or as an amphiphilic polymer with a variable charge density. The important differences when compared with the polymers, which we have discussed so far, are that proteins are monodisperse and that there is much less conformational freedom and variation for proteins. Many proteins are compact macromolecules with a well-defined structure on different levels. Rather different from these globular proteins (such as enzymes, hemoglobin, and albumins) are fibrous proteins (collagen, keratin, etc.) with extended linear structures. Most fibrous and globular proteins become disordered on heating.

Surfactant–Protein Interactions have Broad Relevance

Since surfactants and proteins are both amphiphilic, it is natural that they associate. These interactions show similarities to other surfactant–macromolecule systems, in particular to systems of amphiphilic polymers, such as hydrophobically modified water-soluble polymers. Globular proteins differ from the other polymers we have discussed in that they are monodisperse and in that they are compact and essentially lack conformational freedom. One important difference relates to the reversibility: the surfactant binding to a protein at

higher stages of binding, for ionic surfactants in particular, may lead to conformational changes that are irreversible, that is, the equilibrium conformation is not recovered on removing the surfactant. Protein denaturation by a surfactant is an important aspect in many applications. In studies of interactions, it is a complicating factor, since mixed solutions of surfactants and proteins may involve protein molecules in different conformational states. Complexes involving a denatured protein have close analogies to complexes between surfactants and partially hydrophobic, flexible polymers.

The interactions between small amphiphilic molecules—lipids and surfactants—and proteins have a broad significance in industrial, biological, food, pharmaceutical, and cosmetic systems. Examples of these include the following: lipid-membrane protein interactions in cell membranes; surfactant-induced skin irritation, related to the interaction of surfactant with stratum corneum proteins; the exposure of human hair and wool proteinaeous substrates to surfactants on washing and other processes; protein-surfactant and protein-lipid combinations in edible products; the interactions of surfactants with gelatin in industrial, pharmaceutical, and photographic applications; sodium dodecyl sulfate-polyacrylamide gel electrophoresis as an important technique for the determination of the molecular weight of proteins; emulsification of soil in the detergent industry and oils in personal hygiene products; enzyme-containing washing powders; renaturation of proteins; extraction and purification of proteins assisted by nonionic surfactants; enzyme catalysis in microemulsions.

Surfactants Associate to Proteins and may Change their Conformation

Before considering concrete examples of protein-surfactant association, predictions based on our learning in Chapter 14 on polymer-surfactant interactions in general are relevant. Since proteins are amphiphilic and, in addition, at least for water-soluble proteins, have a net charge, they are expected to interact with surfactants both with hydrophobic and, for ionic surfactants, electrostatic interactions; the latter can, of course, be either attractive or repulsive. Because of hydrophobic groups or domains in the protein we expect a non-cooperative binding at low surfactant concentrations, exactly as for hydrophobically modified water-soluble polymers (cf. Figure 14.13). For ionic surfactants associating with oppositely charged proteins we can expect binding isotherms of the type shown in Figure 14.2, thus with two steps.

We note again that it is important to consider both non-cooperative association and protein induced self-assembly of surfactants; we emphasize, also, that surfactant micelles are dynamic entities and, therefore, a description in terms of polymer-micelle association is not valid. Rather, emphasis should be on any micelle formation that occurs below the critical micelle concentration (CMC).

Cosolutes may have an important influence on protein conformation and solubility. Most water-soluble proteins owe their solubility to a net charge, as can be inferred from the decreased solubility around the isoelectric point (where the protein has no net charge), and salt sensitivity. Binding of an oppositely charged surfactant, therefore, easily leads to precipitation of a protein.

Decreased solubility can also be associated with protein denaturation and surfactant-induced denaturation is an important aspect of protein–surfactant solutions, which we will come back to later.

Surface Tension and Solubilization give Evidence for Surfactant Binding to Proteins

The normal surface tension versus surfactant concentration curve (Chapter 4) is modified by a protein in a way that resembles that observed for weakly polar homopolymers. Thus, Figure 15.1, which gives the surface tension of solutions of sodium dodecyl sulfate (SDS) in the presence of gelatin, shows clear analogies with that shown earlier in Figure 14.1: the surface tension curve has a break far below the CMC, followed by a plateau region and then a further decrease down to values approaching those of the solution of surfactant alone. In the case of a nonionic surfactant, no effect of the protein is seen (Figure 15.1). However, for other cases, a clear interaction between a protein and a nonionic surfactant is indicated from surface tension curves. As discussed in Chapter 14, most polymers do not associate with nonionic surfactants, with the general exception being strongly amphiphilic polymers, such as hydrophobically modified water-soluble polymers.

The solubility of a water-insoluble nonpolar substance, such as a dye, starts to be important above the CMC for a surfactant solution (Chapter 4). In the presence of a polymer, solubilization starts at a lower concentration, thus signifying a polymer-induced surfactant micellization (Figure 14.3). An analogous effect is observed for many protein solutions (Figure 15.2). This indicates that a water-soluble protein can also induce surfactant self-assembly leading to the formation of hydrophobic microdomains well below the CMC.

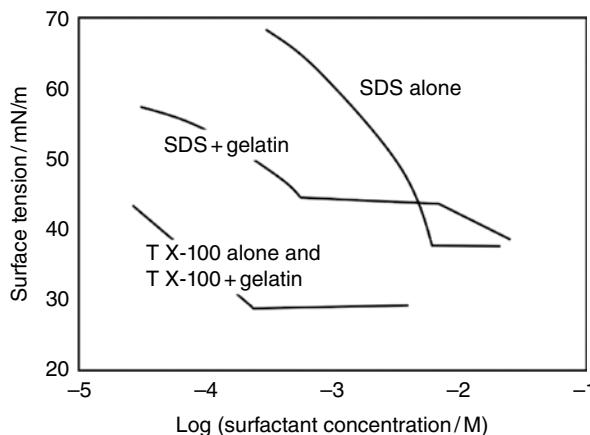


Figure 15.1 The effect of gelatin on the surface tension of solutions of SDS and Triton X-100 (deca(ethylene glycol)mono{octylphenyl ether). (With permission from Knox, Jr, W.L. and Parshall, T.O. (1970) The interaction of sodium dodecyl sulfate with gelatin. Journal of Colloid and Interface Science, 33, 16–23. Copyright Elsevier.)

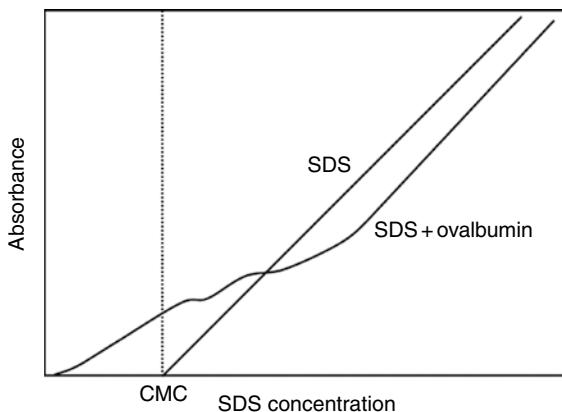


Figure 15.2 Solubilization (measured by the increase in UV absorbance) of dimethyl aminoazobenzene (probe) by ovalbumin–SDS solutions

However, the behavior is not as clear-cut as for many homopolymer systems, and it is difficult to identify a critical association concentration (CAC).

The Binding Isotherms are Complex

The association of surfactants to proteins is directly illustrated in binding isotherms obtained by equilibrium dialysis and other techniques for a few proteins (Figure 15.3). The important features of the binding isotherms are the combination of a low degree of non-cooperative binding at low surfactant concentrations and a massive cooperative binding at higher concentrations. Often binding is described in terms of a low amount of high affinity binding to specific sites, followed in the second stage by cooperative binding.

The interesting analogy with surfactant binding to hydrophobically modified polymers (described in Chapter 14) is illustrated in Figure 15.3b for the case of SDS interacting with lysozyme; at low concentrations, there is a low amount of non-cooperative binding, which is followed by first an anti-cooperative region and then an extensive cooperative binding. In analogy with what we saw for oppositely charged polymers and surfactants (cf. Figure 14.8) the binding curves are shifted to higher surfactant concentrations in the presence of electrolyte; furthermore, the phase separation region becomes smaller.

In considering binding isotherms for oppositely charged protein–surfactant pairs, precipitation phenomena must be noted; so-called *high-affinity binding* at low surfactant concentrations has been shown to involve precipitation of a stoichiometric complex (see below). In the same way as for nonionic polymers, anionic surfactants associate much more strongly than cationic ones, whereas nonionics often show no association. Anionics may also associate to proteins at pH values above the isoelectric point, where the protein has a net negative charge.

Structural and mechanistic descriptions of protein–surfactant complexes are few but it appears that the first step is due to hydrophobic interactions between the surfactant

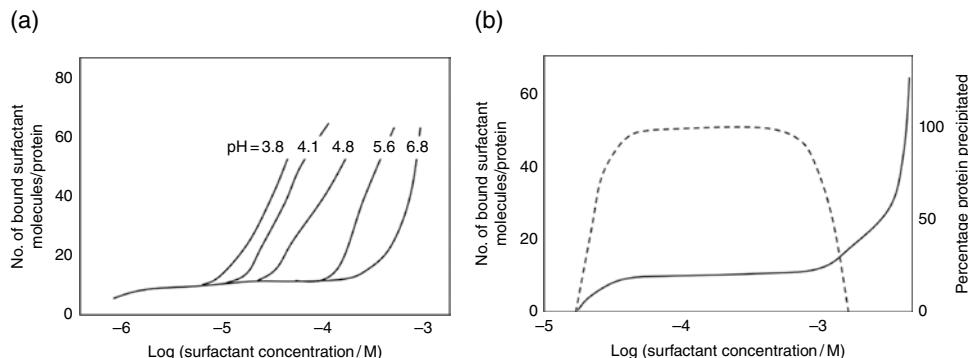


Figure 15.3 Surfactant binding (expressed as the number of surfactant molecules per protein molecule) to bovine serum albumin for SDS at different pH levels (a) and surfactant binding and protein precipitation in dilute mixtures of SDS and lysozyme. The number of bound SDS molecules per lysozyme molecule (continuous curve), as well as the fraction of the protein in the precipitated phase (dashed curve), is shown as a function of the free surfactant concentration (b). (With permission from Reynolds, J.A., Gallacher, J.P. and Steinhardt, J. (1970) Effect of pH on the binding of N-alkyl sulfates to bovine serum albumin. *Biochemistry*, **9**, 1232–1238, Copyright 1970, American Chemical Society, and Fukushima, K., Murata, Y., Sugihara, G. and Tanaka, M. (1981) The binding of sodium dodecyl sulfate to lysozyme in aqueous solution. *Bulletin of the Chemical Society of Japan*, **54**, 3122–3127, Copyright 1961, The Chemical Society of Japan.)

hydrophobic tails and nonpolar residues/patches of the protein, whereas the second stage shows analogies with polymer-induced micellization. In the second stage of binding, there is an unfolding of the protein to expose the hydrophobic interior. Therefore, many globular proteins are gradually converted into random coils and a “pearl necklace” structure, similar to that adopted for simple polymers (Figure 14.5), is frequently used as a model; thus, there are strings of globular micelles decorating the polypeptide backbone. The micelles formed appear to have considerably lower aggregation numbers (and, therefore, a lower solubilization capacity) than the micelles formed by the surfactant alone or in the presence of hydrophilic homopolymers.

Protein–Surfactant Solutions may have High Viscosities

Addition of a surfactant to a solution of gelatin may, for higher protein concentrations, show a marked viscosity increase with a maximum as a function of the surfactant concentration (Figure 15.4). Similar observations have been made for mixed solutions of globular proteins and ionic surfactants. The behavior has analogies with that displayed by solutions of mixtures of surfactants and hydrophobically modified water-soluble polymers (but is not at all so pronounced). This is in line with the amphiphilic nature of the protein. The viscosity effect is related to the formation of micelle-like aggregates cross-linking the protein molecules.

Another interesting manifestation of the amphiphilic character of proteins is when a protein is added to a solution of a hydrophobically modified polymer. As can be seen in

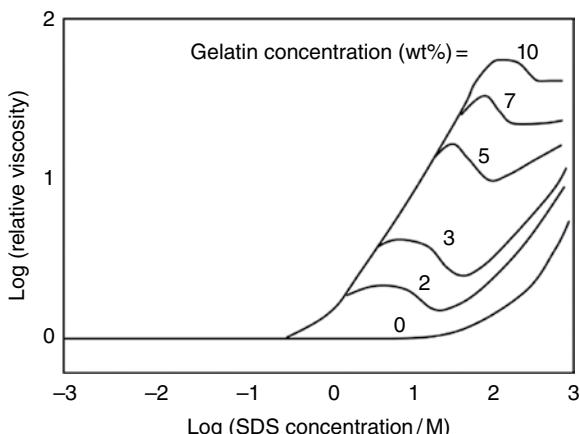


Figure 15.4 Relative viscosity for gelatin solutions of different concentrations as a function of the concentration of added SDS. (With permission from Greener, J., Contestable, B.A. and Bale, M.D. (1987) Interaction of anionic surfactants with gelatin. *Macromolecules*, **20**, 2490–2498. Copyright 1987, American Chemical Society.)

Figure 15.5 for the case of hydrophobically modified polyacrylate and lysozyme, protein addition leads to a very significant viscosity increase; at higher protein concentrations, the viscosity decreases to low levels. There is a very interesting similarity to the effect of surfactant micelles (Figure 14.11 and Figure 14.12), which is in line with both surfactant micelles and proteins having a hydrophobic interior and a hydrophilic surface. For the combination of serum albumin and hydrophobically modified polyacrylate the effects are even more pronounced; a schematic picture of the gelation mechanism is given in Figure 15.5.

Protein–Surfactant Solutions may give rise to Phase Separation

Precipitation of a protein with net positive charge on binding of an anionic surfactant is a common phenomenon; at higher surfactant concentrations, there is a redissolution. The behavior shows analogies with that of mixed systems of an ionic polymer and an oppositely charged surfactant in general (Figure 14.19) but oppositely charged protein–surfactant pairs are more complex, as we will illustrate with mixed solutions of lysozyme and SDS.

As SDS is added to a solution of lysozyme, there is, at low concentrations of SDS, formation of a solid-like neutral complex with excess protein in solution (Figure 15.6). The amount of precipitate reaches a maximum as the number of surfactant molecules per protein is eight, which corresponds to the number of net positive charges on lysozyme. Excess of surfactant leads to redissolution; for surfactants with shorter alkyl chain lengths, more surfactant is needed for redissolution. The latter occurs in the cooperative part of the binding isotherm, when the free surfactant concentration reaches the CMC (Figure 15.3b). Interestingly, the anionic surfactant–lysozyme precipitate can be redissolved not only by an excess of anionic surfactant, due to charge reversal of the complex, but also by a cationic

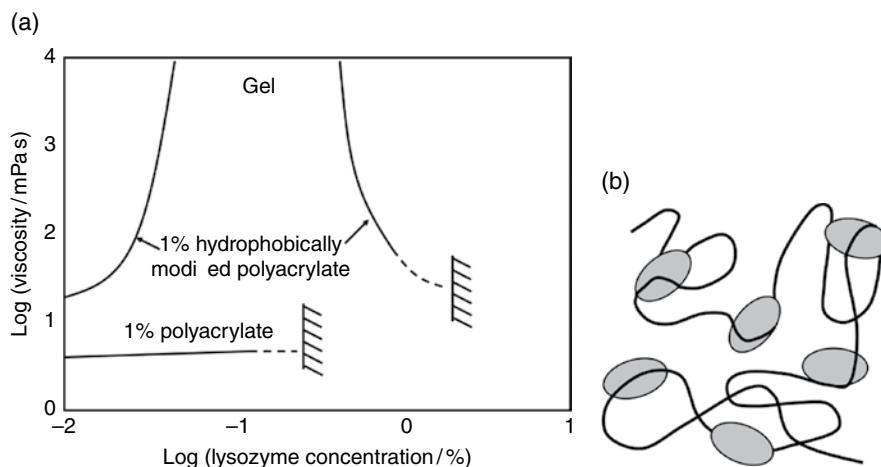


Figure 15.5 (a) Variation of viscosity as a function of lysozyme concentration for 1% solutions of polyacrylate and hydrophobically modified polyacrylate (3% modification by octadecyl groups); (b) schematic illustration of the association between bovine serum albumin and hydrophobically modified polyacrylate. (With permission from Petit, R., Audebert, R. and Iliopoulos I. (1995) Interactions of hydrophobically modified poly(sodium acrylate) with globular proteins. Colloid and Polymer Science, **273**, 777–781, Copyright © 1995, Springer, and Tribet, C., Porcar, I., Bonnefont, P.A. and Audebert, R. (1998) Association between hydrophobically modified polyanions and negatively charged bovine serum albumin. Journal of Physical Chemistry B, **102**, 1327–1333, Copyright 1998, American Chemical Society.)

surfactant. However, the mechanism is then completely different. It is due to a stronger association between the cationic and the anionic surfactant than between the anionic surfactant and the protein.

The low amount of surfactant needed for precipitation, as well as the low amount of water in the precipitate, and the stoichiometry of the complex, is related to the globular nature of the protein. A well-defined tertiary structure favors the formation of well-defined complexes and the water content is low for a neutral precipitate formed by rigid particles; this is in contrast to the gel-like coacervates formed in mixtures of surfactants and hydrophobically modified water-soluble polymers or gelatin and gum-arabic.

The cooperative binding and the precipitation of a neutral complex at low surfactant concentrations can be described in terms of a solubility product (K_s) of the neutral compound, according to:

$$PS_n(s) = P^{n+} + nS^-; K_s = [P^{n+}][S^-]^n \quad (15.1)$$

when considering the case of a negatively charged surfactant (S^-) and a positively charged protein (P^{n+}). The critical surfactant concentration for binding is that where the solubility product is just exceeded. Since the complex involves many surfactant molecules, the critical surfactant concentration depends only weakly on the protein concentration and the binding becomes markedly cooperative.

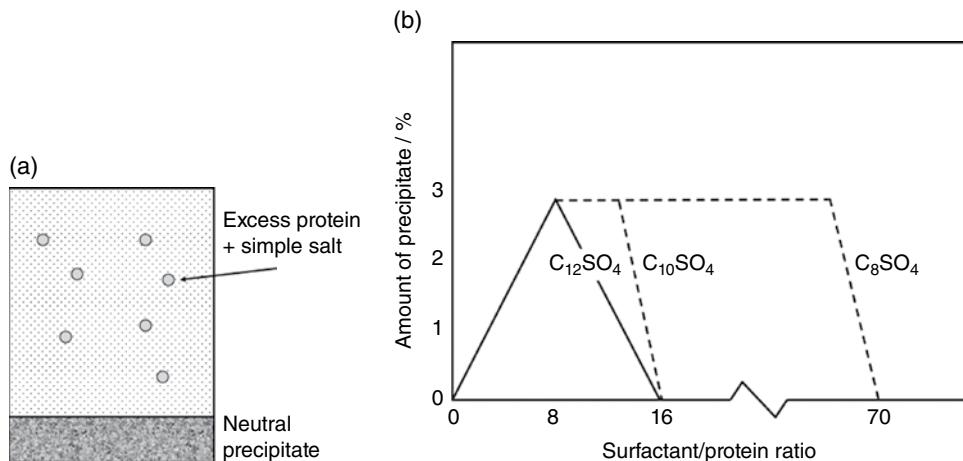


Figure 15.6 (a) Mixed solutions of a cationic protein and an anionic surfactant give, over wide composition ranges, a neutral precipitate in equilibrium with a solution with excess protein; (b) the amount of precipitate in solutions of lysozyme and a sodium alkyl sulfate increases linearly with the surfactant/protein stoichiometry until it reaches eight, the net number of positive charges on the enzyme. Redissolution at higher surfactant concentrations is more efficient with a more strongly associating surfactant. (With permission from Stenstam, A., Khan, A. and Wennerstrom, H. (2001) The lysozyme–dodecyl sulfate system: an example of protein–surfactant aggregation. *Langmuir*, **17**, 7513–7520. Copyright 2001, American Chemical Society.)

The phase behavior is complex, with not only solid and solution phases but also a (blue) isotropic gel phase, occurring over a narrow range around a well-defined surfactant:protein ratio. The effect of progressive surfactant addition is shown in Figure 15.7a, together with a schematic phase diagram (Figure 15.7b). Whereas the associative phase separation shows similarities with that of other polyelectrolyte–ionic surfactant systems, we underline the important additional features. One is the minute amount of surfactant needed for the onset of phase separation. Another is the occurrence of a novel gel phase in which a three-dimensional network is due to partially denatured protein molecules.

There are thus three types of protein–surfactant aggregates in such systems: the insoluble complex salt (precipitate), an electrostatically swollen gel-like state containing macroscopic aggregates, and a soluble complex containing a single protein molecule.

Surfactants may Induce Denaturation of Proteins

Globular water-soluble proteins owe their stability to hydrophobic intramolecular interactions balancing hydrophilic interactions. Weakening the hydrophobic interactions is the cause of denaturation by low molecular weight cosolutes, such as urea or guanidinium chloride.

For surfactants the mechanism of denaturation is completely different. Due to their amphiphilic character they may strengthen the hydrophobic interactions and stabilize a

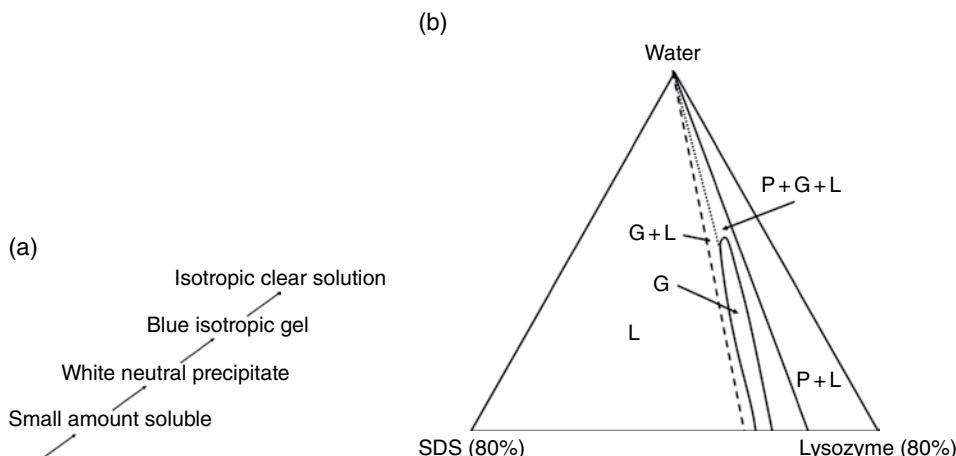


Figure 15.7 (a) There is a sequence of sample characteristics as SDS is progressively added to a solution of lysozyme. (Reproduced by courtesy of Anna Stenstam.) (b) The phase diagram (concentrations in wt%) shows schematically the regions for the occurrence of solution (L), gel (G), and precipitate (P), as well as two- and three-phase regions. (With permission from Morén, A.K. and Khan, A. (1995) Phase equilibria of an anionic surfactant (sodium dodecyl sulfate) and an oppositely charged protein (lysozyme) in water. *Langmuir*, **11**, 3636–3643. Copyright 1995, American Chemical Society.)

protein. For nonionic surfactants, therefore, both stabilization and destabilization is possible. Binding of larger amounts of ionic surfactants, often acting as denaturants at concentrations orders of magnitude below those of urea or guanidinium chloride, will cause an osmotic swelling of the protein overcoming the hydrophobic interactions.

As we have seen, ionic surfactants in general bind to proteins and can then initiate unfolding of the tertiary structure. Anionic surfactants, such as SDS, denature proteins more than cationics. Nonionic surfactants, on the other hand, have minor effects on the tertiary structure of the protein. The unfolding of the protein typically occurs in the region of the binding isotherm, where a significant increase in surfactant binding by nonspecific cooperative interactions starts. SDS is a strong protein denaturant but, interestingly, insertion of oxyethylene groups reduces the effect considerably. Denaturation by SDS is also reduced by the addition of nonionic or zwitterionic surfactants. The role of mixed micelle formation was discussed in Chapter 13. At low binding ratios, surfactants can stabilize proteins against thermally induced unfolding.

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16

Surfactant–Polymer Mixtures at Interfaces

Water-soluble polymers are often present in surfactant-based systems, for example, in personal care products. One role of the polymer is to regulate the rheological behavior of the system; this aspect is covered in Chapters 14 and 19. In this chapter we will demonstrate that polymers and surfactants collaborate or compete with respect to their adsorption on solid surfaces. The interaction of a surfactant with a polymer at surfaces makes it possible to tune the adsorbed layer and to access nonequilibrium trapped states.

Figure 16.1a illustrates that a surfactant can associate with a polymer being adsorbed at a surface, as well as in bulk. There are two important aspects of this phenomenon. The first is that the surfactant–polymer association changes the solubility of the polymer. A surfactant–polymer complex can either have higher or lower solubility compared to the polymer alone. Since solvency is often controlling adsorption, the polymer adsorption might decrease or increase upon association with a surfactant. The second aspect is that of kinetics. As these complexes often form slowly and polymer desorption can be very slow, the order of addition of the components can be important.

Figure 16.1a indicates three scenarios from a thermodynamic point of view:

1. The surfactant associates with the adsorbed polymer layer.
2. The surfactant associates with the polymer to give a soluble polymer–surfactant complex, thus leading to polymer desorption.
3. The surfactant adsorbs strongly to the surface, which leads to polymer desorption.

However, it should be stressed that as for polymer adsorption in general, kinetics often controls the behavior.

Adsorption from surfactant–polymer mixtures is commonly studied with increasing surfactant concentration while keeping the polymer concentration constant (Figure 16.1b).

The adsorption can, in addition to pre-adsorbing the polymer with subsequent addition of the surfactant, also be measured by pre-mixing the surfactant and polymer.

Surfactant interaction with polymers being adsorbed at a surface is not different from the interaction in solution; hence, as the surfactant concentration reaches the critical association concentration (CAC), surfactant self-assemblies start to form in the adsorbed polymer layer. From a kinetic point of view, however, the entire polymer may not be available for the surfactant, as surfactant molecules can be considered to interact only with the polymer loops and tails and not the polymer trains. Thus, a surfactant may not easily interact with the polymer when the polymer has a strong interaction with the surface, such that it is lying down at the surface, because then there are no sites on the polymer to interact with the surfactant. For polyelectrolytes this can be remedied by addition of electrolyte, which weakens the polymer interaction with the surface, creating polymer loops that are available for the surfactants.

If there is a strong attraction between the surfactant and the polymer, such that they show associative phase separation, then there is an enhanced adsorption of the surfactant–polymer complex, as a result of the decreased solvency. If, on the other hand, there is a weak attractive, or repulsive, interaction between the surfactant and the polymer, such that they show segregative phase separation, then the surfactant can displace the polymer from the surface, that is, there is a competitive adsorption, provided that the surfactant interacts directly with the surface. This is typically the case for hydrophobic surfaces, where a surfactant always adsorbs more strongly than a polymer.

Two cases can be distinguished. The first is if only one of the components adsorbs at the surface; the surface is then termed *selective*. The other case is when both components adsorb at the surface. Then the surface is termed *nonselective*. One example is the adsorption of DNA, which is anionic, and a cationic surfactant on a hydrophilic negatively charged surface. Then DNA does not adsorb alone but only in the presence of the surfactant; thus, the surface is selective. In the case of a hydrophobic surface both DNA and the surfactant adsorb; hence, the surface is nonselective. We will below get acquainted with examples from both these cases.

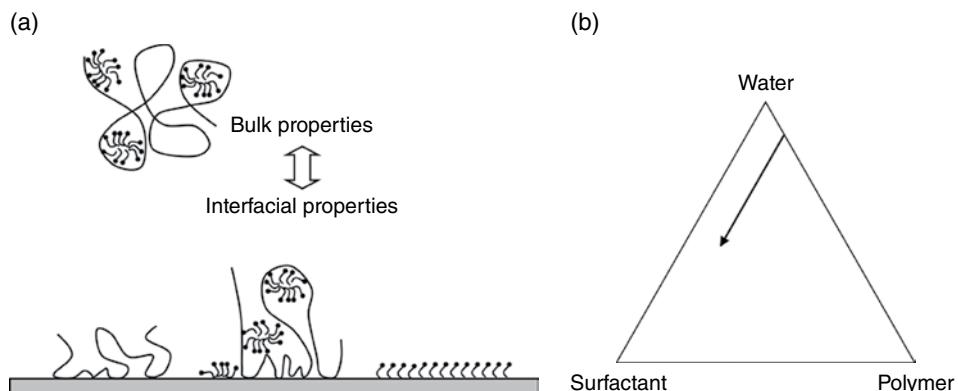


Figure 16.1 (a) Illustration of surfactant–polymer interactions at a surface and in bulk solution. The surfactant forms micelles on the adsorbed polymer loops and tails or directly on a hydrophilic surface. On hydrophobic surfaces the surfactant always adsorbs on the surface (b) Surfactant–polymer complexes at surfaces are commonly studied at increasing surfactant concentration while keeping the polymer concentration constant

The surfactant–polymer complex formation at surfaces differs from that in solution in that complexes form at a lower surfactant concentration at the surface. Also, the aggregate structures might be different (Figure 16.1a). The establishment of equilibrium of these systems can be extremely slow; hence, hysteresis is often observed. One reason is that the polymer is bound to the surface with a number of segments. Changes in the adsorbed layers can take several days. The adsorbed layer structure can also significantly depend on the order of addition of the components.

The slow kinetics also leads to the possibility that complexes can be trapped in non-equilibrium states. For example, if surfactant is added to a polymer being adsorbed at the surface, the complexes are different from the case when polymer is added to a surfactant solution in equilibrium with the surface. This is akin to the addition of a polymer to a colloid dispersion. Addition of the polymer to the colloid dispersion may cause flocculation whereas addition of the colloid dispersion to the polymer solution usually renders steric stabilization of the system (Chapter 18).

Surfactant–Polymer Interactions can both Increase and Decrease Adsorption

An illustration of how the adsorbed layer is governed by the surfactant–polymer interactions is given in Figure 16.2. Here a hydrophobically modified EHEC is adsorbed on a hydrophobic surface followed by addition of SDS. Without surfactant the hydrophobic moieties of the polymer attach to the surface, giving a compact polymer conformation at the surface. On addition of a surfactant the polymer layer swells due to the formation of charged surfactant self-assemblies together with the hydrophobic moieties of the polymer. At the same time the adsorbed amount decreases. At even higher surfactant concentrations the polymer molecules desorb from the surface and only a monolayer of surfactant is left at the surface.

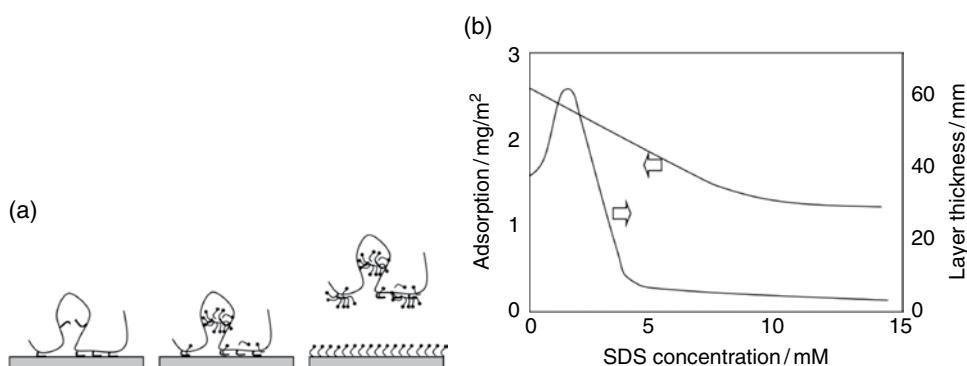


Figure 16.2 (a) Schematic drawing of the effect of adding a surfactant to a hydrophobically modified polymer that is adsorbed at a hydrophobic surface; (b) the effect of SDS addition on the adsorbed amount and thickness of a hydrophobically modified EHEC on hydrophobic silica. (With permission from Joabsson, F., Thuresson, K. and Lindman, B. (2001) *Interfacial interaction between cellulose derivatives and surfactants at solid surfaces. An ellipsometric study*. Langmuir, **17**, 1499–1505. Copyright 2001, American Chemical Society)

Polymer Adsorbs but not the Surfactant

In Chapter 14, we saw that nonionic water-soluble polymers facilitate the formation of micelles in solutions of ionic surfactants (Figure 14.5). The mechanism is that the polymer dilutes the charges at the micelle surface, hence the entropy of the counterions is increased (Figure 3.2). This type of interaction also occurs between surfactants and polymers being adsorbed on a surface. An example of this situation is given in Figure 16.3 for the adsorption of dodecylsulfate ions on a silica surface, with and without pre-adsorbed poly(ethylene oxide) (PEO). The dodecylsulfate ions show no adsorption at a silica surface but if PEO is pre-adsorbed the surfactant ions do adsorb. This is an example of surfactant–polymer complex formation at the surface, where the pre-adsorbed polymer ties the surfactant to the surface.

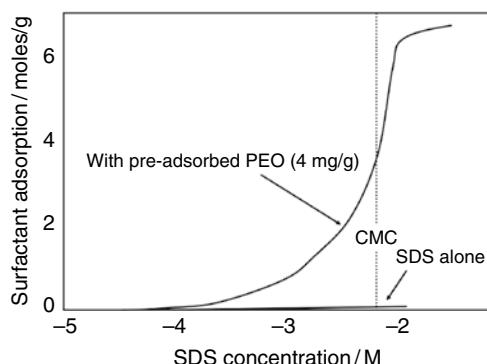


Figure 16.3 Adsorption of dodecylsulfate ions at a silica surface with and without pre-adsorbed PEO. (With permission from Maltesh, C. and Somasundaran, P. (1992) Binding of sodium dodecyl sulfate to polyethylene oxide at the silica water interface. Journal of Colloid and Interface Science, **153**, 298–301. Copyright Elsevier.)

Surfactant Adsorbs but not the Polymer

Another example of how surfactant–polymer interaction affects the adsorption is illustrated in Figure 16.4, showing the simultaneous adsorption of poly(vinyl pyrrolidone) (PVP) and dodecyl sulfate ions on an Fe_2O_3 surface. Also shown is the adsorption of the individual species. In the absence of SDS the polymer shows no adsorption (only in the order of 0.02 mg/m^2) whereas the single surfactant adsorbs at increasing levels up the critical micelle concentration (CMC). In the presence of SDS the polymer adsorbs strongly with increasing SDS concentration. This is due to the interaction between the surfactant and the polymer forming a complex at the surface. However, PVP desorbs from the surface as the SDS concentration is further increased, which is due to the increased solubility of the surfactant–polymer complex caused by the charge given to the complex from the surfactant.

Note that here the surfactant adsorbs at the surface whereas in the previous system the polymer preferentially adsorbs at the surface. In both instances it is the balance of surfactant–polymer interaction at the surface and in the solution that determines the overall behavior.

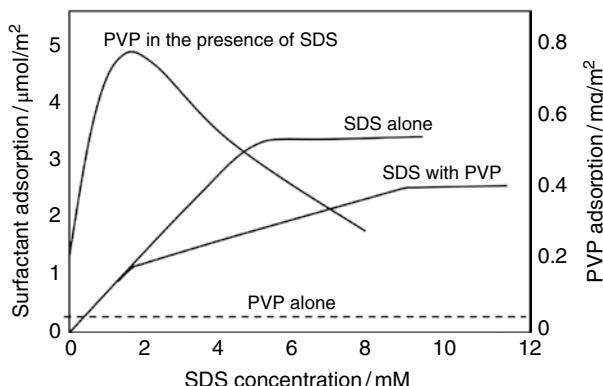


Figure 16.4 The simultaneous adsorption of PVP and dodecylsulfate on an Fe_2O_3 surface, showing that the polymer adsorbs only in the presence of surfactant. At higher SDS concentration the surfactant–polymer complex desorbs due to an increased solubility. Also shown is the adsorption of the two individual components. (With permission from Ma, C. and Li, C. (1989) Interaction between poly(vinylpyrrolidone) and sodium dodecyl sulfate at solid/liquid interface. Journal of Colloid and Interface Science, **131**, 485–492. Copyright Elsevier.)

Surfactant–Polymer Systems Showing Associative Phase Separation Adsorb at Hydrophilic Surfaces

As discussed in Chapter 14, strong polymer–surfactant complexes form when there are opposite charges of the two components giving associative phase separation. Here the driving force is the release of the counterions that are bound to the polymer and to the surfactant micelles. Such systems are commonly studied with increasing surfactant concentration while keeping the polymer concentration constant (Figure 16.5a). Hence, one passes the associative phase separation region.

Figure 16.5b gives the general form of adsorption, where the total adsorbed amount is plotted versus the surfactant concentration, at constant polymer concentration. Here the polymer is of opposite charge to both the surface and the surfactant and the surface is hydrophilic. Hence, the surface is selective since only the polymer adsorbs. An example of the general trends is given in Figure 16.5c, showing the adsorption of the system SDS and cationic hydroxyethyl cellulose (HEC) on a silica surface. In this system the polymer adsorbs but not the surfactant alone.

Beyond a certain surfactant concentration the surfactant binds to the polymer. This is the CAC of the surfactant with the polymer. In the example the CAC is 0.1 mM. The adsorbed amount increases sharply as the CAC of the system is exceeded. The association of the surfactant to the polymer lowers the charge of the polymer, leading to a compaction of the polymer chain and a reduced solubility. This results in a higher adsorption of the polymer (Chapter 11). In this surfactant concentration range there is no difference if the surfactant and the polymer are pre-mixed or if the polymer is pre-adsorbed at the surface with subsequent addition of the surfactant.

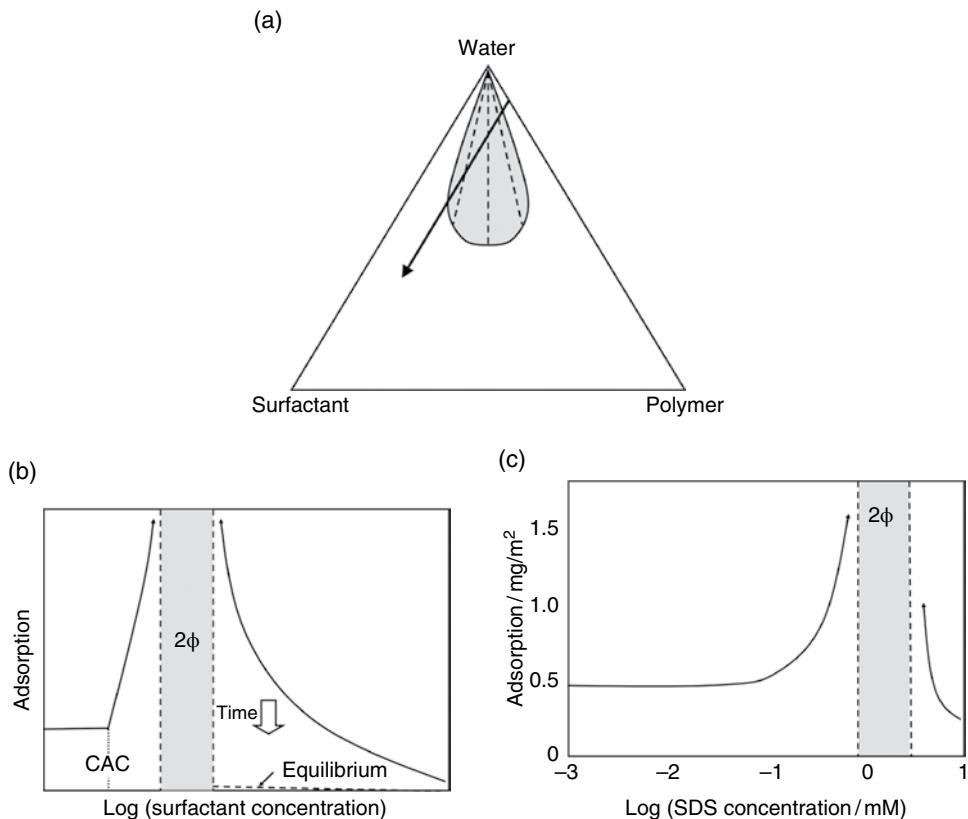


Figure 16.5 (a) Surfactant–polymer complexes at surfaces are commonly studied at increasing surfactant concentration while keeping the polymer concentration constant, hence passing a two-phase region. (b) General form of adsorption where the polymer is of opposite charge to both the surface and the surfactant as exemplified (c) by the adsorption of SDS and cationic HEC on a silica surface with 100 ppm of pre-added polymer. (With permission from Terada, E., Samoshina, Y., Nylander, T. and Lindman, B. (2004) Adsorption of cationic cellulose derivatives/anionic surfactant complexes onto solid surfaces. I. Silica surfaces. *Langmuir*, **20**, 1753–1762. Copyright 2004, American Chemical Society.)

Increasing the surfactant concentration even further takes us into a two-phase region where the surfactant–polymer complex phase separates from the solution. This is an associative phase separation. The adsorption is now at maximum. This phenomenon is used, for example, for microencapsulation of emulsion droplets with surfactant–polymer complexes where the complex adsorbs at the oil/water interface.

At even higher surfactant concentrations the surfactant–polymer complex attains the same charge as the surface and the surfactant–polymer complex becomes soluble. In this surfactant concentration regime there is no adsorption of the pre-mixed complex on silica while for the pre-adsorbed polymer case, with subsequent addition of surfactant, there is an adsorbed amount that only slowly decreases with time. Hence, the apparent inertia of absorbed polymers to desorb causes a nonequilibrium situation (desorption kinetics is normally

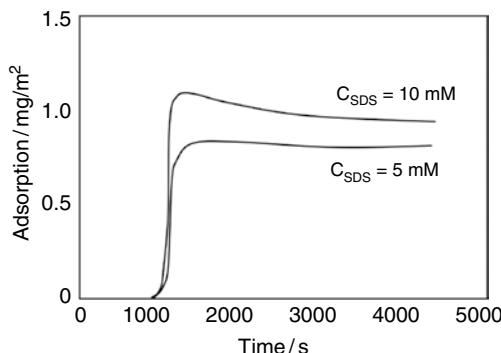


Figure 16.6 Continuous dilution of two pre-mixed SDS + cationic HEC polymer systems at time 1000 s, showing an immediate adsorption, deposition, as the two-phase region is approached. (With permission from Terada, E., Samoshina, Y., Nylander, T. and Lindman, B. (2004) Adsorption of cationic cellulose derivatives/anionic surfactant complexes onto solid surfaces. I. Silica surfaces. *Langmuir*, **20**, 1753–1762. Copyright 2004, American Chemical Society.)

much slower than adsorption kinetics). Given sufficient time the surface will eventually be free from both polymer and surfactant.

The lack of adsorption of the surfactant–polymer complex at higher surfactant concentrations reflects the fact that the complex is now strongly negatively charged, giving a higher solubility due to the counterion entropy (Chapters 3 and 9). A surfactant–polymer complex at the surface of the same charge would create a highly charged surface, resulting in a lowering of the counterion entropy (Figure 3.2), which works against adsorption.

An interesting observation is made on dilution with pure water (Figure 16.6). If a system with low surfactant concentration is diluted, the adsorption keeps intact (not shown in the figure). However, if a system with high surfactant concentration is diluted with water, the solubility decreases and on approach of the two-phase region adsorption is induced; at still higher dilution macroscopic phase separation occurs (Figures 16.5b and 16.5c). Hence, there is a deposition of the complex on the surface as water is added. This is a general observation and is taken advantage of in, for example, formulation of shampoos, dishwashing compounds, and detergents. Here the deposition of polymer on rinsing is of importance for product functionality. This is an example of the delicate balance of interactions between the surfactant–polymer complex in solution and the surfactant–polymer complex at the surface, as well as the interactions of the individual components with the surface.

Surfactant–Polymer Complexes also Adsorb at Hydrophobic Surfaces

The general effects described above apply irrespective of the surface, since the adsorption is mainly governed by the solubility. On hydrophobic surfaces there is, however, an additional feature as surfactants always adsorb at such surfaces. Therefore, surfactant adsorption starts at very low concentrations rather than at the CAC as for hydrophilic surfaces. This infers a competitive adsorption in combination with complex formation in solution and at the surface. The general features are described in Figure 16.7a and an example is given in Figure 16.7b for the simultaneous adsorption of a cationic polymer and SDS on a hydrophobic surface. Except for the surfactant adsorption at low concentrations there are the same

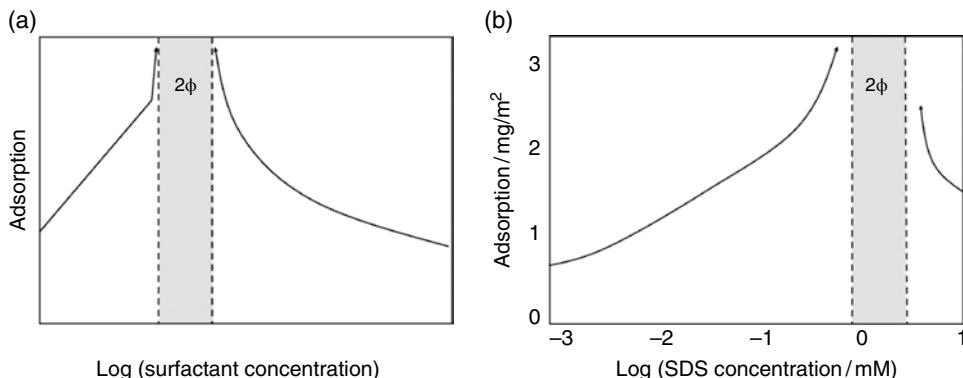


Figure 16.7 (a) General form of adsorption where the polymer is of opposite charge to the surfactant and the surface is hydrophobic as exemplified (b) by the adsorption of SDS + cationic HEC complexes at a hydrophobized silica surface. (With permission from Terada, E., Samoshina, Y., Nylander, T. and Lindman, B. (2004) Adsorption of cationic cellulose derivative/anionic surfactant complexes onto solid surfaces. II. Hydrophobized silica surfaces. *Langmuir*, **20**, 6692–6701. Copyright 2004, American Chemical Society.)

observations as on hydrophilic surfaces, namely an increased adsorption as the SDS concentration approaches the solubility limit of the surfactant–polymer complex. This increase occurs for the same reasons as for the adsorption on hydrophilic silica.

As for the adsorption on hydrophilic silica there is no adsorption of the surfactant–polymer complex at surfactant concentrations above the phase separation region. In this surfactant concentration region the surface is covered with adsorbed surfactant only; the polymer–surfactant complexes do not adsorb because they are negatively charged. The slow decrease with surfactant concentration shown in Figure 16.7b is due to a very slow desorption kinetics of the surfactant–polymer complex. If the surface is exposed to a pre-mixed surfactant polymer system above the precipitation region, then the adsorption is due to SDS alone. Hence, no adsorption of the cationic polymer occurs on the hydrophobic silica in solutions with SDS concentrations above the precipitation region.

Surfactant–Polymer Systems Showing Segregative Phase Separation give Competitive Adsorption

Segregative phase separation typically occurs when the surfactant and polymer have the same charge (Chapter 14). If the surface is selective there is just adsorption of one of the components. If, on the other hand, the surface is nonselective there will be a competition between the surfactant and the polymer for the surface sites. As for the systems showing associative phase separation these systems are normally studied with increasing surfactant concentration while keeping the polymer concentration constant. Thus, one enters the segregative two-phase separation region, but there is no one-phase region at higher surfactant concentrations (Figure 16.8a), as for associative phase separation.

Three examples are given here. The first system is SDS and poly(styrene sulfonate) (PSS), that is, both the surfactant and the polymer are negatively charged. The surface is a

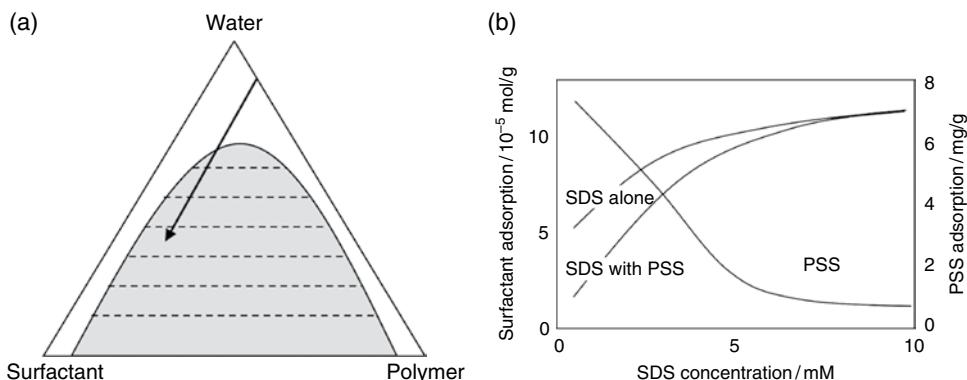


Figure 16.8 (a) Surfactant–polymer systems showing segregative phase separation are commonly studied at increasing surfactant concentration while keeping the polymer concentration constant; (b) simultaneous adsorption of decyl sulfate (SDS) and PSS (constant concentration) on alumina, showing competitive adsorption. (With permission from Esumi, K., Masuda, A. and Otsuka, H. (1993) Adsorption of poly(styrenesulfonate) and ionic surfactant from their binary mixtures on alumina. *Langmuir*, **9**, 284–287. Copyright 1993, American Chemical Society.)

positively charged alumina. Both the surfactant and the polymer adsorb below the CMC of the surfactant, although at lower amounts compared to single component solutions. Above the CMC, however, only the surfactant is present at the surface, and at the same level as without the polymer. Almost all polymer is desorbed in the presence of surfactant above its CMC (Figure 16.8b). This phenomenon is important in, for example, production of paints or coating colors. Here the pigment particles, which could be dispersed with a polyelectrolyte, are mixed with a latex dispersion that is stabilized with surfactants. If the surfactant has a higher affinity for the pigment surface than the polyelectrolyte (as in Figure 16.8b), then the polymer might desorb and the system will be destabilized.

The second system is cetyltrimethyl ammonium bromide (CTAB) and quaternized HEC on negatively charged silica. Also here the polymer is unable to compete with the surfactant for the surface sites. Hence, at sufficiently high surfactant concentrations there is no polymer at the surface.

The third system is given in Figure 11.16b, showing the displacement of poly(vinyl alcohol) (PVA) from a silica surface by addition of the nonionic surfactant octa(ethylene glycol) monononylphenyl ether (NP-E₈). The figure shows that the surfactant progressively adsorbs in place of the polymer as the surfactant concentration increases.

Polymer–Surfactant Mixtures at the Liquid–Air Interface

The effect of a weak surfactant–polymer interaction on the surface tension is exemplified with a neutral polymer and an anionic surfactant in Figure 14.1. Note that there are no surfactant–polymer complexes formed at the surface. The surface tension development with increasing surfactant concentration can be explained by desorption of the polymer from the surface due to competitive adsorption as well as surfactant–polymer complex formation in bulk solution (see Chapter 14).

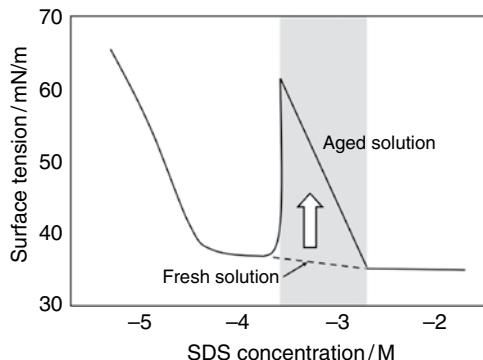


Figure 16.9 Surface tension versus SDS concentration in presence of polyDADMAC showing data of fresh and aged solutions. The shaded area indicates the region of phase separation. (With permission from Campbell, R.A., Arteta, M.Y., Angus-Smyth, A., et al. (2011) Effects of bulk colloidal stability on adsorption layers of poly(diallyldimethylammonium chloride)/sodium dodecyl sulfate at the air-water interface studied by neutron reflectometry. *Journal of Physical Chemistry B*, **115**, 15202–15213. Copyright 2011, American Chemical Society.)

A strong interaction between surfactant and polymer is exemplified with a cationic polymer and an anionic surfactant, for instance polydiallyldimethylammonium chloride (polyDADMAC) and SDS. The driving force giving the strong interaction is due to the release of counterions from both the polymer and the surfactant. Hence, the interaction is based on a gain in entropy of the counterions as described in Chapter 3. Figure 16.9 shows the surface tension versus surfactant concentration in the presence of a constant amount of polyDADMAC. At low surfactant concentrations the surfactant and the polymer form a complex at the liquid–air interface resulting in a drastic lowering of the surface tension compared to the polymer free case. At these low surfactant concentrations the surface tension is independent of the polymer concentration. The sharp increase in surface tension at a specific surfactant concentration is due to phase separation in solution where the components undergo associative phase separation with subsequent precipitation. This leaves the solution, and the surface, depleted from polymer, hence the surface tension shoots up to that of a polymer free system. Above this point the surfactant covers the liquid–air interface. It has been shown that this precipitation is a time-consuming process and the settling process takes several days to reach completion. In the figure it can be seen that fresh systems do not show this rise in surface tension.

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17

Microemulsions

The Term Microemulsion is Misleading

Microemulsions are neither micro, nor emulsions, but the term is so established that it has been kept. Instead, microemulsions are macroscopically homogeneous mixtures of oil, water, and surfactant, which on the microscopic level consist of individual domains of oil and water separated by a monolayer of amphiphile; the typical length scale is in the nanometer range. Microemulsions should not be regarded as emulsions with very small droplet size; microemulsions and (macro)emulsions (including so-called nanoemulsions) are fundamentally different (Figure 17.1). Whereas macroemulsions are inherently unstable systems in which the droplets will eventually undergo coalescence, microemulsions are thermodynamically stable with a very high degree of dynamics with regard to the internal structure. As a thermodynamically stable phase based on surfactant self-assemblies, it has much in common with other surfactant phases, micellar solutions, and liquid crystalline phases. Microemulsions can form in mixtures of surfactant, oil, and water alone but, in many cases, a second surfactant, or a so-called cosurfactant, such as a medium-chain alcohol, is required.

Oil–Water–Surfactant Systems can be Illustrated by Phase Diagrams

The application potential of microemulsions was recognized at an early stage and has triggered a build-up of knowledge about the phase behavior of oil–water–surfactant systems. The phase behavior of a three-component system can, at fixed temperature and pressure, best be represented by a phase diagram, as shown in Figure 17.2. At low surfactant concentrations,

Emulsion	Microemulsion
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Unstable, will eventually separate Large droplets (1–10 µm) Static system Moderately large internal surface, moderate amount of surfactant needed Small oil/water curvature	Thermodynamically stable Small aggregates (about 10 nm) Highly dynamic system High internal surface, high amount of surfactant needed The oil/water interfacial film can be highly curved
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Figure 17.1 Characteristic differences between emulsions and microemulsions

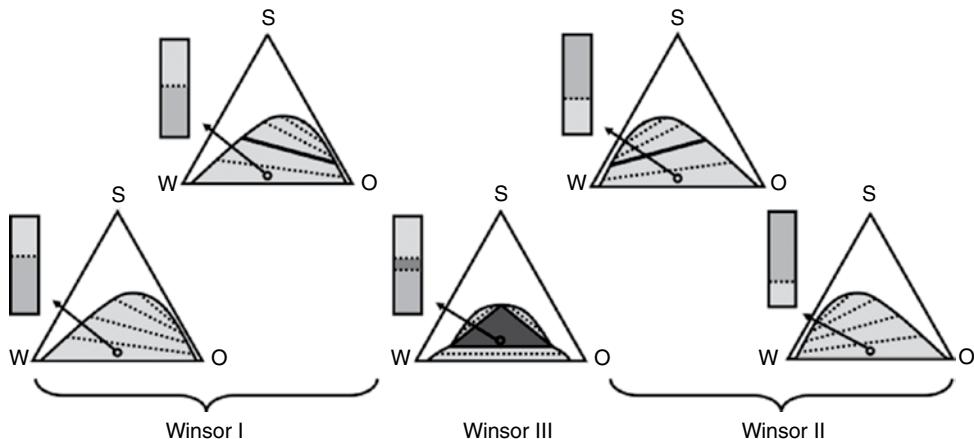


Figure 17.2 Schematic phase diagrams of surfactant–water–oil systems. In the diagram to the left, the surfactant is hydrophilic, to the right it is lipophilic, whereas the phase diagram in the middle corresponds to a balanced surfactant system. The dark triangle is a three-phase region. The black line in the two upper diagrams marks the commencement of the three-phase region. In the lower two-phase region of the middle phase diagrams there is a coexistence of oil and water phases. For efficient surfactants this region is small and often omitted in phase diagrams. A left-to-right transition may be effected by a temperature increase for nonionic surfactant systems and with an increase in salinity for ionic surfactant systems. In the test-tube illustrations the microemulsion phase is indicated with a darker shade

there is a sequence of equilibria between phases, commonly referred to as Winsor phases. A microemulsion phase may be in equilibrium with excess oil (Winsor I, or lower phase microemulsion), with excess water (Winsor II, or upper phase microemulsion), or with both excess phases (Winsor III, or middle phase microemulsion).

For nonionic surfactants, the I–III–II transition may occur by raising the temperature (from left to right in Figure 17.2), whereas for ionic surfactant systems containing an electrolyte, that is, a quaternary system, the transition may be induced by increasing salinity. Winsor I, which represents a composition based on nonionic surfactant at a low temperature, is indicative of the phase behavior of a hydrophilic surfactant. Only small quantities of oil can be solubilized into the oil-in-water (o/w) microemulsion when the surfactant is very hydrophilic, and the microemulsion is in equilibrium with almost pure oil, as indicated by the tie-lines. On raising the temperature the surfactant becomes less hydrophilic and more oil can be solubilized into the microemulsion, but the system is still of the Winsor I type. Figure 17.2 also illustrates Winsor III systems with a three-phase triangle surrounded by two-phase regions. On increasing the temperature, the microemulsion apex moves from left to right. When it is in a central position, that is, at the point where the microemulsion contains equal amounts of oil and water, the system is referred to as balanced. The height of the three-phase triangle at the point where the system is balanced can be seen as a measure of the surfactant efficiency. With a very efficient amphiphile, the microemulsion apex may appear at only a few percent surfactant; the importance of such systems is discussed in Chapter 25 in relation to enhanced oil recovery. Winsor II may be seen as a mirror image of Winsor I. The phase behavior depicted in the diagrams is also visualized by test tubes in Figure 17.2.

In the triangular diagrams of Figures 17.2, temperature is not a variable. In order to illustrate the effect of temperature on the phase behavior of oil–water–surfactant systems, a phase prism, as shown in Figure 5.11, can be used. Characterization of an entire prism is tedious, however, and, to simplify the work, the number of degrees of freedom is often reduced by one, either by keeping the oil-to-water ratio constant, usually at 1:1 (Figure 5.11) or by using a constant surfactant concentration (Figure 5.13).

Figure 17.3 illustrates a section through the phase prism for an oil–water–nonionic surfactant system at a 1:1 oil-to-water ratio, equivalent to the plane cut out of Figure 5.11

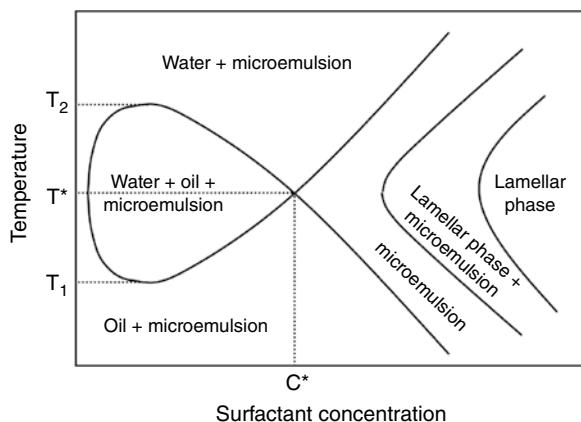


Figure 17.3 Schematic phase diagram of a ternary system based on nonionic surfactant; “lam” denotes a lamellar liquid crystalline phase. The oil-to-water ratio is kept constant and the surfactant concentration is varied. (With permission from Olsson, U. and Wennerström, H. (1994) Globular and bicontinuous phases of nonionic surfactant films. Advances in Colloid and Interface Science, **49**, 113–146. Copyright Elsevier.)

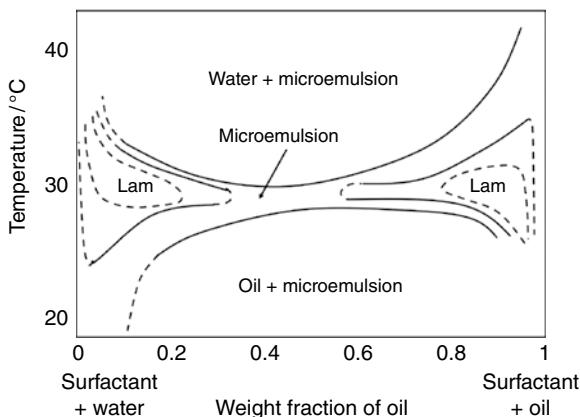


Figure 17.4 Phase diagram of the system $C_{12}F_5-H_2O$ -cyclohexane/hexadecane (1:1) at a constant surfactant concentration of 7.0 wt%. (With permission from Olsson, U., Nagai, K. and Wennerström, H. (1988) Microemulsions with nonionic surfactants. 1. Diffusion process of oil molecules. *Journal of Physical Chemistry*, **92**, 6675–6679. Copyright 1988, American Chemical Society.)

(a “fish cut”). The three-phase region, consisting of a microemulsion in equilibrium with excess oil and water, exists between the temperatures T_1 and T_2 and the temperature range is very dependent on the surfactant concentration. At a surfactant concentration C^* and at the balanced temperature T^* , the three-phase region meets the one-phase microemulsion (the microemulsion apex of the three-phase region). At higher surfactant concentrations, the microemulsion is in equilibrium with the lamellar phase.

The section through the phase prism representing constant surfactant concentration, equivalent to the plane cut out of Figure 5.13, is also a useful tool for studying the phase behavior of nonionic systems. A typical example is shown in Figure 17.4. The diagram illustrates the phase behavior when the temperature and the relative amounts of oil and water are varied.

The phase diagram shows an isotropic solution phase forming a narrow channel, which connects the surfactant in water at lower temperatures with the surfactant in oil at higher temperatures. This diagram illustrates the limited region of existence of the microemulsion phase, which is typical of systems based on nonionic surfactants. The system is balanced at around 28 °C. At higher temperatures, the surfactant is too oil-soluble and an aqueous phase separates out. At lower temperatures, the surfactant is too hydrophilic and oil separates out. The diagram also shows that a lamellar liquid crystalline phase forms at intermediate temperatures, both at high and low weight fractions of oil.

The Choice of Surfactant is Decisive

Depending on the surfactant used the curvature of the oil–water interface of a microemulsion may vary from highly curved toward oil, to zero mean curvature, to highly curved toward water. Contrary to emulsions, the curvature of microemulsions can be considerable

at the scale of the surfactant. This implies that not only the hydrophile–lipophile balance, but also the molecular geometry of the surfactant, is an important factor in finding the optimum microemulsion surfactant.

A popular way of dealing with surfactant geometry is to use the packing parameter concept, introduced in Chapter 4 and discussed further in Chapters 6 and 7. The geometric or packing properties of surfactants depend on their optimal head group area (a) as well as on the hydrocarbon volume (v) and the extended length of the surfactant hydrophobe chain (ℓ_{\max}). The value of a is governed not only by the size of the head group but also by repulsive forces acting between the head groups and attractive hydrophobic forces between the hydrocarbon chains. Steric chain–chain and oil penetration interactions determine v and ℓ_{\max} . As described earlier, the value of the dimensionless critical packing parameter (CPP) ($v/a\ell_{\max}$) can be used to determine what type of aggregate will spontaneously form in solution.

As described below, microemulsions can have different microstructures, oil-in-water (o/w), water-in-oil (w/o), and bicontinuous types (for illustrations see Chapters 4 and 6). From geometrical considerations it may be stated that surfactants with one moderately long, straight-chain aliphatic hydrocarbon tail are best suited to prepare o/w microemulsions, surfactants with rather bulky hydrophobes are good for bicontinuous microemulsions (see below) and surfactants with highly branched hydrophobic tails should be used for w/o microemulsions. Indeed, this has been found to be the case. Often a combination of surfactants is used in the formulation. The surfactant geometry will then be the mean geometry of the species involved. Consequently, a combination of a surfactant with a single straight-chain tail and one with two branched tails, such as the compounds shown in Figure 17.5a and Figure 17.5c, may constitute an ideal mixture to formulate a bicontinuous microemulsion.

For some microemulsion applications, in particular in enhanced oil recovery (Chapter 25), there is a need for surfactants that by themselves, that is, without cosurfactant or cosolvent,

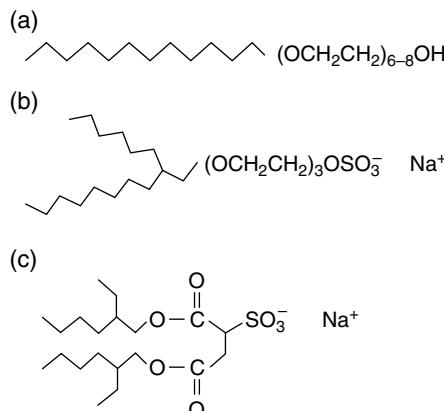


Figure 17.5 Examples of surfactants for different types of microemulsions: (a) an alcohol ethoxylate (used at temperatures well below the cloud point) for o/w microemulsions; (b) a branched-tail ether sulfate for bicontinuous microemulsions; and (c) a double-tail (and branched) sulfonate for w/o microemulsions

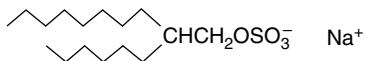


Figure 17.6 Structure of a surfactant, sodium 2-hexyldecylsulfate, with a very high solubilizing capacity for both oil and water

can solubilize large amounts of oil and water. By proper optimization of the surfactant geometry, including the surfactant molecular weight, molecules with extreme solubilizing capacities have been obtained. An example is shown in Figure 17.6. The relatively simple twin-tailed sulfate surfactant used at 1.54 wt% can solubilize 49.2% aqueous NaCl solution and 49.2% hexane, representing 32 times as much water and hexane as surfactant. Even higher solubilizations have been obtained with somewhat larger molecules with tailor-made branching of the hydrophobic chain.

The surfactant of Figure 17.6 has very low solubility in both oil and water. This is an important characteristic of a surfactant to be used with high efficiency in Winsor III systems. Very low saturation concentrations in both excess phases are needed in order to have the surfactant confined to the location where it exerts its action, that is, at the oil–water interface.

Ternary Phase Diagrams can be Complex

For an amphiphile of less pronounced amphiphilic character, such as a short-chain surfactant, the immiscibility of oil and water is overcome only at rather high concentrations of amphiphile. For a stronger amphiphile, such as a long-chain surfactant, lower amounts of surfactant are needed to form a microemulsion and the phase diagram may be more complex, with a three-phase triangle in addition to two-phase regions. Some different appearances of the phase diagram of ternary surfactant–oil–water systems were illustrated in Figure 17.2. (Liquid crystalline phases were omitted there.) The number of phases may vary, as exemplified in Figure 17.3. For an efficient surfactant, that is, one with a very pronounced amphiphilic character, which produces microemulsions at low surfactant contents and a lamellar phase at higher concentrations, the phase diagram is more complex, as exemplified in Figure 17.7. The example is taken for an exactly balanced surfactant (such as C_{12}E_5 with decane at 38.2 °C), that is, the microemulsion that is formed at the lowest surfactant concentration has equal volume fractions of oil and water. The phase diagram is then symmetric around this solvent ratio.

Microemulsions Based on C_mE_n Surfactants and Alkanes Clearly Illustrate the Importance of a Balanced System

We will now consider the microstructure of a microemulsion system as a function of a relevant system parameter, which may be temperature, electrolyte concentration, or surfactant composition of a mixture. It will then be illustrative to present a phase diagram at a fixed surfactant concentration and varying compositions of the solvent mixture. For non-ionics, we consider a Shinoda cut, as illustrated in Figure 5.13 and Figure 17.4. Here, the

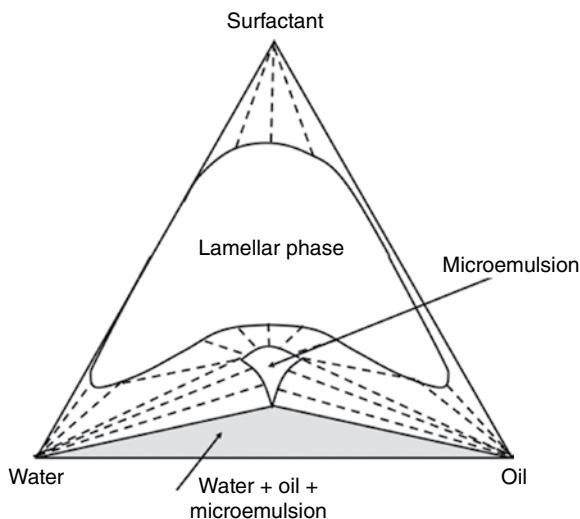


Figure 17.7 Phase behavior for balanced conditions of a surfactant–water–oil system. (The two-phase region at the bottom is very narrow and is omitted here.) (With permission from Kabalnov, A., Lindman, B., Olsson, U., et al. (1996) *Microemulsions in amphiphilic and polymer-surfactant systems*. Colloid and Polymer Science, **274**, 297–308. Copyright © 1996, Springer.)

microemulsion channel goes from the lower left to the upper right; it is possible to form microemulsions at all mixing ratios between oil and water by adjusting the temperature to a proper value.

There is a strong relationship between surfactant structure and the relative partitioning of the surfactant and the formation of microemulsions. Nonionic surfactants of the C_mE_n type together with alkanes are ideal mixtures to illustrate the delicate balance between the solubility in the aqueous phase relative to that of the oil phase as the temperature is varied. The temperature is a powerful tuning parameter for these systems because the water solubility decreases and the oil solubility increases with temperature. Also, the molecular structure can easily be varied, since the hydrophilicity increases with an increase in n and decreases with an increase in m . Changing the alkane solvent to one with a longer chain lowers the surfactant solubility in the alkane phase. Thus, in order to regain the balance between the water and oil phases, we need to raise the temperature, hence the phase inversion temperature (PIT) is raised for the longer alkanes. The general behavior is shown in Figure 5.11, where the cut is at a 50:50 oil-to-water ratio.

Figure 17.8 shows a series of phase diagrams with C_mE_4 , *n*-octane and water with the cut as shown in Figure 5.11. The series clearly illustrates the decrease in PIT as the surfactant hydrocarbon tail gets longer. The minimum amount of surfactant needed to form a microemulsion, that is, where the tail of the fish starts, decreases with increasing length of the hydrophobe, illustrating the fact that the surfactant becomes more efficient. Note that the solubility in the oil increases with the length of the hydrophobe whereas it decreases in the water phase. This imbalance is met by a decrease in temperature, which increases the solubility in the water phase and decreases the solubility in the alkane phase. Also, note the

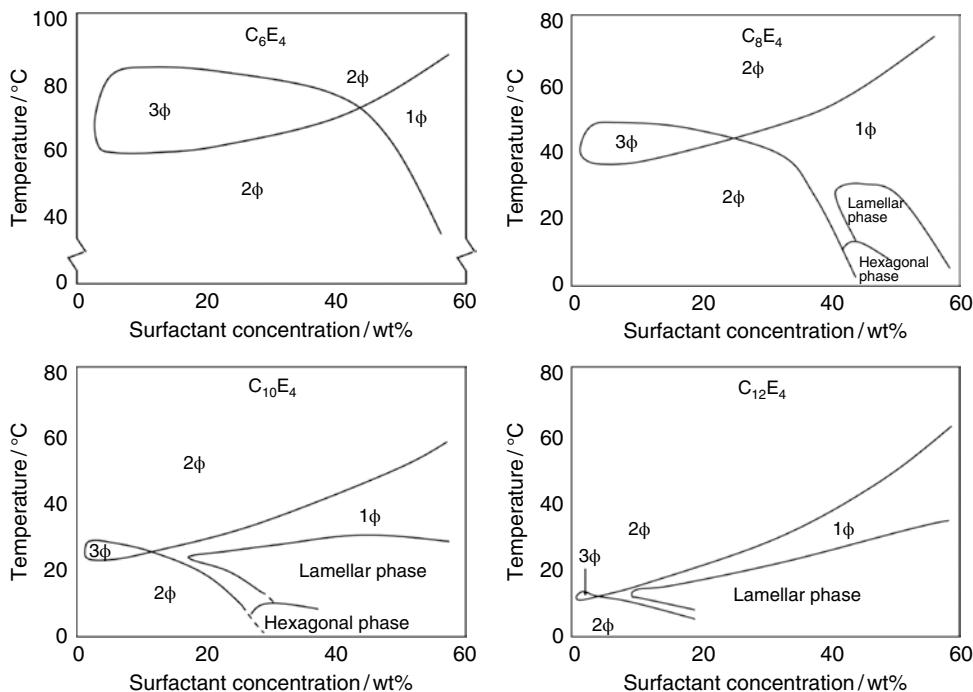


Figure 17.8 Phase diagrams of the systems water–n-octane– C_mE_4 at a 1:1 volume ratio of water to oil, showing the increased efficiency and decreased PIT as the hydrophobic tail of the surfactant increases. (With permission from Kahlweit, M., Strey, R. and Firman, P. (1986) Search for tricritical points in ternary systems: water-oil-nonionic amphiphile. *Journal of Physical Chemistry*, **90**, 671–677. Copyright 1986, American Chemical Society.)

large lamellar region for the surfactants with longer hydrophobes. Here the flexibility of the surfactant film is not sufficient to keep the system in a microemulsion state. This is an illustration of the fact that the necessary molecular structure in terms of the CPP of the surfactant is the same for the formation of a microemulsion and a lamellar liquid crystalline phase (see further below). The presence of a lamellar liquid crystalline phase makes these systems useless for microemulsion formulation unless an additive is introduced that destabilizes the ordered structure of the lamellar phase. Examples of such additives are hydro-tropes such as sodium xylenesulfonate (page 24) and medium-chain alcohols.

The situation where both the surfactant hydrophobe and the hydrophile chain length increase is displayed in Figure 17.9. This series is interesting in that it is an illustration of the increased efficiency of the surfactant as the surfactant polarity difference between the two parts increases in the sense that both the hydrophilic and hydrophobic ends increase. The figure reveals that the efficiency of the surfactant increases in the series, as is seen by the fact that the necessary concentration to create a microemulsion drastically decreases. The figure also reveals the limitation in that a lamellar liquid crystalline phase appears.

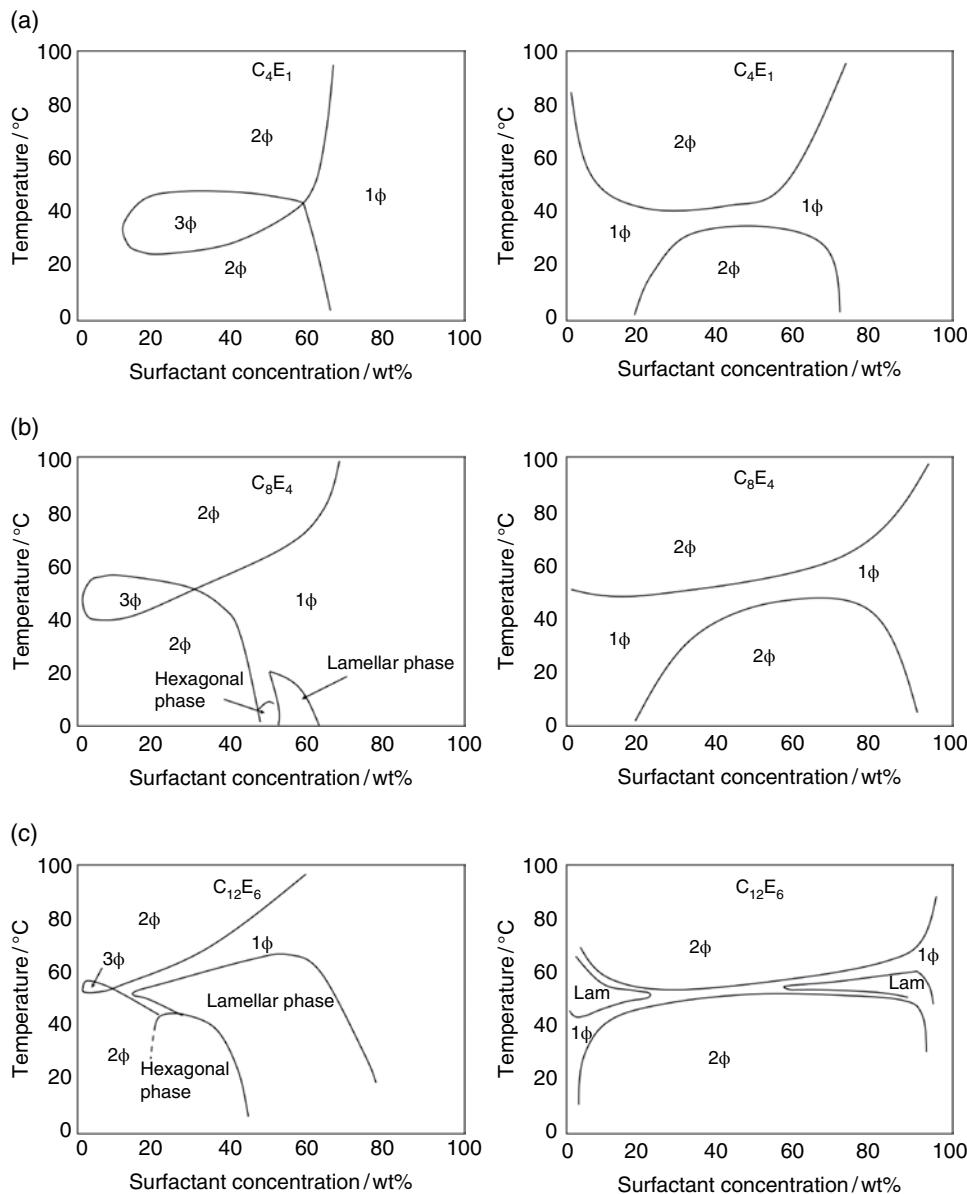


Figure 17.9 Phase diagrams of water-n-decane (1:1 by volume, i.e., $\phi = 0.5$) and CE_j with increasing amphiphilicity of the surfactant. Left is a “fish cut” and right is a “Shinoda cut.” (With permission from Kahlweit, M., Strey, R. and Firman, P. (1986) Search for tricritical points in ternary systems: water-oil-nonionic amphiphile. Journal of Physical Chemistry, **90**, 671–677. Copyright 1986, American Chemical Society.)

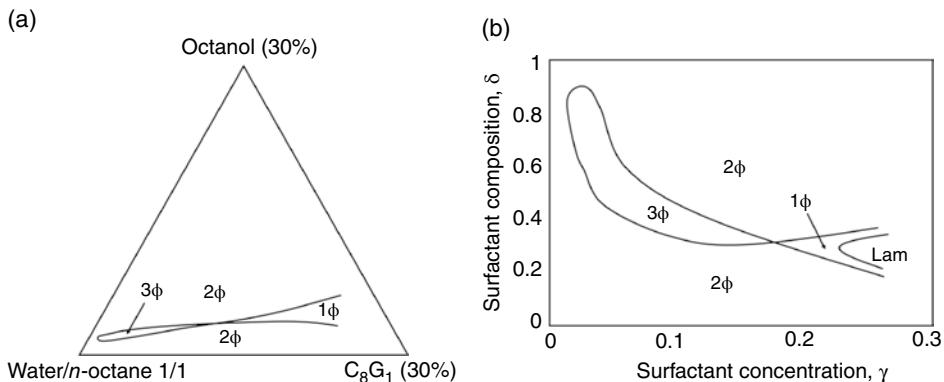


Figure 17.10 (a) Detail of the phase diagram of water-n-octane (1:1 by volume, i.e., $\phi = 0.5$) C_8G_1 , and n-octanol; (b) the same data replotted as surfactant hydrophobicity versus total amphiphile concentration. The surfactant concentration and composition parameters, γ and δ , are defined in Equations 5.3 and 5.4. (With permission from Sottmann, T., Kluge, K., Streij, R., et al. (2002) General patterns of the phase behavior of mixtures of H_2O , alkanes, alkyl glucosides, and cosurfactants. *Langmuir*, **18**, 3058–3067. Copyright 2002, American Chemical Society.)

The general trends for microemulsion formation with these surfactants are that the PIT (page 321) decreases with an increase of the length of the hydrophobic tail of the surfactant, a decrease in the length of the polyoxyethylene chain and a decrease in alkane chain length of the oil. Also, the efficiency increases with mutual insolubility in the aqueous and the oil phases.

Microemulsions with Alkyl Polyglucosides

Alkyl polyglucosides (C_iG_j) are nontoxic and biologically degradable (Chapters 1 and 2). These nonionic surfactants do not have the temperature sensitivity that the polyoxyethylene-containing surfactants have and are, therefore, interesting to use for microemulsion formulations where the temperature is varied. Since temperature cannot be used as a tuning parameter a hydrophobic cosurfactant is used instead. Figure 17.10 displays part of the phase diagram of the quaternary system of water, octane (1:1 by volume, i.e., $\phi=0.5$) C_8G_1 , and n-octanol. The figure shows the typical fish profile, as described in Figure 5.11, illustrating that n-octanol is a suitable cosurfactant for the tuning of the hydrophobicity of the C_8G_1 system. Note here also that the microemulsion formation is hampered by the formation of a lamellar liquid crystalline phase.

Adding a Polymer can Significantly Increase the Efficiency of the Surfactant

On the addition of a polymer to a microemulsion, the polymer can partition into the water, the oil, or the surfactant phase. If the polymer partitions into the water phase or the oil phase, the chemical potential of the water or the oil, respectively, is lowered, hence oil or

water is transferred from the surfactant phase to that phase, thus decreasing the volume of the microemulsion phase (Figure 17.11a). If, on the other hand, the polymer is partitioned into the surfactant phase, for example by associating with the surfactant membrane, the chemical potential of both the water and the oil is lowered in that phase, hence the surfactant phase swells (Figure 17.11).

Adding an amphiphilic polymer can reduce the amount of surfactant needed and also decrease the interfacial tension (Figure 17.12).

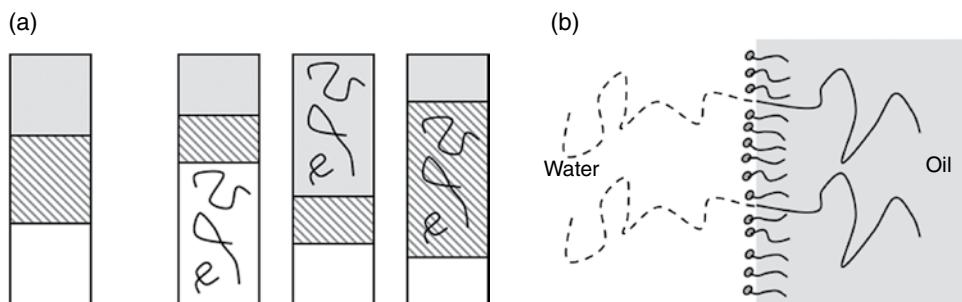


Figure 17.11 An added polymer might partition into the water or the oil phase, whereupon the surfactant phase decreases. The polymer might alternatively partition into the surfactant phase, thus swelling it with oil and water (a). The polymer should attach to the surfactant layer in the surfactant phase in order to bind both water and oil to its tails (b)

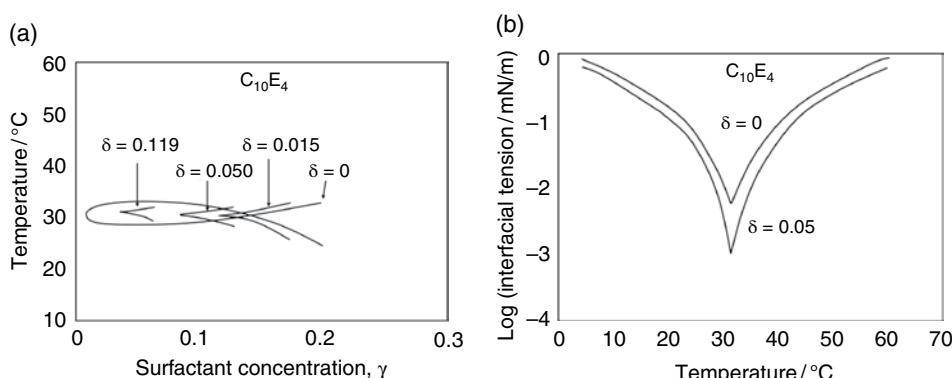


Figure 17.12 To the system water-n-decane- $C_{10}E_4$ ($\phi = 0.5$) is added a block copolymer, $(EO)_5-(PO)_5$ (at the indicated concentrations), which increases the efficiency of the surfactant (a) The addition of the block copolymer also decreases the interfacial tension to extremely low values (b). The surfactant concentration and composition parameters, γ and δ , are defined in Equations 5.3 and 5.4. (With permission from Jakobs, B., Sottmann, T. and Strey, R. (1999) Amphiphilic block copolymers as efficiency boosters for microemulsions. *Langmuir*, **15**, 6707–6711. Copyright 2002, American Chemical Society.)

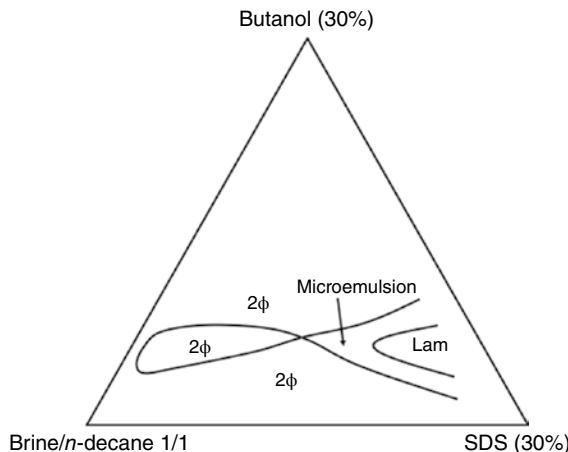


Figure 17.13 Detail of the phase diagram for the system water (with 10% NaCl)/decane(1/1)–SDS–butanol showing the appearance of a fish with two- and three-phase regions as well as microemulsion and lamellar phase. (With permission from Bellocq, A.M., Biais, J., Clin, B., et al. (1980) Three-dimensional phase diagram of the brine-toluene-butanol-sodium dodecyl sulfate. Journal of Colloid and Interface Science, **74**, 311–321. Copyright Elsevier.)

Microemulsions with Single-Chain Ionic Surfactants Usually Require a Hydrophobic Cosurfactant

Ionic surfactants that contain a single hydrocarbon chain of normal length usually require a hydrophobic cosurfactant in order to form microemulsions since they are too hydrophilic in themselves. An alternative to adding a cosurfactant is to add salt but this might not be sufficient in some cases and high salt concentrations may not be possible for the specific application. An alternative route is to increase the surfactant solubility in the oil phase by changing the oil to a more polar type or to a shorter hydrocarbon. Systems with water–oil–surfactant and added cosurfactant are conveniently represented by the cut shown in Figure 5.11, namely at a constant oil:water ratio of 1:1. An example is shown in Figure 17.13 giving the appearance of a fish for the system water (NaCl)–decane–SDS–butanol. A lamellar phase also appears in this system at higher surfactant concentrations.

The Microstructure is Controlled by Surfactant Properties

An efficient surfactant, that is, one forming a microemulsion at low concentration, is characterized by a low concentration of surfactant unimers in both solvents. There is then a very strong segregation into three types of domains: oil and water domains and surfactant monolayer films. This segregation into domains, or pseudo-phases, is the first question relating to microemulsion structure. The second question to address concerns, in analogy with our general discussion of surfactant self-assembly structures (Chapter 6), whether or not the surfactant films give discrete or connected structures. In the early literature, discrete, that is, droplet-type, structures were stressed but it was later realized

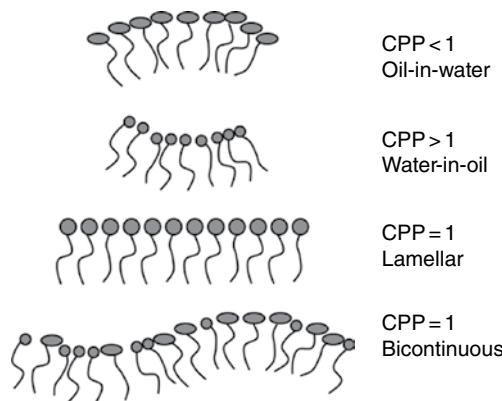


Figure 17.14 An illustration of the relationship between surfactant packing conditions and microstructure of microemulsions

that this picture is inconsistent with several observations, such as the stability over the entire range of solvent mixing ratios.

Having decided whether we have in a particular situation a discrete or a bicontinuous type structure, we address the subsequent question, which relates to the shapes of droplets and type of bicontinuous structure.

From the arguments presented in Chapter 6, and as also discussed above, a value of the CPP below unity will give an o/w structure and a value above unity will give a w/o structure. For a value around one, we can expect either a lamellar liquid crystalline phase or a bicontinuous microemulsion (Figure 17.14). The competition between these two alternatives is general and is decided by the flexibility of the surfactant film, so that a more flexible film favors the microemulsion. As an example, lecithin forms rigid layers and, therefore, a lamellar phase whereas a nonionic surfactant gives more flexible films and, thus, a bicontinuous microemulsion; lecithin films can be made more flexible by a cosolvent, which, therefore, can transform a lamellar phase into a microemulsion.

We can alternatively discuss microstructure in terms of the spontaneous curvature of the surfactant films (Chapter 6). When H_0 is positive, an o/w structure forms while a w/o structure is preferred when H_0 is negative. When the spontaneous curvature is small, we may again have either a lamellar structure or a bicontinuous microemulsion.

Figure 17.15 summarizes the microstructure for a nonionic system (cf. Figure 17.4 and the accompanying discussion); the picture would be analogous for other surfactants, as when temperature is replaced by salinity for an ionic surfactant. Along the microemulsion channel from the lower left to the upper right there is a progressive change in microstructure involving droplet growth, elongation, connection, fully bicontinuous structure, structural inversion, disconnection, and disintegration into smaller droplets. In the perpendicular, narrower, channel there is a bicontinuous structure throughout. We note the proximity of the various bicontinuous structures to a lamellar phase. The main factor, here controlled by temperature, in determining microstructure is the spontaneous curvature or the CPP, while the proportion of the two solvents plays a smaller role.

Figure 17.16 offers another illustration of the microstructure in the two cuts of the phase diagram (Figure 5.11 and Figure 5.13). For a balanced microemulsion system, that is, one where the microemulsion forms at the lowest surfactant concentration for equal volumes of oil and

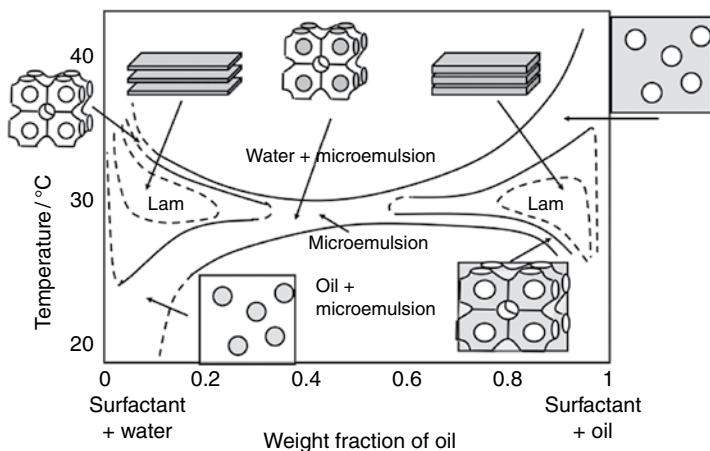


Figure 17.15 Microstructures in different regions of a Shinoda cut of the phase diagram of a nonionic system. (With permission from Kabalnov, A., Lindman, B., Olsson, U., et al. (1996) Microemulsions in amphiphilic and polymer-surfactant systems. Colloid and Polymer Science, **274**, 297–308. Copyright © 1996, Springer.)

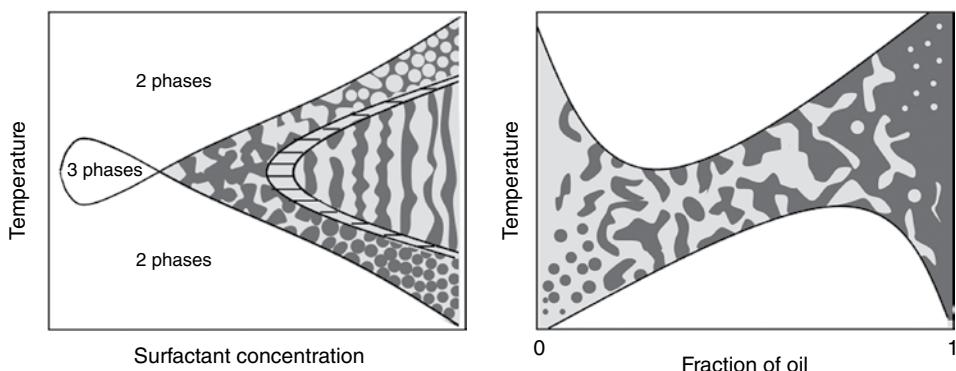


Figure 17.16 An illustration of the microstructure in the two cuts of the phase diagram (see Figure 17.9)

water, the microstructure is bicontinuous. For such a surfactant system, the three-phase triangle in the phase diagram is symmetrical with respect to the water–oil base. It is generally true for three-phase, so-called Winsor III, systems that the middle phase has a bicontinuous structure.

Molecular Self-Diffusion Probes Microstructure

A general and reliable approach for probing microstructure in terms of connectivity is by monitoring the molecular self-diffusion coefficients. This approach is not limited to microemulsions but is more generally applicable and has been instrumental in increasing our understanding of cubic liquid crystals and other isotropic solution phases as well.

In self-diffusion experiments, we investigate the molecular displacements over large distances, from several microns and upward. This means that molecular motions within discrete aggregates, like micelles and microemulsion droplets, will not contribute to the experimental observations.

Self-diffusion of an entity (molecule, aggregate, particle) depends on a number of factors: size and shape of the diffusing entity, friction, and obstruction. At low concentrations in a homogeneous medium, the diffusion coefficient of a spherical entity (radius R) is given by the Stokes–Einstein relationship, as follows:

$$D = \frac{k T}{6 \pi \eta R} \quad (17.1)$$

With a typical viscosity (η) of the order of 1 mPas (1 cP in older units), D will be about $2 \times 10^{-9}/R$, if R is expressed in Å and D in m²/s. This means that a small molecule such as water (R of the order of 1 Å) will have a diffusion coefficient of the order of 10⁻⁹ m²/s. This will apply to the local (short-range) motion. For the case where there is no confinement into closed domains and the molecular species can translate freely, this value will apply also to the long-range motion, which is what is probed in the experiments. For large particles, the diffusion coefficient will be much lower and, as we will see, for the case of microemulsions with discrete droplets, the droplet size is typically of the order of 100 Å; the self-diffusion coefficient will then be of the order of 10⁻¹¹ m²/s.

There are several different ways in which molecular self-diffusion coefficients may be obtained. The most popular ones have been techniques based on radioactive labeling and nuclear magnetic resonance (NMR) spectroscopy. In the former, diffusion is monitored over distances from a few to several millimeters. In the latter, which is the most versatile and convenient technique, the Fourier-transform pulsed-gradient spin-echo NMR (FT PGSE NMR) technique is used to monitor molecular displacements. Here, the motion of the nuclear spins in molecules is monitored in a spatially varying magnetic field. It is then possible to monitor diffusion over distances that are typically in the range 0.001–0.1 mm. The obtained NMR signal (the “spin echo”) contains contributions from the different molecules in the sample containing the spin probe (normally ¹H) but by Fourier transformation these different contributions can be resolved. It is generally possible to obtain the self-diffusion coefficients for all components in a complex liquid mixture with good precision within a few minutes.

Confinement, Obstruction, and Solvation Determine Solvent Self-Diffusion in Microemulsions

Figure 17.17 illustrates how the self-diffusion of oil and water can be used to distinguish between structures with discrete droplets or micelles and structures in which both solvents form domains that are connected over macroscopic distances. A solvent confined to discrete particles will have a D-value orders of magnitude lower than that of a solvent forming connected domains.

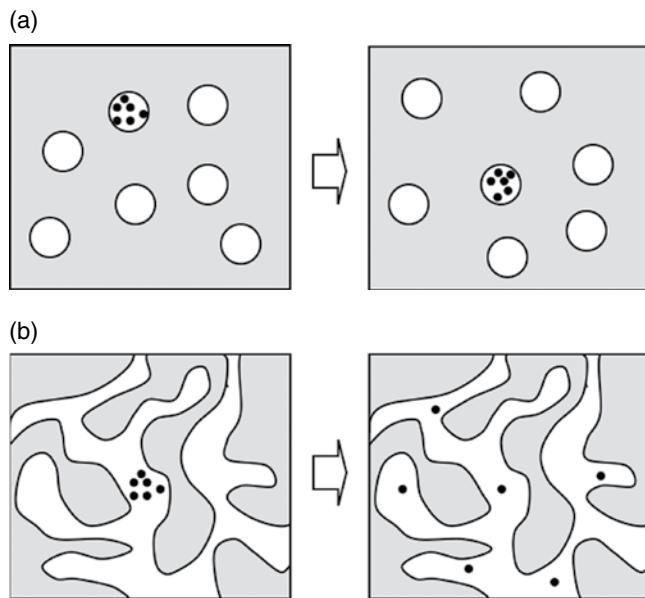


Figure 17.17 Solvent molecules in domains, which are connected over macroscopic distances, can translate rapidly over long distances while solvent molecules, which are trapped in discrete or closed domains, diffuse very slowly. (a) An oil-swollen micelle or an oil-in-water microemulsion and (b) a bicontinuous structure. (We note that bicontinuity can only occur in three dimensions so this is not easily illustrated in two dimensions.) The points represent labeled molecules at the initial time (left figures) and after a certain time (right figures)

The predicted self-diffusion behavior of the principal structures can be summarized as follows:

1. A water-in-oil droplet structure, that is, with discrete water domains in an oil continuum, will have a water diffusion that is much slower than that of oil; oil will have a D-value of the same order of magnitude as that of neat oil. Both water and surfactant diffusion will correspond to the diffusion of the droplets, with D-values of the order of $10^{-11} \text{ m}^2/\text{s}$ or below.
2. An oil-in-water droplet structure will have the opposite relation between the diffusion rates of the two solvents but will otherwise have analogous self-diffusion characteristics.
3. A bicontinuous microemulsion, where both solvents form domains extending over macroscopic distances, will be characterized by high D-values of both solvents. The surfactant diffusion is expected to be of the order of $10^{-10} \text{ m}^2/\text{s}$ (as in a lamellar phase), that is, much more rapid than for a droplet-type microemulsion, since it is uninhibited, but significantly slower than in a simple molecularly-dispersed solution.
4. For the molecularly-dispersed or structureless situation we expect all components to have rapid diffusion (around $10^{-9} \text{ m}^2/\text{s}$ or slightly below).

These simple arguments apply perfectly to a case of complete segregation into oil and water domains and surfactant films and are appropriate for an efficient surfactant, that is, a surfactant with low solubility in both solvents and which can mix large amounts of oil and

water in homogeneous solution. If the confinement is less pronounced, the difference between the D-values will be reduced. In the extreme case of a molecularly-dispersed solution, with no aggregation, all components will be characterized by rapid diffusion.

Both single molecule translation and droplet translation will be affected by the obstruction due to domains that are inaccessible for that particular species. The droplet diffusion is retarded in proportion to the volume fraction (ϕ) of the droplets. For the case of spheres, the relative reduction is approximately given by:

$$\frac{D}{D_0} = 1 - 2\phi \quad (17.2)$$

Solvent molecules in a continuous medium containing spherical droplets are retarded only moderately and the diffusion coefficient relative to the droplet-free case is given by:

$$\frac{D}{D_0} = \frac{1}{1 + \phi/2} \quad (17.3)$$

Also, for elongated droplets, such as those with prolate or cylindrical shapes, the obstruction effect is moderate. This is illustrated in Figure 17.18, where we also see that oblate or disc-shaped droplets retard solvent diffusion very strongly, even at low volume fractions. Indeed, the presence of larger planar obstructing surfaces will reduce the D-value to two-thirds at low volume fractions. The same obstruction effect will apply to the zero mean curvature structures, already referred to in conjunction with sponge and cubic liquid crystalline phases (Chapters 6 and 7). The noted differences in obstruction effects between different obstructing geometries are useful for assigning the microstructures of microemulsions.

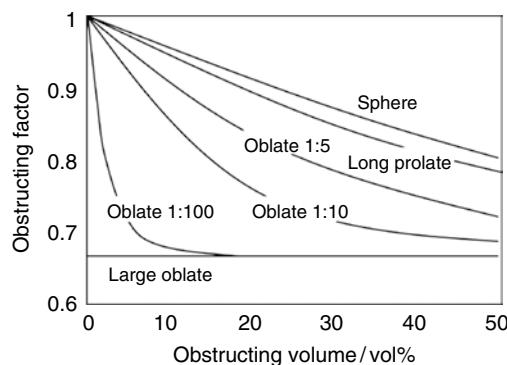


Figure 17.18 The solvent diffusion is retarded strongly by the presence of large oblates or discs, but only moderately by spheres or prolates. The obstruction factor, that is, the ratio between the self-diffusion coefficient in the presence of obstructing particles and that of the neat solvent, is given as a function of the particle volume fraction for spheres, prolates, and oblates, with different axial ratios. (With permission from Jönsson, B., Wennerström, H., Nilsson, P.-G. and Linse, P. (1986) Self-diffusion of small molecules in colloidal systems. Colloid and Polymer Science, **264**, 77–88. Copyright © 1986, Springer.)

The surfactant molecules in the surfactant films will be solvated, which will retard the solvent diffusion further. This retardation will be proportional to the surfactant concentration and can be accounted for.

Self-Diffusion Gives Evidence for a Bicontinuous Structure at Balanced Conditions

Essentially all types of surfactant can form microemulsions provided the conditions are appropriate. Furthermore, the solvent composition of the microemulsion can be varied over wide ranges by varying a suitable parameter, which may be temperature, salinity, cosurfactant, or cosolvent concentration, or the mixing ratio between two different surfactants. Stressing that the microemulsion behavior is general, as an example we choose a nonionic surfactant system. Microemulsions based on nonionic surfactants offer the easiest illustration, as they may be prepared from only three components and since the CPP, and thus also the spontaneous curvature of nonionic surfactant films, can be varied by temperature, rather than by varying the composition.

The self-diffusion behavior at different temperatures in the microemulsion channel of nonionics is illustrated in Figure 17.19. The relationship between the diffusion coefficients of the two solvents is very different at different temperatures. At low temperatures, water diffusion is close to that of neat water while oil diffusion is strongly reduced and gives evidence for oil confinement into closed domains. At high temperatures, the converse situation applies with uninhibited oil diffusion and confinement of water into droplets.

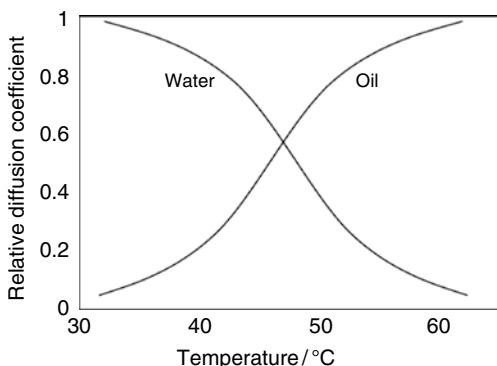


Figure 17.19 As temperature is increased through the microemulsion channel (cf. Figure 17.15) of a nonionic system, water diffusion is reduced from high to very low values, while the opposite applies to oil. The ordinate gives the relative diffusion coefficient, that is, the measured diffusion coefficient (D), over that of the neat solvent at the temperature in question. (With permission from Olsson, U., Shinoda, K. and Lindman, B. (1986) Change of the structure of microemulsions with the hydrophile-lipophile balance of nonionic surfactant as revealed by NMR self-diffusion studies. *Journal of Physical Chemistry*, **90**, 4083–4088. Copyright 1986, American Chemical Society.)

At intermediate temperatures, the relative diffusion coefficients of both solvents are high, which gives evidence for a bicontinuous microstructure, that is, with both oil and water domains being connected over macroscopic distances. It is observed for all types of surfactant that at the crossing point of the water and oil curves we have D/D_0 values of about 0.6. This is close to the theoretical maximum of two-thirds for D/D_0 at the crossing point. Such a situation applies when the obstructing surface is effectively planar, allowing translation only in two directions out of three, or has a zero mean curvature.

Our structural description of bicontinuous microemulsions derives from the minimal surface-type structures often found for cubic liquid crystalline phases (Chapters 6 and 7). But since the microemulsion is a solution without long-range order, a perturbed version of the regular minimal surface structure applies. In fact, the microstructure is close to that of the sponge phase illustrated in Figure 6.7. The main differences are that the sponge phase has bilayer surfactant films while the bicontinuous microemulsion has monolayer surfactant films, and that in the sponge phase all channels are water filled whereas in the bicontinuous microemulsion every second one is filled with oil.

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18

Colloidal Stability

Colloids are dispersions of particles with a size less than 1 µm. There are two reasons for this size limit. The first is that below this limit the surface-to-volume ratio starts to become important. Figure 18.1 shows how the importance of the surface increases as the size decreases. The second reason is that below about 1 µm the particles will only slowly sediment, or cream. Examples of colloids are found in nature (clays), in food (milk), and in technical applications (waterborne paints).

It is important to master the most fundamental principles of colloidal stability in order to be able to handle surfactants and polymers in contact with colloidal dispersions. This chapter is, therefore, a brief account of the basics of colloidal science and technology with focus on colloidal stability. The main concern is that particles attach to each other and form larger agglomerates that, in turn, sediment or cream. Below we first present the attractive forces and then the means to hinder particles from attaching to each other. This is followed by a description of the most common instability mechanisms of dispersions as well as a description of how measurements of the electrophoretic mobility can give insight into colloidal chemistry.

The Attractive Forces

There are many forces that are at play between molecules, such as ion–ion electrostatic forces, ion–dipole, dipole–dipole, ion–induced dipole, dipole–induced dipole, and, finally, induced dipole–induced dipole interactions, which is also termed dispersion force. Common for these forces is that they all are inversely dependent on the dielectric constant of the medium in which the molecules or particles are dispersed. Hence, the attraction between

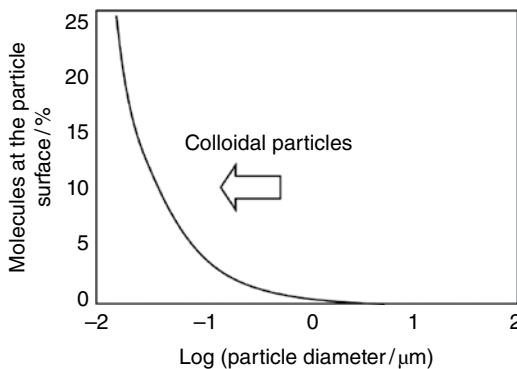


Figure 18.1 Colloidal dispersions contain particles with a size less than $1\text{ }\mu\text{m}$

molecules or particles is largest in vacuum and smallest in high dielectric media such as water. Examples of some dielectric constants are: water (80), ethanol (25), acetone (21), ethyl acetate (6.0), toluene (2.4), and hexane (2.1).

The most important attractive force is the *dispersion force*, which is always present. The electrons in a molecule, or atom, are continuously moving. At one instant there could be an excess of electrons in one part of the molecule and at another instant there could be an excess of electrons in another part. This dynamics creates temporary dipoles that are continuously forming and disappearing and which will induce dipoles in a neighboring molecule that, in turn, induce dipoles in the first molecule, and so on. Note that this type of interaction is independent of whether the molecules are neutral or ionic and whether or not they contain permanent dipoles.

In going from molecules to particles one needs to integrate over all types of interactions as well as over all space of the particles. The obtained attraction force, which is the sum of dipole–dipole, dipole–induced dipole, and induced dipole–induced dipole interactions, is directly proportional to the size of the particles, that is, the larger the size, the larger the attraction. It is also inversely proportional to the distance between the particles. Most of all it is dependent on the material of the particles as is manifested by the *Hamaker constant*. The Hamaker constant (A_H) is a measure of the attraction between particles and depends on the atomic density of the two particles, ρ_1 and ρ_2 , according to:

$$A_H = C \rho_1 \rho_2. \quad (18.1)$$

Here C is an integral over the dipole–dipole, dipole–induced dipole, and induced dipole–induced dipole interactions. Table 18.1 gives a list of Hamaker constants of some materials. The expression of the attraction between two particles is:

$$U = \frac{A_H}{6h} \frac{R_1 R_2}{(R_1 + R_2)} \quad (18.2)$$

where h is the distance between the particles and R_1 and R_2 are their sizes. We first note that if one of the particles has an infinite size, that is, is a flat surface, then the attraction is larger than that between the particles themselves. This explains the fact that particles have a tendency to adhere to solid surfaces.

Table 18.1 Hamaker constants in vacuum and in water

	In vacuum (10^{-20} J)	In water (10^{-20} J)
Water	3.7	—
<i>n</i> -Octane	4.5	0.41
<i>n</i> -Decane	5.0	0.51
Polystyrene	6.5	0.95
Polytetrafluoroethylene	3.8	0.33
SiO_2 (quartz)	8.9	1.0
SiO_2 (silica)	6.5	0.46
Al_2O_3	15.2	3.7
TiO_2	15.3	5.4

Secondly, there is a profound effect of the solvent. Figure 18.2 is an illustration of the solvent effect. When two particles approach each other the solvent needs to be removed. As illustrated in the figure there is a net effect of the attractive forces between the particles minus the attractive forces of the imaginary solvent that would take the place of the particles. The net effect is:

$$A_{131} = (A_{11} - A_{13}) + (A_{33} - A_{13}) = (\sqrt{A_{11}} - \sqrt{A_{33}})^2 \quad (18.3)$$

where index 1 represents the particles and index 3 the medium. In the latter equality we have used the geometric mean, that is: $A_{ij} = \sqrt{A_{ii}A_{jj}}$, which is a valid approximation for dispersion forces. Equation 18.3 implies that the Hamaker constant of a material submerged into a medium is always smaller than in vacuum and is always positive:

$$A_{11} \text{ (in vacuum)} = (\sqrt{A_{11}})^2 > A_{131} \text{ (in water)} = (\sqrt{A_{11}} - \sqrt{A_{33}})^2 \quad (18.4)$$

Hence, there cannot be a net repulsion between uncharged and bare particles in a medium. This is the reason why particles suspended in a medium need to be stabilized by either counterions or polymer molecules. Table 18.1 reveals that the Hamaker constant of particles submerged into water is about one-tenth of the Hamaker constants in vacuum.

Thirdly, we note that seemingly related materials may have very different Hamaker constants. Alumina (Al_2O_3), for example, has a Hamaker constant of 3.7×10^{-20} J when

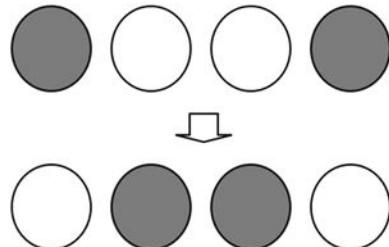


Figure 18.2 When two particles approach each other the solvent needs to be replaced. The black rings are particles and the non-filled rings represent solvent.

Table 18.2 Hamaker constants for two different materials separated by a medium (units of 10^{-20} J).

Water and air in octane	0.5
Octane and air in water	-0.3
Quartz and air in octane	-0.9
Quartz and air in water	-1.0
Polystyrene and air in water	-1.1

dispersed in water, whereas the Hamaker constant of silica (SiO_2) is only 0.46×10^{-20} J. There is, therefore, no point in having SiO_2 as a model colloid for Al_2O_3 since one needs to stabilize against much stronger forces in the alumina case.

Finally, the interaction between two particles of different material (indexes 1 and 2) in a medium (index 3) is given by:

$$A_{132} = (A_{11} - A_{13}) + (A_{33} - A_{23}) = (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}}) \quad (18.5)$$

We note with interest that this interaction can either be positive or negative, implying that there could be systems where there is either an attraction or repulsion between two unlike materials. The requirement for repulsion is that the Hamaker constant of the medium should be in between the Hamaker constants of the two materials. Table 18.2 gives some examples of Hamaker constants between different materials in a medium. The table shows that there are attractive forces between air bubbles and water droplets in octane, while there are repulsive forces between air bubbles and octane droplets in water. Repulsive Hamaker forces are sometimes a problem in flotation processes. They can also be taken advantage of. At least theoretically, self-lubricating systems can be achieved if the fluid between two hard surfaces has a Hamaker constant between those of the hard materials.

Instabilities of Colloidal Dispersions—Six Routes to Destabilize Dispersions

There are several different ways dispersions can be destabilized. Six destabilizing mechanisms are covered under separate headings in this chapter. The first is through coagulation (Figure 18.3a). This is the process where particles attract each other and where the stabilization mechanism is not sufficient. The destabilization is initiated by lowering the osmotic barrier that is caused either by counterions or by attached polymers.

The second destabilization mechanism is flocculation (Figure 18.3b). On flocculation the particles adhere to each other and form a network whereas in coagulation massive lumps are formed. Flocculated particles attach to each other at a certain distance, which means that, contrary to coagulates, they can usually be redispersed under suitable conditions. Flocculation is frequently induced by the addition of a polymer.

The third and fourth destabilization mechanisms are sedimentation and creaming, respectively, where the dispersed particles either sink down or float up in the vessel. These instabilities are driven by the difference in density of the particles to that of the liquid in which they are dispersed. There are several means where this process can be slowed down or even hindered.

The fifth destabilizing mechanism is coalescence and occurs in emulsions and foams. Here the emulsion droplets, or gas bubbles, merge into bigger droplets or larger gas bubbles. The mechanism is based on a breakage of the thin film separating the droplets or

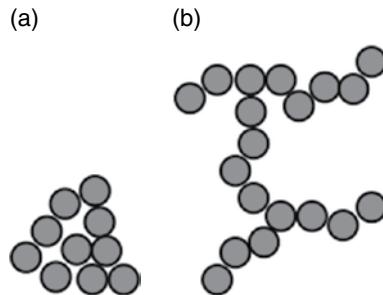


Figure 18.3 (a) Coagulation and (b) flocculation occur when there is a net attraction between the particles

bubbles and is, for surfactant-stabilized systems, related to the surfactant structure, or, expressed differently, to the critical packing parameter (CPP).

The sixth destabilizing mechanism is Ostwald ripening. This destabilization mechanism is based on the fact that the chemical potential, or pressure, of a substance inside small particles is higher than inside larger particles, as described by the Young–Laplace (Equation 12.3). Hence, there will be a transport of substance from small to large particles.

Instability can be manifested in an increase in viscosity. The reason for this is that flocks, or coagulates, include water, hence the effective volume fraction of the dispersed phase becomes higher than in the original dispersion. From Figure 19.6 we conclude that this higher volume fraction is associated with a higher viscosity.

In some applications there is a need for particles to adhere to each other. Clay particles, for example, adhere by a face-edge mechanism (Figure 18.4a). The faces are negatively charged whereas the edges are positively charged at normal pH values. Detaching the particles by decreasing the ionic strength is termed *peptization*. This is a well-known phenomenon in nature. For instance, clay that is exposed to heavy rain may lose its stiffness and start to flow due to peptization, causing landslides (Figure 18.4b).

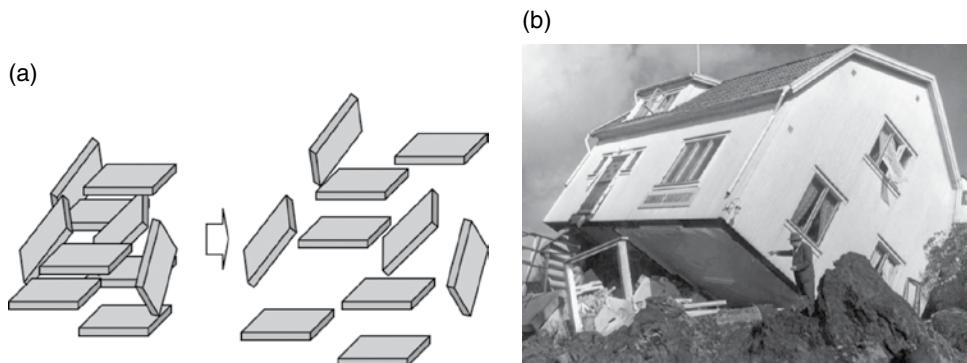


Figure 18.4 On dilution with de-ionized water the net attraction between clay particles decreases, leading to instability, peptization (a), as is experienced in landslides after heavy rainfall (b). (From http://commons.wikimedia.org/wiki/File:Landslide_in_Sweden_%28Surte%29_1950,_2.jpg)

Stabilization against Coagulation through an Osmotic Barrier

There are two main routes to stabilize a colloid against coagulation. One is through the presence of counterions outside a charged particle surface and the other is through attaching a polymer to the particle surface. The first route is termed *electrostatic stabilization* and the latter route is termed *steric stabilization*. There is also the possibility of combining these two routes, *electrosteric stabilization*. The basic physics is the same for these alternatives, that is, the creation of an osmotic barrier. Charged particles have counterions close to the surface and when two particles approach each other the counterion concentration will be high between the particles where the counterion clouds overlap (Figure 18.5a). This higher counterion concentration will cause the surrounding water to move into the region between the particles, hence the particles will separate. The stabilizing factor is the osmotic force of water, which seeks to dilute this region. An analogous mechanism is at work when polymer molecules are attached to the particles. Here the polymer segment concentration will be higher in the region between the particles when they approach each other, hence the water will seek to dilute this region (Figure 18.5b).

There is a second stabilizing contribution in the case of adsorbed polymers. Upon approach of two such particles there is a limited volume available for the polymers, resulting in a lowering of the conformational entropy. This contribution is in operation regardless of whether the polymers become compressed or penetrate when the particles come close to each other (Figure 18.6).

The DLVO Theory is a Cornerstone in the Understanding of Dispersion Stability

The DLVO theory, named after the four scientists behind it—Derjaguin, Landau, Verwey, and Overbeek—describes the interplay between van der Waals attractive force between particles and the osmotic barrier due to the counterion layer outside the particles. It is the competition between these forces that determines the stability of a dispersed system. Figure 18.7 shows an interaction energy curve. The curve is composed of an attractive van der Waals interaction and a repulsive interaction, due to the presence of counterions. The attractive

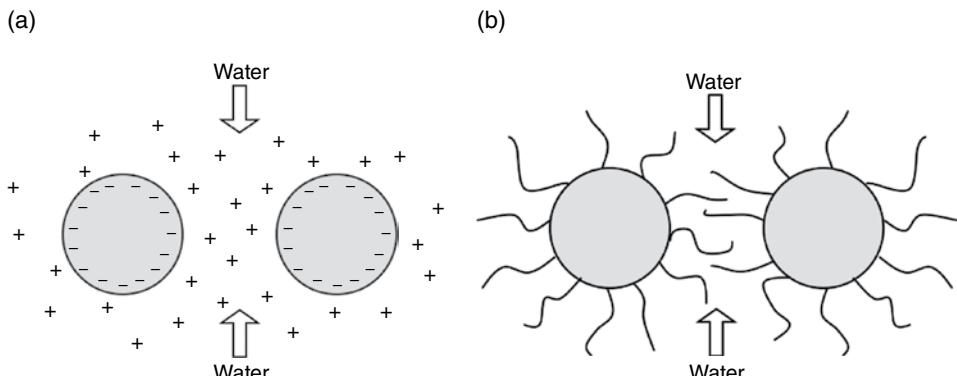


Figure 18.5 (a) Electrostatic and (b) steric stabilization of dispersed particles, illustrating the flow of water, driven by an osmotic force, that keeps the particles apart

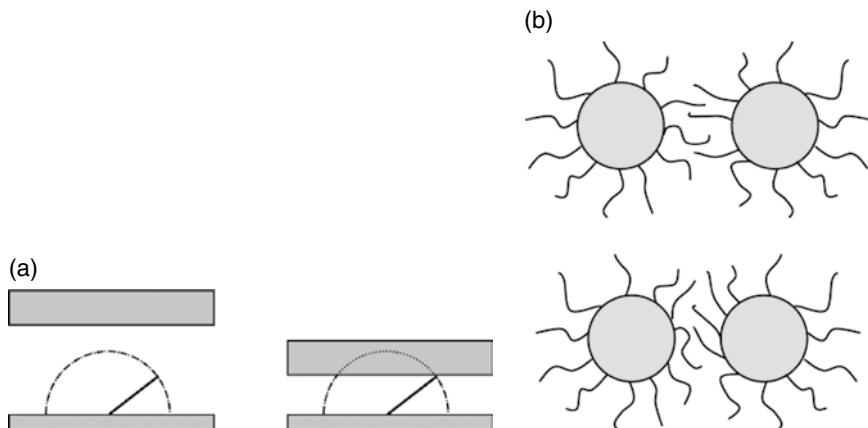


Figure 18.6 (a) An adsorbed stiff rod experiences limited freedom of motion and, hence, lower entropy as a second surface is approached. (With permission from Mackor, E.L. and van der Waals, J.H. (1952) The statistics of the adsorption of rod-shaped molecules in connection with the stability of certain colloidal dispersions. Journal of Colloid Science, 7, 535–550. Copyright Elsevier.) (b) Both on interpenetration and compression the polymer loses conformational entropy

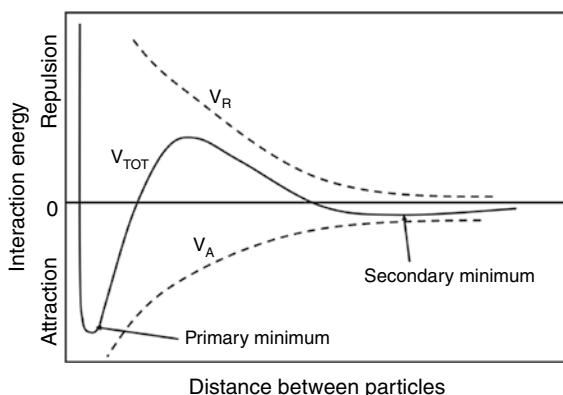


Figure 18.7 Potential energy as a function of distance between two particles. V_A , V_R and V_{TOT} stand for attractive van der Waals interaction, repulsive electrostatic interaction, and resulting curve, respectively. This figure is an illustration of a system where salt is present, thus giving a balance between the attractive and repulsive forces and, hence, a secondary minimum

forces dominate at small distances between the particles, thus causing a primary minimum in the interaction (when the particles come very close together there is a strong repulsion due to overlapping of electron clouds, the *Born repulsion*). In salt-free systems the repulsive force dominates at large distances. When salt is present, as in the figure, there is a balance such that there could be a secondary minimum at larger distances. In between, the repulsive osmotic barrier can take over provided that the surfaces are highly charged and the electrolyte concentration in the continuous phase is not too high.

Coagulation is when particles get stuck in the primary minimum whereas flocculation is when particles attach at the secondary minimum. If this energy minimum is weak, the flocculation is reversible, that is, the particles can easily be redispersed by the action of shear forces. The figure reveals that dispersions are thermodynamically unstable. Sooner or later, sometimes after years of storage, all emulsions, suspensions, and foams will coagulate.

How to Attain Charges at a Particle Surface

We will here give a short account on how to attain charges at the surface of colloidal particles. We will briefly present seven routes, that is, (i) adsorption of an ionic surfactant, (ii) adsorption of a polyelectrolyte, (iii) adsorption of multivalent ions, (iv) incorporation of potential determining ions, (v) isomorphic substitution, (vi) dissociation of surface groups, and (vii) incorporation of ionic comonomers in latex recipes.

The adsorption of ionic surfactants at solid surfaces is described in Chapter 8. The charge density thus obtained can amount to about 2–3 charges/nm², corresponding to 30–40 Å² per charge for surfactants with one charge per molecule. The more hydrophobic surfactants, with lower critical micelle concentration (CMC), will have larger adsorption energy and for such surfactants the surface charge can be considered permanent at the particle surface.

The adsorption of polyelectrolytes is described in Chapter 11. In that chapter the technique on how to obtain a metastable polymer layer with a high surface charge was described. Adsorbing a polyelectrolyte renders electrosteric stabilization, as will be described later in this chapter.

Adsorption of multivalent ions is more effective the higher the valence of the ion. Higher valency ions are often strongly hydrated. Sodium hexametaphosphate (SHMP) is an example of a multivalent ion. SHMP is a commonly used dispersion agent because it has a strong affinity for cationic surfaces, such as the edges of clay particles, and carries six charges per molecule.

Incorporation of potential determining ions is pertinent for salt crystals, such as silver iodide (AgI). The principle is very simple: If one has an excess of silver ions (e.g., through addition of silver nitrate (AgNO₃)), then these give an excess at the silver iodide surface, hence forming cationic particles. If, on the other hand there is an excess of iodide ions (e.g., through addition of sodium iodide (NaI)), then we will have an anionic surface. Figure 18.8 shows the zeta potential as a function of the silver ion concentration (zeta potential and electrophoretic mobility are discussed later in this chapter). As the silver ion concentration increases, the zeta potential goes from negative to positive due to the incorporation of silver ions into the lattice. The concentration at which the surface changes sign is termed the point of zero charge. This point is strongly dependent on the counterion of the silver, as shown by the following examples with the isoelectric points given within the parentheses: AgCl (4.0), AgI (5.6), and Ag₂S (10.2).

Isomorphic substitution is when one ion in a lattice is substituted for another ion of the same size. If the two ions have different valency, the charge of the lattice will be affected. One industrially important example is the incorporation of Al³⁺ ions in the lattice of SiO₂ nanoparticles, which gives rise to a more negatively charged surface because tetravalent silicon is replaced by trivalent aluminum. Other examples are found in nature for various clay minerals. The charges emanating from isomorphic substitution are permanent and not dependent on pH.

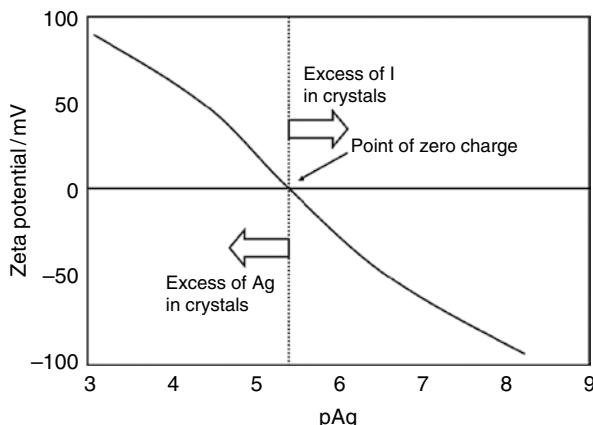


Figure 18.8 The zeta potential of silver iodide crystals versus the silver ion concentration

Another way to attain charged surfaces is through dissociation of surface groups. Oxides, for example, have groups that are able to dissociate, hence the pH is the tool to obtain a charged surface. Examples of the isoelectric point, that is, the pH at which the zeta potential changes sign, for some oxides are: SiO_2 (2.0), MnO_2 (5.3), Fe_3O_4 (6.6), Fe_2O_3 (8.2), Al_2O_3 (9.1), ZnO (9.2), and MgO (12.4).

Finally, charges can be incorporated in a latex surface by adding an ionic monomer at the end of the latex polymerization. Examples of ionic comonomers are acrylate, methacrylate, itaconate, and styrene sulfonate.

Sensitivity to Salts is a Feature of Electrostatically-Stabilized Colloids

Electrostatically stabilized colloids are sensitive to an increase in ionic strength as realized upon considering the stabilization mechanism given in Figure 18.5a. If the solution contains a high concentration of ions there will be only a small, or no, osmotic driving force for water molecules to enter the region between the colliding particles, hence the mechanism behind separation of the particles will be lost. Increasing the salt content is, therefore, an effective way to destabilize such dispersions.

The presence of the electrolyte screens the charge of the surface and this effect increases with the salt concentration (Figure 18.9) The distance at which the potential has dropped to $1/e$ of the potential at the surface is termed the *Debye length*. The Debye length decreases strongly as the ionic strength increases (Table 18.3). The table reveals that at a salt concentration of about 0.1 M the Debye length is virtually zero. A lesson to learn from this is that electrostatic stabilization can be extremely efficient in model systems but often less useful in practice because of the high and often uncontrolled electrolyte content that is present in many technical applications.

When a particle is subjected to an electric field it will move toward the electrode of opposite charge with a speed, termed *electrophoretic mobility*, which is proportional to the charge of the particle. There will also be a stagnant layer of water that moves along with the particle. Hence, the electrophoretic mobility will be a measure of the potential, not at the surface but at a distance further out from the surface, as indicated in Figure 18.9. This

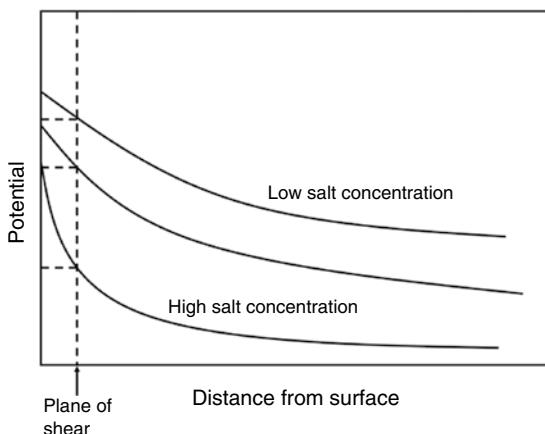


Figure 18.9 The decline of the potential from a surface at three different salt concentrations, illustrating that the zeta potential decreases with salt content, see text

Table 18.3 The Debye length as a function of ionic strength for a 1:1 electrolyte and as a function of the valency of the counterion at an ionic strength of 1 mM

Ionic strength (M)	Debye length (Å)
0.0001	295
0.001	96
0.01	30
0.05	14
0.1	10
At I = 1 mM	
NaCl	96
CaCl ₂	39
AlCl ₃	27

is termed the *plane of shear*. We note that as salt is added the measured potential at the plane of shear decreases. The measurement of electrophoretic mobility is treated later in this chapter.

Table 18.3 also shows the Debye length for divalent and trivalent counterions, illuminating that higher valency ions have a tendency to be more attracted to the charged surface and, hence, to be more efficient in decreasing the stability. Exchanging monovalent counterions for ions of higher valency will reduce the number of ions. This will, in turn, lower the osmotic barrier, leading to a poorer stability. An every-day example of the power of divalent ions as flocculants is the clarity of salt water compared to the water in lakes. The ions in seawater, in particular calcium and magnesium, flocculate the humus and other colloidal particles in the water. Salts of trivalent ions, such as aluminum, are used as flocculants in water purification and to decrease the stability of sludge in sewage plants.

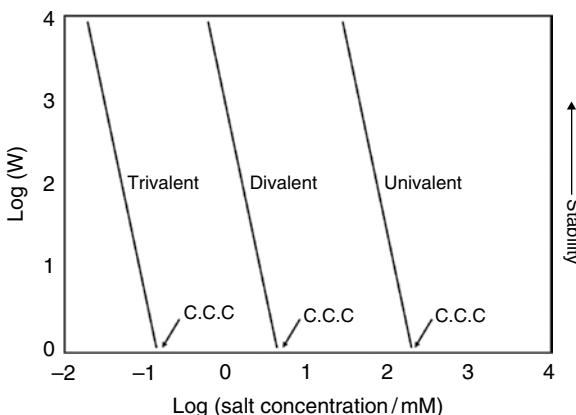


Figure 18.10 The effect of adding three different types of salts on the stability of a colloid showing the difference in valency of the counterion

Figure 18.10 shows the effects of adding salts on the stability of a colloid. The stability is here defined as:

$$\text{Stability} = \log(W) = \log\left(\frac{\text{maximum rate of coagulation}}{\text{measured rate of coagulation}}\right) \quad (18.6)$$

The maximum rate of coagulation is obtained when every particle collision leads to an attachment. This is achieved above a critical salt concentration termed the *critical coagulation concentration* (c.c.c.). The rate of coagulation is typically determined through a change in light absorbance. There is a dramatic effect of the valency of the counterion, as shown in the figure. The reason is the lower number of counterions leading to a lower osmotic suction force, since there are fewer ions between the colliding particles to attract water from the surroundings. The c.c.c. relates to the valency (z) of the counterion through the *Schulze-Hardy rule*:

$$\text{c.c.c.} \propto z^{-6} \quad (18.7)$$

The c.c.c. is not a unique quantity since it depends on experimental conditions, such as the elapsed time between the salt addition and measurement of the rate of coagulation, the method of mixing, the method of determining the coagulation, the solid contents, the polydispersity of the sample, and the Hamaker constant of the material.

The intolerance to salts has two further implications. The first is that electrostatically stabilized colloids cannot be obtained at high volume fractions of the dispersed phase for the simple reason that as the volume fraction increases so does the ionic strength. The second implication is that electrostatically stabilized colloids exhibit poor freeze-thaw stability. During the formation of ice crystals the ion concentration in the remaining liquid water increases with coagulation as a result. We conclude that the stability of colloidal dispersions can be decreased by lowering the surface charge, raising the ionic strength, and choosing counterions with high valency.

How to Attach a Polymer at a Particle Surface

Adsorption of polymers at solid surfaces was discussed in Chapter 11. Adsorbing a polymer in order to attain steric stabilization is not trivial, as illustrated in Figure 18.11. On the one hand, a strong attachment to the surface is needed. Strong adsorption energy, however, leads to a conformation where the polymer lies down at the surface, which of course is useless for steric stabilization. On the other hand, low adsorption energy leads to the desired polymer conformation at the surface (Figure 18.11). However, in such systems there is a pronounced risk that the polymer molecules desorb upon collision of two particles, hence the steric stabilization will be lost.

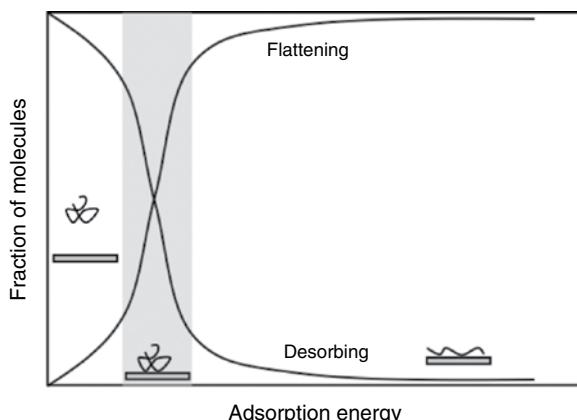


Figure 18.11 Illustration of the problem of attaining steric stabilization with adsorbing homopolymers. Only in the shaded region can steric stabilization be obtained

One solution to the problem is to use copolymers (Figure 18.12). One segment attaches to the surface while the other segment protrudes into the solution rendering steric stabilization. Nonionic surfactants can be regarded as low molecular weight analogues to copolymers in this respect, with the hydrocarbon chain attaching to the surface and the polyoxyethylene chain protruding into the aqueous solution.

An alternative to physical adsorption of a polymer is to chemically graft a polymer to the surface (Figure 18.13a). This method is termed *grafting to*. The “grafting to” process is not very efficient, however, since once there are a few polymer molecules grafted at the surface

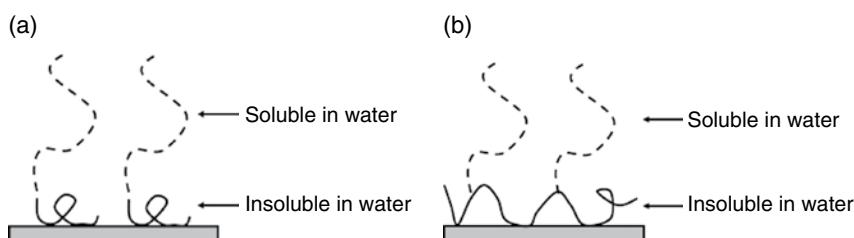


Figure 18.12 Adsorption of (a) block or (b) comb copolymers at a particle surface can give effective steric stabilization of the dispersion

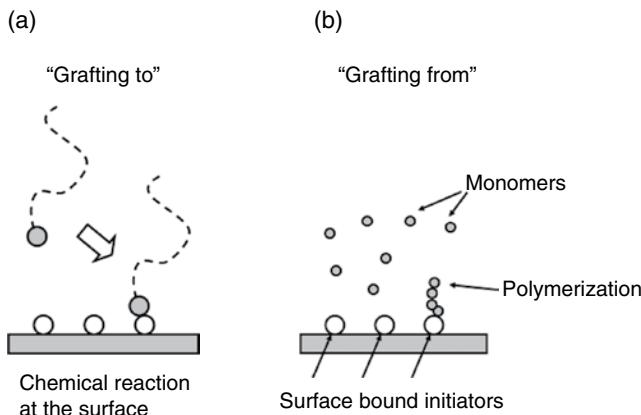


Figure 18.13 The principles of “grafting to” and “grafting from”

they hinder other polymer molecules approaching. An alternative method is *grafting from*, where an initiator is attached to the surface and monomer is added to the solution rendering a polymerization that starts at the surface (Figure 18.13b). The success of the method lies in the control of the polymerization process, that is, control of the molecular weight, the chemical composition, and the confinement to the surface. One technique is atomic transfer radical polymerization (ATRP), where the initiator, being attached at the surface, is activated by a transition metal in its lower oxidation state, such as Cu(I) bound to ligands. The choice of transition metal as well as the choice of ligands determines the polymerization process.

Instability at Theta Temperatures is a Feature of Sterically-Stabilized Colloids

In Chapter 9 we concluded that a dispersion where the particles are covered with polymers behaves as if it was a polymer solution with infinitely high molecular weight. Three conditions must be fulfilled for such systems: (i) the polymer must be sufficiently strongly attached to the surface, (ii) the surface must be fully covered with the polymer, and (iii) the polymer molecular weight must be sufficiently high that it masks the attractive forces between the particles.

Thus, a colloidal dispersion is stable when the polymer–solvent interaction is more favorable than the theta conditions and it flocculates when the polymer–solvent interaction is worse than the theta conditions (Figure 18.14). This has been proven true, without any exceptions, for numerous systems, both aqueous and nonaqueous. Knowledge of the theta conditions is, therefore, of fundamental importance when designing a dispersed system stabilized with polymer. Hence, stable dispersions are found at temperatures that are above the theta temperature (Θ_u), associated with the UCST of the polymer solutions, and below the theta temperature (Θ_l), associated with the LCST of the polymer solutions (see Figure 5.2 for the definitions of UCST and LCST). This is valid only for the stabilizing moiety of a polymer. Hence, for a block copolymer one should only consider the theta condition for the block that is protruding into the solution and not the whole copolymer. Interestingly, dispersions can be flocculated by changing the temperature accordingly and then be redispersed by going back in temperature. Naturally, the change in solution properties can also be achieved by adding salt, or a nonsolvent.

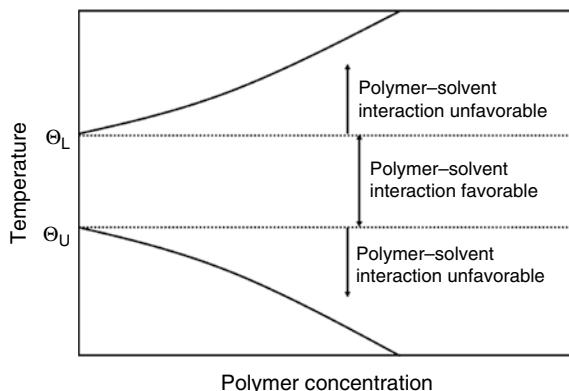


Figure 18.14 Illustration of the region where sterically stabilized dispersions are obtained, that is, when the polymer–solvent interaction is favorable (see text). The figure shows a general phase diagram for a polymer of infinitely high molecular weight, displaying both an upper and a lower critical point, Θ_U and Θ_L .

Electrosteric Stabilization is Powerful

Dispersions are often stabilized by more than one mechanism. In many systems electrostatic and steric stabilization are combined. Such a combination is sometimes called *electrosteric stabilization*. Electrosteric stabilization can be achieved by the adsorption of both an ionic and a nonionic surfactant. Electrosteric stabilization is a powerful means to stabilize a colloid, since use is made of both the osmotic force of the counterions and the fact that there is a contribution from the nonionic surfactant or polymer chains that protrude into the solution.

Electrosteric stabilization can also be achieved by adsorption of a polyelectrolyte where the charged polymer chains protrude into the solution, as is depicted in Figure 18.5b. The adsorption of polyelectrolytes is described in Chapter 11, in which the technique of how to obtain a metastable polymer layer with a high surface charge was described. One important parameter is the intrinsic solubility of the polymer backbone, that is, the solubility of the uncharged polymer. The best stability is achieved when the polyelectrolyte backbone is soluble in the aqueous phase even if the charges are neutralized. Hence, polysaccharides are excellent candidates as electrosteric stabilizers.

A typical relationship between the adsorption of a polyelectrolyte, such as sodium polyacrylate, and the viscosity of a dispersion is illustrated in Figure 18.15. The minimum amount of polymer needed in order to disperse particles in suspensions can easily be monitored by viscosity measurements.

Comparison of Electrostatic and Steric Stabilization

Despite the fact that both electrostatic and steric stabilization rest on osmotic forces, there are some fundamental differences between the two (Table 18.4). Electrostatically stabilized dispersions are very sensitive to high ionic strengths. Hence, such colloids cannot be obtained at high volume fraction of the dispersed phase and they do not show any freeze–thaw stability (Figure 18.16). In both cases this can be referenced to the fact that the ionic strength increases. These limitations are not present in sterically-stabilized

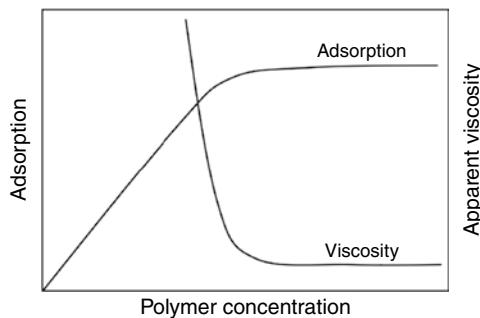


Figure 18.15 As a polyelectrolyte adsorbs at the surface of the particles in a suspension the viscosity of the suspension decreases. This is due to a lowering of the interaction between the particles when polymer is adsorbed

Table 18.4 Comparison of the properties of electrostatically and sterically stabilized dispersions

Electrostatic stabilization	Steric stabilization
Coagulates on addition of electrolytes	Insensitive to electrolytes
Only effective in aqueous solutions	Effective in aqueous as well as nonaqueous media
Only effective at low volume fractions	Effective at high as well as low volume fractions
Freezing induces irreversible coagulation	Freeze-thaw stability can be attained
Sensitive to shear	Stable at high shear

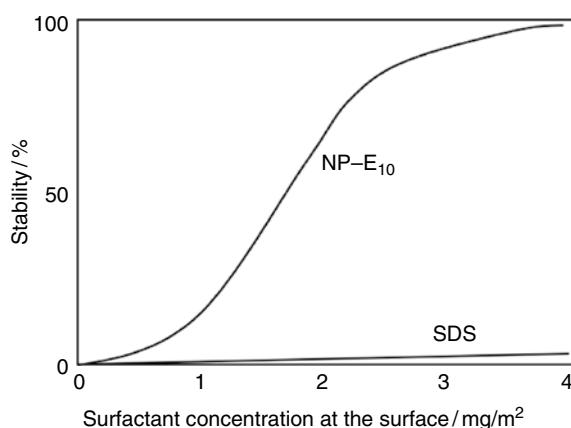


Figure 18.16 Freeze-thaw stability of a latex suspension that is electrostatically stabilized with SDS or sterically stabilized with NP-E₁₀

dispersions. Sterically stabilized dispersions also have the advantage that they can be induced to flocculate and then redispersed by changing the solvent conditions for the stabilizing polymer, as discussed above.

Another difference is that electrostatic stabilization only works in aqueous solutions whereas steric stabilization can be obtained in both aqueous and nonaqueous systems.

Thus, nonaqueous dispersions need steric stabilization and the protruding chains must have good solubility in the continuous phase.

Finally, strong shearing may force electrostatically-stabilized particles to collide, inducing irreversible coagulation. Sterically stabilized systems are much more stable toward high shear.

Flocculation Occurs on the Addition of Polymers

Above we noted that flocculation of a sterically stabilized dispersion can be induced by changing the temperature to theta conditions. This type of flocculation is reversible, that is the dispersion can be restabilized by changing the temperature back to stable conditions. Flocculation can also occur as a result of nonequilibrium processes, such as when added polymer molecules adsorb on more than one particle and bring these together (Figure 18.17a). This type of flocculation is often used to clear wastewater from particles. The formation of flocs will cause these to sediment, or cream, leaving the supernatant clear of particles.

There are three types of irreversible flocculation. The first is when polymer molecules adsorb at more than one particle, bringing the particles together. This is *bridging flocculation* (Figure 18.17a). Bridging flocculation is a dynamic phenomenon and depends on the route of adding the polymer and the colloid. If the colloid is added to the polymer solution, each particle will be immersed in an excess of polymer and there is little chance for the polymer molecules to adsorb at more than one particle. This could, in fact, lead to a sterically-stabilized system. If, on the other hand, the polymer solution is added to the colloid dispersion, then each polymer will be surrounded by colloids and there is a good chance that a polymer molecule adsorbs on more than one particle, resulting in flocculation. Bridging flocculation is normally only of importance for polymers with high molecular weights ($>10^6$).

The second type of flocculation occurs on adding a low molecular weight polyelectrolyte of opposite charge to that of the particle surface. This is *patch flocculation* (Figure 18.17b).

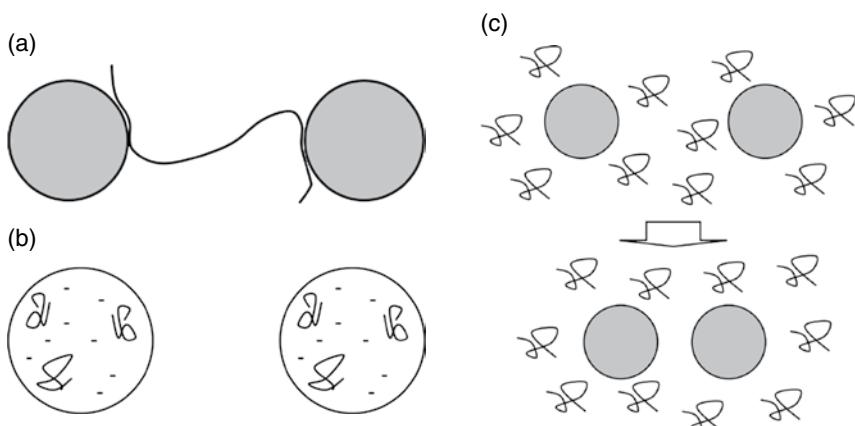


Figure 18.17 Illustration of (a) bridging flocculation, (b) patch flocculation, and (c) depletion flocculation

The mechanism is that the polymer molecules adsorb in patches at the particle surface and only partially neutralize the surface. Oppositely charged patches on different particles may then attract each other, which may lead to flocculation. This flocculation mechanism is particularly important for low additions of polyelectrolyte.

The third type of flocculation occurs when there is an excess of nonadsorbing polymer. This is *depletion flocculation*. The mechanism is to be found in osmotic forces, as is illustrated in Figure 18.17c. When two particles approach in a solution of an excess of non-adsorbing polymer, then there will be a point where there is no longer room for polymer molecules between the particles. That induces an osmotic force driving the water out of this area in order to dilute the surrounding polymer-rich solution, causing the particles to flocculate. This phenomenon is sometimes seen in applications such as waterborne paints.

In *selective flocculation* the polymer adsorbs only on one type of particle in a mixture of particles. This is a way to separate one type of particles from a mixture. This technique is used in separation of minerals for example.

Heterocoagulation is the phenomenon where a mixture of two dispersions is not stable due to the attractive forces between the different types of particles. The reason could be that the two different dispersions are stabilized with different types of surfactants or polymers. It could also be a matter of a rearrangement of adsorbed layers where molecules desorb from one type of particle and adsorb on the other type. Such a reorganization, or competitive adsorption, may occur over a long period, hence the instability could go undetected in the laboratory.

Sedimentation or Creaming

The rate of unhindered sedimentation or creaming of a single particle (v) is given by Stokes law:

$$v = \frac{\Delta\rho d^2 g}{18\eta} \quad (18.8)$$

where $\Delta\rho$ is the difference in density of the particle and the medium, d is the particle diameter, g is the gravitational constant, and η is the viscosity of the medium. The equation illustrates the influence of particle size, density difference, and viscosity of the medium.

Consequently, on decreasing the particle size the sedimentation or creaming will be slowed down. Brownian motion counteracts the sedimentation or creaming and if the particle size is of the order of 100 nm or less the sedimentation or creaming will be hampered considerably.

The equation also reveals that there are other ways to hinder, or at least hamper, sedimentation or creaming. One obvious way is to match the densities of the dispersed phase and the dispersion medium. Adding salts to the aqueous phase or adding high-density oils to the organic phase are ways to match the densities.

An obvious way to decrease the sedimentation or creaming is to increase the viscosity of the medium. This is normally achieved by adding high molecular weight polymers to the medium. Adding a polymer that has some affinity to the particle surface will slightly flocculate the dispersion and the dispersion will form a network throughout the whole system. Such a network will hinder the sedimentation or creaming. This is often achieved in

commercial colloidal systems, such as ketchup or waterborne paints. On stirring, or shaking, the flocks are broken up and the dispersion will flow. If, on the other hand, there is a strong adsorption of the polymer such that the particles stick together to form larger agglomerates, the sedimentation or creaming will become faster.

Coalescence

Foams and emulsions have many features in common, among which are coalescence and Ostwald ripening. The analogy between emulsions and foams is especially clear for emulsions where oil droplets are emulsified in water. Coalescence is the process where emulsion drops merge into bigger drops. The process also occurs in foams, where foam bubbles merge into larger bubbles. Coalescence continues until the whole system is separated into an oil and an aqueous phase or until the foam has disappeared. The process of coalescence is dependent on the stability of the thin film that separates the drops or bubbles upon collision. If the film is stable there is no coalescence. If, on the other hand, there is an instability in the sense that there is a hole formed in the film, then the film will retract immediately and coalescence is a fact. Stabilizing against coalescence is, therefore, a matter of stabilizing the thin film separating the emulsion droplets or foam bubbles. If a hole is created in the film, then the pressure inside the film in the vicinity of the hole will be large due to the curvature of the hole (Figure 18.18). The liquid in the film therefore retracts and the hole expands in size.

To create a hole in the film separating two droplets it is necessary to bend the surfactant monolayer at the oil/water, or air/water interface. The curvature of this hole is significant, hence the energy of the hole formation strongly depends on the surfactant molecular structure. Figure 18.19 displays a hole in a water film separated by oil. As seen, one would expect a higher energy in creating a hole with a surfactant with a low CPP, as in Figure 18.19b, compared to a surfactant with a high CPP (Figure 18.19a). It is, therefore, more likely that holes are created with hydrophobic surfactants and, thus, o/w emulsions with such surfactants are less stable. This molecular mechanism is in accordance with Bancroft's rule (Chapter 24). Of course, the reasoning also holds for w/o emulsions with the conclusion that a water hole in the oil layer separating two droplets is more easily formed with hydrophilic surfactants rendering unstable emulsions.

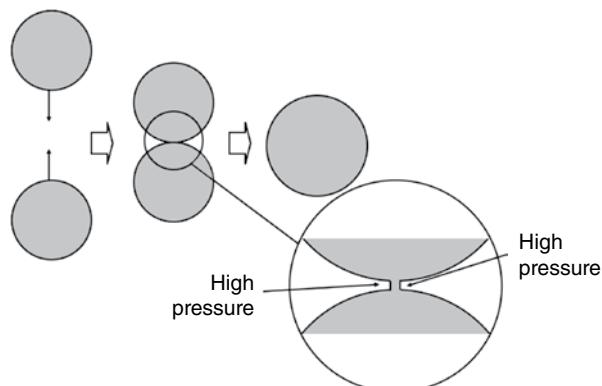


Figure 18.18 The coalescence of two oil droplets starts with the formation of a hole in the thin film separating the droplets

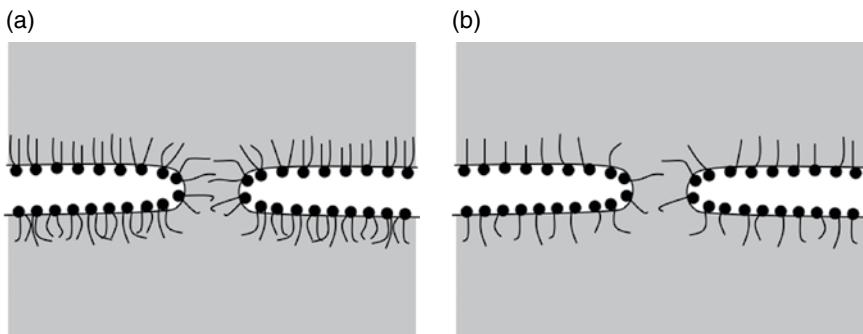


Figure 18.19 The formation of a hole in the thin aqueous film separating two emulsion oil droplets gives rise to a highly curved monolayer of the surfactant film stabilizing the emulsion droplets. The energy required for a hydrophobic surfactant (high CPP) as in (a) is smaller than for a hydrophilic surfactant (low CPP) as in (b). (Adapted with permission from Kabalnov, A. and Wennerström, H. (1966) Macroemulsion stability: the oriented wedge theory revisited. *Langmuir*, **12**, 276–292. Copyright 1996, American Chemical Society)

Ostwald Ripening

The second instability specific for emulsions and foams is Ostwald ripening. This phenomenon rests on the fact that the chemical potential, or pressure, of small droplets or bubbles, is larger than in larger droplets or bubbles (Equation 12.3). Hence, there will be a transport of molecules from the small droplets or bubbles to the large ones (Figure 18.20a). For emulsions the process continues until the dispersion ends up in two separate phases, an oil and an aqueous phase. This process can be very slow and continue for years.

The factors influencing the rate of Ostwald ripening are: (i) the particle size distribution; (ii) the solubility of the internal phase in the continuous phase; (iii) the type of surfactant in the continuous phase; (iv) the presence of substances in the dispersed phase that are insoluble in the continuous phase; and (v) the presence of polymeric surfactants at the interface.

If the emulsion, or foam, is very polydisperse from the start, then the Ostwald ripening will be fast. If, on the other hand the emulsion is perfectly monodisperse there will be no difference in chemical potential of the substance in the droplets and, hence, no transport between the droplets. This is, however, very unlikely since there is always a variation in droplet size, even in seemingly “monodisperse” size distributions.

The effect of solubility of the internal phase in the continuous phase is illustrated in Figure 18.20b, showing the average growth of droplets of *n*-alkanes emulsified in water. The solubility decreases by an order of magnitude as the alkane chain is lengthened by two carbon atoms. Hence, Ostwald ripening is not an issue with very insoluble oils, such as long-chain triglycerides.

If there is an excess of surfactant in the continuous phase, then the dispersed phase material might be transported as solubilized in micelles. Hence, solubilization will enhance the speed of Ostwald ripening. The surfactant also affects the rate through its effect on the interfacial tension. Surfactants rendering a high interfacial tension will give rise to a higher rate of degeneration of an emulsion as seen from the Young–Laplace equation (Equation 12.3). The role of surfactant molecular structure in Ostwald ripening is not completely clear, however.

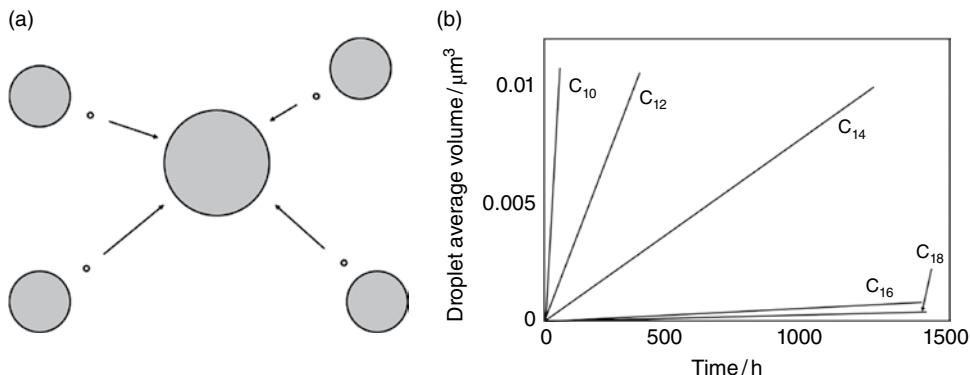


Figure 18.20 (a) Ostwald ripening is the process where material is transported from the small droplets, or bubbles, to the larger ones. (b) Droplet volume as a function of time for five n-alkane emulsions illustrating that the rate decreases with decreasing solubility of the alkane. (With permission from Weiss, J., Herrmann, N. and McClements, D.J. (1999) Ostwald ripening of hydrocarbon emulsion droplets in surfactant solutions. *Langmuir*, **15**, 6652–6657. Copyright 1999, American Chemical Society.)

These are the two alternative ways to hamper Ostwald ripening in an emulsion or foam (Figure 18.21). The first is to add a small amount of a component that dissolves in the dispersed phase but which has extremely low solubility in the continuous phase. As material is transported from the smaller droplets to the larger ones the concentration of the insoluble species increases in the small and decreases in the large droplets. This is entropically unfavorable and the continued Ostwald ripening will cease. For many oil-in-water emulsions, hexadecane is useful as such an extra added component.

The second alternative to hinder Ostwald ripening is to use surface active polymers, such as proteins, polysaccharides, or synthetic polymers. These species adsorb irreversibly at the interface and the polymer surface concentration is the same on small droplets as it is on large droplets. However, when material is transported from the small to the large droplets the surface concentration increases in the small droplets and decreases in the large droplets, with the consequence that the interfacial tension becomes smaller in the smaller droplets and larger in the large droplets. This hampers the Ostwald ripening process, since the pressure in the smaller droplets becomes lower compared to the pressure in the larger droplets (Equation 12.3).

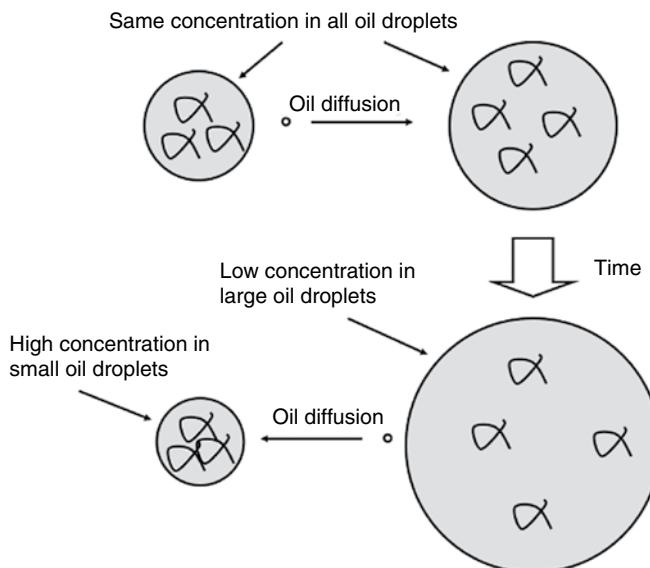
Stabilization with Particles

Solid particles can be used to stabilize emulsions and foams. The particles should be small in comparison to the size of droplets or bubbles. Best effect is obtained with particles that form a 90° contact angle with the oil–water or air–water interface. Such particles are wetted by both phases and, therefore, attach well to the surface of the droplets.

The stabilization energy can be written as:

$$\Delta E = \pi r^2 \gamma (1 - |\cos \theta|)^2 \quad (18.9)$$

(a)



(b)

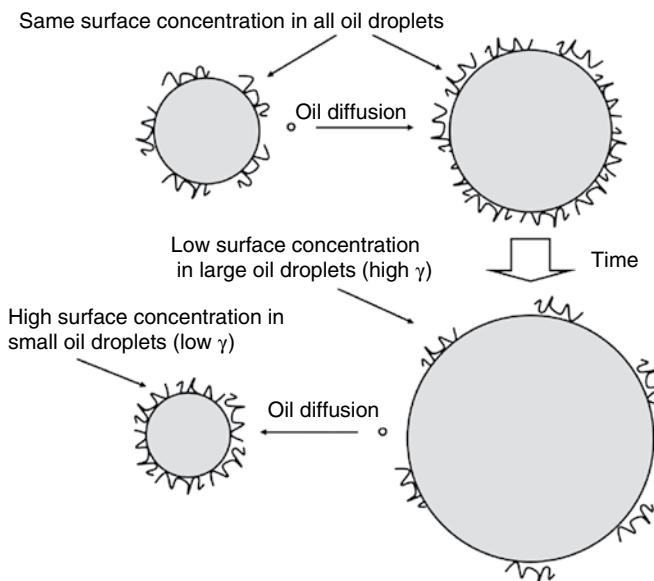


Figure 18.21 Ostwald ripening can be hampered (a) by addition of a second material that is insoluble in the continuous phase but soluble in the dispersed phase or (b) by using surface active polymers that do not desorb from the surface

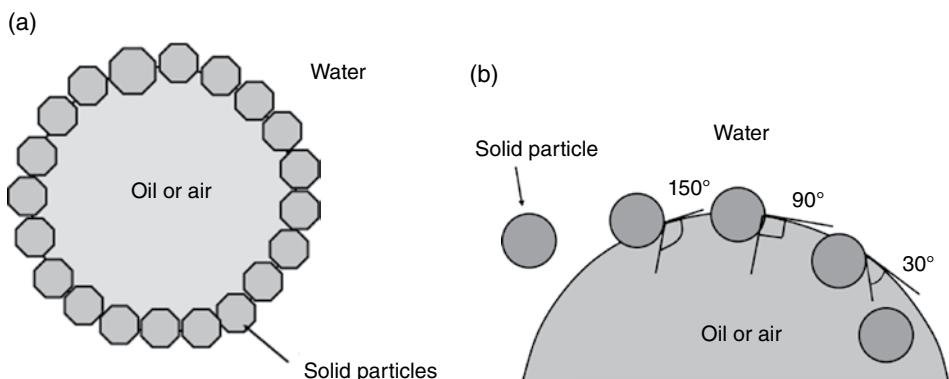


Figure 18.22 (a) An oil droplet, or foam bubble, covered by small, hydrophobic particles; (b) best stabilization is achieved if the contact angle of the particle on the surface of the droplet is around 90°

Here r is the radius of the small particles, γ the interfacial tension, and $\cos \theta$ the contact angle that the particle makes at the surface. It can immediately be seen that the stabilization energy is at maximum for $\theta = 90^\circ$. It can also be seen that large particles and a high interfacial, or surface, tension are beneficial. From a stabilization point of view it is, therefore, better not to use a surfactant in combination with the particles. However, without an additive that reduces the interfacial tension it may be difficult to disintegrate the dispersed phase into small drops. A combination of a surfactant and hydrophobic particles is, therefore, often used if the emulsification is not made with a device that gives a high energy input. Also, choosing the optimal value of r is not straightforward because particles that are too large have difficulties in reaching the interface in a reasonable time. In practice, particles with a diameter 10–100 times smaller than that of the emulsion droplets are commonly used. Figure 18.22 illustrates the concept.

Stabilization by Lamellar Liquid Crystals

Surfactants can pack in multilayers around the dispersed phase, forming lamellar liquid crystals (Chapter 6). Such a multilayer arrangement is stable and can provide very long-lived dispersions. Formation of lamellar liquid crystals can sometimes also be the key to making emulsions or foams with a minimum of energy input, so-called *spontaneous emulsification* (page 443). Figure 18.23a illustrates lamellar liquid crystals at the surface of an oil droplet. The formation of lamellar liquid crystalline phases is due to a balanced interaction between the surfactant, oil, and water, hence the stability of emulsions is very dependent on the choice of oil. Figures 18.23b and 18.23c show the effect of changing an aromatic to an aliphatic type of oil. The phase diagrams show the three-phase region (in black) where there is an equilibrium between water, oil and a mesophase. Hence, for the aromatic oil there needs to be much less emulsifier in order to reach the three-phase region. This is because of the good swelling of the aromatic oil in the lamellar phase of the emulsifier (NP-E_{10}).

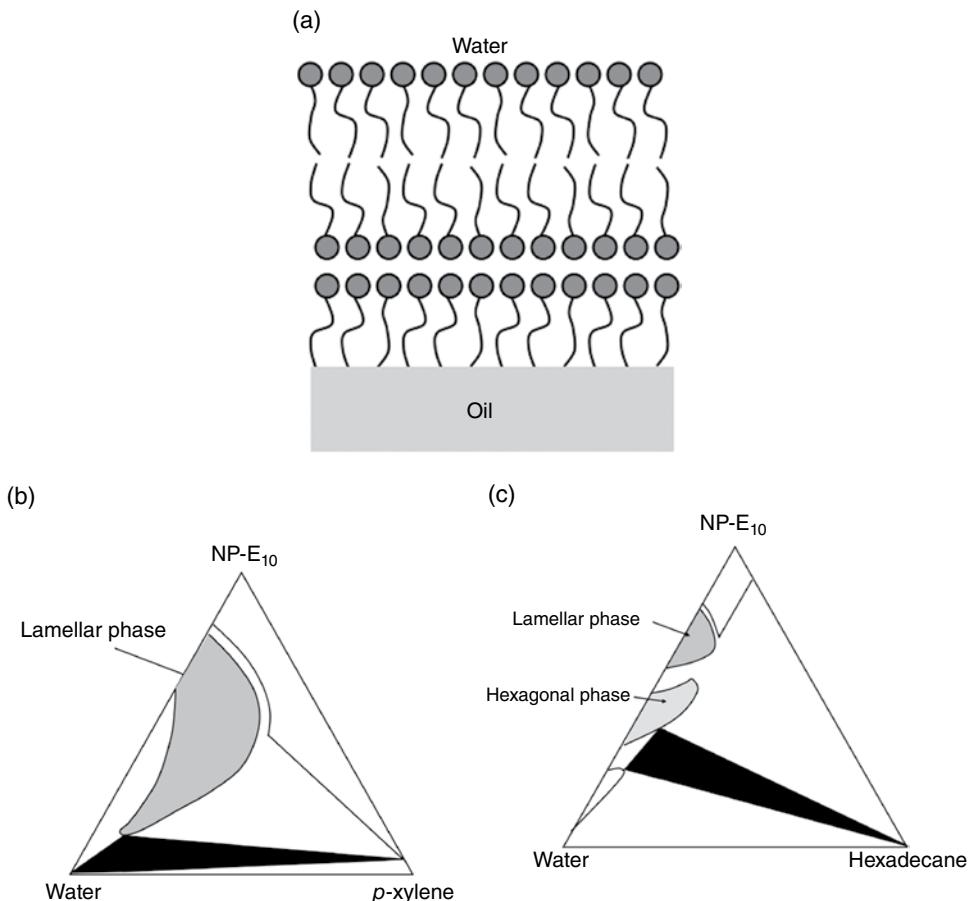


Figure 18.23 (a) Stabilization of an emulsion by a multilayer of surfactant, which may extend into a lamellar liquid crystal. The formation of a lamellar liquid crystalline phase is highly dependent on the choice of oil, here exemplified with (b) *p*-xylene and (c) hexadecane. The concentration of surfactant needed in order to reach the three-phase region, in which one of the phases is a mesophase (the black triangle), is much less in the former system. (With permission from Friberg, S. and Solans, C. (1986) Surfactant association and the stability of emulsions and foams. *Langmuir*, **2**, 121–126. Copyright 1986, American Chemical Society)

Electrophoretic Mobility—A Versatile Tool in the Assessment of Colloids

The electrophoretic mobility of a particle is obtained by measuring the particle speed in an electric field (Figure 18.24a). Through measuring the electrophoretic mobility of colloidal particles a plethora of information can be gained. One of the advantages of the technique is that the electrophoretic mobility is independent of particle size and shape and is solely a function of the electrical potential at the slipping plane just outside the particle surface. Note that the electrophoretic mobility does not give the surface potential but rather the potential at the slipping plane just outside the surface (Figure 18.9 and Figure 18.24b). This is termed the zeta potential.

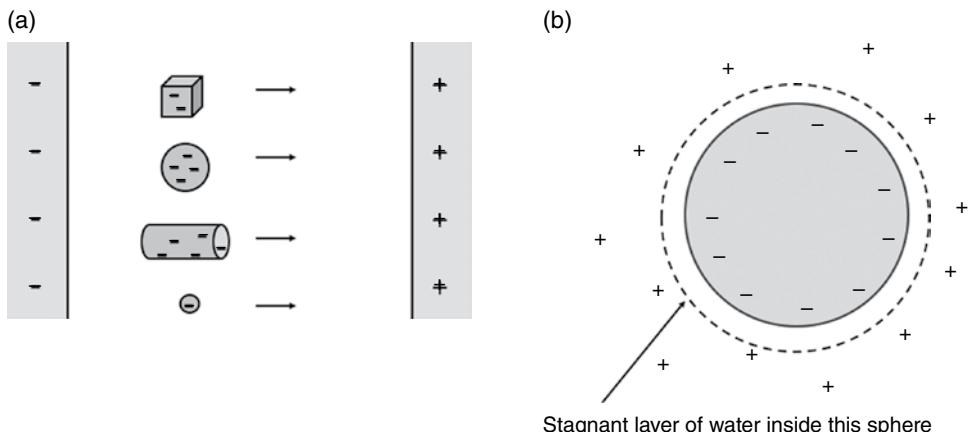


Figure 18.24 (a) The principle of electrophoretic mobility illustrating that the mobility is independent on both size and shape of the particles and is only a function of the surface charge. (b) An illustration of that the zeta potential is obtained at a distance outside the surface of the particle, the slipping plane

As was discussed earlier, many particles have an isoelectric point, that is, a pH where the zeta potential is zero. Figure 18.25a shows the zeta potential as a function of pH of a mineral for which the isoelectric point is independent of the amount of salt added. The lower zeta potential at higher salt concentration is a consequence of the compression of the double layer, as is illustrated in Figure 18.9. However, if the salt interacts with the surface, the situation will be as is shown in Figure 18.25b. Here there is no common isoelectric point, since the surface potential changes as a function of the concentration of adsorbing ions. The pH dependence on salt addition, as illustrated in Figure 18.25 is, therefore, used to discern whether or not a salt is inert with respect to the particle surface.

Measurements of the electrophoretic mobility can be used to investigate the adsorption of surfactants, as shown in Figure 18.26, which shows the adsorption of alkyl ammonium

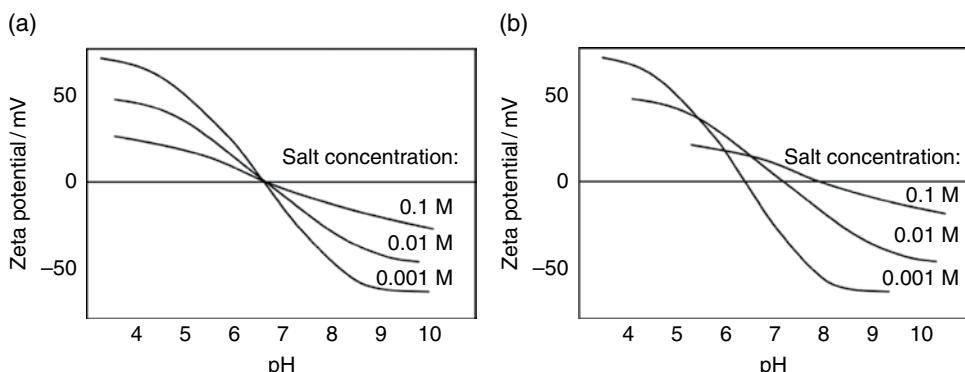


Figure 18.25 Illustration of the zeta potential versus pH for particles with (a) an inert salt and (b) a salt that adsorbs at the particle surface

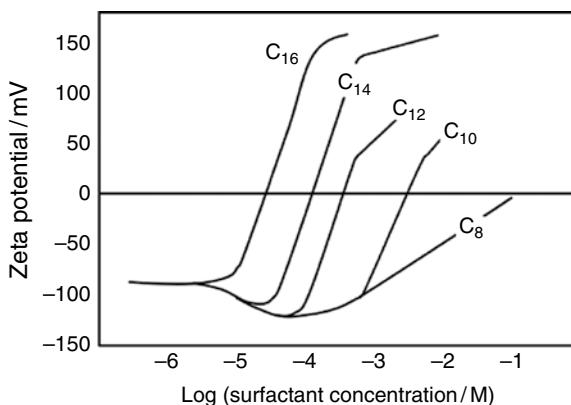


Figure 18.26 Adsorption of cationic surfactants (alkyl ammonium acetates) on quartz as investigated with electrophoretic mobility measurements. (With permission from Fuerstenau, D.W. (2002) Equilibrium and nonequilibrium phenomena associated with the adsorption of ionic surfactants at solid-water interfaces. *Journal of Colloid and Interface Science*, **256**, 79–90, Copyright 2002, American Chemical Society, and Somasundaran, P., Healy, T. and Fuerstenau, D. (1964) Surfactant adsorption at solid-liquid interface: dependence of mechanism on chain length. *Journal of Physical Chemistry*, **68**, 3562–3566, Copyright 1964, American Chemical Society)

ions. The figure reveals that the cationic surfactants first reduce and eliminate the surface charge, then reverse the charge of the surface, and that the efficiency increases with the alkyl chain length, as expected.

Electrophoretic mobility is also a useful tool for studying adsorption of polyelectrolytes at particles. It can even be used to investigate the adsorption of neutral polymers. An adsorbed neutral polymer will shift the slipping plane further out from the particle surface (Figure 11.19a). This results in a decreased electrophoretic mobility as shown in Figure 11.19b.

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19

An Introduction to the Rheology of Polymer and Surfactant Solutions

The flow properties are in focus in most applications of polymer and surfactant solutions as well as for mixed systems. In a number of previous chapters we have already touched on the rheological aspects of different types of systems. While it is not possible to go deep into the advanced topic of rheology, we wish to give some central aspects and, thereby, achieve a comparison between the rheological properties of different systems.

Rheology Deals with how Materials Respond to Deformation

Solid bodies, liquids, and gases can respond in different ways to a deformation; they can be elastic, they can flow, or they can fracture. It is a large and important subject not least for colloidal systems. Here, we are interested in the flow properties of dispersions, as well as simple and complex solutions, and the elasticity of solutions and gels. The steady-state behavior will be in focus but it should be recalled that time-dependent effects are most significant for applications.

Rheology is not an easy subject. Experiments that give relevant information need to be carefully designed, the mathematics is quite difficult to master, and even minute changes in composition (as we saw *inter alia* in Chapter 14) and in aggregation can dramatically change the rheological properties. Here we mainly introduce basic relationships and definitions, as well as consider the rheology of simple colloidal dispersions and solutions.

Viscosity Measures how a Simple Fluid Responds to Shear

In this chapter we only consider one simple type of deformation, shear, as introduced in Figure 19.1. Under so-called “nonslip” conditions, the layer of the liquid closest to the wall is stationary with respect to the latter. Different systems respond very differently to shear, for example, a fluid (liquid or gas) by viscous flow, or a solid by an elastic deformation. For a fluid, the deformation is irreversible, while for a solid it is reversible. For many of the systems we are interested in here the situation is intermediate (viscoelastic): there is both a viscous and an elastic response.

We will only consider laminar (i.e., nonturbulent) flow and first we look at the simplest (so-called Newtonian) behavior. With reference to Figure 19.1, we can define the following:

$$\text{Shear stress: } \tau = \frac{F}{A} \text{ (often also denoted } \sigma \text{) (units of Pa)}$$

$$\text{Shear strain: } \frac{dx}{dy} \text{ (alternatively, } \gamma\text{)}$$

$$\text{Flow rate: } v = \frac{dx}{dt}$$

$$\text{Shear rate: } D = \frac{dv}{dy} = \frac{d}{dt} \left(\frac{dx}{dy} \right) \text{ (units of s}^{-1}\text{)}$$

For two parallel plates at a constant separation, there is a linear variation in the flow rate in the y -direction, that is, D is the same in all layers. For a cylindrical tube (with Poiseuille flow), v is a parabolic function of r , largest at the center and zero at the wall, while D is zero at the center and largest at the wall (Figure 19.2).

For the simplest case, which we call a Newtonian fluid, the shear stress and the shear rate are proportional to each other (Figure 19.3); the proportionality constant is the viscosity, η :

$$\frac{F}{A} = \eta \frac{dv}{dy} \quad \text{or} \quad \tau = \eta D \quad (19.1)$$

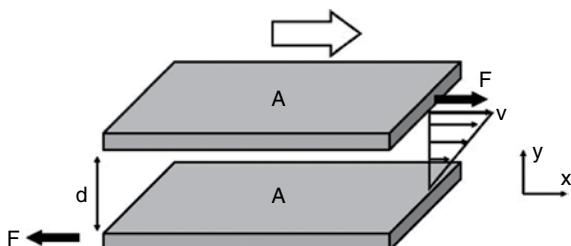


Figure 19.1 Two parallel planes, each of area A , located at $y = 0$ and $y = d$. The space between the planes is filled with a sheared fluid. The upper plane moves with a velocity v relative to the lower one and the lengths of the arrows between the planes are proportional to the local velocity in the fluid. The applied shearing force is F

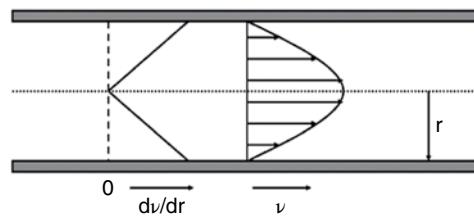


Figure 19.2 For the flow of a fluid in a cylindrical tube, the velocity (v) is a parabolic function of the radius (r) with a maximum in the center. The shear rate (dv/dr) is a linear function of r , largest at the wall and zero at the center

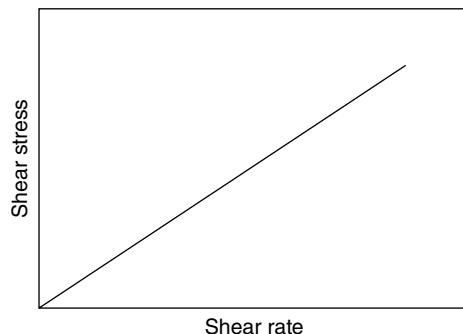


Figure 19.3 For a Newtonian fluid, the shear stress is proportional to the shear rate

The viscosity, which is defined as the resistance against deformation for a fluid, can vary widely between different materials, as illustrated in Table 19.1. The larger the viscosity, then the larger is the shear stress required for a certain shear flow.

Simple liquids are generally Newtonian, while colloidal systems, dispersions or solutions, may or may not be Newtonian. The rheological nature may also change with concentration and shear rate; the latter is very different for different processes (Table 19.2).

For solutions, it is often convenient to discuss different derived functions, such as relating the viscosity to that of the neat solvent or normalizing it with respect to concentration. The relevant parameters are the relative viscosity (viscosity ratio), the specific viscosity, the reduced viscosity (viscosity number), and the intrinsic viscosity (limiting viscosity number) (Table 19.3).

The viscosity can be measured by a number of different shear experiments, suitable for different systems and purposes. In the capillary, or Ostwald, viscometer the measured flow time gives the viscosity. The flow time (t) depends on the viscosity as well the density (ρ) of the liquid and, generally, the instrument is calibrated by measurements with a liquid of known viscosity. The following relationship applies for two liquids, 1 and 2:

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2} \quad (19.2)$$

Table 19.1 The viscosity of some common fluids

Liquid	Approximate viscosity (Pa s)
Glass	10^{40}
Molten glass (500°C)	10^{12}
Bitumen	10^8
Molten polymers	10^3
Golden syrup	10^2
Liquid honey	10^1
Glycerol	10^0
Olive oil	10^{-1}
Bicycle oil	10^{-2}
Water	10^{-3}
Air	10^{-5}

After Barnes, H.A., Hutton, J.F. and Walters, K. (1989) *An Introduction to Rheology*, Elsevier Science, Amsterdam.

Table 19.2 Shear rates typical of some common materials and processes

Situation	Typical range of shear rates (s^{-1})	Applications
Sedimentation of fine powders in a suspending liquid	10^{-6} – 10^{-4}	Medicines, paints
Leveling due to surface tension	10^{-2} – 10^{-1}	Paints, printing inks
Draining under gravity	10^{-1} – 10^1	Painting and coating
Extruders	10^0 – 10^2	Polymers
Chewing and swallowing	10^1 – 10^2	Foods
Dip coating	10^1 – 10^2	Paints, confectionary
Mixing and stirring	10^1 – 10^3	Manufacturing liquids
Pipe flow	10^0 – 10^3	Pumping, blood flow
Spraying and brushing	10^3 – 10^4	Spray drying, painting
Rubbing	10^4 – 10^5	Application of creams and lotions
Milling pigments in fluid bases	10^3 – 10^5	Paints, printing inks
High speed coating	10^5 – 10^6	Paper
Lubrication	10^3 – 10^7	Gasoline engines

After Barnes, H. A., Hutton, J. F. and Walters, K. (1989) *An Introduction to Rheology*, Elsevier Science, Amsterdam.

Table 19.3 Important derived functions used to characterize viscosity behavior including the IUPAC names

Functional form	Symbol	Common name	IUPAC name	$\lim(c=0)$
—	η	Viscosity	—	η_0
η/η_0	η_r	Relative viscosity	Viscosity ratio	1
$\eta/\eta_0 - 1$	η_{sp}	Specific viscosity	—	0
$(\eta/\eta_0 - 1)/c$	η_{red}	Reduced viscosity	Viscosity number	[η]
$\ln(\eta/\eta_0)/c$	η_{inh}	Inherent viscosity	Logarithmic viscosity number	[η]
$\lim \eta_{red}$ or $\lim \eta_{inh}$	$[\eta]$	Intrinsic viscosity	Limiting viscosity number	—

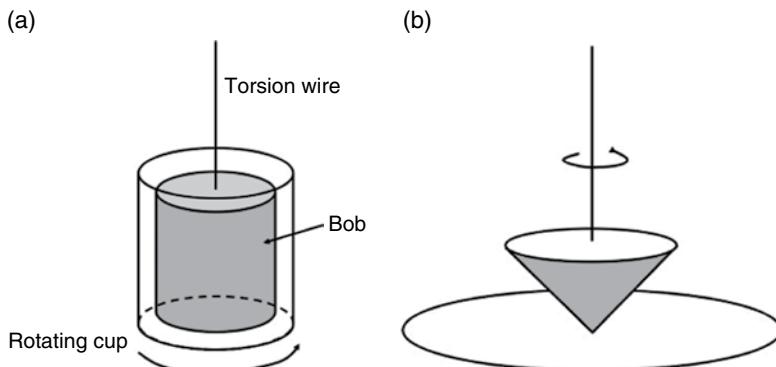


Figure 19.4 Schematic representations of (a) the concentric-cylinder and (b) the cone-and-plate viscometer

For dilute solutions or dispersions, there is no difference in density between the solution and the neat solvent, so:

$$\frac{\eta}{\eta_0} = \frac{t}{t_0} \quad (19.3)$$

In the concentric-cylinder and cone-and-plate viscometers illustrated in Figure 19.4, the viscous fluid is enclosed in the gap between two surfaces. As one of them moves, for example, by rotation of the outer cylinder in the concentric-cylinder viscometer, the viscous resistance will be transmitted through the fluid and produces a torque on the stationary surface, which is related to the viscosity. By varying either the width of the gap or the angular velocity, the shear rate can be varied.

The Presence of Particles Changes the Flow Pattern and the Viscosity

If colloidal size particles are introduced in a liquid, the flow pattern is changed, as illustrated in Figure 19.5. If a nonrotating particle is inserted, the liquid must be slowed down since the layers on opposite sides of the particle must have the same velocity, which must be the same as that of the particle. The overall velocity gradient is thus reduced and, since the shear is the same, this corresponds to an increased viscosity. For a rotating particle there will also be a reduced velocity gradient.

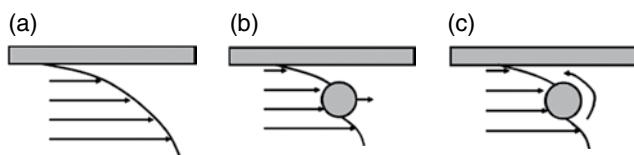


Figure 19.5 Illustration of the flow pattern near a stationary wall for a neat liquid (a), and in the presence of particles, nonrotating (b), or rotating (c)

The increase in viscosity due to the particles depends on their concentration and for a Newtonian colloidal system the relationship can be expressed as a power series in the particle concentration. For low concentrations and low shear rates, we therefore have:

$$\frac{\eta}{\eta_0} = 1 + k_1 c + k_2 c^2 + k_3 c^3 + \dots \quad (19.4)$$

where η_0 is the viscosity of the medium (absence of particles) and c the concentration of particles. The constant k_1 depends on the particle shape and k_2 on the particle–particle pair interactions, with numerical values depending on the concentration units chosen (k_1 equals the intrinsic viscosity or limiting viscosity number defined above).

It is illustrative to choose the volume fraction (ϕ) of particles as the concentration unit. For rigid, spherical particles, at low concentrations, we have:

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi \quad (19.5)$$

which is known as Einstein's equation of viscosity of dispersions, that is, the intrinsic viscosity $[\eta]_\phi = 2.5$.

The relative viscosity and the reduced viscosity as a function of the volume fraction of spherical particles are illustrated in Figure 19.6. In Figure 19.6a, the slope gives the intrinsic viscosity, while in Figure 19.6b it is given by the intercept on extrapolation to $\phi = 0$. Equation 19.5 has been verified for a wide range of particles.

The Einstein theory is based on a model of dilute, unsolvated spheres. Deviations can be due to a high concentration, to nonspherical shape of particles, or to particle swelling due to solvation. For rigid nonspherical particles, $[\eta]_\phi > 2.5$, with theoretical equations available for simple ellipsoidal shapes. Absorption of solvent and solvation leads to an increase of $[\eta]_\phi$, but the Einstein equation is still valid if the effective volume of the particle, including absorbed solvent, is considered. This effect becomes very important for flexible polymers. If solute adsorption occurs, then there is an analogous effect and the effective volume of the particle, including adsorbed molecules, needs to be considered.

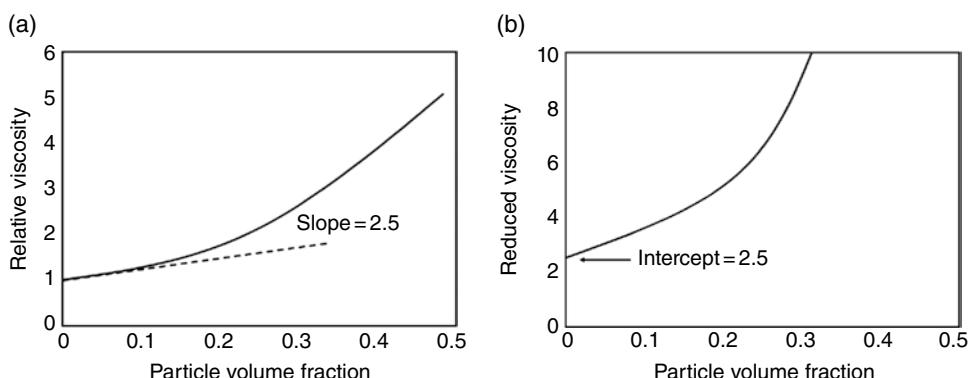


Figure 19.6 (a) Relative and (b) reduced viscosity versus volume fraction of spherical particles; the slope and intercept, respectively, give the intrinsic viscosity

For a polymer molecule the effective volume per unit of mass is very large and, therefore, $[\eta]$ is very large compared to particles. This is discussed in Chapter 9, where the Mark–Houwink equation is presented (Equation 9.3). Different particle shapes and different solvency conditions give different exponents, as exemplified by rigid spheres giving 0, rigid long rods 1.8, and flexible polymer chains in a theta (θ) solvent (for an explanation of theta solvent, see Chapter 9) 0.5 and in an athermal solvent 0.8.

The Rheology is Often Complex

We have considered above the simple Newtonian behavior, where there is proportionality between the shear stress and the shear rate. For colloidal systems, this simple relationship generally breaks down and we have a non-Newtonian liquid. However, we can then define an apparent viscosity as follows:

$$\tau = \eta_{\text{app}} D \quad (19.6)$$

For a non-Newtonian liquid, the value of η_{app} depends on the shear stress (or shear rate), a dependence that will interest us now.

However, let us first mention another complication. The apparent viscosity generally varies with time at a given shear rate (or stress); thus, η_{app} depends on the history of the solution. Above, we have assumed that a certain shear rate produces a certain shear stress, which does not change as long as a constant shear rate is applied. After some time, at constant D , or τ , a *stationary state* often develops, where η_{app} is constant and independent of the history of the system.

The relationship between shear rate and shear stress is different for different systems, as exemplified in Figure 19.7. For a shear-thinning (or *pseudo-plastic*) system, η_{app} decreases with increasing shear rate; plastic liquids are characterized by a finite yield value, that is, a minimal yield stress needed before they start to flow. A shear-thickening (or *dilatant*) system is characterized by an apparent viscosity that increases with increasing shear rate.

Non-Newtonian behavior can arise from many different mechanisms, some of which are illustrated in Figure 19.8. For dilute systems, shear-thinning can be due to flow orientation

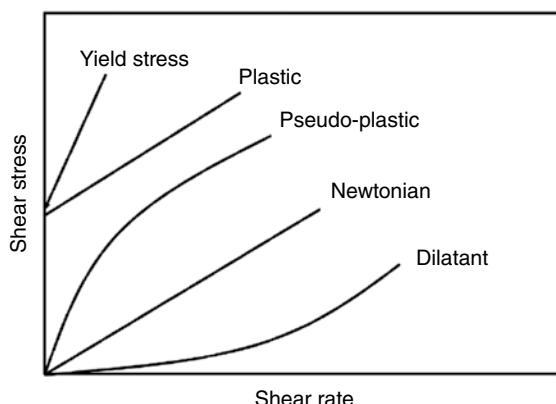


Figure 19.7 Different relationships between shear stress and shear rate for the stationary state

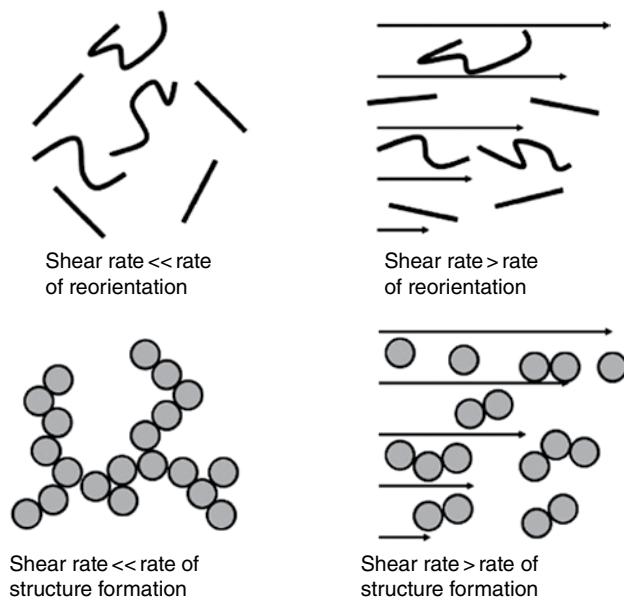


Figure 19.8 Examples of the origin of shear-thinning for dilute (top) and concentrated (bottom) systems, showing schematic structures for low and high shear rates. (Courtesy of Lennart Piculell.)

of the particles or change in conformation of the polymer molecules. Thus, when the shear rate is larger than the rate of thermal reorientation of the particles, they will be aligned in the flow direction. For concentrated systems, shear-thinning appears when the shear rate is larger than the rate of build-up of the equilibrium supra-particulate structures.

The behavior of shear-thinning systems is illustrated in Figure 19.9, and as can be seen there are two Newtonian plateaus where η_{app} is independent of shear rate and shear stress. The plateau value for low shear rates is called the zero shear viscosity. The shear-thinning behavior of polymer solutions depends strongly on concentration (Figure 19.10).

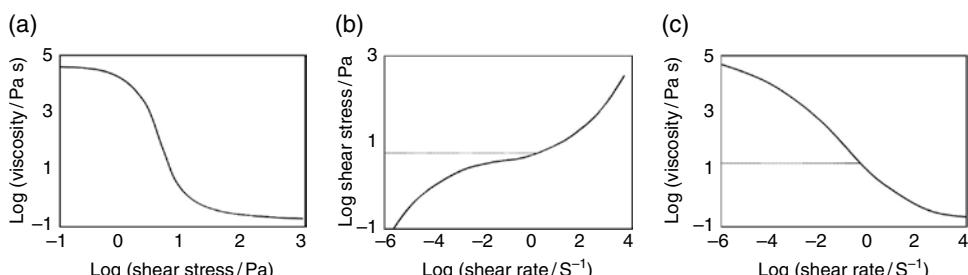


Figure 19.9 Illustrations of the typical behavior of a non-Newtonian liquid: (a) viscosity versus shear stress; (b) shear stress versus shear rate (the dotted line representing the ideal yield stress, or Bingham plastic, behavior); (c) viscosity versus shear rate. (With permission from Barnes, H.A., Hutton, J.F. and Walters, K. (1989) An Introduction to Rheology, Elsevier Science, Amsterdam. Copyright Elsevier.)

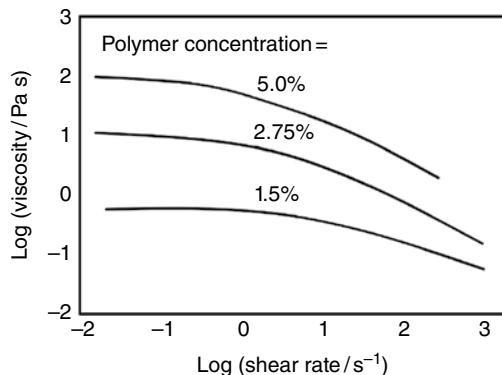


Figure 19.10 Shear-thinning for concentrated polysaccharide solutions, illustrated for λ -carrageenan at three concentrations (in wt%). (With permission from Morris, E.R., Cutler, A.N., Ross-Murphy, S.B. and Rees, D.A. (1981) Concentration and shear rate dependence of viscosity in random coil polysaccharide solutions. Carbohydrate Polymers, 1, 5–21. Copyright Elsevier.)

The viscosity can either increase or decrease with time and these changes can be reversible or irreversible. A common case is *thixotropy*, where the viscosity decreases with time. Thixotropy typically occurs when the solution is shear-thinning, with the opposite applying for shear-thickening situations. For such cases, the flow history of the sample must be taken into account. The opposite case to thixotropy is called *rheopexy*.

Viscoelasticity

In defining the viscosity from the simple shear experiment, we saw that for the simple case of a Newtonian liquid the shear stress is proportional to the shear rate. For a solid body subjected to shear, there will be deformation rather than flow; the shear stress is proportional to the shear or deformation rather than the shear rate:

$$\tau = G \frac{dx}{dy} \quad (19.7)$$

where G (units of Pa) is called the *storage modulus* (a solid is elastic). A characteristic of many surfactant and polymer systems is that they have both types of responses simultaneously; they are both viscous and elastic, that is, *viscoelastic*.

Viscoelasticity can be investigated in oscillating measurements. Considering Figure 19.4, the outer cylinder (or the plate) is oscillated sinusoidally; the torque experienced by the inner cylinder (giving the shear stress) is measured as a function of time. For an elastic body, the shear stress is largest at the maximum deformation, that is, at the extreme points of the oscillation, while it is zero when the deformation is zero; the shear stress varies in phase with the deformation, that is, the phase angle $\delta = 0$. For a viscous liquid, the shear stress is largest at the maximum shear rate, and therefore this occurs for zero deformation.

When the deformation is at a maximum, the shear rate is zero and so, too, is the shear stress. The shear stress is thus out-of-phase with respect to the deformation, and the phase angle is 90° .

For a viscoelastic liquid the phase angle has an intermediate value, $0^\circ < \delta < 90^\circ$. It is characterized by the in-phase and out-of-phase components of the modulus:

Shear storage modulus:

$$G' = G_0 \cos \delta \quad (19.8a)$$

Shear loss modulus:

$$G'' = G_0 \sin \delta \quad (19.8b)$$

Viscoelastic systems are also characterized by two other parameters, namely:

Dynamic shear modulus:

$$G^* = \left[(G')^2 + (G'')^2 \right]^{1/2} \quad (19.9a)$$

Dynamic viscosity:

$$\eta^* = \frac{G^*}{\omega} = \frac{\left[(G')^2 + (G'')^2 \right]^{1/2}}{\omega} \quad (19.9b)$$

The limiting types of behavior are an elastic gel and a Newtonian liquid. For an elastic gel, the elastic component dominates, thus $G' \gg G''$ and G' is independent of frequency. The dynamic viscosity (η^*) approaches G'/ω , which is inversely proportional to the frequency. For a Newtonian system, the viscous component dominates and the (dynamic) viscosity is independent of frequency. This is exemplified later in Figure 19.15.

The Rheological Behavior of Surfactant and Polymer Solutions Shows an Enormous Variation: Some Further Examples

Surfactant Systems

The viscosity of surfactant solutions is only weakly affected by surfactant self-assembly into spherical aggregates. On the other hand, as we investigated in Chapter 6, growth into cylindrical or thread-like aggregates is accompanied by major increases in viscosity. In Figure 6.1, the viscosity is shown for the case of spherical aggregates. At low volume fractions, the viscosity follows the Einstein equation for hard spheres. For higher concentrations, there is agreement with models that take into account crowding and other particle-particle interactions. An illustration for the case of microemulsions composed of spherical droplets is given in Figure 19.11, again showing the weak increase in viscosity with droplet volume fraction.

The increase in viscosity due to uni-dimensional growth of micelles was illustrated earlier in Figure 6.2. The dramatic increase in viscosity with concentration is due to a

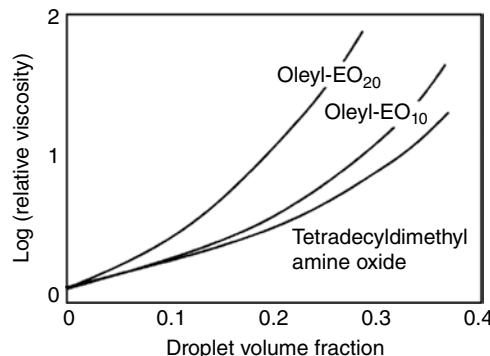


Figure 19.11 Relative viscosity as a function of the droplet volume fraction (volume fraction of surfactant plus oil), for oil-in-water (o/w) microemulsions composed of surfactant, decane, and water. (Adapted with permission from Gradzielski, M. and Hoffmann, H. (1999) *Rheological properties of microemulsions*, in *Handbook of Microemulsion Science and Technology* (eds P. Kumar and K.L. Mittal), Marcel Dekker, New York, pp. 357–386. Copyright Taylor and Francis Group LLC Books.)

combination of micellar growth and micelle–micelle interactions; the viscosity enhancement relative to neat water may exceed 10^7 . Such solutions are typically viscoelastic. Cationic surfactants with certain organic counterions may give particularly strong effects, as illustrated in Figures 19.12 for hexadecylpyridinium in the presence of salicylate. Figure 19.12a shows the zero shear viscosity data, while Figure 19.12b shows the storage and loss moduli data.

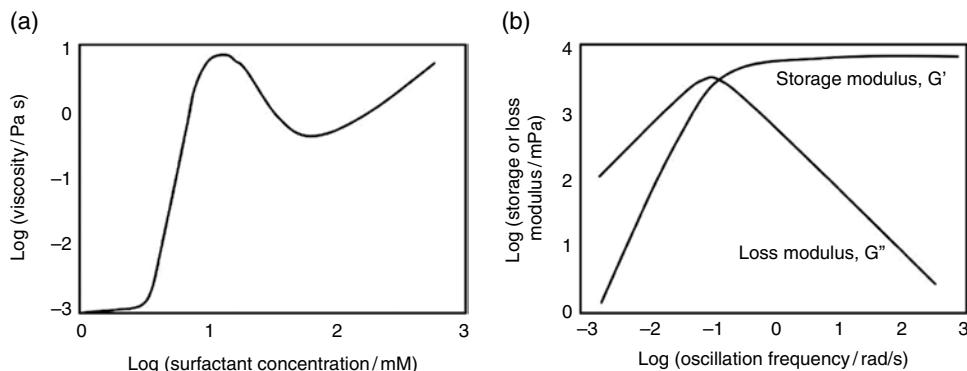


Figure 19.12 (a) The concentration dependence of the viscosity extrapolated to zero shear rate for equimolar concentrations of hexadecylpyridinium chloride and sodium salicylate and (b) the storage and loss moduli (G' and G'' , respectively) for a solution of 80 mM hexadecylpyridinium salicylate. (With permission from Hoffmann, H., Löbl, M., Rehage, H. and Wunderlich, I. (1986) *Rheology of surfactant solutions*. Tenside-Detergents, **22**, 290–298, Copyright 1986, Carl Hanser Verlag GmbH & Co. KG.)

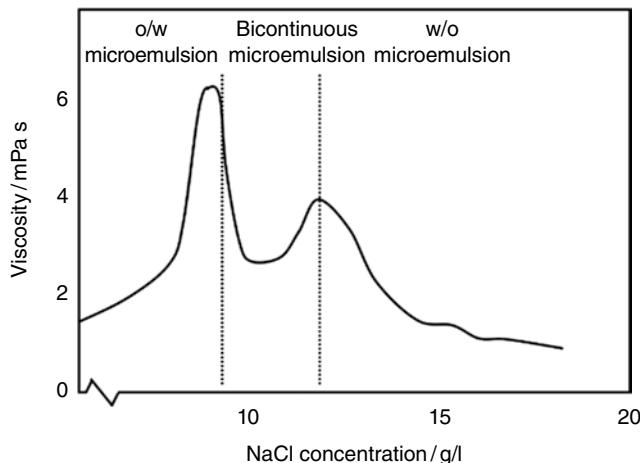


Figure 19.13 Viscosity (at low shear rates) as a function of salinity for a system of a commercial petroleum sulfonate (TRS 10-80), octane and alcohol. As the salinity increases there is a change over from an o/w to a bicontinuous and finally to a w/o microemulsion. (Data from Kaler, E.W., Bennett, K.E., Davis, T. and Scriven, L.E. (1983) Toward understanding microemulsion microstructure: a small-angle x-ray scattering study. *Journal of Chemical Physics*, **79**, 5673–5684.)

There are also cases of reversed micellar growth leading to similar effects. For lecithin–water–oil systems, addition of water to a solution of lecithin in oil can lead to viscosity increases by a factor of 10^6 because of this.

Bicontinuous and L_3 (sponge) phase surfactant solutions are characterized by a Newtonian behavior and moderate viscosities, even at relatively high volume fractions. Similarly, the structurally related bicontinuous microemulsions also show low viscosities and simple Newtonian flow behavior. In Figure 19.13, the relationship between microstructure and viscosity is illustrated for a microemulsion system where a transition from an oil-in-water (o/w) to a bicontinuous and finally to a water-in-oil (w/o) structure can be induced by the addition of salt. Irrespective of the microstructure, the viscosity is low and does not vary much with changes in the microstructure. The low viscosity illustrates the dynamic character of microemulsions (Chapter 17). In microemulsion systems, where one can pass between different types of structures, it is typically observed that there is a maximum in viscosity around the transition from the droplet to the bicontinuous microstructure, as illustrated in Figure 19.13.

For liquid crystalline phases there is a relationship between rheology and composition but the most important factor is phase structure. Of the common phases, the lamellar one has the lowest viscosity, while the cubic ones (both discrete micellar and bicontinuous types) have the highest viscosities. In fact, cubic phases are characterized by very high viscosities and may even possess a yield value. They exhibit elastic properties and have a solid-like appearance. When subjected to shear, the liquid crystalline phases present complex rheological responses, which are due to microstructural rearrangements; for lamellar phases, there is a complex interplay between extended bilayer stacks, bilayer fragments,

and multilamellar vesicles, “onions.” Concentrated lamellar phases may be changed on shear into highly viscous dispersions of onion-type multilamellar vesicles.

Polymer Solutions

As we have already touched upon above, as well as in Chapters 6 and 9, polymers have a broad range of applications for rheology control. We have also seen that the viscosity depends on a number of factors, such as molecular weight, concentration, solvency conditions, and extension of polymer molecules. Special attention will be paid here to the properties of associating polymers.

The discussion above regarding the exponent in the Mark–Houwink equation illustrates the role of solvency. For polyelectrolytes the extension of polymer molecules is determined by the counterion entropy, and is thus strongly influenced by salt, as well as polymer concentration. Due to electrostatic screening, polyions adopt a more compact conformation in the presence of salt as well as at higher polyion concentration; this explains the decrease in reduced viscosity, shown in Figure 19.14.

Associating amphiphilic polymers can give rise to a wide range of rheological behavior depending on the polymer architecture and we have already alluded to two cases in Chapters 7 and 14.

The block copolymer case of Figure 7.15 is of a special nature. Here self-assembly into the same type of structures as for surfactant systems controls the rheological behavior. Thus, the dramatic increase in viscosity with increasing temperature (sometimes referred to as *thermal gelation*) is due to a phase transition from a micellar solution to a cubic liquid crystalline phase.

The shear-thinning behavior of polysaccharide solutions was exemplified above in Figure 19.10. An illustration of the widely different types of behavior that can be

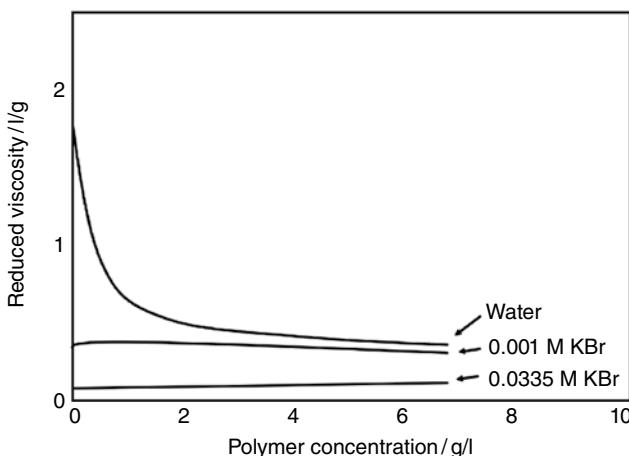


Figure 19.14 The reduced viscosity of poly(*N*-butylvinylpyridinium) solutions with bromide as the counterion as a function of polymer concentration. The figure illustrates the increased screening effect with the ionic strength, originating from either the counterion or the polymer itself

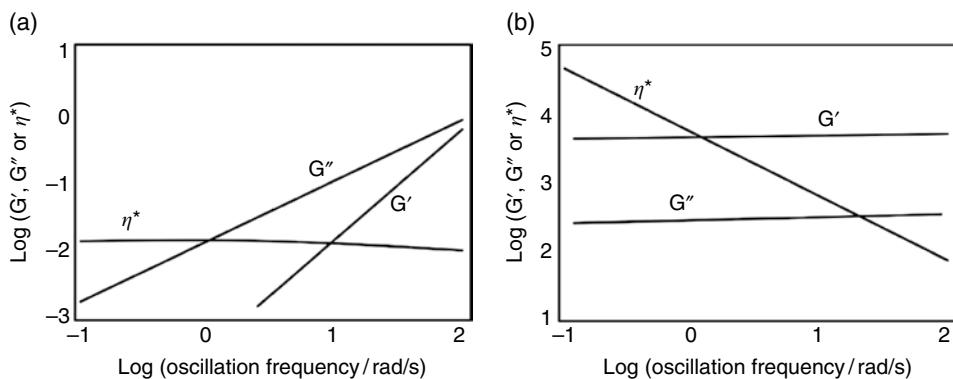


Figure 19.15 Storage and loss moduli (G' and G'' , respectively) and complex viscosity (η^*) as a function of frequency for (a) a dextran solution and (b) an agarose gel. The solution in (a) shows a Newtonian behavior, while the gel in (b) displays strongly elastic properties. (Adapted with permission from Morris, E.R. and Ross-Murphy, S.B. (1981) Chain flexibility of polysaccharides and glycoproteins from viscosity measurements, in Techniques in the Life Sciences, Volume B3, Elsevier/North Holland, Amsterdam, p. 310. With permission from Elsevier.)

encountered for chemically similar aqueous polysaccharide systems is provided in Figure 19.15. This figure presents the *mechanical spectra* of G' , G'' , and η^* plotted logarithmically against the frequency. Figure 19.15a shows the data obtained for a polymer (dextran) solution, which approximates a purely viscous system, while Figure 19.15b illustrates a gel (agarose), responding, to a good approximation, as an elastic solid. For the solution case, $G'' \gg G'$, both increasing with frequency, and the viscosity is independent of frequency over a wide range. In the gel case, $G' \gg G''$, both independent of ω , with the dynamic viscosity decreasing with frequency.

Mixed Polymer–Surfactant Systems

The rheological behavior of mixed polymer–surfactant solutions is, as for polymer solutions in general, strongly dependent on polymer concentration; however, for the mixed systems much more dramatic changes are seen. The case of dilute solutions is illustrated in Figure 19.16 for the case of a nonionic polymer associating with an ionic surfactant. The reduced viscosity increases with the polymer molecular weight and, in particular, with the binding of the surfactant (starting at the critical association concentration (CAC)). As the ionic surfactant binds, the polymer is effectively transformed into a polyelectrolyte, with a more extended conformation.

The dramatic viscosity changes for mixed semi-dilute solutions of a hydrophobically modified water-soluble polymer and a surfactant were discussed in some detail in Chapter 14 in terms of mixed aggregate formation. The viscosity is very sensitive to the stoichiometry of the micellar-type self-assemblies. Similar cross-linking effects and a very efficient gelation has been observed with vesicles instead of micelles.

Mixed polymer–surfactant solutions are typically viscoelastic; for certain systems there may be a change-over from the dominance of viscous effects to the dominance of elastic

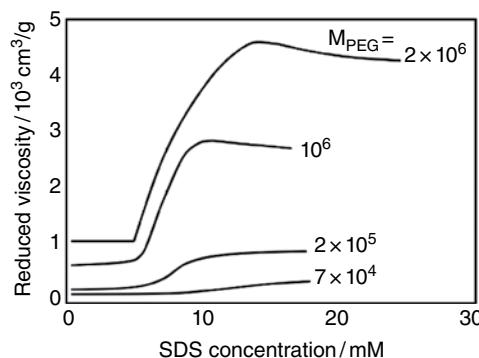


Figure 19.16 Reduced viscosity data obtained for solutions of poly(ethylene glycol) (PEG) as a function of the concentration of added sodium dodecyl sulfate (SDS) for four different molecular weights. (With permission from Francois, J., Dayantis, J. and Sabbadin, J. (1985) *Hydrodynamic behavior of the poly(ethylene oxide)-sodium dodecylsulphate complex*. European Polymer Journal, **21**, 165–174. Copyright Elsevier.)

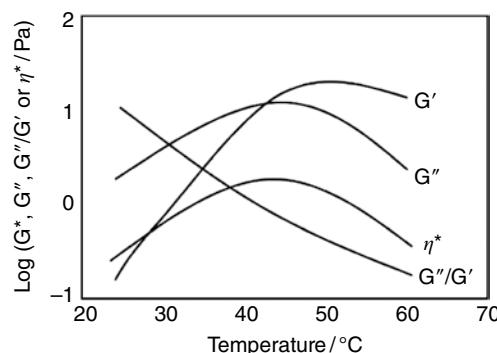


Figure 19.17 Viscoelastic properties as a function of temperature for a solution (1 wt%) of the nonionic polymer ethylhydroxyethylcellulose (EHEC) and the cationic surfactant hexadecyltrimethylammonium bromide. (With permission from Carlsson, A., Karlström, G. and Lindman, B. (1990) *Thermal gelation of nonionic cellulose ethers and ionic surfactants in water*. Colloids and Surfaces, **47**, 147–165. Copyright Elsevier.)

properties as the temperature increases. This may occur for nonionic polymers, which become less polar at higher temperature and show a clouding behavior, as illustrated in Figure 19.17; this system shows a temperature-induced gelation.

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20

Wetting and Wetting Agents, Hydrophobization and Hydrophobizing Agents

Liquids Spread on Surfaces

Wetting is the ability of a liquid to spread on a surface, either a solid surface or another liquid with which the drop is immiscible. The degree of wetting, often referred to as *wettability*, depends on the nature of both the drop and the surface. The wettability is governed by the ratio between adhesive forces between molecules in the drop and the surface, which favor wetting, and cohesive forces within the drop, which work against wetting.

A drop of liquid placed on a solid surface may spread so as to increase the liquid–solid and liquid–gas interfacial areas. Simultaneously, the solid–gas interfacial area decreases and the contact angle (θ) between the drop and the solid is reduced. If a drop of water spreads readily over a surface, that is, if the θ value is low, it is a sign of the surface being hydrophilic. If the θ value is around 90° or higher, the surface is hydrophobic. A *superhydrophobic* surface is a surface at which the contact angle of water is $>150^\circ$. Such surfaces are attracting considerable current interest and can be achieved either through chemical means, such as fluorination of the surface, or by inducing a special surface topography, or by a combination of the two. The superhydrophobicity obtained for hydrophobic surfaces with a specific roughness is called *the Lotus effect* after the flower, whose leaves stay clean because of their special microstructure. The regular pattern of indentations in the micrometer scale gives the effect that the drop is standing on air compartments separated by hydrophobic walls. Many plants, not only the Lotus flower, and also many insect wings, and so on, have this type of architecture. Figure 20.1 illustrates different degrees of wetting of a drop of water on a surface.

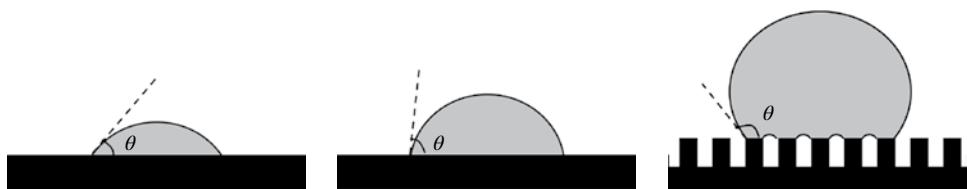


Figure 20.1 A drop of water on a hydrophilic surface giving low contact angle (left), on a hydrophobic surface giving a contact angle of around 90° (middle), and on a superhydrophobic surface with controlled roughness giving a very high contact angle (right). In the right-hand figure, the drop stands on the tops of the asperities, sometimes called the Cassie–Baxter state

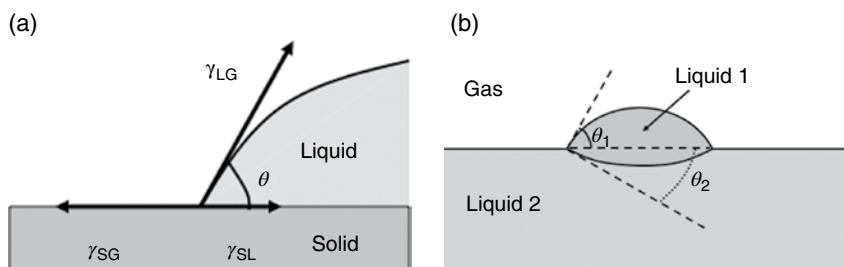


Figure 20.2 (a) Surface forces involved in spreading. (b) A drop of liquid L_1 on liquid L_2

Spreading continues until the system has reached equilibrium. The degree of spreading is governed by the surface tension of the liquid (γ_{LG}), the surface tension (usually referred to as the surface free energy) of the solid (γ_{SG}), and the interfacial tension between the solid and the liquid (γ_{SL}). The forces involved are illustrated in Figure 20.2a.

The surface free energy of the solid (γ_{SG}) strives to spread the drop, that is, to shift the three-phase point outward. Thus, spreading is favored on high-energy surfaces. The interfacial tension (γ_{SL}) and the horizontal component of the surface tension (γ_{LG}) of the liquid (i.e., $\gamma_{LG} \cos \theta$) act in the opposite direction. At equilibrium, the resultant force is zero:

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos \theta \quad (20.1)$$

This trigonometric relation between the contact angle and the forces acting on a drop on a solid surface is generally known as Young's equation, although Thomas Young formulated it in words, not as a mathematical equation. It dates back to 1805 and it has become the basis for the understanding of the phenomenon of spreading on *solid surfaces*.

Wetting may also be connected with the relative adhesion of the liquid to itself as compared to the solid. If W_A is the work of adhesion of the liquid to the solid, then it can be shown that:

$$W_A = \gamma_{LG} (1 + \cos \theta). \quad (20.2)$$

Equation 20.2 is known as the Young–Dupré equation. It tells that the free energy involved in spreading a liquid drop on a solid surface can be determined from two measurable parameters, the surface tension of the liquid and the contact angle that the liquid makes on that surface.

Spreading of *one liquid on top of another* (assuming immiscible liquids) can be treated in an analogous way. Since the liquid–liquid interface is not planar, however, the angle of contact, θ_2 , must also be taken into consideration (Figure 20.2b). At equilibrium:

$$\gamma_{L_2G} = \gamma_{L_1L_2} \cos \theta_2 + \gamma_{L_1G} \cos \theta_1 \quad (20.3)$$

It can easily be seen that if the interface between the liquids becomes planar—as it will do if L_2 is a high viscous material—then $\cos \theta_2$ is equal to 1. Equation 20.3 is then identical to Young's equation (Equation 20.1).

A spreading coefficient (S) defined as:

$$S = \gamma_{SG} - \gamma_{SL} - \gamma_{LG} \quad (20.4)$$

is often used. Spreading will then occur spontaneously as long as $S > 0$. For spreading of one liquid on another the spreading coefficient can be written analogously, as follows:

$$S = \gamma_{L_2G} - \gamma_{L_1L_2} - \gamma_{L_1G} \quad (20.5)$$

For the situation of one liquid drop on top of another liquid the value of S can easily be obtained since the surface tensions γ_{L_1G} and γ_{L_2G} , as well as the interfacial tension $\gamma_{L_1L_2}$, can either be found in tables or measured by standard techniques. Thus, it is possible to estimate whether or not one liquid will spread on another.

However, it must be noted that considerations of spreading behavior based on literature values of surface and interfacial tensions may not always be accurate. Firstly, the theory is based on total *mutual insolubility*. Even immiscible liquids always dissolve in each other to some extent, however, and this affects the γ -values greatly. The spreading coefficient will, therefore, vary with time. In some cases this may result in reversal of spreading. As, under the initial spreading process, the liquid phases become mutually saturated, the spreading coefficient may be reduced to below zero. This will result in contraction of the film with the formation of flat lenses on the surface.

Secondly, *impurities* in the liquid phases will have a dramatic effect on the spreading behavior. In a liquid–liquid system $\gamma_{L_1L_2}$ will normally be reduced by impurities in either the oil or the aqueous phase. Impurities in the water phase will usually also cause a reduction of the γ_{LG} value. Impurities in the oil phase normally do not influence γ_{LG} to the same extent. In addition, impurities in one phase will normally partition between the phases and, thus, influence all γ -values. Prediction of the net influence of contaminants on spreading is, therefore, difficult.

A good example of the effect of impurities on spreading behavior is the important issue of whether or not oil, for instance from an oil spill, will spread on water. If the surface and interfacial tension values are known, S can be calculated from Equation 20.5. One should then keep in mind that the surface tension of water is higher for salt water than for freshwater, that is, the value of S is larger for salt water, meaning that oil spreads easier on salt water than on freshwater. Impurities in the oil phase may reduce the interfacial tension considerably, which also increases S . Thus, contaminated oil, or oil containing large amount of resin or other surface active components, will spread more easily than pure hydrocarbon oil on a water surface.

The Critical Surface Tension of a Solid is a Useful Concept

It is often more difficult to quantify wetting on solid surfaces than on liquid surfaces because it is difficult to assess the γ_{SG} and the γ_{SL} terms of Equation 20.1. On high energy materials, such as metals, oxides, glasses, and ceramic surfaces, this is not an issue, however. One normally obtains full wetting, that is, the contact angle becomes zero. On low energy solids, such as polymeric surfaces, wood, and so on, the degree of wetting is often an important issue, however, and needs to be quantified. Sometimes good wetting is required. For instance, good adhesion of a glue, a coating, or a printing ink requires proper wetting of the substrate. Sometimes, one wants poor wetting. One approach to the problem of fouling of ships is to coat the hull with a fluorocarbon- or a silicone-based paint. Barnacles and other marine organisms have difficulties in wetting such surfaces and without proper wetting the adhesion becomes weak.

The wettability of low energy solids is usually assessed by the procedure introduced by Zisman in the 1950s. Zisman demonstrated that the contact angle of a drop of liquid on a surface decreases with decreasing surface tension of the liquid for a wide range of surfaces. For a homologous series of liquids, the increase in $\cos \theta$ with decreasing liquid surface tension is linear for a given solid (Figure 20.3). Even for nonhomologous liquids, a plot of γ_{LG} against $\cos \theta$ shows points lying in a narrow rectilinear band. However, the line may exhibit curvature if hydrogen bonding can take place between the liquid molecules and molecules in the solid surface. In practice, linear alkanes are usually employed for *Zisman plots*.

A *critical surface tension* (γ_c) is defined as the point where the plotted line intersects the zero contact angle line, that is, the line representing complete wetting. In the plot in Figure 20.3, γ_c is 18.5 mN/m. Liquids with a γ_{LG} equal to or lower than γ_c will then spread on that surface. The γ_c -value is characteristic of the wettability of the specific solid and it is a practically important value. If a water-based formulation needs to wet a substrate with a critical surface tension of, say, 35 mN/m it does not matter if the high surface tension of pure water (72 mN/m) is reduced to below 35 mN/m by the help of surfactant or by addition

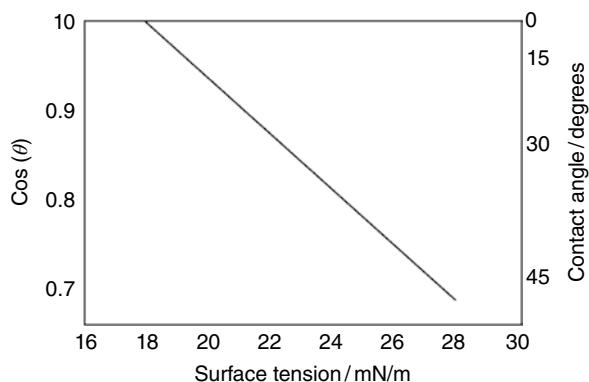


Figure 20.3 A Zisman plot for n-alkanes on polytetrafluoroethylene. θ is the contact angle

of a water miscible cosolvent. The aqueous formulation will wet the substrate if the resulting surface tension becomes lower than 35 mN/m.

The use of a Zisman plot to determine the critical surface tension is relatively straightforward and has become a widely used method to characterize a low energy solid with respect to surface free energy. Zisman plots can be made also for high energy solids. However, for such substrates these plots are not important since the γ_c -values obtained, from 500 mN/m and higher, are so much higher than the surface tension of all normal liquids. Table 20.1 gives critical surface tension values for some common polymers, while Table 20.2 shows the values for various functional groups. The latter values have been calculated from a large collection of experimentally determined γ_c -values for polymers.

As can be seen from Table 20.2, the value of γ_c for a solid is indicative of the molecules making up its surface. The surfaces with the lowest value of γ_c , and hence the lowest surface energy, consist of closely packed CF_3 groups. Replacing one fluorine atom by hydrogen considerably raises the value of γ_c . This low value of γ_c indicates the generally low adhesion between liquids and surfaces containing trifluoromethyl groups. (Sometimes, however, the introduction of a terminal CF_3 group does not decrease the wettability much, since the introduction of the dipole associated with the CF_3-CH_2 group gives an effect in the other direction.) Another observation that can be made from Table 20.2 is that CH_3 groups have very low values compared with CH_2 groups. This implies that surfaces rich in methyl groups should have low surface tensions, which indeed is true. The most common type of silicone oil, polydimethylsiloxane (Figure 20.9), which is discussed later, is probably the best example of an agent for making a methyl-rich surface.

Table 20.1 Critical surface tension (γ_c) values for various polymers at 20°C

Polymer	γ_c (mN/m)
Poly(1,1-dihydroperfluoroctyl methacrylate)	10.6
Poly(hexafluoropropylene)	16.2
Polytetrafluoroethylene	18.5
Poly(trifluoroethylene)	22
Poly(vinylidene fluoride)	25
Poly(vinyl fluoride)	28
Polyethylene	31
Polytrifluorochloroethylene	31
Polystyrene	33
Poly(vinyl alcohol)	37
Poly(methyl methacrylate)	39
Poly(vinyl chloride)	39
Poly(vinylidene chloride)	40
Poly(ethylene terephthalate)	43
Cellulose	45
Poly(hexamethylene adipamide)	46

Table 20.2 Critical surface tension (γ_c) values in relation to surface constitution at 20°C

Surface groups	γ_c (mN/m)
<i>Fluorocarbon surfaces</i>	
$-\text{CF}_3$	6
$-\text{CF}_2\text{H}$	15
$-\text{CF}_2-\text{CF}_2-$	18
$-\text{CF}_2-\text{CFH}$	22
$-\text{CF}_2-\text{CH}_2-$	25
$-\text{CFH}-\text{CH}_2-$	28
<i>Hydrocarbon surfaces</i>	
$-\text{CH}_3$ (crystal)	20–22
$-\text{CH}_3$ (monolayer)	22–24
$-\text{CH}_2-\text{CH}_2-$	31
$-\text{CH}-$ (phenyl ring edge)	35
<i>Chlorocarbon surfaces</i>	
$-\text{CClH}-\text{CH}_2-$	39
$-\text{CCl}_2-\text{CH}_2-$	40
$=\text{CCl}_2$	43

The Critical Surface Tension can be Applied to Coatings

The concept of critical surface tension of a solid is useful for many practical applications, for example, surface coatings. For a coating to spread on a substrate, the surface tension of the liquid coating must be lower than the critical surface tension of the substrate. (In addition, since a liquid is easier to break up and atomize when the surface tension is low, lower surface tension means better sprayability of the coating.) Contaminants on the surface usually have lower critical surface tension than the surrounding areas, thus putting extra demand on the coating with regard to low surface tension.

The polymer and the solvent largely determine the surface tension of the coating. The polymers used as binders have relatively high surface tensions, with values between 35 and 45 mN/m being typical. The organic solvents may have surface tension values in the 23–25 mN/m range although some common solvents, such as glycols, glycol ethers, and aromatic hydrocarbons, have slightly higher values. Surface tension values for some relevant solvents have been compiled in Table 20.3.

In general, among solvents within the same solvent class faster evaporating solvents usually have lower surface tension values than their slower evaporating counterparts. Furthermore, increased branching of the solvent molecule leads to a lowering of the surface tension.

It is evident from the surface tension values of Table 20.3 that the higher the solvent content of the coating, then the lower the surface tension. It is also obvious that wetting problems may arise when the relative amount of solvent is reduced, as is generally wanted for environmental reasons. With such formulations one may risk getting a surface tension of a paint formulation that is higher than the critical surface tension of the substrate. Problems may particularly arise if the surface to be painted is not clean enough. Oily soil and skin fat from fingerprints can give locally very low γ_c values. So called *high solids*

Table 20.3 Surface tension (γ) values for selected solvents used in coatings at 20°C

Solvent type	γ (mN/m)
Isopropanol (<i>alcohol</i>)	23
Butyl acetate (<i>ester</i>)	25
2-Butanone (methyl ethyl ketone (MEK); <i>ketone</i>)	24
Ethylene glycol (<i>glycol</i>)	43
Di(ethylene glycol)monoethyl ether (ethyl diglycol; <i>glycol ether</i>)	34
Decane (<i>aliphatic hydrocarbon</i>)	24
<i>o</i> -Xylene (<i>aromatic hydrocarbon</i>)	30
Water	72

coatings are, therefore, extremely sensitive to contaminants on the surface and paint defects, such as *cratering* and *picture framing*, occur more frequently with high solids than with conventional systems.

Water is a liquid of high surface tension and obviously not suitable for wetting of surfaces. Use of waterborne paints would have been very limited had it not been possible to use surfactants in the formulations. A good surfactant reduces the surface tension of the aqueous formulation down to 28–30 mN/m, that is, to the same range as that of solvent-based paints and lacquers.

Capillary Forces are Related to Wetting

Water can rise high against gravity in narrow tubes and channels; the phenomenon is known as capillary action. Capillary flow is important both in nature and in many practical applications, for instance in diapers. The height, h , of the rise of a liquid in a column is given by the expression:

$$h = \frac{2\gamma_{LG} \cos\theta}{\rho g r} \quad (20.6)$$

where ρ is the density of the water, g the gravitational constant (9.81 m/s²), and r the radius of the column.

It can immediately be seen from Equation 20.6 that complete wetting, that is, $\theta=0$, is required for strong capillary rise. It can also be seen that the surface tension (γ_{LG}) should be high, which means that a surfactant cannot be used as wetting agent. The improvement of the wetting, if needed, must be achieved by other means, such as surface modification by plasma or corona treatment, or by irreversible adsorption of a polymer. By such procedures the surface may become very hydrophilic without a concomitant reduction of the surface tension.

Surface Active Agents can Promote or Prevent Wetting and Spreading

From Equation 20.4 it can be seen that spreading of a liquid on a solid surface can be promoted in two different ways. Addition of a surface active agent will lead to a reduction of both the surface tension (γ_{LG}) and the interfacial tension between the solid and the drop (γ_{SL}). Thus, the spreading coefficient (S) will be increased. The situation is illustrated in Figure 20.4.

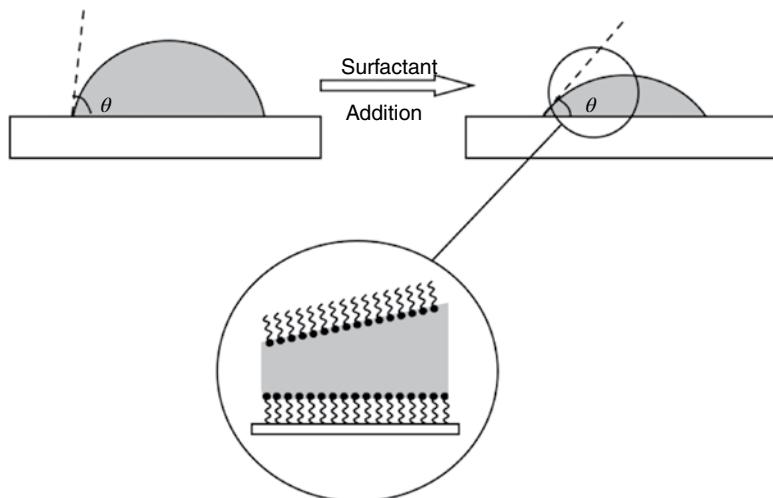


Figure 20.4 Addition of a surfactant to a drop of water on a hydrophobic solid surface will reduce both γ_{LG} and γ_{SL} .

An alternative way of promoting wetting is shown in Figure 20.5. By hydrophilizing the surface γ_{SL} is reduced and γ_{SG} is increased. Both changes work in the direction of promoting wetting, that is, increasing the S value, according to Equation 20.4.

If, on the other hand, a hydrophilic material, for example, paper or paperboard or a textile such as cotton, needs to be made water resistant one should aim at minimizing wetting.

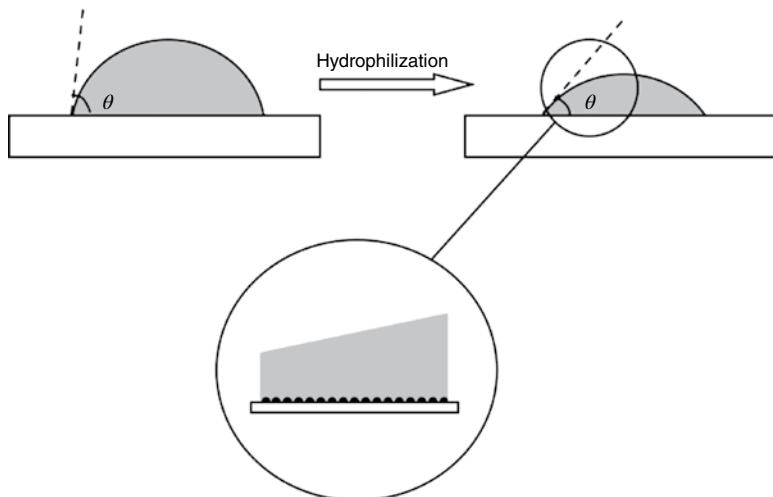


Figure 20.5 Hydrophilization of the surface will reduce γ_{SL} and increase γ_{SG} . The hydrophilization can, for instance, be made by some kind of chemical or physical surface modification, with the net result being that the surface becomes rich in hydrophilic groups.

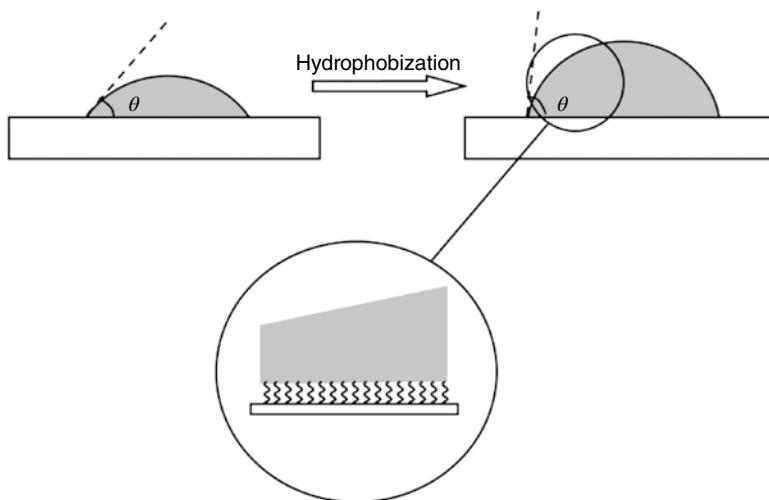


Figure 20.6 Hydrophobization of the surface will increase γ_{SL} and decrease γ_{SG} . The hydrophobization can be made by chemical or physical surface modification and the process results in an uncharged and apolar surface

This is normally done by hydrophobization of the surface, which leads to an increase in γ_{SL} and a decrease in γ_{SG} , both effects contributing to reducing the spreading coefficient (S), as is shown in Figure 20.6.

Wetting Agents

Wetting is a highly dynamic process and when the wetting liquid spreads over the substrate the surface active molecules must diffuse rapidly to the moving boundary between liquid and substrate. Therefore, a good wetting agent must: (i) have a strong driving force to go the solid–liquid interface; (ii) effectively reduce the surface tension; (iii) have a reasonable concentration of free, that is, nonmicelle bound surfactant; and (iv) move rapidly to the newly created surface. To fulfill these requirements, a good wetting agent is a surfactant that is fairly small and quite hydrophobic (often on the borderline of water solubility) but still not having very low critical micelle concentration. Wetting agents are often branched surfactants because these do not form micelles as readily as their straight-chain counterparts. Both nonionic and anionic surfactants are used in commercial formulations. Figure 20.7 shows the structure of two common wetting agents.

More recently, the concept of *superspreading* has been introduced. A *superspreader* is a surfactant which, when added in small amounts to an aqueous solution, enables the liquid to spread spontaneously and rapidly on very hydrophobic surfaces, such as a solid paraffin wax surface (Parafilm). For example, it has been demonstrated that the nonionic silicone-based surfactant shown in Figure 20.8 has a surface-covering rate on Parafilm of $10\text{ cm}^2/\text{min}$ for a 0.01 g aqueous drop containing 0.1 wt\% surfactant. Such rapid spreading is not very common and the mechanism of action of superspreaders is not completely clear. It was

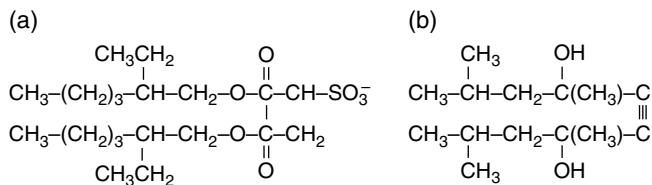


Figure 20.7 Two surfactants that are commonly used as wetting agents, (a) sodium bis(2-ethylhexyl)sulfosuccinate (AOT) and (b) an acetylene glycol

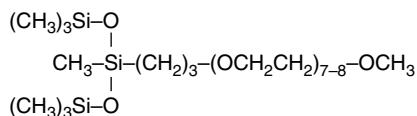


Figure 20.8 A silicone-based superspread

found that the covered area in the early stage of spreading increases monotonically with increasing wt% surfactant and time. In addition, the total area covered when spreading stops is proportional to the concentration of surfactant in the dispersion. (The superspread has very low water solubility and is usually applied as a dispersion.) It seems that spreading stops when all of the surfactant is deposited as a bilayer on the substrate.

In some respects, such as the need for rapid movement to a newly created interface and high concentration of nonmicellized surfactant, the requirements on wetting agents resemble those on foaming agents (Chapter 23).

Hydrophobizing Agents

Paraffin wax, silicones, silanes, and fluorinated hydrocarbons are examples of efficient hydrophobizing agents (with efficiency approximately increasing in that order). In addition, cationic surfactants are often used for this purpose. Figure 20.9 shows the structure of the most common silicone oil, polydimethylsiloxane. The conformation of the silicone on the surface is such that the siloxane backbone interacts with the surface and the methyl groups are oriented away from the surface, as also illustrated in this figure. Thus, the silicone treatment is effectively a surface methylation. As can be seen from Table 20.2, methyl groups render a surface extremely hydrophobic.

Figure 20.10 shows the structure of a glass (or silica) surface hydrophobized with dichlorodimethylsilane. This reagent and other silanes are common hydrophobizing agents for mineral surfaces that contain silanol groups. As with the silicones, the treatment is effectively a surface methylation. Silanes with one long alkyl chain, such as alkyltrialkoxysilane or alkyltrichlorosilane, are also commonly used.

Since both paper and textile fibers normally have a negative net charge, long-chain cationic surfactants are commonly used to impart water repellency. The surfactants also give a

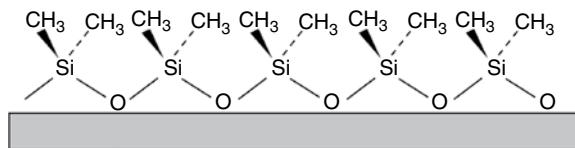


Figure 20.9 Polydimethylsiloxane, a powerful hydrophobizing agent

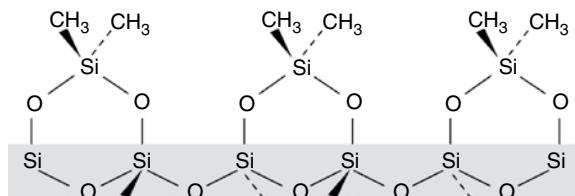


Figure 20.10 A glass or silica surface treated with dichlorodimethylsilane (or dimethoxy- or diethoxydimethylsilane). The surface modification is idealized; not all silanes will give two bonds with the surface

debonding effect, that is, the fiber–fiber attractions are considerably reduced. The most common textile softeners are quaternary ammonium compounds containing two C_{16–18} hydrocarbon chains and two methyl or other short substituents on the nitrogen atom. Due to environmental demands (increased rate of biodegradation), the traditional hydrolytically stable surfactants of this type, *dialkyl quats*, have, to a large extent, been replaced by ester-containing surfactants of similar structure, *dialkyl esterquats*. (For further discussion, see Chapter 2.) The structures of both a traditional dialkyl quat and a dialkyl esterquat are shown in Figure 1.10.

It may be expected that proper surface hydrophobization requires a densely packed layer of the hydrophobizing agent. This seems not to be the case, however. Only a partial coverage by the hydrophobizing agent seems to be needed to form a nonwater-wetting surface. Water will not spread easily on a surface that is partially covered with hydrophobic domains. In many cases it seems that a coverage of 10–15% is enough. This is the reason why hydrophobizing agents are effective already in amounts that correspond to less than monolayer coverage.

Measuring Contact Angles

The contact angle of a drop of liquid on a solid, planar surface has traditionally been measured directly on either a drop resting on a horizontal plane (a sessile drop) or an adhering gas bubble captured at a solid–liquid interface, in both cases using a goniometer (Figure 20.11). The angle of contact is read with the help of a microscope objective to view the angle directly. For larger drops the shape is no longer spherical because gravitational forces come into play. This can be taken advantage of as a method to determine surface tension (Chapter 12).

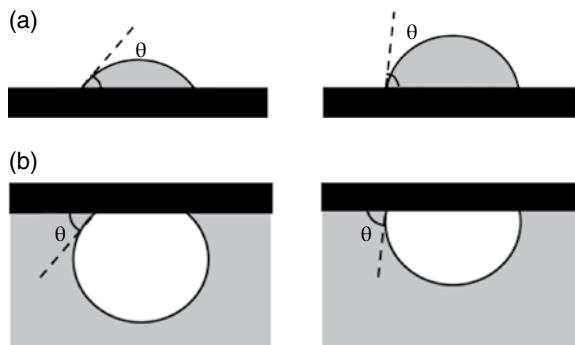


Figure 20.11 Measuring contact angle using (a) a sessile drop or (b) an adhering bubble

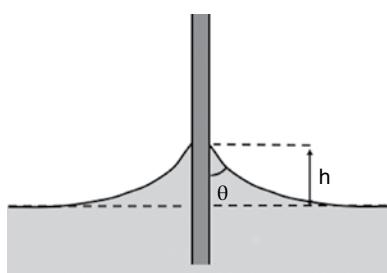


Figure 20.12 The liquid rise method to determine the contact angle (θ)

Contact angle measurements using either sessile drops or adhering bubbles are today usually automatized and computerized; this enables values of contact angles to be determined with a high degree of reproducibility. With modern, fast, and computerized instruments, contact angles can be determined also on penetrating substrates, such as paper. By using instruments that record several hundred times per second, the apparent contact angle of a drop on a highly absorbing paper can be measured as a function of time. By extrapolating to time zero the contact angle of the paper before penetration has started can be obtained. This is a useful way to determine the effect on the surface free energy of various types of additives used in paper production.

An indirect method of determining the contact angle is by measuring the rise of a liquid at a vertical plate that is partially immersed (Figure 20.12). A solid surface is aligned vertically and brought into contact with the liquid and measurement of the height (h) of the liquid gives the contact angle (θ) from the following equation:

$$\sin \theta = 1 - \frac{\rho g h^2}{2} \gamma_{LG} \quad (20.7)$$

where ρ is the density of water and g the gravitational constant. This method is particularly effective for measuring contact angles as a function of rate of advance and retreat and for determining the temperature coefficient of θ .

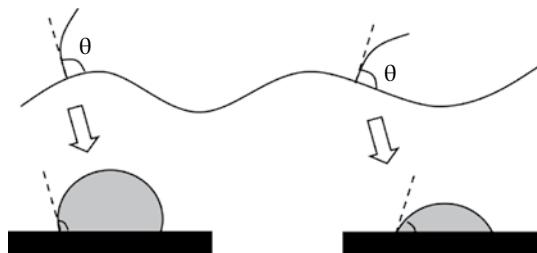


Figure 20.13 Different θ -values may be measured on rough surfaces

Contact angle measurement is, however, not as straightforward as one would imagine. Regardless of the method used a number of complications may arise:

1. Few solid surfaces are effectively flat on the scale of observation. The angles that a drop of liquid makes with a solid are directly dependent on the macroscopic geometry of the solid. This is illustrated in Figure 20.13. Roughness on the scale that affects contact angle measurements can be observed with scanning electron microscopy. If the surfaces are too rough, there are no techniques that give reliable values of the contact angle. Attempts have, for instance, been made to measure the contact angle on powders by pressing the powder into a tablet. However, in most cases the roughness of the surface has been too high to give accurate results.
2. Many organic surfaces, for instance many plastic materials, will expose different groups depending on if the surrounding medium is air or water. Polar groups in a polymer might be buried into the material when the surface is exposed to air but will make their way into the surface when water is the surrounding medium.
3. The phases must be in equilibrium in order to give accurate θ -values. If, for instance, a drop of water is put on a mobile polymer surface, as discussed in the paragraph above, it may first give a high θ -value, indicative of a hydrophobic surface. The water may cause conformational changes in the uppermost surface layer; polar groups may appear in the surface and the contact angle may gradually become lower. Thus, the equilibrium contact angle will be much lower than the initial contact angle. This is an example of *contact angle hysteresis*.

In practice, the conditions under which contact angles are measured are far from ideal. In most cases, the observed contact angle will depend greatly on whether the liquid is *advancing* over a dry surface or *receding* from a wet surface. This is also referred to as *contact angle hysteresis* and it is noticeable on all rough or dirty surfaces.

Many surfaces exhibit both roughness and heterogeneity and on such surfaces both advancing and receding contact angles should be measured. Measuring the rise of a liquid at a vertical plate, as described above, is a commonly used method of making contact angle hysteresis measurements. In general, it can be stated that on a heterogeneous surface the advancing angle is a measure of the wettability of the low-energy part of the surface and the receding angle is more characteristic of the high-energy part of the surface.

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Solid Dispersions

The term *solid dispersions*, that is, dispersions of solid particles in a liquid, are often referred to as *suspensions* or as *slurries*. The particles in a suspension are sufficiently large for sedimentation, that is, 1 µm and above. This distinguishes a suspension from a colloid, where the particles are smaller and, hence, do not settle. However, there is no strict definition with respect to particle size. Dispersions of latex particles, which are often in the 200–800 nm size range, are often referred to as suspensions. The term *fine suspension* is sometimes used to describe a suspension of submicron size particles. Solid dispersions may also be termed *sols*; this term is commonly used for dispersions of noble metals, such as gold, and of certain metal oxides, such as silica. There are some fine distinctions between these terms. A slurry can be a dispersion of solid particles of all dimensions—also far above the colloidal dimension—a sol is a dispersion of very small particles, usually less than 100 nm in size. The small size is beneficial for the colloidal stability. A famous example is Michael Faraday's gold sols, which after 160 years are still intact. Solid dispersions are very common in technical systems and there are a number of different materials that can be obtained in a particulate form, such as clays, oxides, silicates, metals, organics, and polymers.

Compared to emulsions there are some features that can only be obtained in solid dispersions. Particle shapes other than spherical can be obtained, for example needles. The particles may also be hollow. The shape of the suspended particles can be very important for technical applications. A second feature is that the surface of the suspended particles might change with time. In suspensions of minerals, for example, metal ions may leak out into the solution, which affects the surface properties of the mineral (Figure 21.8b). A third feature is that suspensions can be obtained in dry form. One application is ceramics where the particles are sintered into one piece. Even nonsintered solid dispersions are of interest. Here a phenomenon termed capillary condensation might occur. This phenomenon occurs, for

example, when hydrophilic particles are dispersed in a nonpolar medium. Water will condense in the crevices of the agglomerates. This phenomenon also occurs for powders, namely suspensions in air.

Synthesis of Particles

Colloidal particles can be formed either *top-down*, that is through milling, or *bottom-up*, that is through nucleation and growth. Milling only gives relatively coarse particles with a large size distribution. The breakup of a material, or breaking up of aggregates from smaller particles, is most often performed in a liquid that dissipates the heat evolved from the process. The milling is facilitated by addition of a grinding aid. The role of the grinding aid is to penetrate into cracks and channels between particles in an agglomerate in order to lower the free energy of the surface (Figure 21.1). This process will hinder the particles from relaxing back to their original state, hence preventing spontaneous healing of cracks. This is an example of the *Rehbinder effect*. An efficient grinding aid should diffuse fast to the surface and have a good affinity for the surface. Small aromatic molecules, such as benzoic acid, are efficient in both these aspects. Other examples of grinding aids are cationic surfactants, glycols, fatty acids, or amines.

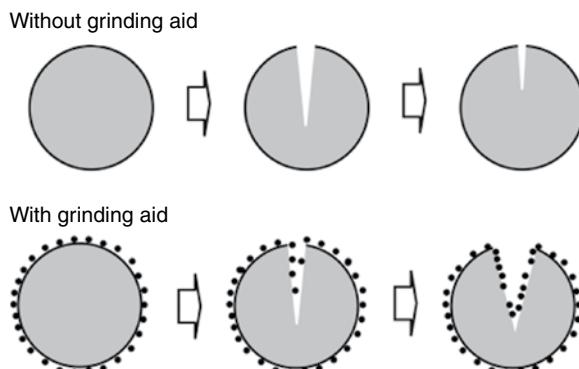


Figure 21.1 The mechanism of a grinding aid is to adsorb in cracks of the particles and, thereby, lower the surface energy. This reduces the tendency for spontaneous healing of the cracks (the Rehbinder effect)

Control of Nucleation and Growth is the Key to Monodispersity

The formation of particles through nucleation and growth can lead to monodisperse particles with sizes down to the nanometer scale. Gold sols, as well as silica sols, are examples of bottom-up colloids. Latices (plural form of latex) are another very important example of colloidal dispersions made by a bottom-up process, emulsion polymerization. Latices are suspensions of particles made up of organic polymers and stabilized by surfactants.

In the synthesis of particles the starting material is brought into a state of supersaturation, whereupon particles nucleate and grow in size. In terms of phase diagrams (Figure 5.1)

one passes the binodal and when the spinodal is reached there will be a nucleation of primary particles in the system. The state of supersaturation can be achieved by a concentration build-up by a chemical reaction, a change in temperature, or addition of a nonsolvent. The need for supersaturation can be understood from considering the two contributions to the free energy of particle formation. The first is the contribution due to the lower free energy of the solid particle (Δf). This contribution is the driving force for phase separation into particles, or to a separate macroscopic phase. The second contribution counteracts the first one and is due to the formation of an interface between the particle and the medium. It is thus proportional to the surface area of the particle. Since the first contribution is proportional to the volume of the particle and the second to its surface, the total energy of particle formation goes through a maximum as a function of particle size (Figure 21.2a). The maximum in the figure implies that there needs to be a certain degree of supersaturation in order to form nuclei that, in turn, will grow into particles.

The concentration build-up is shown in Figure 21.2b, which is termed a *La Mer diagram* after its originator. New particles are nucleated in the time period where the concentration exceeds the limiting supersaturation concentration, that is, when the system has reached the spinodal. This insight leads us to three requirements for the formation of a monodisperse dispersion. The first is that the nucleation should occur at the same time in the whole sample. Hence, there are requirements such as clean system (no nuclei in the solution to start with) and homogeneous system with respect to temperature and concentration (no temperature or concentration gradients). Secondly, the nucleation period should be as short as possible. The third requirement is that the feed of new material should not be so fast that a second generation of nuclei is formed, that is, the feed of new particle material should be slower than the maximum growth rate (*starved conditions*). These principles will be illustrated below for the formation of latex and silica particles. Synthesis of particles in water-in-oil (w/o) microemulsions is covered in Chapter 22.

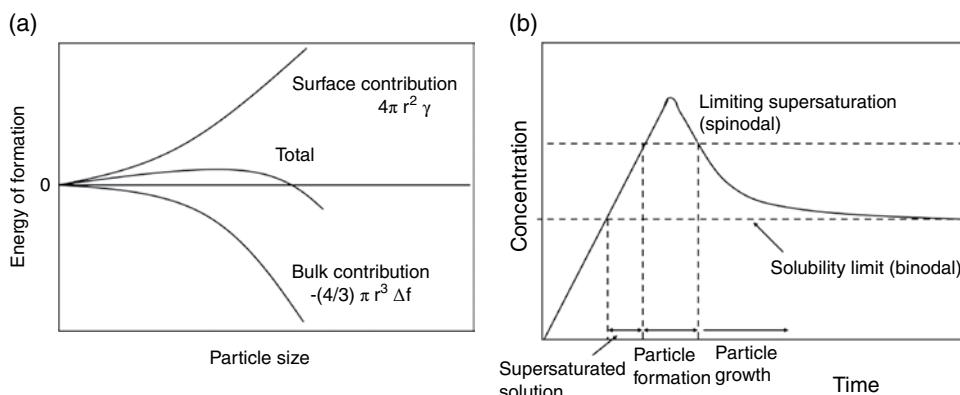


Figure 21.2 (a) The total energy of particle formation goes through a maximum as a function of particle size. (b) The concentration versus time plot illustrating the time intervals for nucleation and subsequent growth (La Mer diagram) (Binodal and spinodal are described in Chapter 5)

Latex Synthesis

Latex particles are synthesized in a process termed *emulsion polymerization*. This term is a misnomer as it eludes to the polymerization occurring in emulsion droplets, which is not the case. The synthesis occurs in the aqueous phase and the polymerization is started by an initiator, which must be water soluble. The monomer is present in the form of emulsion drops, thereby giving the name to the process. It is important, however, to realize that the polymerization occurs in the aqueous phase and not in the emulsion droplets. (The process where polymerization of monomer takes place inside emulsion droplets is termed *suspension polymerization*.) Normally a latex batch has a solids content of 50–60% and a particle size in the range 50–500 nm. However, in the synthesis of model latices, as described here, the solids content is 5–10%. As in all free radical polymerization processes there are four different steps, namely initiation, propagation, termination, and chain transfer. In the initiation step a free radical is formed in the aqueous phase. The most frequently used initiator is potassium persulfate, which, at elevated temperatures, decomposes into two free radicals according to:



The free radical formed initiates the polymerization. In the polymerization step the free radical attacks the double bond of the monomer and a new free radical is formed at the end of the reaction product. This process continues until two such free radical polymers meet and react, thus terminating the polymerization. An alternative fate is that the free radical is transferred to another polymer, which in turn continues the polymerization, that is chain transfer. The original initiator forms a sulfate group at the end of the polymer chain. The principle is illustrated in Figure 21.3a.

The figure illustrates that the initiator and a few monomer molecules form surface active molecules. These agglomerate into nuclei as the polymerization progresses (Figure 21.3b).

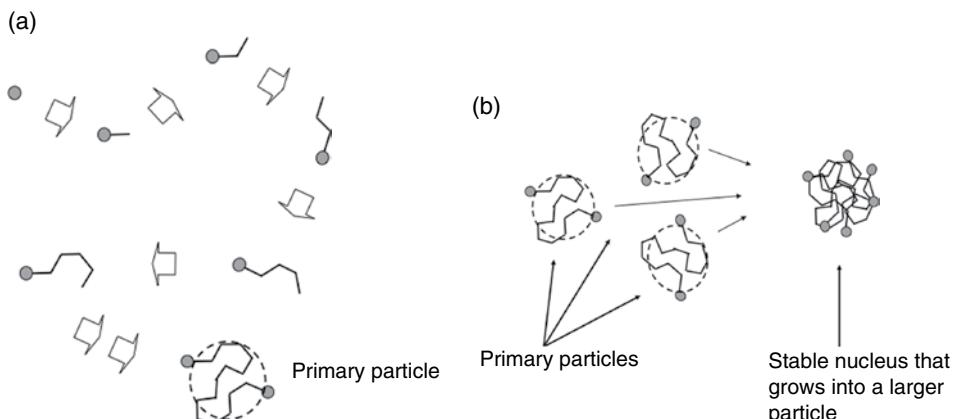


Figure 21.3 Illustration of the emulsion polymerization process without surfactant. (a) The free radical initiates the polymerization forming an unstable primary particle. The primary particles agglomerate until a stable nucleus is obtained. (b) Such nuclei grow into a latex particle

The agglomeration continues until the charges, emanating from the initiator, are in a sufficient number at the surface of the particles to provide colloidal stability. (The surface charge density grows faster than the volume of the particles.) These nuclei are then the loci of further polymerization of the monomer.

In Figure 21.4a the number of particles in the process is given as a function of time, or conversion. The graph illustrates that the number of particles in the beginning of the polymerization period reaches a peak and suddenly falls to a low and constant number. This is the process that is illustrated in Figure 21.3. There is a critical period where primary particles coalesce and form nuclei that finally attain colloidal stability (as depicted in Figure 21.3b). Critical for obtaining a monodisperse sample is that this initiation period occurs simultaneously in the vessel and that further initiation renders surface active molecules that adsorb at the particles already present instead of forming new primary particles. Hence, no new primary particles are allowed to form after this first initiation period. We then have a dispersion where all the particles have been formed simultaneously and where they all grow at the same rate. This will result in a monodisperse latex.

In commercial emulsion polymerization the process is very different. Here a surfactant is present during the whole process. This has the effect that the coalescence of primary particles into stable nucleus in the initiation period, as is depicted in Figure 21.3b, does not occur. Instead, the primary particles are stabilized by the surfactant. The presence of surfactant also means that new radicals that give rise to surface active fragments need not be taken care of by the particles. They could as well be stabilized by the surfactant. Hence, there are new nuclei formed during the whole process. This will lead to polydisperse latices. The effect of the surfactant on the number of particles and on their size is shown in Figure 21.4b. Another effect of having a surfactant present is that a higher colloidal stability is obtained. This allows higher solids content, such as 50%, compared to 5–10% for surfactant-free synthesis.

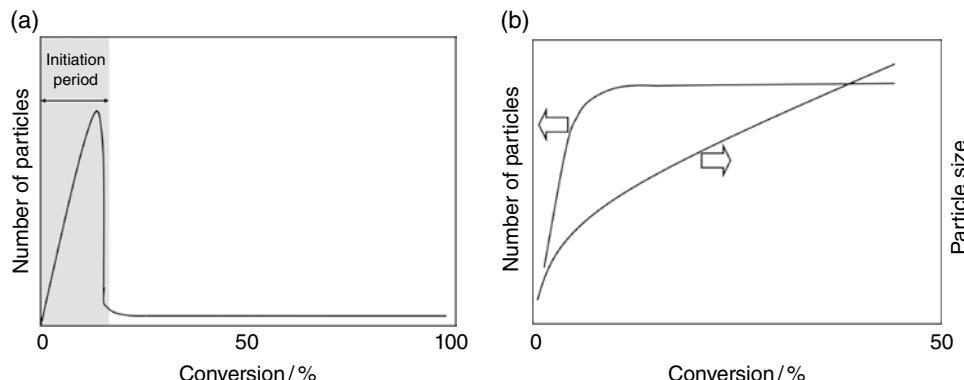


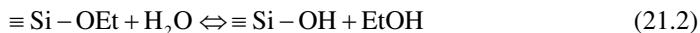
Figure 21.4 Number of particles as a function of time (or conversion) (a) for a surfactant-free system and (b) for a system with surfactant. (b) also shows how the particle size depends on the degree of conversion

Silica Particle Synthesis

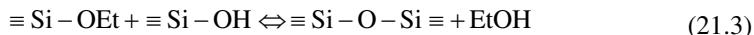
There are several methods to synthesize silica particles and here two will be mentioned. In the first method the synthesis starts with sodium silicate, or water glass. The sodium ion is exchanged via an ion exchanger for protons, whereupon silicic acid is formed. The formed silicic acid then polymerizes into particles by a condensation reaction. The size is regulated with ionic strength and pH. Almost monodisperse samples can be obtained by controlling that the nucleation occurs simultaneously in the whole sample and that no further nucleation occurs after the first one, as discussed in the introductory part of this chapter.

The second method is the so-called Stöber process. In the synthesis, tetraethyl orthosilicate (TEOS) dissolved in an alcohol–water mixture is used as silica source. The pH is raised to 11–12 by addition of ammonia, which leads to hydrolysis of TEOS and subsequent condensation reactions according to:

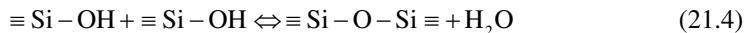
Hydrolysis:



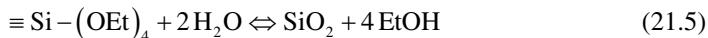
Condensation reaction 1:



Condensation reaction 2:



Overall reaction:



The silicic acid formed polymerizes into particles by further condensation of silanol groups into siloxane bridges. Also, here the nucleation and growth follow the La Mer pattern outlined in Figure 21.2b.

Stabilization of Suspensions with Polymers

Suspensions are frequently stabilized with polymers, such as poly(acrylic acid) (PAA), poly(methacrylic acid) (PMAA), carboxymethyl cellulose (CMC), or lignosulfonates. These polymers are, together with several other polymers, introduced in Chapter 9. The role of the polymer is twofold: it acts as dispersing agent in the preparation of the suspension and it stabilizes the dispersion once it is formed. Such polymers are, therefore, usually referred to as dispersing agents, or dispersants, but one must not forget their important role of maintaining the integrity of the dispersed particles. One may draw a parallel to emulsifiers, which are surfactants that are needed to generate an emulsion but which also play an important role for increasing the lifetime of the dispersion formed.

The majority of the dispersants act via a combination of electrostatic and steric stabilization, namely, electrosteric stabilization (Chapter 18). Lignosulfonates, for example, are used as dispersants for cement/aggregate slurries for concrete production. Using a good

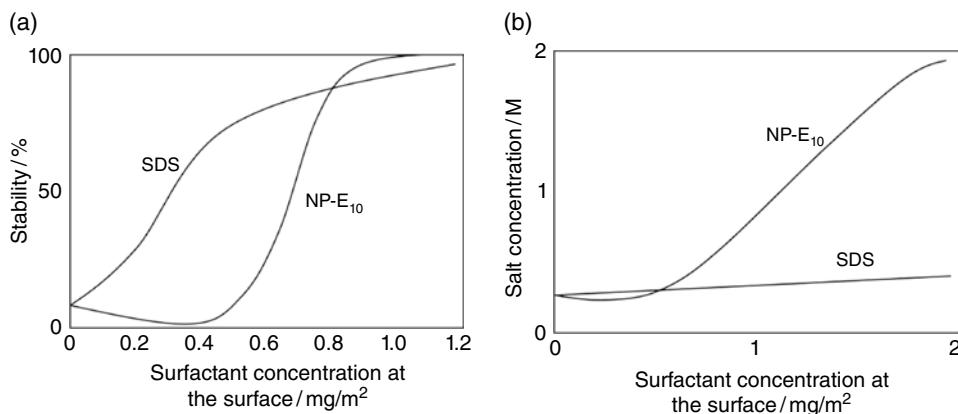


Figure 21.5 (a) Mechanical and (b) salt stability (the salt concentration that induces coagulation) obtained for a latex to which either SDS or NP-E₁₀ has been added

dispersant allows less water to be used in the slurry while still maintaining proper flow. Less water gives stronger concrete. Lignosulfonates are also used as dispersants for other types of particles, such as carbon black or pesticides. (Other types of dispersants, such as sulfonated melamine-formaldehyde resins, are also used in concrete production.)

There are numerous methods to evaluate a dispersant, such as viscosity (Figure 18.15), electrophoretic mobility (Figure 18.24 and Figure 11.19), freeze-thaw stability (Figure 18.16), mechanical stability, salt stability (Figure 18.10 and Figure 21.5) and sediment density (Figure 21.9). It is important to choose a method that is relevant for the intended application of the suspension.

Stabilization of Suspensions with Surfactants

Particle dispersions can also be stabilized by adsorption of surfactants. Both ionic and nonionic surfactants are used for the purpose, either alone or in combination. When used together it is relevant to know that the composition of the surface depends on the solution composition (see, for example, Figure 13.9 and Figure 13.10). Ionic surfactants render electrostatically stabilized suspensions whereas nonionic surfactants render steric stabilization through the polyoxyethylene chains that protrude into the aqueous solution.

Colloidal stability can be measured through shearing of the suspension, by adding salts, or by dilution with water. The values obtained are often referred to as mechanical (or shear) stability, salt stability, and dilution stability, respectively. The relative amount of coagulate arising from such treatments is a measure of the colloidal stability. Figure 21.5 displays mechanical and salt stability of a latex to which either SDS or NP-E₁₀ has been added.

This figure shows that SDS provides good mechanical stability while it does not enhance the stability with respect to addition of salt. The nonionic surfactant NP-E₁₀, on the other hand, gives good resistance against both treatments, if present at sufficiently high concentration. Mechanical stability, for example, is achieved at surface concentrations above 0.6–0.8 mg/m². This value corresponds to a surfactant monolayer where the surfactant molecules are lying down flat on the surface. Above this surfactant concentration, the polyoxyethylene chains start

to protrude into the aqueous solution, which will produce stability against coagulation by stirring. This should be contrasted to freeze–thaw stability (Figure 18.16) that is not obtained until the surface concentration is $2\text{--}2.5\text{ mg/m}^2$, corresponding to a complete surfactant monolayer on the surface, where the surfactant molecules are standing up with their hydrocarbon moieties in contact with the surface and the polyoxyethylene chains protruding into the solution.

Dilution instability of a suspension relates to the fact that for a surfactant adsorbed at a surface there is always an equilibrium between the surface and the bulk. On dilution the bulk phase increases in volume and this will drive the equilibrium toward desorption from the surface. At some point there will not be enough surfactant at the particle surface to provide stability. In general, the more hydrophobic the surfactant, the better is the dilution stabilization. (However, a hydrophobic surfactant is normally not a good dispersing agent.) The resistance to dilution is also influenced by the size of the dispersant, the larger the molecule the better the resistance. Polymeric dispersants usually provide better dilution stability than normal surfactants.

The Shape of Particles can be Regulated with Surfactants

The growth of crystals can be regulated by adsorption of ions, as well as of surfactants. Each crystal face is different with respect to its tendency to adsorb surfactants and it, therefore, has its own adsorption isotherm. The surfactant adsorbs at the crystal faces and affects the growth rate by blocking surface sites. An illustration is given in Figure 21.6 for the growth of adipic acid during precipitation. Addition of a cationic surfactant limits the growth of the negatively charged surfaces giving plate-like particles. On the other hand, adsorption of an anionic surfactant on the positively charged edges gives needle-like particles. Such preferential adsorption of ionic surfactants is frequently used industrially to control crystal morphology during precipitation.

The ability of surfactants to interact with crystal surfaces has technical implications. For instance, calcium carbonate scaling, which is a considerable problem on heat exchangers,

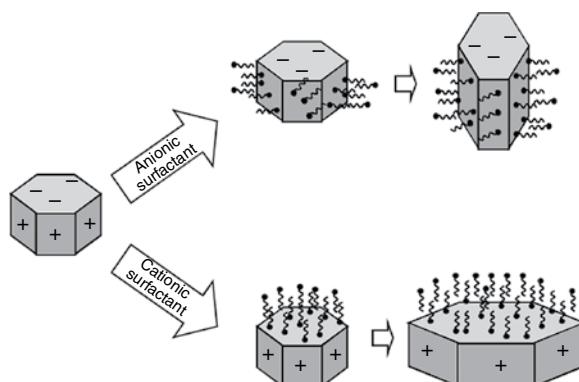


Figure 21.6 In the crystallization of adipic acid the crystals have negative surfaces and positive edges. Adding anionic or cationic surfactants will regulate the crystal growth

boilers, and other warm surfaces (CaCO_3 becomes less soluble at higher temperatures), can be suppressed by the action of a surfactant that interacts strongly with the growing calcium carbonate crystal. An EO–PO diblock polymer with a diphosphate group attached at one of the ends is an example of a surfactant found useful for the purpose. The effect is most pronounced around the cloud point of the surfactant; it is likely that the surfactant binds to the calcium carbonate crystal face by a combination of hydrophobic interaction and complex formation with lattice calcium (Figure 21.7).

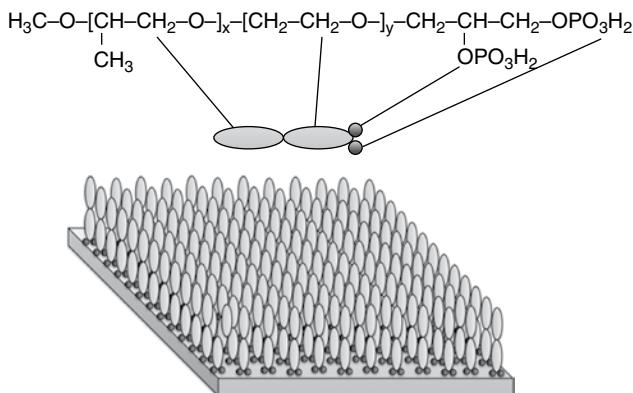


Figure 21.7 Calcium carbonate scaling can be suppressed by addition of a surfactant such as an EO–PO diblock copolymer with a diphosphate group attached at the terminal end of the EO block. (With permission from Kjellin, P., Holmberg, K. and Nydén, M. (2001) A new method for the study of calcium carbonate growth on steel surfaces. *Colloids and Surfaces A*, **194**, 49–55. Copyright Elsevier.)

The Surface of Particles can be Manipulated

We have already seen in Chapter 18 that there are several ways in which a surface can be given a charge. Also, the surface can be manipulated by the adsorption of metal ions, or metal hydroxides. This is utilized, for example, in the flotation process where the collector, which can be an anionic surfactant, is persuaded to adsorb at the surface by the presence of an adsorbed metal ion. Figure 21.8a shows the pH dependence of the flotation recovery of a copper oxide mineral, chrysocolla, using octylhydroxamate as collector. The optimum in flotation recovery coincides with the maximum concentration of CuOH^+ species (Figure 21.8b). These species are adsorbed from solution rendering adsorption sites for the collector. The copper ions in solution come from leakage from the particles.

Ceramic Processing Relates of Surface Chemistry

In ceramic processing the ceramic powder is dispersed in water with the aid of a dispersant. In the slip-casting technique the dispersion is poured into a mold, which draws water from the dispersion, thus forming a solid cast (green body) that is later sintered at high

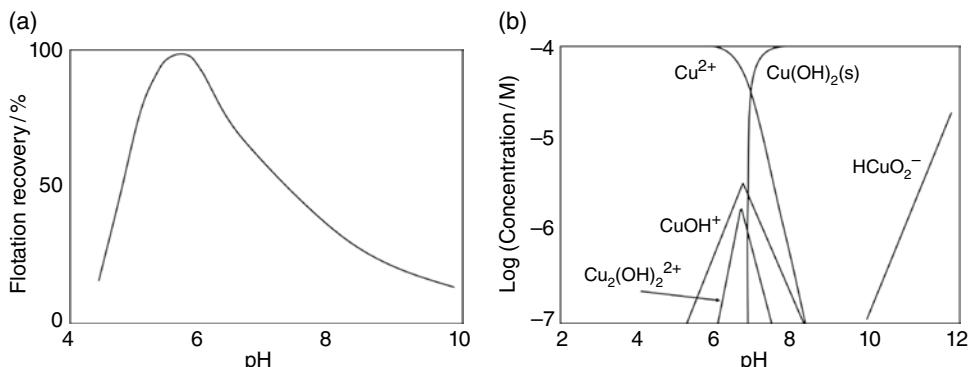


Figure 21.8 The pH dependence for flotation recovery of a copper oxide mineral in the presence of 3.3×10^{-4} M octylhydroxamate as collector and 10^{-4} M CuCl (a) and the species diagram for Cu^{2+} and its hydroxides in 10^{-4} M CuCl . (Reproduced with permission from Fuerstenau, M.C. and Palmer, B.R. (1976) Anionic flotation of oxides and silicates, in Flotation (ed. M.C. Fuerstenau), Volume 1, American Institute of Mining, Metallurgical, and Petroleum Engineers, New York, pp. 148–196. With permission from AIME.)

temperatures. It is important that the dispersion can compact sufficiently in order to prevent shrinkage on sintering. Hence, the use of a proper dispersant is essential for obtaining a high quality product.

A common dispersant is PAA and Figure 18.15 illustrates that polyelectrolyte drastically reduce the apparent viscosity when the surface is totally covered with the polymer. Figure 21.9 shows the sediment density as a function of pH of a BaTiO_3 suspension with and without PAA. PAA gives the particles electrosteric stabilization (Chapter 18), which enables the particles to pass one another at close distances without attaching to each other, hence forming a very dense sediment. Systems forming dense sediments also give high-density casts in the mold.

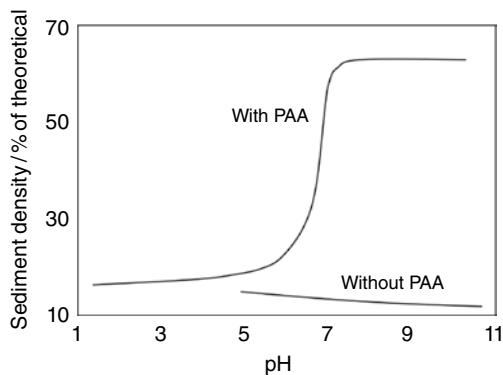


Figure 21.9 Sediment density of a BaTiO_3 suspension as a function of pH, with and without added PAA. (With permission from Chen, Z.-C., Ring, T. and Lemaître, J. (1992) Stabilization and processing of aqueous BaTiO_3 suspension with polyacrylic acid. Journal of the American Ceramic Society, 75, 3201–3208. Copyright 2005, John Wiley.)

Particles Attach to Surfaces

In Chapter 18 it was shown that the attraction between a particle and a flat surface is larger than the attraction between two particles of the same size. Particle attachment/detachment is seen in everyday life such as xerography, removal of soil from surfaces, dirt film on cars, retention of fines and fillers in papermaking, deinking, and so on. Particle adhesion to surfaces is also termed particulate fouling. The adhesion of particles to substrates depends on the character of both the particle and the surface, such as degree of hydrophobicity and surface charge. It is also influenced by the size of the particle and the roughness of the surface. Detachment of particles is facilitated by adsorption of polymers or surfactants. The adsorption usually leads to the same charge of the particle and the surface, leading to a concentration of counterions between the particle and the substrate that will be so high that there will be an osmotic driving force for water to penetrate into the region and separate the particle from the substrate (Figure 25.1).

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22

Surfactant Assemblies as Templates

Nature frequently uses amphiphilic molecules, often together with polymers, as templates for building supramolecular structures. Many of the fascinating objects that we see around us, not least in the marine environment, are synthesized by having inorganic salts such as silicate, phosphate, and carbonate precipitate around an organic template of self-assembled molecules. A composite material is formed. The organic matter may disappear with time, leaving an inorganic object built with a very high degree of precision. Some examples of such structures are shown in Figure 22.1.

Mesoporous Materials

Zeolites are porous aluminosilicates made by Nature by a templating procedure. Their pores are in the Angstrom range and suitable for adsorption of gases and for accommodation of certain cations. Today the majority of the zeolites used are synthetic, made by crystallization of a silica–alumina gel in the presence of alkali and an organic template. The template molecule used in zeolite synthesis is a small, nonamphiphilic species, often a quaternary ammonium compound such as tetrapropyl ammonium bromide. The template is removed after the synthesis by a hydrothermal treatment.

The pores of zeolites, usually referred to as micropores, are too small for many applications. The pore dimensions above that of the zeolites' are named mesopores and the materials with this pore dimension are termed “mesoporous materials.” According to IUPAC's definition, microporous materials (such as zeolites) have pores with a diameter less than 2 nm, mesoporous materials have pores in the range 2–50 nm, and above a diameter of 50 nm the pores are referred to as macropores.

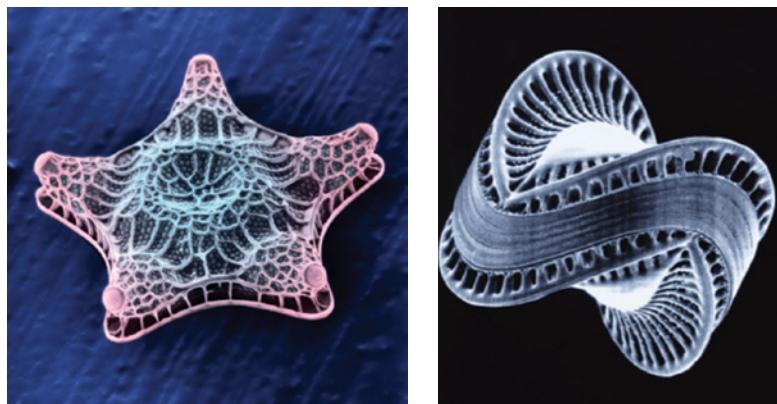


Figure 22.1 Diatoms are a major group of algae. Their shell is essentially silica and created by a templating procedure. The figure shows two out of a plethora of amazing structures

Synthetic mesoporous materials were introduced in the beginning of the 1990s. They were siliceous materials made under alkaline conditions with a cationic surfactant, such as dodecyltrimethyl ammonium halide, as the templating agent and with the tetraethyl ester of orthosilicic acid or tetramethyl ester of orthosilicic acid (TEOS and TMOS, respectively) used as silica source. The structure of TEOS is $\text{Si}(\text{OC}_2\text{H}_5)_4$. Ethanol (from TEOS) or methanol (from TMOS) is generated during the synthesis and is continuously evaporated. The organic template, that is, the self-assembled cationic surfactant, is subsequently removed by thermal treatment. The mesoporous materials produced this way are referred to as MCM (Mobil Composition of Matter) materials, with MCM-41 and MCM-48 being two particularly well-known types. MCM-41 has a hexagonal geometry and MCM-48 has a bicontinuous cubic structure. The oil company Mobil Corporation was instrumental in developing the preparation procedure but the first reported synthesis was from Japanese laboratories. Although the walls separating the pores are amorphous, MCM materials possess a long range ordered framework with uniform mesopores, as can be seen from Figure 22.2.

MCM materials can be seen as a natural extension of zeolites. The two synthesis procedures are similar in many respects with the main difference being that whereas zeolites are made with small templates that are not surface active, the templates used for synthesis of mesoporous materials are surfactants. It is important to realize that it is not the difference in size between the two templating molecules as such that is responsible for the large difference in pore size between typical microporous and mesoporous materials. The surfactant self-assembles during the synthesis and it is the self-assembled surfactant, the micelle, which acts as template. The size of such a micelle is, of course, much larger than that of the individual template salt or molecule used in the zeolite synthesis.

MCM materials have pore sizes in the lower range of the mesopore dimension. A somewhat later development where block copolymers of EO–PO–EO type were used instead of the cationic surfactants gave mesoporous materials with larger pores and with excellent possibilities to tailor the pore size by the choice of block copolymer template. The mesoporous materials produced this way are known as SBA materials, named after the airport code of Santa Barbara. A particularly well-known type is SBA-15, which is a

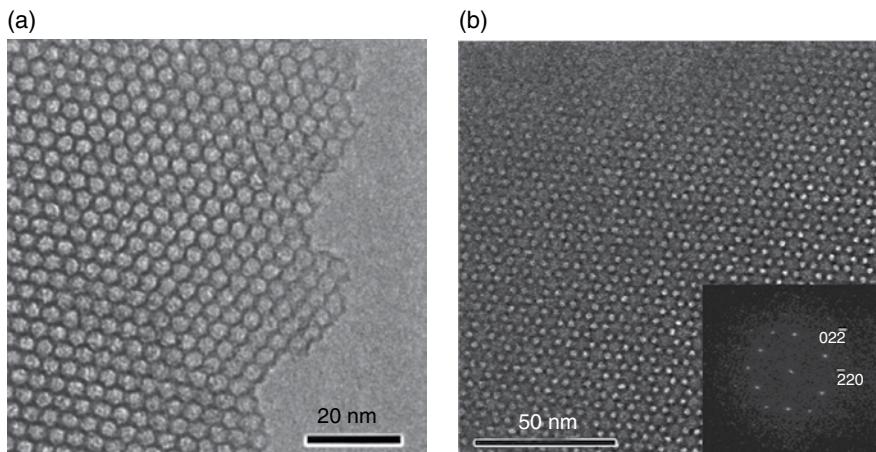


Figure 22.2 Transmission electron microscopy (TEM) micrographs of (a) MCM-41, showing a hexagonal pattern of the pores, and of (b) MCM-48, showing a bicontinuous cubic structure. The insert in the right image is a Fourier diffractogram, confirming the space-group symmetry. (With permission from Jaroniec, M., Kruk, M., Shin, H.J., et al. (2001) Comprehensive characterization of highly ordered MCM-41 silicas using nitrogen adsorption, thermogravimetry, X-ray diffraction and transmission electron microscopy. Microporous and Mesoporous Materials, **48**, 127–134, Copyright 2001, American Chemical Society, and Kaneda, M., Tsubakiyama, T., Carlsson, A., et al. (2002) Structural study of mesoporous MCM-48 and carbon networks synthesized in the spaces of MCM-48 by electron crystallography. Journal of Physical Chemistry B, **106**, 1256–1266, Copyright 2002, American Chemical Society.)

material with the pores organized in a regular, hexagonal pattern. Whereas the synthesis of MCM materials is carried out at high pH, where there is a strong electrostatic attraction between the negatively charged silica and the cationic surfactant, SBA materials are prepared at low pH, where the silica is close to its point of zero charge. Figure 22.3 shows the sequence of events leading to SBA-15.

Mesoporous Thin Films

The mesoporous materials are usually prepared as particles ranging in size from a few hundred nanometers to a few micrometers. They are often elongated and partly aggregated. Mesoporous thin films can also be prepared by a similar type of procedure using an amphiphile as templating agent. A common method for preparing a thin mesoporous silica film on a solid surface is to dissolve a formulation of a surfactant liquid crystalline phase containing dissolved silica in a volatile solvent with high solvency for the amphiphile. For an EO–PO–EO block copolymer, ethanol may be used as solvent. This low viscosity solution is then applied on a solid substrate, for instance by spin coating. As the volatile solvent evaporates from the applied film, the original liquid crystalline structure is regenerated. This procedure is called “evaporation-induced self-assembly.” Calcination leads to a mesoporous film.

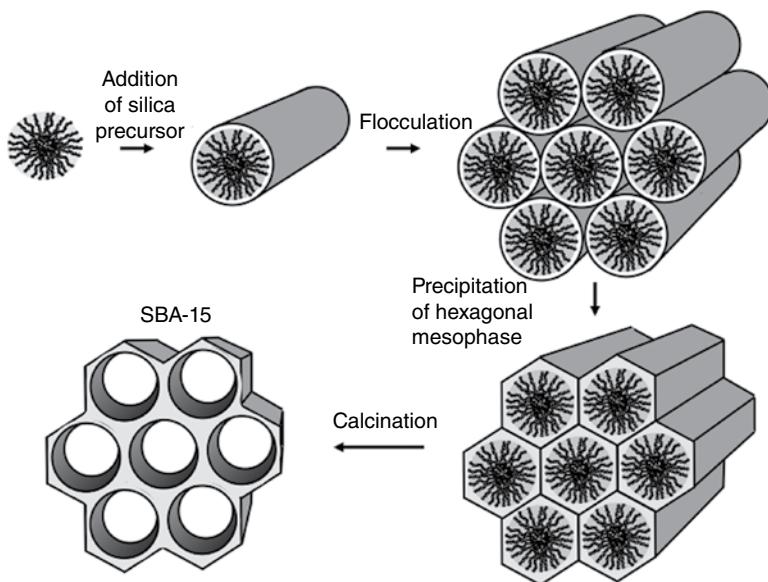


Figure 22.3 Preparation of the hexagonally ordered mesoporous material SBA-15 starting with micelles of a block copolymer of EO–PO–EO type to which the silica precursor is added, generating a sphere-to-rod transition of the surfactant aggregates. With time the rod-like, silica-coated micelles start to interact and eventually arrange into a structure with hexagonal symmetry. The organic matter, that is, the template, is subsequently removed by calcination. (With permission from Gustafsson, H. (2013) Enzyme immobilization in mesoporous silica, PhD thesis, Chalmers University of Technology, Göteborg, Sweden.)

The Silica Precursor

The common silica precursors TEOS and TMOS are relatively expensive. It has been shown that well-ordered mesoporous silica can also be prepared from a simple sodium silicate solution, commonly referred to as water glass. The water glass is first exposed to a cation exchange resin where sodium is replaced by protons causing the pH to drop to around three. This solution is then mixed with the EO–PO–EO block copolymer and the sequence of events is the same as shown in Figure 22.3.

Mesoporous Materials other than Silica

Silica is the most studied mesoporous material but a range of other mesoporous oxides, such as alumina and titania, have also been prepared and studied. Mesoporous carbon can be made from a double templating procedure. Mesoporous silica is first prepared and then used as template (or mold) for making mesoporous carbon. The pores of the mesoporous silica are filled with a carbon-rich organic substance, such as furfuryl alcohol. After pyrolysis a composite silica–carbon material is formed. Removal of the silica by etching with an acid, such as hydrofluoric acid, gives mesoporous carbon with a well-ordered structure. The series of events is shown in Figure 22.4. Mesoporous metals, for example, platinum, can be prepared by a related double templating procedure.

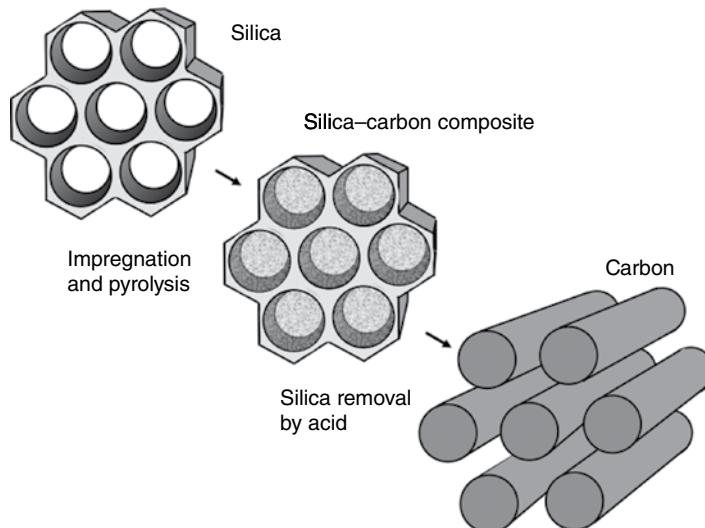


Figure 22.4 Mesoporous carbon can be made by a double templating procedure. Mesoporous silica is first generated using an EO–PO–EO block copolymer as template. After removal of the template, the pores are filled with a carbonaceous material. After pyrolysis a silica–carbon composite is formed from which mesoporous carbon can be obtained by removal of the silica by treatment with hydrofluoric acid

Pore Dimension

The mesoporous materials prepared by an amphiphile as templating agent can be tailored with a great deal of precision. Since the pores of materials of the MCM type represent the space once occupied by the aggregated surfactant tails, the dimension should correspond to twice the length of the hydrophobic tail. Thus, the pore size is governed by the choice of template molecule.

The pore dimension of SBA materials represents the space once occupied by the aggregated PO segments of the block copolymer. The larger the PO block, the larger the pores of the calcined material. The EO blocks, that is, the two polyoxyethylene chains, constituting the corona of micelles of block copolymers of EO–PO–EO type are not aggregated in the silica solution. They will protrude as individual chains through the silica domain. During the calcination step also these chains will be removed. Thus, the silica walls separating the mesopores will not be entirely solid but contain micropores.

Knowledge of the solution behavior of the templating amphiphile is taken advantage of in tailor-making the porous materials. Addition of a solvent with good solvency for the hydrophobic tail of a surfactant is a way to swell the core of the micelle. Likewise, addition of such a solvent in the synthesis of mesoporous material is a way to increase the size of the compartments occupied by the organic template, which, in turn, means that after calcination a material with larger pores is obtained. The reverse temperature dependence of EO–PO–EO block copolymers (Chapter 7), can also be taken advantage of. The hydrophobic segments will grow in size and the hydrophilic segments will contract as the temperature is increased. The effect of temperature on the pore size of SBA materials is, therefore,

substantial. Increasing the temperature in the synthesis of SBA-15 from 80 to 150°C results in an increase of the pore diameter from 5 to 9 nm.

Disordered Mesoporous Silica

The self-assembly of amphiphiles in systems containing oil in addition to a silicate solution can also be used for making mesoporous silica. Porous particles with very small diameters (40–50 nm) can be obtained from emulsions of oil in water. The oil phase consists of TEOS and a hydrocarbon. The surfactant used as emulsifier, which may be cationic or nonionic, also solubilizes water in the oil drops. In doing so one can anticipate that the more hydrophilic fraction of the technical surfactant will dominate at the surface of the oil drops while the more hydrophobic fraction will dominate at the interface between the solubilized water droplets and the oil. Thus, the oil drops of the emulsion can be regarded as a water-in-oil (w/o) microemulsion (which is more or less true for all emulsions). TEOS hydrolyzes in contact with water and because the many small water droplets inside the oil drops give a very large oil–water interface, the hydrolysis and the subsequent silica condensation predominantly occur in the water droplets inside the emulsion drops. The silica condensation continues and an interpenetrating silica network is formed in the drops. Subsequent removal of the organic phase gives porous silica particles. The pores are in the meso range but they are not ordered as in MCM and SBA materials. Such products are interesting because the pore area per particle volume is very large. The pores may have an average size of 10 nm and the particle may have a diameter of 40–50 nm. Thus, there are not many pore openings in the periphery of each particle. Figure 22.5 shows electron microscopy images of such particles.

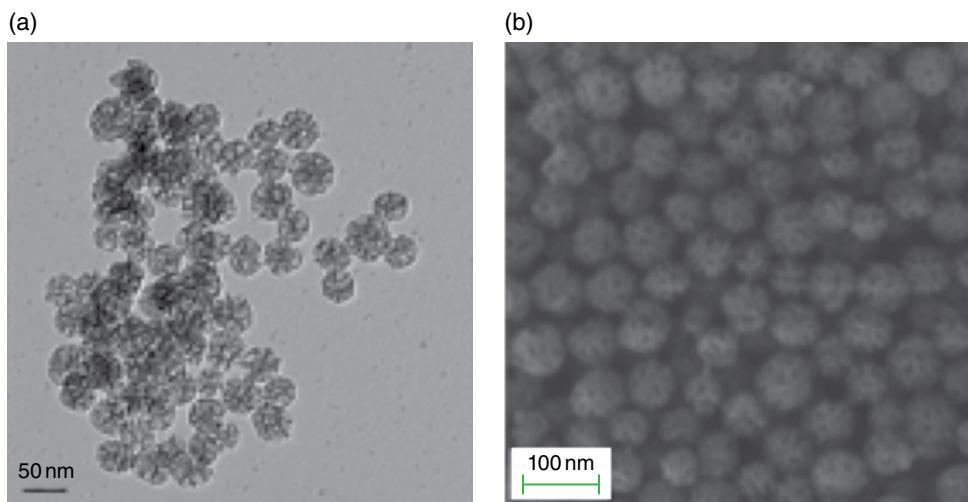


Figure 22.5 Mesoporous silica particles prepared from emulsions of an oil phase consisting of TEOS and an inert hydrocarbon: (a) a transmission electron microscopy image and (b) a scanning electron microscopy image. The surfactant used as emulsifier and to create the water-in-oil microemulsion inside the oil droplets was hexadecyltrimethyl ammonium bromide. (With permission from Gustafsson, H., Isaksson, S. and Holmberg, K. (in print).)

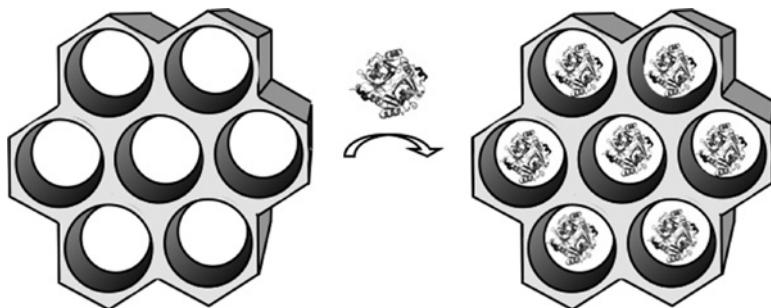


Figure 22.6 Immobilization of an enzyme into the pores of a mesoporous material with hexagonal ordering of the pores. (With permission from Gustafsson, H. (2013) Enzyme immobilization in mesoporous silica, PhD thesis, Chalmers University of Technology, Göteborg, Sweden.)

Applications of Mesoporous Materials

The interest in mesoporous materials, and in particular those with an ordered pore structure, has taken off rapidly since a convenient synthesis was published in the beginning of the 1990s. The materials have a wide spectrum of potential uses, ranging from heterogeneous catalysis, via separation of organic molecules, to applications within the biotechnology and the medical fields. The pores can be used as hosts for active substances, such as drugs, and the release rate can be adjusted by surface modifications of the pore walls, which will affect the retention of the guest molecule. The release rate can also be reduced by applying a lid, for instance a polyelectrolyte layer, on top of the pores. The possibility of tailoring the pore dimension with a great deal of precision and the fact that the pore size is very uniform is particularly interesting for immobilization of proteins and other large and well-defined biomolecules. It has been found that enzymes entrapped in pores of a suitable dimension are very resistant to leakage and, at the same time, retain good activity over long periods. Figure 22.6 shows a schematic of such an immobilization.

Inorganic Nanoparticles

Microemulsions, particularly of the w/o type, can be used for synthesis of inorganic nanoparticles. The method has been used for preparation of a wide range of metals, metal salts, and metal oxides. The synthesis principle is straightforward. In the simplest case, involving two reactants that are soluble in water but insoluble in hydrocarbon, one reagent is dissolved in the water pools of microemulsion A, while the other reagent is dissolved in the water pools of microemulsion B. The two microemulsions are subsequently mixed. As discussed in Chapter 17, microemulsions are highly dynamic systems and the interfaces form and disintegrate constantly. Due to their small size, the droplets are subject to Brownian motion. They collide continuously and in doing so dimers and other aggregates will form. These aggregates are short lived and will be transformed into droplets of the original size. As a result of the continuous coalescence and decoalescence process, the content of the water pools of microemulsion A and microemulsion B will eventually be distributed evenly over

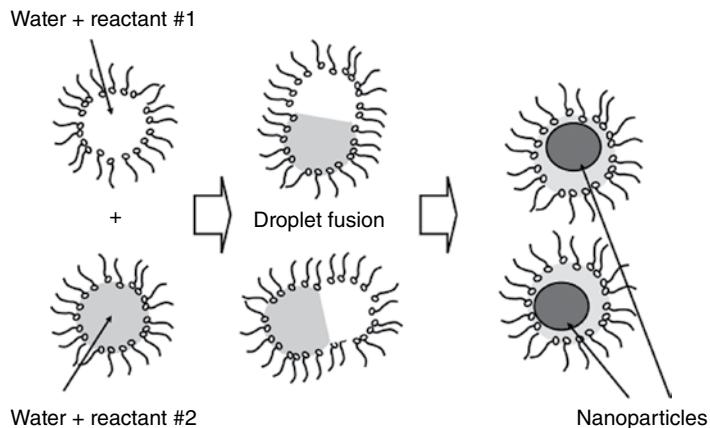


Figure 22.7 The microemulsion-based method to make nanoparticles. (With permission from Holmberg, K. (2004) Surfactants-templated nanomaterials synthesis. Journal of Colloid and Interface Science, **274**, 355–364. Copyright Elsevier.)

the entire droplet population. If the two reactants form a product, this product will be generated within the droplets. Thus, each of the droplets, typically 5–10 nm in diameter, may act as a nanoreactor. The result is that nano-sized particles will form as a surfactant stabilized suspension that coexists with a microemulsion of w/o type, where the drops are essentially pure water (if equimolar amounts of the two reactants are used and the reaction goes to completion). The principle is shown in Figure 22.7.

Assuming that the reaction between the reactants in the microemulsions A and B is fast, then the rate of the microemulsion-based process will be governed by the interdroplet exchange rate. This will vary between different types of surfactants. If the surfactant has good solubility in the continuous oil domain, as is often the case for normal nonionic surfactants, then the rate of reaction may be fast because of the high dynamics of the surfactant film around the water droplets. Ionic surfactants, on the other hand, are usually poorly soluble in apolar oils, which means that they give rise to a less dynamic interfacial monolayer. It has been found that the rate of formation of nanoparticles is higher when a nonionic surfactant is used as amphiphile in the microemulsion formulation than when an ionic surfactant is used.

Size and Shape of the Nanoparticles

The size of the particles formed is often of the same order of magnitude as that of the starting microemulsion droplets. This is particularly true for systems with droplets of small size, below 5–6 nm. However, the nanoparticles formed are not uniform in size and several factors other than the microemulsion droplet size appear to influence the dimension of the particles formed. It seems that an increase in the concentration of the reactants within the droplets leads to an increase in particle size and a large excess of one of the reactants leads to a decrease in size of the particles formed. An increased flexibility of the surfactant film not only gives a faster rate of reaction, as was discussed above, it sometimes also leads to larger particles. The factors governing the size of the generated particles are not fully understood, however.

Also, the shape of the nanoparticles formed may vary and the factors governing the morphology are far from understood. When inert surfactants are used, which is the normal case, the nanoparticles formed are usually spherical. When the surfactant takes an active part in the reaction, which is the case for anionic surfactants with a counterion that becomes reduced to the metal, the particles formed may have a different shape, for instance rod-like. It has also been found that the presence of salts can have a profound effect. The choice of anion is particularly important. An illustrative example is the formation of copper nanocrystals made from copper bis(2-ethylhexyl)sulfosuccinate, that is, the double-tail anionic surfactant AOT with sodium as counterion exchanged by the divalent cupric ion. Reduction with hydrazine was made in the presence of NaF, NaCl, NaBr, or NaNO₃. The presence of F⁻ gave small cubes, Cl⁻ gave long rods, Br⁻ resulted in cubes, and NO₃⁻ gave a variety of shapes (Figure 22.8). The addition of salt did not much affect the internal structure of the microemulsion, however, so the effect is not due to direct templating. The control of the morphology must be related to selective adsorption of the ions on different facets during the crystal growth.

Mixed Nanoparticles

The microemulsion-based synthesis is also an excellent way to make alloys of metals or mixtures of metals with extremely small dimensions of the individual domains. To prepare an alloy or a mixture of two metals one may simply mix three microemulsions, one containing a salt of the first metal, one containing a salt of the second metal and one containing the reducing agent. Alternatively, one may combine the two metal salts into one microemulsion and mix this microemulsion with one containing the reducing agent. As an example, mixed platinum–palladium nanoparticles in the size range of 5–10 nm can be prepared by mixing a microemulsion containing both a platinum and a palladium salt in the water pools with a hydrazine-containing microemulsion. The nanoparticles formed consist of a crystalline platinum core onto which very small amorphous palladium particles are bound. The reason why platinum was formed in the core of the particle is that a platinum salt is reduced somewhat

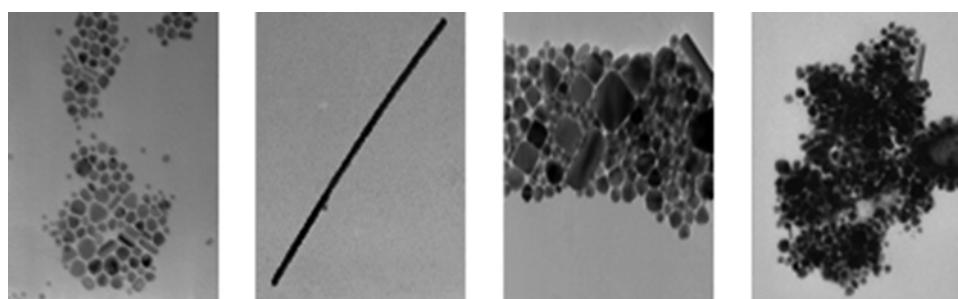


Figure 22.8 Presence of salts plays a decisive role in the shape of copper nanoparticles formed from w/o microemulsions using Cu(AOT)₂ as surfactant and hydrazine as reducing agent. The salts, added at a concentration of 10⁻³ M were, from left to right: NaF, NaCl, NaBr, and NaNO₃. (With permission from Filankembo, A., Giorgio, S., Lisiecki, I. and Pilani, M.P. (2003) Is the anion the major parameter in the shape control of nanocrystals? Journal of Physical Chemistry B, **107**, 7492–7500. Copyright 2003, American Chemical Society.)

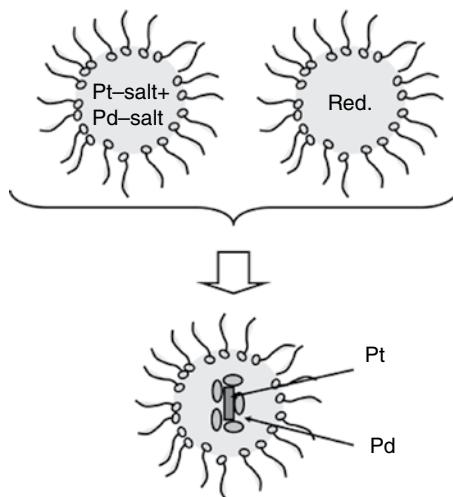


Figure 22.9 Preparation of mixed platinum–palladium nanoparticles, see text. “Red” stands for a reducing agent, such as hydrazine or sodium borohydride. (With permission from Yashima, M., Falk, L.K.L., Palmqvist, A.E.C. and Holmberg, K. (2003) Structure and catalytic properties of nano-sized alumina supported platinum and palladium particles synthesized by reaction in microemulsion. Journal of Colloid and Interface Science, **268**, 348–356 and Holmberg, K. (2004) Surfactants-templated nanomaterials synthesis. Journal of Colloid and Interface Science, **274**, 355–364, Copyright Elsevier.)

easier than the corresponding palladium salt, that is, platinum is a more noble metal. Figure 22.9 illustrates the process for the case where three microemulsions are combined. Sometimes true alloy nanoparticles are obtained when two metal salts are combined in the microemulsion-based synthesis. Nanoparticles consisting of an alloy of gold and silver can be obtained from water soluble gold and silver salts together with a reducing agent.

Deposition on a Solid Support

There are many potential applications for the nanoparticles prepared by the microemulsion route: heterogeneous catalysis, magnetic recording, microelectronics, high-performance ceramics, and so on. Common to most of these uses is that the nanoparticles, which are formed as a suspension, need to be deposited onto some kind of solid support. For catalysis the particles, often noble metals such as platinum or palladium, are deposited onto a carrier material, such as γ -alumina, silica, or titania. There are various ways in which this can be done. One procedure is to add a solvent that dissolves the surfactant and is miscible with both oil and water. The surfactant will then be removed from the surface of the small particles, which will cause the particles to precipitate due to gravitational forces. Tetrahydrofuran is one suitable solvent for the purpose. The support material, in the form of a powder, is usually added first and the solvent is subsequently poured into the mixture, which is vigorously stirred. The ready-made catalyst, that is, the support onto which the noble metal particles are deposited, can be filtered off and the surfactant can subsequently be removed by rinsing with more solvent. Figure 22.10 shows a typical micrograph of a calcined $\text{Pt}/\text{Al}_2\text{O}_3$ sample prepared by this procedure.

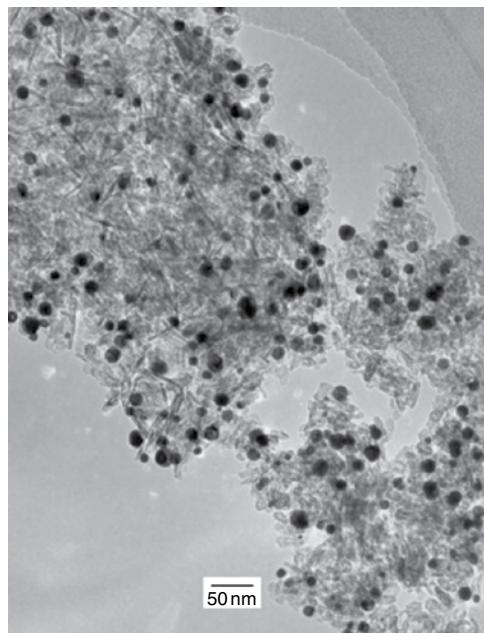


Figure 22.10 Platinum nanoparticles (black spots) deposited on alumina. (With permission from Härelind-Ingelsten, H., Beziat, J.-C., Bergkvist, K., et al. (2002) Deposition of platinum nanoparticles, synthesized in water-in-oil microemulsions, on alumina supports. *Langmuir*, **18**, 1811–1818. Copyright 2002, American Chemical Society.)

A Microemulsion can be used as Reaction Medium for Organic Synthesis

Overcoming Reactant Incompatibility

A common practical problem in synthetic organic chemistry is to attain proper contact between a polar and an apolar reactant. For instance, a large lipophilic organic molecule is usually not compatible with an inorganic salt. There are many examples of important reactions where this is a potential problem: hydrolysis of esters with alkali, oxidative cleavage of olefins with permanganate-periodate, addition of hydrogen sulfite to aldehydes and to terminal olefins, preparation of alkyl sulfonates by treatment of an alkyl chloride by sulfite or by addition of hydrogen sulfite to an α -olefin oxide. The list can be extended further. In all examples given there is a compatibility problem to be solved if the organic component is a large apolar molecule.

There are various ways to solve the problem of poor phase contact in organic synthesis. One way is to use a solvent or a solvent combination capable of dissolving both the organic compound and the inorganic salt. Polar, aprotic solvents are sometimes useful for this purpose but many of these are unsuitable for large-scale work due to toxicity and/or difficulties in removing them by low vacuum evaporation.

Alternatively, the reaction may be carried out in a mixture of two immiscible solvents. The contact area between the phases may be increased by agitation. Phase transfer reagents, in particular quaternary ammonium compounds, are useful aids in many two-phase

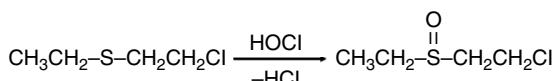
reactions. Also, crown ethers are very effective in overcoming phase contact problems; however, their usefulness is limited by high price. (Open-chain polyoxyethylene compounds often give a “crown ether effect” and may constitute practically interesting alternative phase transfer reagents.)

Microemulsions are excellent solvents both for hydrophobic organic compounds and for inorganic salts. Being macroscopically homogeneous yet microscopically dispersed, they can be regarded as something in-between a solvent-based one-phase system and a true two-phase system. In this context microemulsions should be seen as an alternative to two-phase systems with phase transfer reagents. This is illustrated below by the use of a microemulsion for detoxification of “half-mustard” ($\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$), which was used instead of real “mustard” ($\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$) in order to reduce the toxicity.

Mustard is a well-known chemical warfare agent. Although it is susceptible to rapid hydrolytic deactivation in laboratory experiments, where rates are measured at low substrate concentrations, its deactivation in practice is not easy. Due to its extremely low solubility in water, it remains for months on the water surface. Oxidation of half-mustard with hypochlorite turned out to be extremely rapid in both o/w (oil-in-water) and w/o microemulsions. In formulations based on either anionic, nonionic, or cationic surfactants, oxidation of the half-mustard sulfide to sulfoxide was complete in less than 15 seconds. The same reaction takes 20 minutes when a two-phase system, together with a phase transfer reagent, is employed. The reaction is shown in Figure 22.11.

The use of microemulsions as reaction media can be seen as an alternative to phase transfer catalysis. The two approaches may also be combined, that is, addition of a phase transfer agent has been found to be a way to speed up the reaction in a microemulsion further.

Organic reactions in microemulsions need not be performed in one-phase systems. It has been found that most reactions work well in the two-phase Winsor I or Winsor II systems (Chapter 17). The transport of reactants between the microemulsion phase, where the reaction takes place, and the excess oil or water phase is evidently fast compared to the rate of the reaction. This is a practically important aspect on the use of microemulsions as media for chemical reactions because it simplifies the formulation work. Formulating a Winsor I or Winsor II system is usually much easier than formulating a one-phase microemulsion of the whole reaction mixture.



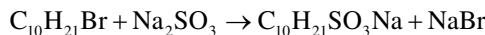
Time for destruction of half-mustard		
In water		months
In a two-phase system with added phase transfer agent		minutes
In a microemulsion		seconds

Figure 22.11 Oxidation of half-mustard by hypochloride yielding a nontoxic sulfoxide. (With permission from Menger, F.M. and Elrington, A.R. (1990) Rapid deactivation of mustard via microemulsion technology. *Journal of the American Chemical Society*, **112**, 8201–8203. Copyright 1990, American Chemical Society.)

Specific Rate Enhancement

By a proper choice of surfactants, a rate enhancement analogous to micellar catalysis (page 37) can be obtained. In microemulsion systems the effect may be referred to as “microemulsion catalysis.”

The importance of the choice of surfactant on the reaction rate can be illustrated by the reaction between decyl bromide and sodium sulfite to give decyl sulfonate, a useful surfactant:



Reactions were carried out in microemulsions based on decyl bromide dissolved in dodecane as the oil component, a solution of Na_2SO_3 as the water component, and either a nonionic surfactant or a nonionic surfactant with a small amount of a cationic surfactant added as the amphiphilic component. The reaction profiles are shown in Figure 22.12.

As can be seen, the reaction was extremely slow in a surfactant-free mixture of the oil and water components and relatively fast in the microemulsions. One would have expected the presence of cationic charges at the interface to increase the rate because of accumulation of the negatively charged sulfite ion in the interfacial layer. This was found when acetate was used as surfactant counterion. With chloride as counterion the rate was somewhat more sluggish than with the nonionic surfactant only and with bromide as counterion the retardation was very pronounced.

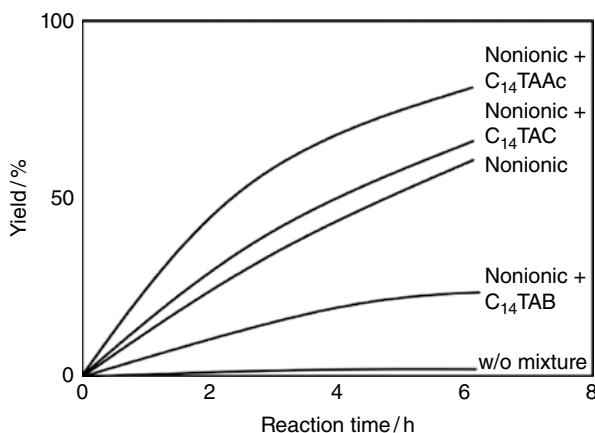


Figure 22.12 Reaction profiles for synthesis of decyl sulfonate from decyl bromide and sodium sulfite. The reactions were carried out in microemulsions based on only the nonionic surfactant $\text{C}_{12}\text{F}_{5}$, C_{12}F_5 with a small amount of tetradecyltrimethylammonium acetate (C_{14}TAAc) added, C_{12}F_5 with a small amount of tetradecyltrimethylammonium chloride (C_{14}TAC) added, or C_{12}F_5 with a small amount of tetradecyltrimethylammonium bromide (C_{14}TAB) added. As reference, the reaction was performed in a surfactant-free two-phase system (w/o mixture). (With permission from Holmberg, K., Oh, S.-G. and Kizling, J. (1996) Microemulsions as reaction medium for a substitution reaction. Progress in Colloid and Polymer Science, **100**, 281–285. Copyright © 1996, Springer.)

Evidently, the choice of counterion is decisive for the reaction rate. A large, polarizable counterion, such as the bromide ion, interacts so strongly with the surfactant palisade layer that approach of the anionic reactant, the sulfite ion, is prevented. Interaction with the acetate ion is much weaker and sulfite ions are allowed to diffuse into the interfacial region where the reaction occurs. This type of electrolyte effect at an interface is quite general and analogous to that discussed on page 37 for alkaline hydrolysis of cationic surfactants of ester quat type.

Microemulsions are Useful as Media for Enzymatic Reactions

Hydrolytic enzymes often catalyze the reverse reaction, that is, condensation, in media of low water activity. Lipases are of particular interest in this respect. When the water activity is low, formation of esters, as well as transesterifications, are catalyzed by lipases and this type of bioorganic reactions is practically important. When media of low water activity are used, most enzymes can be employed at higher temperatures than normally possible. This is also useful from a commercial point of view because higher temperatures mean shorter reaction times.

However, most enzymes require some water around them in order to attain their desired conformation. Microemulsions of the w/o type are then of interest as reaction media and a large number of enzymatic reactions have been performed with the enzyme confined in the water pools and with an aliphatic hydrocarbon as the oil component. Since the size of the water droplets is easily adjusted by the ratio of water to surfactant in the formulation, reaction media can be designed so that each droplet houses only one enzyme molecule. Both the reactant(s) and the product must partition into the hydrocarbon, otherwise the water pools would be crowded. Figure 22.13 shows the principle of an enzymatic reaction in a w/o microemulsion with the enzyme present in the water pools. The figure also illustrates the fact that there is usually an optimum in droplet size of the microemulsion, in the figure expressed as water-to-surfactant molar ratio. In many instances maximum activity occurs

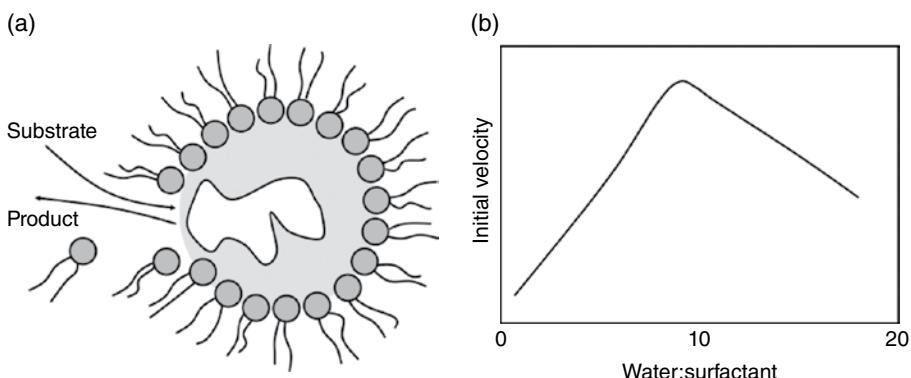


Figure 22.13 (a) A bioorganic reaction with the enzyme confined in the water pools of a microemulsion of the w/o type and (b) enzymatic activity versus molar ratio of water to surfactant in the microemulsion used as reaction medium

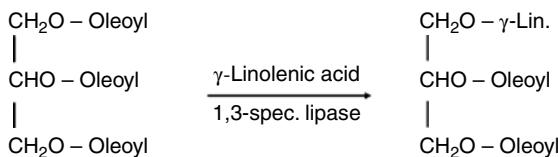


Figure 22.14 Transesterification of triolein with γ -linolenic acid in a w/o microemulsion. γ -Linolenic acid is a nutritionally valuable fatty acid that is not produced in the body but can be supplied in the form of a synthetic triglyceride.

around the water-to-surfactant ratio at which the size of the droplet is somewhat larger than that of the entrapped enzyme. Smaller droplets do not provide space enough for the enzyme to attain its preferred conformation. Larger droplets require an unfavorable transport of hydrophobic molecules to and from the active site of the enzyme.

The use of enzymes in water-poor media is not unnatural. Many enzymes, including lipases, esterases, dehydrogenases, and oxidoreductive enzymes, often function in the cells in microenvironments that are hydrophobic in nature. Also, the use of enzymes in microemulsions is not an artificial approach *per se*. In biological systems many enzymes operate at the interface between hydrophobic and hydrophilic domains, and these interfaces are often stabilized by polar lipids and other natural amphiphiles.

Enzymatic catalysis in microemulsions has been used for a variety of reactions, such as synthesis of esters, peptides, and sugar acetals, transesterifications, various hydrolysis reactions, and steroid transformations. The enzymes employed include lipases, phospholipases, alkaline phosphatase, pyrophosphatase, trypsin, lysozyme, α -chymotrypsin, peptidases, glucosidases, and oxidases.

By far the most widely used class of enzyme in microemulsion-based reactions is lipases—of microbial as well as of animal origin. Figure 22.14 shows a typical reaction performed in a water-poor microemulsion: transesterification of a triglyceride with a fatty acid. The 1,3-specific lipase resides in the water droplets and the two substrates, as well as the products, are hydrophobic and partition into the continuous domain.

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23

Foaming of Surfactant Solutions

A foam is a dispersion of a gas in a liquid or solid; here we will discuss liquid foams. The ratio of gas to liquid determines the appearance of the foam; this ratio is called the *foam number*. At low foam numbers, the gas bubbles are spherical and the liquid lamellae between the bubbles are very thick. Well-known examples of such foams are whipped cream or shaving foams, where the average bubble size is around $50\text{ }\mu\text{m}$. At higher foam numbers, the gas bubbles are separated by thin and planar liquid lamellae. The region where three such lamellae meet is called the *Plateau border* after the Belgian physicist Joseph Plateau.

There are Transient Foams and Stable Foams

There are two types of foams and they require different methods of characterization. These are unstable foams, or so-called transient foams (e.g., champagne), and stable foams (e.g., beer). Transient foams are commonly characterized by the Bikerman method. Here a gas is blown through the liquid in a column with a sintered glass frit at the bottom and the foam height, or foam volume, is recorded when the foam height has reached a steady state (Figure 23.1a). This is repeated at different gas flows and the foam volume is normally linearly dependent on the gas flow. The slope of a plot of the foam volume versus the volumetric gas flow is termed the *foaminess* and interpreted as the average lifetime of a foam bubble, or a foam lamella. It is essential that there is excess liquid at the bottom of the cell at all times, since otherwise the foam volume will be limited by the amount of liquid available.

Stable foams, on the other hand, are characterized by their foam ability, that is, their foam producing power, and their foam stability, that is, their durability. A measure of the foam ability (usually written *foamability*) is the foam volume immediately after the

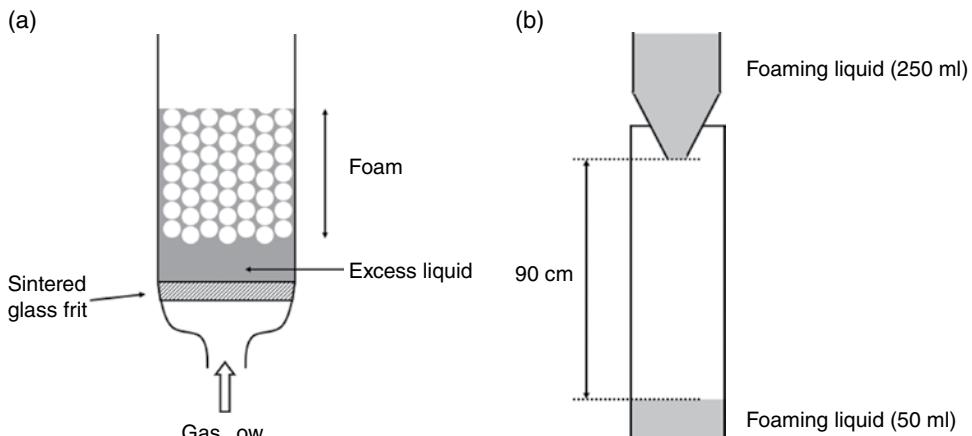


Figure 23.1 (a) In the Bikerman method, gas is continuously blown through the liquid in a column. (b) In the Ross–Miles foam test (ASTM D 1173-63), a specified amount of liquid is poured into a foam column and the immediate foam height, as well as that formed after 5 or 10 min, is recorded

generation of the foam, while a measure of the foam stability is the lifetime of the formed foam. Some protein solutions, for example, show low foamability and high foam stability, whereas some surfactant solutions show high foamability but low foam stability.

The foam volume, formed after shaking the liquid in a test tube, can be used to characterize the foamability of stable foams. This method has the disadvantage of being dependent on the operator, viscosity, and volume of the liquid, as well as the size and shape of the container. An alternative method is the Ross–Miles characterization method, which is an ASTM standardized method that gives both a measure of the foaming ability and the foam stability in a reproducible manner (Figure 23.1b). In this method, foaming liquid is poured into the foam column and the immediate foam volume is recorded, giving a measure of the foamability. The foam volume is then again recorded after 5 or 10 min, giving a measure of the foam stability.

Two Conditions must be Fulfilled for a Foam to be Formed

Foams are always formed from mixtures; pure liquids never foam. There are two important conditions that have to be fulfilled in order for a liquid mixture to foam. The first condition is that one component must be surface active. The lowering of the surface tension upon adding the second component is a measure of the surface activity. Since most organic compounds have a relatively low surface tension compared to that of water (Chapter 12), it is not surprising that aqueous solutions with organic additives foam relatively easily.

The second condition is that the foam film must show surface elasticity, that is, there must be a force pulling back the foam film if it has been stretched (Figure 23.2). The surface

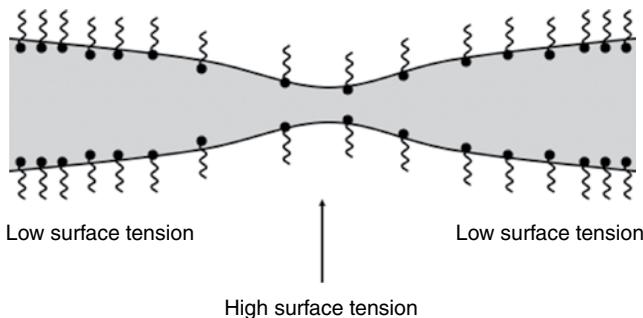


Figure 23.2 When a foam lamella is stretched, by mechanical vibrations or thermal instability, the surfactant concentration at the surface, that is, at the stretched part, is suddenly lowered, thus resulting in an increased surface tension and, hence, a restoring force

elasticity (E) originates from the increase in surface free energy, or the surface tension, as the surface area (A) is increased, that is, as the lamella is stretched:

$$E = A \frac{d\gamma}{dA} \quad (23.1)$$

When stretched, the foam lamella now experiences a force trying to pull back the lamella, thus reducing this higher surface energy. This condition of a surface elasticity must be valid on the time-scale during which the lamella is stretched and restored. Thus, it is a prerequisite for foaming that the transport of the surface active component from the bulk solution to the newly created surface is sufficiently slow. If this is not the case, the adsorption at the surface will decrease the surface tension and the temporary stretch of the foam lamella will be made permanent with a weakening of the lamellae as the result.

Thus, in order to attain elasticity, the foaming agent, for example a surfactant, is not allowed to diffuse from the interior of the lamellar film to the newly created surface before the film retracts. Surfactants with a very high critical micelle concentration (CMC), that is, surfactants that give high concentrations of unimer, will not form stable foams. This is because the high bulk concentration will allow the newly created surface to be covered with surfactant, diffusing from the interior of the lamellar film, before the film retracts. In addition, aqueous solutions of solutes that do not form micelles show low foamability. An example is aqueous solutions of ethanol that do not foam, despite the fact that ethanol lowers the surface tension of water, as shown in Figure 12.10.

Another example is given in Figure 23.3, showing the foaming of butanol–water mixtures. The reason for the increase in foam height at low alcohol concentration is obvious, namely the increased availability of surface active species. The subsequent decrease in foam is due to the effect outlined above, that is, a diffusional transport of surface active material from the bulk liquid that surpasses the transport from surface diffusion, leading to a decreased elasticity. The solubility limit is marked in the figure and at higher concentrations there is no foam. The reason is that the droplets of alcohol act as foam killers, as described by the mechanism given at the end of this chapter.

Foaming increases with surfactant concentration and levels off at concentrations above the CMC. One reason it does not level off at exactly the CMC is that surfactant is depleted

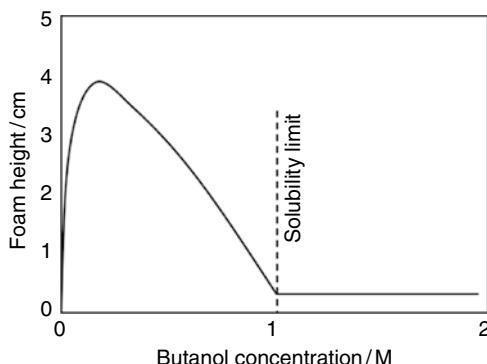


Figure 23.3 Foaming of butanol solutions in water. (With permission from Sasaki, T. (1938) On the nature of foam: I. Stability of the foam produced by the aqueous solutions of alcohols and acids. Bulletin of the Chemical Society of Japan, **13**, 517–526. Copyright 1938, The Chemical Society of Japan.)

from the bulk to the extra surface that is being created by the foam. Other reasons are that the packing of the surfactants at the surface continues to increase above the CMC, since the ionic strength increases for ionic surfactants and the hydration decreases with concentration for nonionic surfactants. Thus, the packing, and hence the cohesion, of the surfactant layer continues to increase above the CMC.

There are Four Forces Acting on Foams

Table 23.1 lists the four most obvious forces acting on foams. The first one is the gravitational force, causing drainage of the liquid between the air bubbles. The drainage can be slowed down by either increasing the viscosity of the bulk liquid or by adding particles, either solid particles or emulsion droplets. These particles become trapped in the Plateau borders, so hindering further drainage by a local increase in the viscosity, as shown in Figure 23.4.

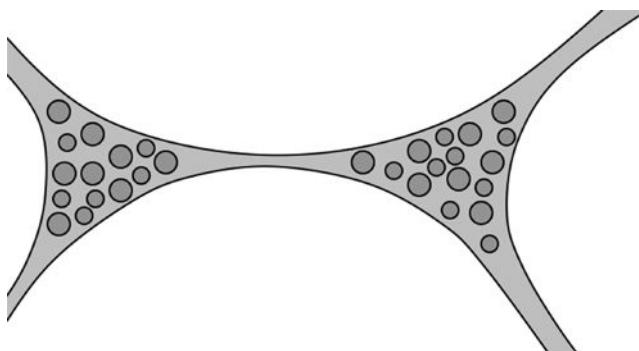
Foaming of an emulsion is a matter of the inability of the emulsion droplets to reach the surface. If they enter the surface they might function as foam killers (see further below). There are three factors that could prevent emulsion droplets reaching the surface. The first is based on the thermodynamic reasoning that the system must gain energy in order to enter the surface. Hence, the entering coefficient (E) must be larger than zero:

$$E = \gamma_{w/o} + \gamma_w - \gamma_o > 0 \quad (23.2)$$

Here $\gamma_{w/o}$ is the interfacial tension between the oil and the foaming liquid, γ_w and γ_o are the surface tensions of the aqueous solution and the oil, respectively. The second factor is the condition of the so-called pseudo-emulsion film formed between the droplet and the surface. Parameters of importance are the interfacial viscosity and surface tension gradients. The third condition is that there could be a net repulsion between the oil droplet and the air across the water, as described in Chapter 18. Hence, an oil droplet dispersed in water

Table 23.1 A summary of the four forces acting on foams

Force	Effect
Gravitation	Drainage to foam base
Pressure difference in lamellas and Plateau borders	Drainage to Plateau borders
Pressure difference of the gas in bubbles of different size	Diffusion of gas from small to large bubbles
Overlap between the electrical double layers	Increase in foam stability

**Figure 23.4** Emulsion droplets, or suspended particles, hinder further drainage of the foam liquid if they are trapped in the Plateau borders

could have a negative Hamaker interaction with the air, that is, a net repulsion toward the surface (Table 18.2).

For stable foams, that is, those with high foam numbers, where thin lamellae form, the drainage due to the gravitational force will gradually be substituted by the second force acting on foams, that is, drainage due to capillary forces. This force originates from the fact that the hydrostatic pressure in the Plateau borders is lower than in the lamellae. This lower pressure is caused by the negative curvature of the liquid surface at the Plateau borders. Thus, there is a driving force for the liquid to flow from the lamellae to the Plateau borders, further decreasing the stability of the foam.

The third force acting on foams is less obvious. It stems from the fact that the gas pressure inside a bubble is inversely proportional to the size of the bubble (Chapters 12 and 18). Thus, small bubbles have higher pressures than larger ones. There will, therefore, be molecular transport of gas from the small to the large gas bubbles through the liquid. It is thus possible for a foam to collapse without any lamellae breaking. The mechanism of transport is by dissolution of the gas followed by diffusion through the lamellae. Transport through the liquid is consequently proportional to the solubility of the gas in the liquid. The foam stability of argon, or fluorinated hydrocarbons, in aqueous solutions is, therefore, higher than of carbon dioxide in the same system, since carbon dioxide is more water soluble than argon or fluorinated hydrocarbons.

The fourth force acting on foams comes into play in very stable foams, where the lamellae become very thin. Here there will be an overlap between the electrical double layers originating from the surfactant molecules adsorbed at the liquid–air interface. This overlap causes repulsion, so preventing further thinning of the lamellae. This phenomenon occurs at distances of the order of 10–100 nm, depending on the ionic strength of the system.

The addition of salt compresses the electrical double layer, whereby the stability is diminished. On the other hand, as will be discussed later, salt addition also increases the critical packing parameter (CPP) of ionic surfactants and, hence, also the surface activity, in most cases causing an increased tendency for the solution to foam. Hence, there are two counteracting effects of salt and the literature can sometimes be confusing on this matter.

Finally, a factor that has an obvious effect on foam life is the surface viscosity of the liquid. Many types of foams are very stable, such as whipped cream or shaving cream, due to high surface viscosity. It is not necessary that the bulk liquid is viscous as long as the air–liquid interfacial layer has a high viscosity. This is the case for foams formed with proteins, for example.

Micelles with divalent counterions are more stable than those with monovalent counterions, since they have a smaller loss in entropy from the counterion binding. (Only half the number of entities that are involved, see further Chapter 3.) This increased stability is also apparent at the liquid–air interface. For example, addition of a magnesium salt strongly increases the stability of foams formed from an SDS solution. This effect is due to the increased stability of the liquid–air interface, as well as to a reduced drainage rate in the lamellae due to the long-lived micelles.

The Critical Packing Parameter Concept is a Useful Tool

The packing of surfactant molecules at the surface is of vital importance for the stability of a foam. As the CPP of the surfactant increases, the surfactant at the air–water interface packs closer together and a higher cohesion is attained. This gives the liquid lamellae good strength, increasing both the surface elasticity and viscosity, resulting in a high foamability and proper foam stability. Thus, according to this mechanism the foamability should continuously increase with increasing CPP.

On the other hand, the foamability is not only determined by the cohesion of the surfactant monolayer. Foams are broken by coalescence, that is, destruction of the thin liquid film separating the bubbles. The origin of coalescence is the formation of a hole in the film and is described in Chapter 18 (Figures 18.18 and 18.19). Thermal and mechanical fluctuations in the foam films lead to the formation of transient holes of molecular size. Once a hole is formed the film is not stable and the hole will propagate through the whole film. The formation of holes is, in turn, closely related to the molecular structure of the surfactant, namely the CPP. These holes are more easily formed with surfactant systems where the CPP is large. This is because the curvature of the hole is very large and the energy of forming a hole for surfactant systems with low CPPs is much larger than for surfactants with high CPPs (Figure 18.19). Hence, according to this mechanism the foaming ability, and the foam stability, should decrease as the CPP is increased.

Therefore, we have two counteracting phenomena acting on the foam as the CPP of the surfactant is increased. The cohesion within the lamellae will increase with the CPP and

cause a higher foaming ability while the ease of hole formation will also increase but cause a lower foaming ability. The foaming ability therefore displays a maximum as the CPP is varied (Figure 23.5). At this maximum the two phenomena balance each other. At higher CPP values, the ease of hole formation dominates, whereas at lower CPP values the lack of cohesion in the surfactant monolayer dominates. This general behavior is illustrated below with a few examples.

The CPP of nonionic surfactants is easily altered by changing the length of the polyoxyethylene chain. Figure 23.6a shows the foaming ability of aqueous solutions of nonylphenol ethoxylates, NP-E_n. This figure displays a pronounced maximum when the surfactant contains 80 wt% polyoxyethylene, corresponding to NP-E₂₀. Hence, for nonylphenolethoxylate surfactants with a shorter polyoxyethylene chain, the ease of hole formation dominates, whereas for surfactants with longer polyoxyethylene chains the inability to form a highly cohesive surfactant monolayer dominates.

The CPP of nonionic surfactants can also be altered by changing the temperature. At low temperatures, the polyoxyethylene chain expands, thus resulting in a large head group and, hence, a low CPP, while at higher temperatures the polyoxyethylene chain contracts, giving an increased CPP value (Chapter 7). The foaming ability shows a maximum at temperatures below the cloud point, in accordance with the mechanisms just outlined. Increasing the temperature above the cloud point causes the solution to separate into two phases, one that is poor in surfactant and one that is rich in surfactant. The surfactant rich phase forms droplets in the solution and these act as defoamers, according to the mechanism shown in Figure 23.9.

The CPP can be changed by altering the hydrocarbon chain length of the surfactant, which is demonstrated in Figure 23.6b, where the foam volume of aqueous solutions of alkyl sulfates at 60°C is plotted versus the number of carbon atoms in the alkyl chain. This figure shows a maximum in foam volume when the surfactant alkyl chain contains 16 carbons. For shorter-chain surfactants the disability to form a highly cohesive surfactant monolayer dominates, while for longer-chain surfactants the ease of hole formation dominates. These experiments were performed at 60°C in order to be well above the Krafft point of the surfactants.

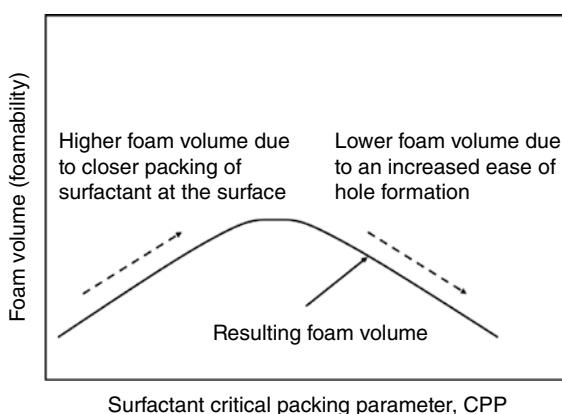


Figure 23.5 Two opposing effects are acting on a foam as the CPP of the system is altered, leading to a maximum in foaming ability

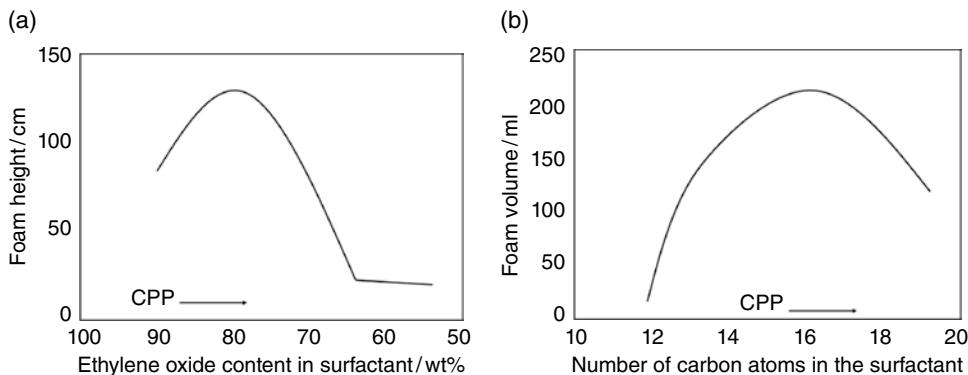


Figure 23.6 (a) Nonylphenol ethoxylates show a maximum in foamability when the polyoxyethylene chain constitutes about 80 wt% of the surfactant. The immediate foam height as determined from a Ross–Miles test. (b) Foam volume for a series of alkyl sulfates showing a maximum when the surfactant alkyl chain contains 16 carbons. ((b) Reproduced with permission from Bikerman, J.J. (1973) *Foams*, Springer-Verlag, Berlin, p. 114. Copyright © 1973, Springer.)

The CPP of an anionic surfactant system can be adjusted by addition of a nonionic long-chain amphiphile, such as a fatty acid or an alcohol. These compounds increase the CPP of the total system and the foaming ability is therefore increased if the CPP of the original surfactant is small. This is demonstrated in Figure 23.7, which shows that a foam from an aqueous solution of a soap is sensitive to changes in pH. At high pH values, the fatty acid is dissociated (forming a soap with low CPP), resulting in a poor foaming ability due to the inability to form a highly cohesive surfactant monolayer. On the other hand, at low pH, where the undissociated fatty acid dominates, there is also poor foaming ability. This is due to the ease of hole formation in these systems because the CPP value is now large. Note that

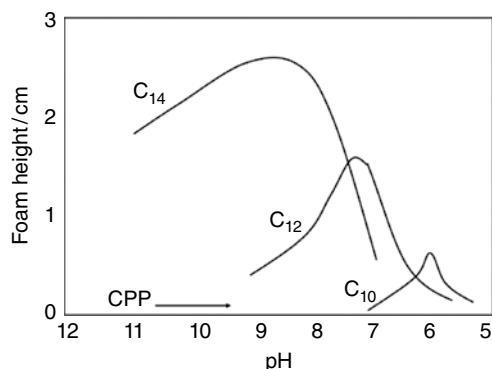


Figure 23.7 The pH dependence (at 50°C) of the foam volume of some fatty acids, showing a maximum at intermediate pH values. (Reproduced with permission from Bikerman, J.J. (1973) *Foams*, Springer-Verlag, Berlin, p. 111. Copyright © 1973, Springer.)

the foam maximum is moved toward larger pH values for the longer alkyl chains. When lengthening the alkyl chain, the CPP is increased; thus, more charged species (higher pH) are needed in order to balance the above two forces.

Foam boosters, which are used in many commercial products, work according to the principle above. Common foam boosters are alkanolamides and alcohol ether sulfates. Another foam booster is dodecyl alcohol. It is well known that technical SDS normally contains a few percent dodecyl alcohol and such solutions show much more stable foams than pure SDS solutions.

Mixing surfactant solutions such that a liquid crystalline phase is formed is a way to produce very stable foams. The liquid crystalline phase will be present in the Plateau borders and decreases the drainage through its high viscosity. Hence, the large effect of the presence of liquid crystalline phases is on the foam stability and to lesser degree on the foamability. A further possible mechanism is that the liquid crystalline phase in the Plateau borders acts as a reservoir of surfactant with the optimal composition to stabilize the foam film.

In conclusion, the formation of a foam is very sensitive to the CPP of the system, showing a maximum somewhere as the CPP is changed. There are pitfalls in this approach, however. One example is revealed when studying the effect of electrolytes on foams. In ionic surfactant systems, the addition of salt increases the CPP. Thus, for systems with low CPP values the foaminess should increase with salt addition. This is not always observed, however, since an increased salt content also lowers the double-layer repulsion between the two liquid-air interfaces in the lamellae, thereby decreasing both the foaminess and the foam stability.

Addition of Polymers might Increase or Decrease Foam Stability

Water-soluble polymers are present in many technical applications of surfactant solutions and it is of interest to know how the interaction between polymers and surfactants influences the formation and the stability of foams. Adding a water-soluble polymer to a surfactant solution can either increase or decrease the foamability and the foam stability. In the case where there is a weak surfactant–polymer interaction, such as between SDS and PEO, the presence of the polymer increases both the foamability and foam stability. The local high concentration of the polymer in the lamellae gives both a steric repulsion and a high viscosity.

If there is a strong surfactant–polymer interaction, such as between oppositely charged surfactant and polymer, then the foamability is usually lowered due to depletion of surfactant molecules from the surface as association structures are generated between surfactant and polymer in bulk. In some cases, however, gels are formed at the surface and these can give rise to both higher foamability and better foam stability. Normally the surfactant–polymer complexes are not moving sufficiently fast to the surface to influence the foamability. The foam stability on the other hand is increased for such systems. At surfactant:polymer ratios where precipitates are formed there is no foam, since the hydrophobic precipitates act as foam killers. At even higher surfactant:polymer ratios there is free surfactant to render good foamability, as well as proper foam stability. The stability is larger than for a polymer-free system since the solubilized complex gives a high viscosity to the bulk solution, which hampers the drainage.

Particles and Proteins can Stabilize Foams

Particles and surface active polymers, such as proteins, are two other groups of foam stabilizers besides surfactants. In Chapter 18 it was demonstrated that particles showing a contact angle with the liquid of around 90° are efficient stabilizers. However, particles showing a lower contact angle, down to 75° , also enhance the foam stability. This is because they adhere to the surface of the lamellae, or Plateau borders, and thereby hamper the drainage.

Similarly, proteins stabilize foams when the pH is close to the isoelectric point. Highly charged proteins far from the isoelectric point are in general easily soluble in water and do not show much surface activity. At pH values close to the isoelectric point, on the other hand, the protein is less soluble. In Chapter 12 it was demonstrated that the surface activity of polymers increases as the bulk solubility decreases. This is the case for proteins as well. Hence, proteins partition to the surface as the pH approaches the isoelectric point. Also, the net cohesion and the surface viscosity are highest at this point. This increased surface activity gives an increased foamability. If the pH is changed even closer toward the isoelectric point, the protein will precipitate and no foam will form.

Various Additives are Used to Break Foams

Foams in industrial processes are generally not wanted and can sometimes be the bottleneck for a high production rate. When unwanted foam appears it is common to add a *foam killer* (often also referred to as an *antifoamer* or a *defoamer*). These are surface active compounds, or systems, that break foams by spreading on the foam lamellae. For example, a foam stabilized by an ionic surfactant can easily be broken down by spraying a medium-chain alcohol, such as octanol, on top of the foam. The octanol droplets have a very low surface tension, which means that they spread on the foam lamellae. This process carries with it a layer of liquid, below the surface, thus thinning the lamellae to the point of breakage (Figure 23.8). Note that octanol can only be used by a spraying application. Mixing it with the system might instead stabilize the foam, since the addition of octanol might lead to the formation of a lamellar liquid crystalline phase, which can be incredibly efficient in stabilizing foam lamellae. Octanol should, therefore, be used with caution, since the

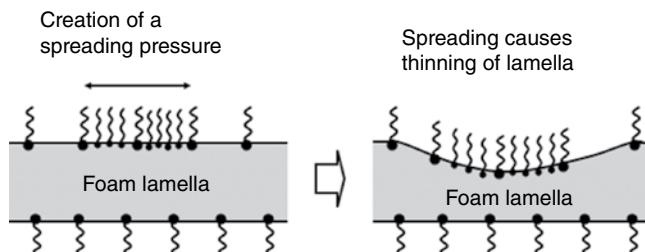


Figure 23.8 In the most common defoaming mechanism, the defoamer spreads on the surface of a foam lamella pulling with it a layer of liquid, below the surface, thus thinning the lamella to the point of breakage

final system might give an even more stable foam. Another mechanism of foam breaking using octanol can be that the total CPP of the system increases locally because the added molecules partition into the hydrocarbon part of the surfactant monolayer at the surface. The ease of hole formation is thereby increased, so leading to reduced foaming ability. Small branched substances such as tributylphosphate and 2-ethylhexanol are also used as defoamers. They act by decreasing the rigidity of the monolayer.

This spreading mechanism is also used in machine dishwashing formulations. Here, very hydrophobic block copolymers of EO–PO–EO or PO–EO–PO type have traditionally been used. Due to poor biodegradation characteristics they have now to a large extent been replaced by other nonionic surfactants. These surfactants are only dispersible in water and act by the mechanism described above.

Another common type of foam breaker is based on silicone oil, or a hydrophobic mineral oil. The oil droplets spread on the surface (Figure 23.9a) and since the oil itself does not show any surface elasticity, it will cause the foam film to break. The condition for an oil droplet to spread on the surface of a foam lamella is that the spreading coefficient (S) should be positive (see page 379):

$$S = \gamma_w - \gamma_{w/o} - \gamma_o > 0 \quad (23.3)$$

Here γ_w and γ_o are the surface tensions of the foam liquid and the oil, respectively and $\gamma_{w/o}$ is the interfacial tension between the foam liquid and the oil. Normally the surface tension of organic compounds is in the range 25–40 mN/m, which is roughly that of the foam liquid if it is stabilized by surfactants. Thus, a prerequisite for spreading is that the oil shows a very low interfacial tension toward the aqueous solution. If not, the oil will just

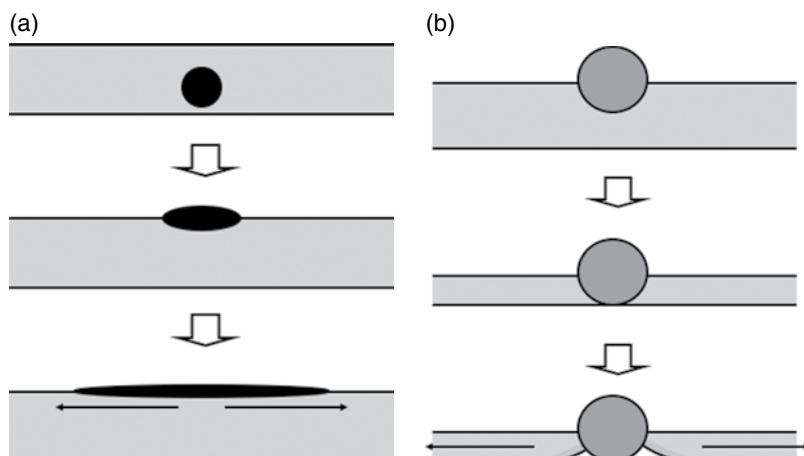


Figure 23.9 (a) Foam breaking mechanism of an oil droplet entering and spreading on the surface of a foam lamella and (b) the effect of hydrophobic particles on the stability of thin liquid films. As the film thins through drainage, the lower surface of the film comes in contact with the particle surface and the particle dewets. The lower contact line approaches the upper contact line, and the film ruptures when the contact lines meet. The arrows show the liquid flow generated by the Laplace pressure

form a lens at the water surface. Silicone oils are well suited as foam breakers since they have low surface tension, as well as very low interfacial tension toward water. In some applications, the use of silicone oil interferes with the performance of the product, which means that nonsilicone substitutes have to be used. The most common substitutes are mineral oils. Such oils usually have higher interfacial tension toward water and may, therefore, not spread spontaneously. In order to achieve spreading, surface active compounds, such as long-chain fatty amides, can be added to the mineral oil. These adsorb at the oil–water interface, thereby decreasing the interfacial tension. These additives must not be soluble in the aqueous phase, otherwise they will be depleted from the mineral oil, thereby decreasing the efficiency of the foam breaker. An important prerequisite for dispersed oil foam killers is that they must be able to enter the water–air interface. Accordingly, it is necessary that the Hamaker constant of the oil is such that it does not give repulsive forces with the air (Table 18.2).

Particles are often also added to the foam-killing oils. The purpose of the particles is to break a so-called pseudo-emulsion film that is sometimes created between the oil droplet and the air. This pseudo-emulsion film prevents the oil droplet from entering the surface, despite the fact that energy would be gained by the process. The mechanism is most likely related to the high viscosity of this pseudo-emulsion film.

Finally, hydrophobic particles can be used to break a foam according to the mechanism shown in Figure 23.9b. Here the particle penetrates the foam film and the foaming liquid dewets the surface of the particle. This is also the mechanism in action when hydrophobic tools, such as knives, are used to break a foam.

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24

Emulsions and Emulsifiers

Emulsions are Dispersions of One Liquid in Another

An emulsion is a dispersion of one liquid in another liquid. This means that the two liquids must be immiscible. Contrary to microemulsions, which are considered one-phase systems, emulsions contain at least two phases. Almost all emulsions contain water as one phase and an organic liquid as the other phase. The organic phase is normally referred to as the “oil” but it by no means needs to be an oil in the normal meaning of the word. Hydrocarbons are the most common oil in emulsions.

There are two main types of emulsions, oil-in-water (o/w) and water-in-oil (w/o). Oil-in-water emulsions are by far the most important and common examples are paints, glues, milk, bitumen emulsions, agrochemical formulations, and so on. Spreads (margarines) are well-known examples of w/o emulsions. The droplets in an emulsion are referred to as the dispersed phase, while the surrounding liquid is the continuous phase. There also exist so-called double emulsions, which may be w/o/w or o/w/o. Such systems are of interest for drug delivery.

If an oil is dispersed in water without any amphiphile or other kind of stabilizer added, the life-time of the emulsion will be short. The oil droplets are unstable in two senses. One is that they will cream, that is, ascend to the top of the container. The rate of creaming depends on a number of parameters, such as the size of the droplets, the difference in density between the two phases, and the viscosity of the continuous phase. The second instability is that droplets will coalesce on collision, thus increasing the droplet size. Both creaming and coalescence were discussed in Chapter 18. The droplet size is particularly important because the rate at which individual droplets move due to gravity is proportional to the square of the droplet radius. For an emulsion of a typical hydrocarbon oil in water a $0.1\mu\text{m}$ droplet moves 0.4 mm/day , a drop of $1\mu\text{m}$ moves 40 mm/day , and a drop of $10\mu\text{m}$ moves 4 m/day . Calculations show that the half-life of a droplet of a typical hydrocarbon of $1\mu\text{m}$

size, assuming a 1:1 oil-to-water ratio and a viscosity of the continuous water phase of 1 mPas, is 0.77 s. Six months shelf-life means a half-life of 1.6×10^7 s. From these calculations, it can clearly be understood that the droplets need to be stabilized. As we shall see, there are various ways to stabilize emulsions.

Emulsifiers are Surfactants that Assist in Creating an Emulsion

Surfactants that are added in order to assist in forming and stabilizing an emulsion are referred to as *emulsifiers*. For this purpose other types of compounds can be used also, such as amphiphilic polymers, small particles, and so on. Surfactants are also used to create the emulsion, that is, to help in finely dispersing either oil into water or water into oil. In order to achieve this, two requirements must be fulfilled: the surfactant must reduce the oil–water interfacial tension to low values and the surfactant must rapidly diffuse to the newly created interface. The last requirement is crucial; only if the new interface is rapidly covered by a surfactant monolayer will that interface be stable against coalescence. High molecular weight polymers, hydrophobic particles, proteins close to their isoelectric point, and liquid crystals may be good at stabilizing an oil–water interface but these are all large species that diffuse slowly to the newly formed interface. Low molecular weight surfactants are, therefore, superior when it comes to creating emulsions. Other substances may then play a larger role in stabilizing the system. (Compare the discussion about the role of Emulsan, page 198.)

The PIT Concept

As discussed in some detail in Chapter 7, the physicochemical properties of nonionic surfactants based on polyoxyethylene chains are very temperature dependent. The same surfactant may give a water-continuous emulsion at low temperatures and an oil-continuous one at high temperatures (Figure 24.1). The concept of using the *phase inversion temperature* (PIT) as a more quantitative approach to the evaluation of surfactants in emulsion systems has been found very useful. As a general procedure, emulsions of equal parts of oil and aqueous phase and approximately 5% nonionic surfactant are prepared by shaking during a rise in temperature. The temperature at which the emulsion inverts from o/w to w/o is defined as the PIT of the system. The phase inversion can easily be detected by an abrupt drop in conductivity when the emulsion transforms from a water-continuous to an oil-continuous system.

In laboratory work the PIT is often first determined with model nonionic surfactants that are *homologue-pure*. It is important in this context to note that the PIT of such a surfactant is somewhat different from the PIT of a technical surfactant of the same average degree of ethoxylation. The difference is particularly large for surfactants with short polyoxyethylene chains. The reason for this difference is that for the surfactant with a broad homologue distribution the fraction of amphiphilic molecules with short polyoxyethylene chains, that is, the hydrophobic fraction, will preferentially partition into the oil phase, whereas the fraction with long polyoxyethylene chains will, to a large extent, dissolve in the aqueous phase. The oil is normally a better solvent for the hydrophobic fraction than the water for the hydrophilic fraction. A larger fraction will, therefore, be “lost” in the oil phase than

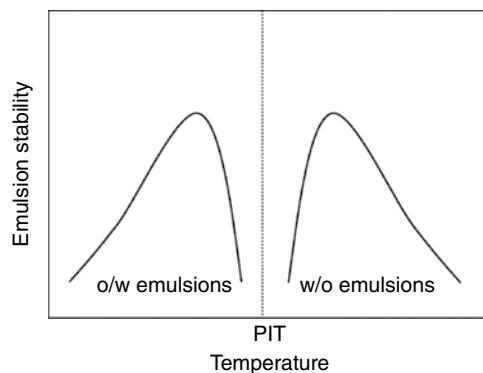


Figure 24.1 At low temperatures nonionic surfactants based on polyoxyethylene chains give o/w emulsions whereas w/o emulsions are obtained at high temperatures. The temperature where the inversion occurs is termed the “phase inversion temperature” (PIT)

in the water phase and the resulting surfactant at the interface will be more hydrophilic than the average surfactant added to the system. Hence, the PIT will be higher than if no fractionation had occurred. Partitioning into the oil and water phases occurs for the homologue pure surfactant as well, but in this case the PIT is not affected since all molecules, that is, those in the oil phase, those in the water phase and those residing at the interface, are the same. The situation is illustrated in Figure 24.2.

It is important to realize that the PIT value is not associated with the surfactant *per se*. It relates to the oil–water–surfactant system, that is, to the emulsion at the point when the hydrophilic–lipophilic properties of the nonionic surfactant used as the emulsifier just

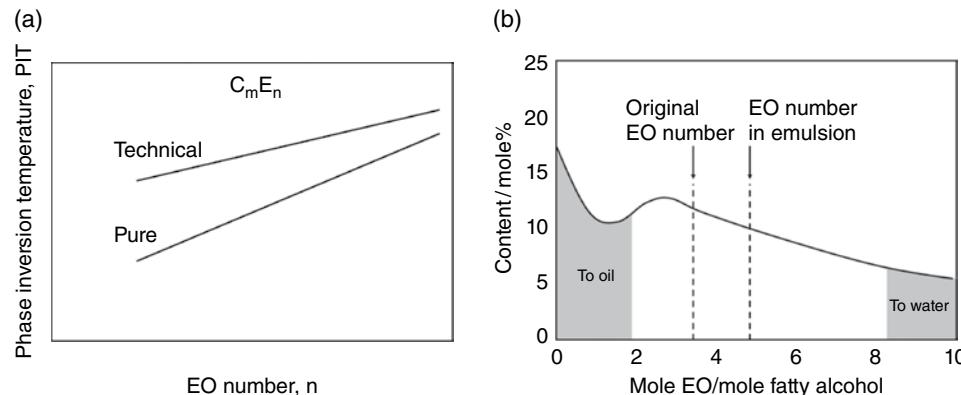


Figure 24.2 (a) A schematic graph showing that a technical fatty alcohol ethoxylate has a higher PIT than a homologue-pure surfactant of the same average degree of ethoxylation. The difference is due to partitioning of the hydrophobic and hydrophilic fractions into oil and water, respectively. (b) in the system $C_{12}E_{3.5}$ – decane – water a larger fraction of the surfactant partitions into the oil than into the water. This means that the oil–water interface will be occupied by surfactants with a longer polyoxyethylene chain than that of the added surfactant

balances. Nonionic surfactants are sometimes classified according to their hydrophilic-lipophilic balance (HLB) and assigned a HLB number. The HLB number scale ranges from 0 (hydrophobic end) to 20 (hydrophilic end). The HLB number for fatty alcohol ethoxylates is calculated as the weight % ethylene oxide in the molecule divided by a factor of five. In general, low HLB surfactants are used as emulsifiers for w/o emulsions and high HLB surfactants are used for making o/w emulsions. Calculating the HLB number of other polyoxyethylene-based surfactants, such as alkylphenol ethoxylates and fatty amide ethoxylates, is not equally straightforward and attempts to transfer the concept to other classes of surfactants have not been very successful.

There is, of course, a correlation between the PIT and the HLB number. Increasing the length of the polyoxyethylene chain in nonionic surfactants gives higher HLB numbers and leads to an increase in the PIT. Other factors that affect the PIT are:

Nature of the oil. The more nonpolar the oil, then the higher the PIT. For instance, ethoxylated nonylphenol with 9.6 EO has a PIT in benzene–water 1:1 of around 20°C. When benzene is replaced by cyclohexane, the PIT is raised to 70°C and with hexadecane as oil the PIT is above 100°C.

Electrolyte concentration and type of salt. The PIT decreases with addition of most, but not all, salts. Replacing distilled water by a 5% sodium chloride solution gives a PIT reduction of the order of 10°C. The salt dependence is the same as that discussed in Chapter 7 for the cloud point.

Impurities in the oil. Substances that make the oil more polar, such as fatty acids or fatty alcohols, can give a considerable reduction in the PIT. Such compounds are typical byproducts in technical surfactants and may partition into the oil. These impurities tend to assemble at the o/w interface, hence there need only be small amounts in order to give appreciable changes in the PIT. Very water-soluble substances, such as poly(ethylene glycol) and sugar, do not affect the PIT much.

Relative volumes of oil and water. The PIT for homologue-pure surfactants can usually be regarded as constant for oil-to-water volume ratios of 0.2–0.8. For technical surfactants that contain amphiphiles with varying HLB values, the oil-to-water ratio will affect the distribution of species between the phases, leading to increased PIT with increasing oil-to-water ratio. If the PIT is measured at different oil-to-water ratios and the values extrapolated to an oil-to-water ratio of zero, the value obtained will roughly correspond to the cloud point of the surfactant.

A rule of thumb in emulsion technology is that water-soluble emulsifiers tend to give o/w emulsions and oil-soluble emulsifiers w/o emulsions. This is known as *Bancroft's rule* and dates 100 years back. The statement above, that is, that surfactants with low HLB values give w/o emulsions and those with high HLB values o/w emulsions, is obviously in agreement with Bancroft's rule. Also, the four factors discussed above that affect the PIT are in harmony with Bancroft's rule of emulsifier solubility governing what type of emulsion that will form. For instance, the addition of a polar, oil-soluble organic substance leads to an increase in oil polarity that, in turn, leads to increasing solubility of the surfactant in the oil. Bancroft's rule states that this will favor formation of a w/o emulsion. Thus, addition of the additive lowers the PIT. Figure 24.3 illustrates the point. In order to achieve a balanced system, water solubility of the surfactant then needs to be improved. This is done by lowering the temperature. (Polyoxyethylene-based nonionics become more water soluble at lower temperatures.)

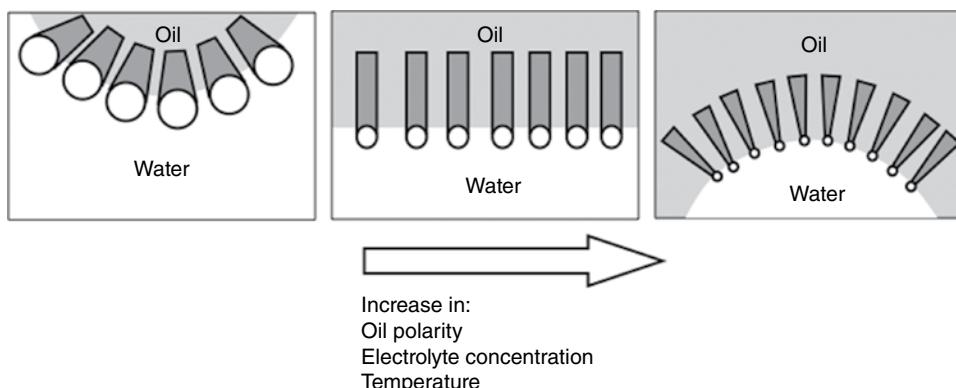


Figure 24.3 Effect of oil polarity, electrolyte concentration, and temperature on the curvature of the oil–water interface

The PIT Method of Selecting Emulsifier is Often Useful

The oil–water interfacial tension is at a minimum at the PIT (Fig 12.15). Emulsions made at this temperature will, therefore, have the finest particle size. Such emulsions are not stable to coalescence, however (Figure 24.1). In the *PIT method of emulsification* a non-ionic emulsifier (or better still, a surfactant mixture) is chosen that gives a PIT of around 40°C above the storage temperature of the ready-made emulsion (equal parts oil and water, 5% surfactant). The emulsification is carried out at some 2–4°C below the PIT, and the emulsion is then rapidly cooled down to the storage temperature at which the coalescence rate is lower (Figure 24.1). An efficient way to bring about rapid cooling is to carry out the emulsification with a relatively small amount of water, and subsequently add cold water.

One may also make the emulsion slightly above the PIT, in which case a w/o emulsion is formed. Subsequent addition of cold water will give a phase inversion into an o/w system. This is a useful way of emulsifying very viscous oils, such as alkyds and other resins, but the droplet size will normally not be as small as by the PIT method without phase inversion.

Nonionic Surfactants are Versatile Emulsifiers

Alkylphenol ethoxylates have traditionally been widely used as emulsifiers. With the increasing concern about biodegradability and aquatic toxicity, these surfactants have to a large extent been replaced by fatty alcohol ethoxylates of similar HLB numbers. Sometimes, such a replacement is not straightforward, a fact that may be attributed to the differences in the hydrophobic tail of the two surfactant types. Whereas fatty alcohol ethoxylates are normally based on a straight-chain, aliphatic hydrocarbon, alkylphenol ethoxylates (in practice octyl- or nonylphenol ethoxylates) have a bulky and polarizable tail. Figure 24.4 shows the structures of the two types of compounds. It is likely that the many methyl groups in the alkyl chain of the nonylphenol ethoxylate shown in the figure are of importance for the properties of this surfactant class. As was discussed in Chapter 20, methyl

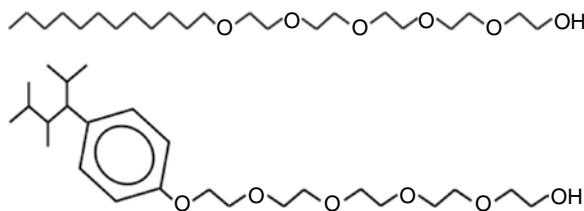


Figure 24.4 Structures of (top) a fatty alcohol ethoxylate and (bottom) a nonylphenol ethoxylate

groups in a surface render the surface very hydrophobic. (Compare the values of critical surface tension of polydimethylsiloxane (normal silicon oil) of 24.5 mN/m with that of polyethylene of 31 mN/m.) It is likely that the many methyl groups in the low molecular weight silicone surfactants are decisive of their efficiency as wetting agents (page 385). By the same reasoning the methyl groups in the tail of the alkylphenol ethoxylates provide strong hydrophobicity to the surfactant, and this is an important characteristic of an amphiphile. The ideal emulsifier should have maximum hydrophilicity of the polar head group and maximum hydrophobicity of the hydrophobic tail. Then the losses into the bulk phases will be minimized. However, there are limits. Firstly, there is a solubility limit. Increasing the hydrophilic as well as the hydrophobic moieties will eventually cause insolubility due to solidification of the emulsifier. Secondly, the diffusion will be slowed down as the molecules get larger and this will disqualify them as emulsifiers (see the later section on Bancroft's Rule).

For a surfactant to align properly at an interface, the molecular structure is important. The oil–water interface of an emulsion droplet is relatively planar at the surfactant dimension. Consequently, in order to obtain optimum packing, and hence cohesiveness, at this interface, which is beneficial for emulsion stability, the surfactant should have a geometry such that the size of the polar head matches that of the hydrophobic tail. It can easily be seen, for example, by viewing molecular models, that the volume of the hydrocarbon tail is much smaller than that of the polar head group for linear fatty alcohol ethoxylates of the type normally used as emulsifiers for o/w systems. For the corresponding alkylphenol ethoxylates the volume of the hydrophobic tail is usually also smaller than that of the polar head but the difference in size is not so pronounced. Consequently, linear fatty alcohol ethoxylates pack less efficiently at interfaces (unless these are strongly curved convex against water) than alkylphenol ethoxylates. Another way of viewing this difference is that the driving force for the fatty alcohol ethoxylates to align at interfaces is smaller than for alkylphenol ethoxylates.

Nonionic surfactants based on branched alcohols have a more balanced geometry than their linear counterparts. So-called *Guerbet alcohols*, namely alcohols with long side chains at the two-carbon atom (made by the Guerbet reaction—a kind of aldol condensation) constitute an example of raw materials of interest in this respect. Guerbet alcohol ethoxylates have been found useful as replacers of alkylphenol ethoxylates in some applications. *Oxo alcohols* represent another important type of branched alcohols. Oxo alcohols are produced by reacting an olefin with syngas ($\text{CO} + \text{H}_2$) over a catalyst (the hydroformylation or the oxo process) followed by hydrogenation of the generated

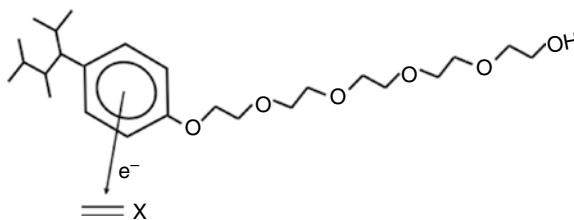


Figure 24.5 An EDA complex may form between nonylphenol ethoxylate and an unsaturated moiety in an oil or at a solid surface

aldehyde. 2-Ethylhexanol and 2-propylheptanol are examples of surfactant hydrophobes made by the oxo process.

Another difference between nonylphenol ethoxylates and fatty alcohol ethoxylates is the presence of the six π -electrons in the hydrophobic tail of the former. These are likely to affect the interactions between these surfactants and unsaturated components of the oil. Phenols are known to be able to act as donors in electron donor–acceptor (EDA) complexes, donating π -electrons to suitable acceptor molecules. It is reasonable to assume that EDA complex formation will play a role in the interaction between alkylphenol ethoxylates and unsaturated components in the oil phase. No such contribution is, of course, present in the case of fatty alcohol ethoxylates. It is often difficult to replace alkylphenol ethoxylates as dispersants for solid particles and it is likely that the lack of this type of interaction is one of the reasons why fatty alcohol ethoxylates often do not provide the same dispersing power. Figure 24.5 illustrates the formation of an EDA complex involving a nonylphenol ethoxylate.

The electronic effect is not as general as the effect of the geometrical packing. EDA complexes can only form with oils containing components that can function as π -electron acceptors. Olefins and aromatics, particularly those that contain electron-withdrawing substituents, may act as acceptor molecules. Many emulsions, both in the food area and for industrial applications, are based on oils that contain unsaturated components. Formation of such EDA complexes will enhance the interactions between the emulsifier and the oil phase. This, in turn, enables the formulator to use surfactants with slightly longer polyoxyethylene chains than would otherwise be possible. Longer polyoxyethylene chains mean a higher water solubility of the surfactant. Without the extra contribution to the interactions involving the hydrophobic tail, such surfactants would partition too much into the water phase. The longer chains are beneficial as such since the steric repulsion between the droplets, which helps to prevent coalescence, will be enhanced.

Ionic Surfactants have Analogous Behavior

Ionic emulsifiers normally give o/w emulsions since they are, in general, hydrophilic. However, decreasing their hydrophilicity by, for example, adding salt will lower the solubility in the aqueous phase and force the surfactant into the oil phase, hence forming w/o emulsions. The temperature dependence is negligible, however, which means that in contrast to systems based on nonionic surfactants, heating or cooling

cannot be used as a way to obtain phase inversions. The effect of the oil is similar to that for nonionic surfactants in the sense that the solubility of the surfactant in the oil increases with the polarity of the oil. Therefore, in order to keep the same conditions when changing to a longer alkane one needs to force the surfactant into the oil phase, for example by adding salt, which will reduce the solvency of the aqueous phase. Alcohols with a chain length above four carbon atoms partition to the oil phase and render the oil more polar. Hence, an o/w emulsion may invert to a w/o emulsion on the addition of a medium chain alcohol (compare Figure 24.3).

Using Surfactant Mixtures as Emulsifiers

Often mixtures of emulsifiers are used to create and stabilize emulsions. The emulsifiers are often chosen such that one should be abundant in the continuous phase and act as an emulsifier according to the description below, where Bancoff's rule is explained in terms of the Marangoni effect. The other component should have low solubility in the continuous phase and, therefore, be effective in reducing the interfacial tension. One example is a mixture of a hydrophilic anionic surfactant with a hydrophobic nonionic amphiphile, such as a medium-chain length alcohol or amine, where the role of the latter is to lower the interfacial tension. Another approach is to mix an anionic surfactant with a nonionic surfactant based on a polyoxyethylene chain (Figure 24.6). This creates an electrosterically stabilized emulsion with excellent stability. Stabilization of spreads

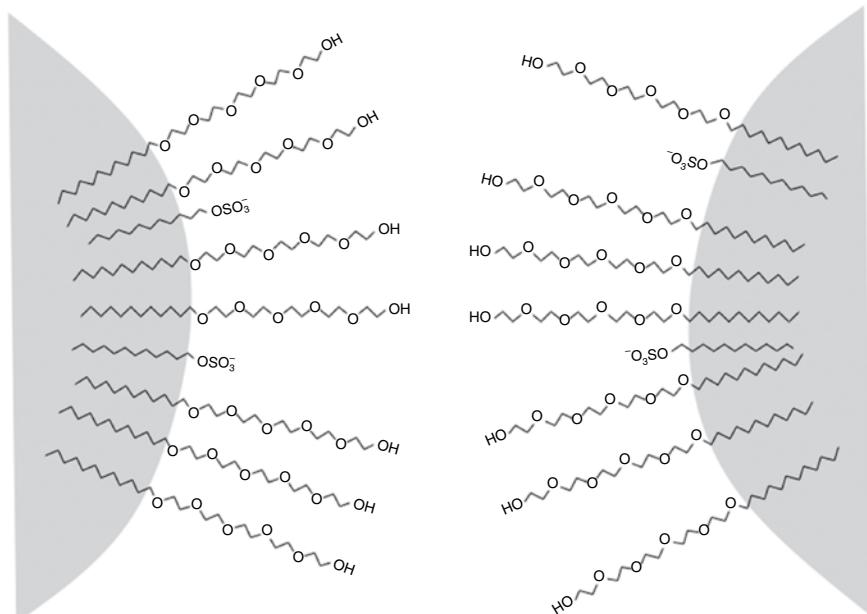


Figure 24.6 An o/w emulsion stabilized by a combination of a fatty alcohol ethoxylate and sodium dodecyl sulfate. (The surfactants are not drawn to scale.)

(margarines) may have three contributions: a biopolymer gives steric stabilization, fat crystals provide particle stabilization, and an anionic phospholipid gives electrostatic stabilization. The latter contribution is small, however, because the continuous medium has a low dielectric constant.

Another reason to use surfactant mixtures is to create lamellar liquid crystalline phases that are excellent in stabilizing emulsions (Chapter 18). When using lipids it is common to use mixtures in order to prevent crystallization. In using mixtures of emulsifiers one should realize that the surfactant composition at the interface depends on (i) the surfactant composition (Chapter 13), (ii) the total surfactant concentration, and (iii) the oil-to-water ratio.

Some general rules for mixtures are: if one surfactant has a pronounced affinity for the aqueous phase and the other a pronounced affinity for the oil phase, the two surfactants will act more or less independently; if neither of the two surfactants has a good affinity for either phase, a third phase of high surfactant concentration will be formed, called the surfactant phase, which contains most of the two surfactants; in some cases lamellar liquid crystalline phases can form giving good stability to the emulsion.

Bancroft's Rule may be Explained as a Marangoni Effect

Figure 24.7 illustrates an attempt to explain Bancroft's rule regarding what type of emulsion is formed with a specific surfactant. By applying shear to a mixture of oil and water, the oil–water phase boundary has been extended, having “oil fingers” in water and “water fingers” in oil, as shown in the left-hand figure. This situation is unstable. If the oil fingers break up, an o/w emulsion will form and if the water fingers break, a w/o emulsion will be created. In order to stabilize the newly formed droplets—regardless of what type of structure is being formed—enough time must be available to allow the emulsifier to go to the interface and adsorb there in an amount sufficient to prevent immediate coalescence.

In the experiment of Figure 24.7 the emulsifier is water soluble. The following discussion is based on the fact that adsorption of surfactant at a newly formed oil–water interface is not instantaneous. The oil finger breaks up and immediately afterwards the situation, shown in the right-hand figure, may appear. The interfacial concentration of emulsifier is uneven. It is higher on the relatively older top and bottom sides and lower in the regions

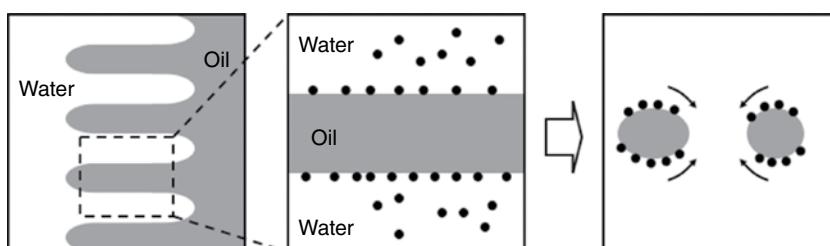


Figure 24.7 Dynamic interpretation of Bancroft's rule; the dots represent emulsifier molecules. (With permission from Lyklema, J. (1994) Adsorption at solid-liquid interfaces with special reference to emulsion systems. *Colloids and Surfaces A*, **91**, 25–38. Copyright Elsevier.)

between the droplets, because these interfaces were formed more recently. The emulsifier molecules have not yet had time to reach these sites. Transient gradients in interfacial tension are created, thus leading to a flow of water toward the gap by viscous traction, an example of the *Marangoni effect*. A further consequence is that the oil droplets are transiently pushed apart, so giving them enough time to stabilize. Thus, it is the hydrodynamics in the system, driven by a gradient in interfacial tension, that is responsible for the survival of the initially formed oil droplets, not the interfacial tension-reducing effect by the surfactant. If, instead, the water fingers had broken up, the emulsifier molecules would have been inside the droplets and coverage of the interface would have been equal all around. No Marangoni effect would then be operative to assist in separating the droplets during the critical initial period.

This description of the mechanism behind emulsion formation also explains why an emulsifier is normally a low molecular weight amphiphile. The emulsifier must move quickly in the solution and small molecules diffuse more rapidly than large molecules. As mentioned earlier in this chapter, larger species, such as macromolecules or hydrophobic particles, are often used in emulsion formulations. However, their role is not to act as emulsifier and contribute to a Marangoni flow. Instead, these species will go slowly to the interface and replace emulsifier molecules.

Bancroft's Rule may be Related to the Surfactant Geometry

An alternative approach to explain Bancroft's rule is that of the surfactant geometry being decisive of whether o/w or w/o emulsions form. Surfactants with large critical packing parameter (CPP) values need more space on the oil side; thus, they should give w/o emulsions. Surfactants with large head groups have the opposite requirement and should favor o/w emulsions. Ideas along this line were among the early attempts to explain why some surfactants give oil-continuous emulsions while others give water-continuous systems. However, when considering and comparing the dimensions of emulsion droplets and surfactants, it is obvious that at the scale of the surfactant molecule the oil–water interface is almost planar. Thus, the energy difference between the two different orientations of surfactant must be very small.

A striking example of how the curvature concept can be used to explain the type of emulsion formed is in oil–water–surfactant systems close to the PIT where the surfactant is a polyoxyethylene-based nonionic. As discussed in Chapter 17, such mixtures may give rise to three phases, namely a microemulsion in equilibrium with excess oil and water phases. If the microemulsion phase, which contains most of the surfactant, is removed and the remaining two phases are subjected to agitation, either an o/w or a w/o emulsion may form. Which type of emulsion will form depends entirely on whether the experiment is made above or below the PIT of the system. Below the PIT, the spontaneous curvature of the microemulsion is convex against water, that is, the surfactant CPP is slightly smaller than one, and an o/w emulsion is formed. Above the PIT, the curvature is convex against oil, that is, the surfactant CPP is slightly larger than one, and a w/o emulsion is formed. In this case, the relative surfactant solubility in oil and water seems not to play any role. A normal fatty alcohol ethoxylate, such as $C_{12}E_5$, has a molecular solubility several orders of magnitude higher in hydrocarbons than in water.

Hydrodynamics may Control what Type of Emulsion will Form

At very low surfactant concentration or when a very weak amphiphile is used, the type of emulsion formed, oil-in-water or water-in-oil, is controlled by the mixing procedure rather than by the choice of surfactant. In such systems Bancroft's rule may or may not be obeyed. For instance, addition of oil to a solution of a nonionic surfactant in water may lead to an oil-in-water emulsion, also at temperatures above the PIT if the surfactant concentration is very low. These hydrodynamics-controlled emulsions usually have poor stability, however, and are not of much practical importance.

Other Stabilizing Agents for Emulsions

Particle-stabilized emulsions can become extremely long-lived and are, therefore, of considerable industrial interest (Chapter 18, see for instance Figure 18.22). They are, for instance, widely used for food applications. Proteins that have precipitated around their isoelectric point and triglyceride crystals are examples of edible particles useful for the purpose. One well-known example is homogenized milk, where casein is deposited on the surface of the fat globules. Particle stabilized emulsions are also frequently used in the cosmetics field. For technical applications, hydrophobized silica nanoparticles are often employed. The particle stabilized emulsions are commonly referred to as *Pickering emulsions* after S.U. Pickering, who described the phenomenon in 1907. (The effect had actually been recognized by W. Ramsden a few years earlier.)

Formation of lamellar liquid crystalline layers around the emulsion droplets also renders emulsions with an extremely high stability (Figure 18.23), illuminating the close connection between emulsion stability and phase behavior.

Emulsions can be Very Concentrated

Most technical emulsions have a concentration of dispersed phase in the range 25–50%. The viscosity experienced by each individual particle is the same viscosity as that of the continuous phase, whereas the viscosity of the emulsion as a whole is much higher, as illustrated in Figure 19.6. Since a high viscosity of the continuous phase is advantageous for emulsion stability, it is common practice to add a polymer or some other additive that increases the viscosity of this phase.

For emulsions of monodisperse droplets, 50% disperse phase means rather close packing of the particles. In many cases the particles in such emulsions may, in fact, reside in the secondary minimum (Figure 18.7). The theoretical maximum for random packing of spheres is 64 vol% internal phase and for hexagonal packing the value is 74 vol%. Nevertheless, emulsions can contain far above 90 vol% disperse phase. For spherical droplets, this requires a broad distribution of droplet sizes so that smaller droplets can fill the spaces between larger ones.

One technically important example of such concentrated emulsions is emulsion explosives. These are w/o emulsions containing around 90% water in which ammonium nitrate is dissolved. Ammonium nitrate oxidizes the surrounding hydrocarbon oil to give carbon dioxide, water, and nitrogen, all gaseous components that require a large volume.

In extreme cases emulsions can have 99% disperse phase. Such concentrated emulsions are “gel-like” and their structure resembles that of concentrated foams with a polyhedral rather than a spherical structure of the droplets/air bubbles (Figure 24.8a). There are two factors that may contribute to the stabilization of concentrated w/o emulsions. The first is the fact that the dispersed aqueous phase contains a salt that is insoluble in the organic phase that separates the aqueous domains. This gives stabilization against Ostwald ripening because when water diffuses from the small domains to the larger ones the salt concentration in the small domains increases, creating a driving force back (see Chapter 18 on Ostwald ripening). The second stabilizing contribution is that salts increase the refractive index of the aqueous phase, which may then approach that of the oil phase. According to Lifshitz’s theory the attraction (A) between two bodies is at minimum when the refractive indexes of the droplets match that of the medium:

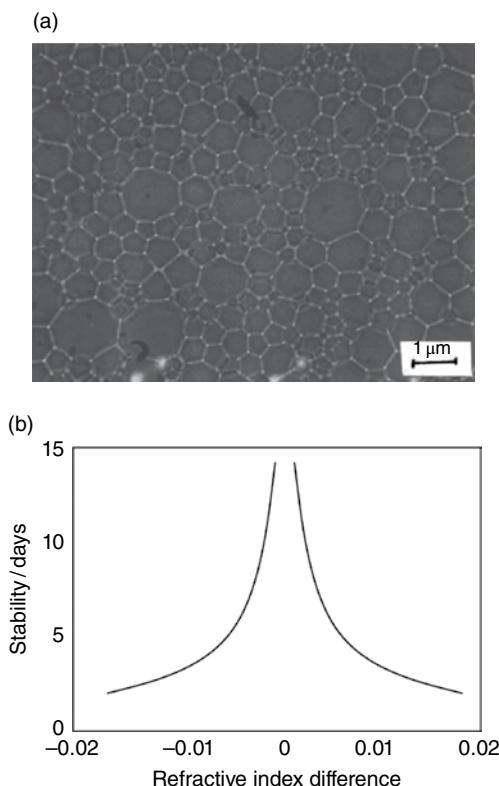


Figure 24.8 (a) In extremely concentrated emulsions the structure resembles that of a dry foam. (b) The stability (given in days before complete phase separation) of a concentrated w/o emulsion versus the refractive index difference between the dispersed and the continuous phase. (With permission from Kizling, J. and Kronberg, B. (1990) On the formation and stability of concentrated water-in-oil emulsions, a phrons. Colloids and Surfaces, **50**, 131–140 and Kizling, J. and Kronberg, B. (2001) On the formation of concentrated stable w/o emulsions. Advances in Colloid and Interface Science, **89–90**, 395–399. Copyright Elsevier.)

$$A = a \left(\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right) + b \frac{(n_1^2 - n_2^2)^2}{(n_1^2 + n_2^2)^{3/2}} \quad (24.1)$$

where n_i and ε_i are the refractive index and the dielectric constant, respectively, of phase i and a and b are constants. In the concentrated w/o emulsions the refractive index of the aqueous phase can be varied by the salt concentration and by the type of ions. Even water-soluble organics, such as glycerol, can be used to increase the refractive index of the aqueous phase. Transparent emulsions are obtained when the refractive indexes of the aqueous phase and the oil match. The stability of concentrated w/o emulsions as a function of the refractive index difference between the aqueous and oil phases is illustrated in Figure 24.8b. Here the salt concentration increases when going to the right in the diagram. The figure clearly shows that the stability increases drastically as the refractive indexes of the dispersed phase and the continuous phase approach the same value.

Spontaneous Emulsification

One way to make emulsions of very small droplets in a continuous phase, so-called miniemulsions, is to use the concept of *spontaneous emulsification*. A *miniemulsion*, sometimes referred to as a *nanoemulsion*, is a system that contains droplets in the size range of 50–300 nm. The concept should not be mixed up with that of a *microemulsion*. Whereas a microemulsion is thermodynamically stable, a miniemulsion, like a regular emulsion, is not thermodynamically stable and will sooner or later undergo phase separation.

One mechanism behind spontaneous emulsification is shown in Figure 24.9. The system consists of hexadecane, water, the nonionic surfactant $C_{12}E_6$, and an alcohol, *n*-octanol, which can be seen as a cosurfactant. Large drops of some 100 μm in diameter, containing oil, surfactant, and cosurfactant, are injected into water. The temperature is kept above the PIT, which means that the surfactant prefers the oil phase and that a reversed curvature, that is, w/o, is favored. Water diffuses into the drops and the cosurfactant diffuses out into the water. A water-in-oil microemulsion forms inside the drops and continued diffusion of water into the drops and of *n*-octanol out of the drops transforms the w/o microemulsion into a bicontinuous system. Almost all the surfactant remains in the drops. The increasing ratio of surfactant to cosurfactant in the drops makes the drop interior increasingly more hydrophilic. At one point the microemulsion cannot solubilize all the oil. Instead, oil droplets start to form and the large drops now consist of a microemulsion coexisting with these droplets. Eventually the microemulsion disappears and only oil droplets remain. Spontaneous emulsification can occur in different types of system and a common denominator of most of them is that the creation of the small oil droplets is due to spontaneous diffusion of components in the system across interfaces. It has been claimed that one of the formation mechanisms requires transient local negative values of interfacial tension, but this has been difficult to verify experimentally.

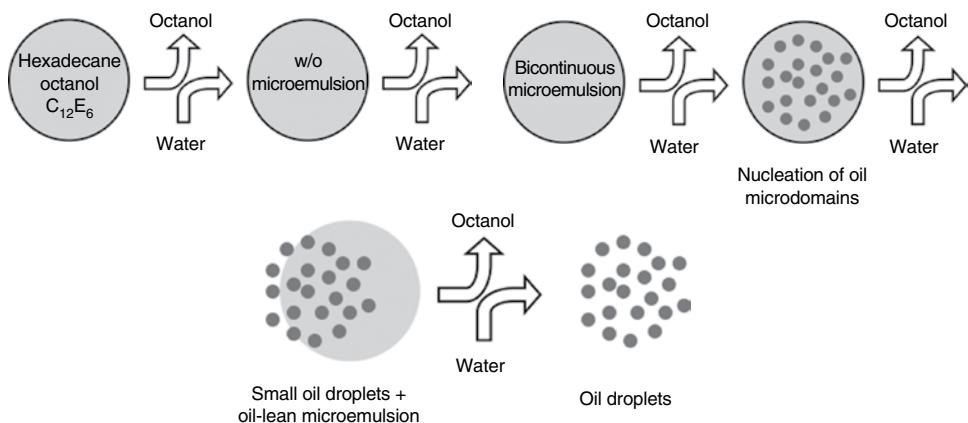


Figure 24.9 Spontaneous emulsification initiated by addition of large drops of a mixture of hexadecane, n-octanol and the nonionic surfactant $C_{12}E_6$ to water. See text for explanation of the process. (Reproduced with permission from Rang, M.J. and Miller, C.A. (1998) Spontaneous emulsification of oil drops containing surfactants and medium-chain alcohols. Progress in Colloid and Polymer Science, **109**, 101–117. With kind permission from Springer Science+Business Media.)

Ouzo Emulsions

Emulsions of o/w type are normally formed by disintegration of an oil component into small fragments in water, a kind of top-down process. Such emulsions may also be produced by a bottom-up process. The self-emulsification process described above can be regarded as an example of that but an even more genuine example of a bottom-up procedure for making o/w emulsions is the so-called *Ouzo procedure*, named after the Greek alcoholic drink. Ouzo is a transparent liquid that becomes turbid when mixed with water. An emulsion has formed without any input of mechanical energy. Another name for the Ouzo process is *the solvent shifting process*.

The principle of the Ouzo procedure is the following. A hydrophobic substance, such as hexadecane, is dissolved in a water-miscible solvent, for example, ethanol, and a surfactant is added. The surfactant needs to be hydrophilic in order for an o/w emulsion to form (see the previous discussion about Bancroft's Rule). This solution is poured into an excess of water. The hexadecane will not be soluble in the water–ethanol mixture and will form oil nuclei in the solution. These will grow into small oil droplets that will be stabilized by the surfactant and the size of the droplets will depend on the hexadecane-to-surfactant ratio. The procedure is illustrated in Figure 24.10.

Emulsions made in this way can be very uniform in size, which means that Ostwald ripening (Chapter 18) can be suppressed. A drawback of the procedure is that the emulsions need to be very dilute in order to have reasonable stability. Nevertheless, the procedure is of interest for emulsions in the pharmaceutical and cosmetics fields, where hexadecane is replaced by a hydrophobic active substance. In real Ouzo both the hydrophobic substance and the amphiphile are natural ingredients in anise.

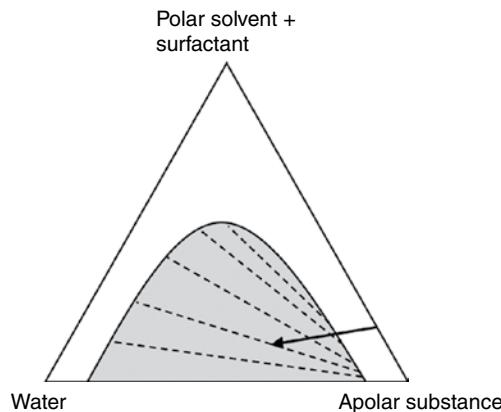


Figure 24.10 An ouzo emulsion is made by adding water to a solution of an apolar substance and a surfactant in a polar solvent. The arrow illustrates the dilution path. The tie-lines in the (dark) two-phase region show the composition of the two phases formed

Other Types of Emulsions

Nonaqueous emulsions also exist. In such systems the two organic liquids need to have very different polarity. The apolar component may be the continuous phase, such as in dimethylformamide-in-hydrocarbon emulsions. The polar component may also be the continuous phase and examples include hydrocarbon in formamide or in dimethylsulfoxide emulsions. Polymeric surfactants are particularly efficient in stabilizing these systems. Fluorocarbons are generally not compatible with hydrocarbons and fluorocarbon-in-hydrocarbon emulsions exist.

There are also examples of emulsions of two aqueous phases. In such systems the two phases are normally solutions of two different polymers, such as dextran and poly(ethylene glycol) (the phase diagram in Figure 9.11). The formation of emulsions in such systems is based on the fact that aqueous solutions of different high molecular weight polymers normally undergo segregative phase separation (page 191).

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25

Microemulsions for Soil and Oil Removal

A Detergent Formulation is Complex

Removal of soil from fabric, that is, detergency, is a complex process involving interactions between surfactants, soil, and the textile surface. The choice of surfactant is the key to success and surfactant-based cleaning compositions are one of the oldest forms of formulated products for both household and industrial use. The traditional surfactants are sodium and potassium salts of fatty acids, made by saponification of triglycerides. Soaps are still included in small amounts in many detergent formulations, in particular as foam depressants, but the bulk surfactants in detergents of today are synthetic nonionics and anionics with alcohol ethoxylates, alkylaryl sulfonates, alkyl sulfates, and alkyl ether sulfates being the most prominent.

The soil present on fabric may vary widely and different mechanisms are responsible for removal of different types of soil components. The term oily soil refers to petroleum products, such as motor oil, and vegetable oil, for example, butter, but also skin sebum. Surfactants play a key role in removing oily soil, as will be discussed in this chapter, but hydrolytic enzymes, which are present in most detergent formulations today, are important for hydrolysis of triglycerides, proteins, and starch.

Some stains, such as those from tea and blood, may be difficult to remove even with optimized surfactant–enzyme combinations. Bleaching agents are often effective in eliminating these spots. They normally act by oxidizing the stain chromophores into noncolored products which may, or may not, be removed by the action of surfactant.

A detergent formulation also contains a large amount of so-called “builders,” such as zeolite or phosphate, which function as sequestering agents for divalent ions, thus preventing surfactant precipitation as calcium or magnesium salts in areas of hard water.

Other additives are antiredeposition agents, fluorescing agents, perfumes, and so on. The antiredeposition agents are interesting from a surface chemistry point of view. They are usually anionic polyelectrolytes and they act as dispersants for the released soil in the washing solution. In doing so they prevent the soil from resettling on the fabric, which is very important for the washing result. Carboxymethylcellulose is a commonly used antiredeposition agent.

In the following, the discussion is focused on the action of surfactants on oily soil but a brief description of how surfactants work on particulate soil is also given. The need for builders, the action of enzymes on triglyceride soil, the bleaching, and so on, lie outside the scope of the topic.

Particulate Soil Removal

Soil attached to a fabric or some other surface is often subdivided into particulate soil and oily soil. Surfactants are useful for the removal of both types of soils but the mechanisms are completely different. Particulate soil usually comes off more or less spontaneously if both the particle and the surface carry a negative net charge, which is often the case. If the two surfaces have opposite charges, detachment of the particles is not so facile. However, a simple and often useful approach is to raise the pH of the surrounding water. Increasing the pH may deprotonate neutral functional groups, such as carboxylic or phenolic groups, at the surfaces. It may also transform positively charged ammonium groups into neutral amino groups. Thus, treatment with alkali is a way to induce a negative net charge on both surfaces, which greatly simplifies the removal of the particles. Alumina particles attached to textile fibers is a typical example. Alumina has an isoelectric point in the range 7–8. During normal washing condition the mineral will be negatively charged and will easily desorb from negatively charged fiber surfaces.

The mechanism by which a charged particle desorbs from a surface of similar charge should not be referred to as charge repulsion. As discussed in some detail in Chapter 3, the process is driven by the entropy of the counterions. When there are negative charges both on the substrate and on the attached particles, there will be an accumulation of positively charged counterions in and around the contact zone. This will lead to an osmotic flow of water into that zone which, usually with the help of some mechanical energy, will cause the particles to desorb. This is exactly the mechanism behind “electrostatic stabilization” of dispersed systems, as discussed in Chapters 18 and 21.

Problems often arise when hydrophobic particles are attached to a relatively hydrophobic surface. Carbonaceous particles, for example, originating from incomplete fuel combustion, attached to a synthetic textile fiber is a typical example. Elevated pH is usually not enough to remove such particles. However, an anionic surfactant may be very useful. The surfactant will adsorb in a monolayer at the surfaces of the particles as well as the substrate, rendering both highly negatively charged. Water, driven by an osmotic force, will flow into the region between the particles and the substrate, and this flow will often be sufficient to make the particles detach (Figure 25.1).

Thus, anionic surfactants are particularly efficient for removing oily soil and the effect is due to the increased counterion entropy. Cationic surfactants can also be used for this purpose although the risk of redeposition of the detached particles, which will be positively

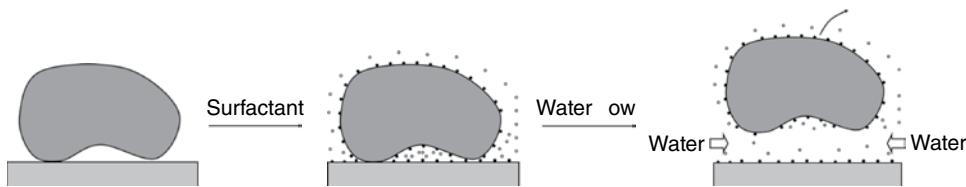


Figure 25.1 Addition of an anionic surfactant will induce negative charges on the surfaces of attached hydrophobic particles and a hydrophobic substrate. The high concentration of counterions in the contact region will induce an osmotic flow that may cause the particles to detach

charged, may then be larger because many surfaces carry a net negative charge. In principle, nonionic surfactants can also give the same effect and the flow of water, which will cause particle detachment, will then be driven by a high concentration of polyoxyethylene chains in the region between the particles and the substrate, an effect related to *steric stabilization* of dispersed systems, discussed in Chapters 18 and 21.

Oily Soil Removal

Removal of the other type of soil, oily soil, is more complex. If the soil is attached to a very hydrophilic surface, the removal is usually easy because of poor wetting (high contact angle, Chapter 20), which leads to poor adhesion between the soil and the substrate. Mechanical action alone may be sufficient for the detachment.

If the substrate is moderately hydrophilic giving a contact angle for the oily soil of around or above 90° , a surfactant is usually needed in order to make the soil detach. The mechanism is then similar to the one discussed above for removal of hydrophobic particles from a relatively hydrophobic surface. The surfactant will enter the crevices between the soil and the substrate and adsorb at both surfaces. The resulting osmotic flow may act to detach the soil, just as in the case of particulate soil discussed above. This detachment principle, sometimes referred to as the “roll-up mechanism,” is shown in Figure 25.2. A common example where the roll-up mechanism applies is removal of oily soil from cotton fibers.

If the substrate is hydrophobic the oily soil may wet the surface, that is, the contact angle will be low. This is typically the case for oily soil on polyester and other more apolar fabrics. Then the roll-up mechanism discussed above will not be important. Instead, the removal is based on achieving a low interfacial tension between the oil and the surrounding water. Thus, the action by the surfactant will then be on the oil–water interface, and the surfactant adsorption at the substrate–water interface will be less important for the soil removal.

If a low enough interfacial tension can be achieved by the action of surfactant, the soil may be removed by two different mechanisms, which are independent of each other but which may work in parallel. Both are independent of the nature of the fabric:

1. Emulsification (Figure 25.3).
2. Solubilization (Figure 25.4).

According to the emulsification mechanism the low interfacial tension, together with mechanical agitation, induces a deformation of the soil patches. One may draw a parallel

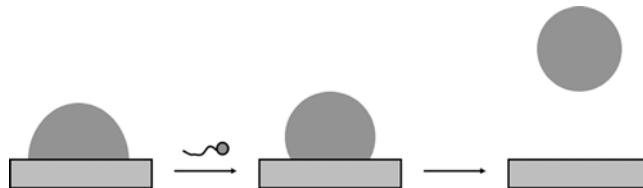


Figure 25.2 The roll-up mechanism for removal of oily soil from a moderately hydrophilic substrate. See text for discussion



Figure 25.3 The emulsification mechanism of removal of oily soil from a substrate. The surfactant acts on the oil–water interface and the soil leaves the surface as a surfactant-stabilized drop



Figure 25.4 The solubilization mechanism of removal of oily soil from a substrate. The surfactant acts on the oil–water interface and the soil becomes solubilized in a microemulsion that is generated around the surface of the soil

to the pendant drop method for measuring interfacial tension (page 247). The lower the interfacial tension, the more elongated the drop. At some point the elongated oil patch becomes “necked” and an oil drop, stabilized by a monolayer of surfactant, leaves the substrate. There are often small patches of oily soil remaining on the substrate, as illustrated on the figure, and this accounts, at least partially, for the gradual graying of many white textiles on repeated washing. (Another reason for graying is redeposition of soil on the fabric.)

Whereas the emulsification mechanism requires mechanical action, soil removal according to the solubilization mechanism is a spontaneous event (even if the convection induced by agitation may speed up the process). This is the reason why removal of oil from a porous rock, that is, the enhanced oil recovery (EOR) process that goes under the name of surfactant flooding, only relies on the solubilization mechanism. Down in the reservoir the mechanical energy input is probably not sufficient to remove oil by the emulsification mechanism.

The solubilization process involves *in situ* formation of a microemulsion. To obtain maximum efficiency the surfactants, often a mixture of a nonionic and an anionic amphiphile, should generate a bicontinuous microemulsion. This bicontinuous microemulsion will then be in equilibrium with the oily soil and with the surrounding washing water. Thus, this is a

practical example of a Winsor III system (page 316), but the middle-phase microemulsion is extremely small compared to the sizes of the two excess phases. The generation of a microemulsion, which should preferably have a bicontinuous microstructure and in which the soil constitutes the oil component, is exactly the same as in EOR, which is discussed at the end of this chapter.

As discussed in some detail in Chapter 17, the key for creating a three-phase system with a middle-phase microemulsion in equilibrium with excess oil and water is to have an amphiphile system that, under the conditions used, has a critical packing parameter, CPP, around one. This applies to all types of surfactants and, as was also discussed in Chapter 17, for ionic surfactants the CPP can be adjusted by addition of electrolytes, while for nonionic surfactants based on a polyoxyethylene head group temperature is the parameter that is primarily used for fine-tuning. In the following the concept will be illustrated for nonionic surfactants but the same reasoning can be applied to anionic and cationic surfactant-based systems.

How can the Low Interfacial Tension Be Achieved?

The oil–water interfacial tension is at minimum at the phase inversion temperature (PIT, Chapter 24) of an oil–water–surfactant system. When applied to oily soil removal, the soil constitutes the oil component of the ternary system.

Nonionic surfactants are often characterized by their cloud points (Chapter 7). However, the cloud point value, which is given for a surfactant, does not take into account the presence of the oil. It is important to realize that it is the PIT of the oil–water–surfactant system, and *not* the cloud point of the aqueous surfactant solution, that is the temperature of relevance for solubilization. What correlation is there then between the cloud point and the PIT?

1. For an oil that penetrates the surfactant hydrocarbon layer, the effect of adding oil to a micellar solution of surfactant will be that the hydrocarbon volume (v) in the expression $\text{CPP} = v/(a \ell_{\max})$ (Chapter 6) increases. The CPP will increase and the change in geometry will be manifested as a shift toward more elongated micelles (Figure 25.5).
2. Oils that do not enter into the surfactant hydrocarbon layer will form an oil core in the micelle. As shown in Figure 25.6, this will lead to increased area per surfactant head group, that is, to an increase in a , which, in turn, means a decrease in the CPP. The effect on micelle geometry will be that of a shift toward a more spherical aggregate.

Small oil molecules generally penetrate and mix with the surfactant hydrocarbon chains while large oil molecules do not. For straight-chain aliphatic oils and straight-chain surfactants, oil molecules of chain lengths smaller or equal to that of the surfactant hydrocarbon tail tend to mix well. Longer chain length oils form a separate core.

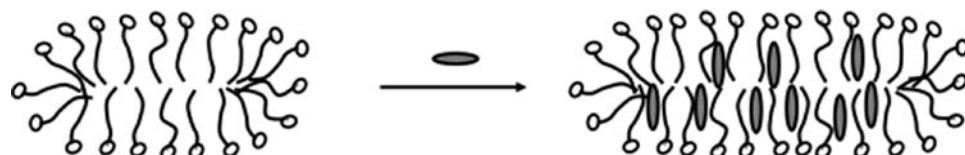


Figure 25.5 Solubilization of a small hydrocarbon oil that can penetrate the surfactant hydrocarbon region leads to elongation of the micelles

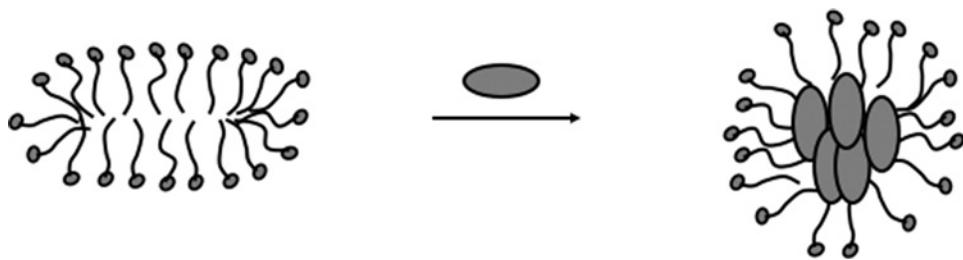


Figure 25.6 Solubilization of a large hydrocarbon oil that cannot enter into the surfactant hydrocarbon region leads to more spherical micelles because the oil incorporated forms a core

Figure 25.7 illustrates the effect on the cloud point of addition of a low molecular weight aliphatic hydrocarbon. As can be seen, there is a substantial drop in the cloud point, which is consistent with the view that the added hydrocarbon penetrates into the surfactant tail region, leading to an increase in the CPP value. At high amounts of added hydrocarbon, there is a cloud point increase that indicates saturation of the surfactant tail region, forcing excess oil to form a micelle core.

The effect on the cloud point of addition of a high molecular weight aliphatic hydrocarbon is shown in Figure 25.8. The hydrocarbon does not mix with the surfactant tail region and the almost linear increase in the cloud point correlates with the increase in a and decrease in the CPP value discussed above.

To summarize, in order to obtain maximum solubilization, washing should be done at a temperature corresponding to the PIT of the oil–water–surfactant system, in which the oily soil constitutes the oil. When the oil molecules are larger than the surfactant tail (which is the normal situation), the PIT is higher than the cloud point. As an example, the best result in removing motor oil stains (with cleaning formulations based on nonionic surfactant) is often obtained at some 20°C above the surfactant cloud point. At this temperature the surfactant–water mixture present in the initial washing bath is typically a dilute dispersion of a lamellar

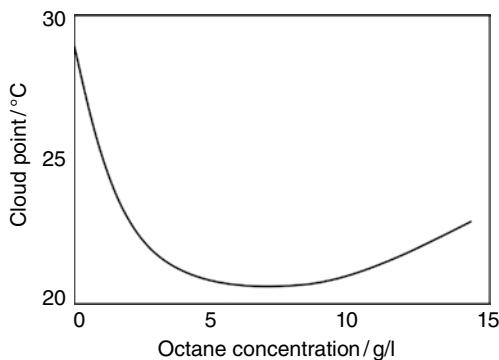


Figure 25.7 Effect on the cloud point of a nonionic surfactant of the addition of a low molecular weight hydrocarbon, octane

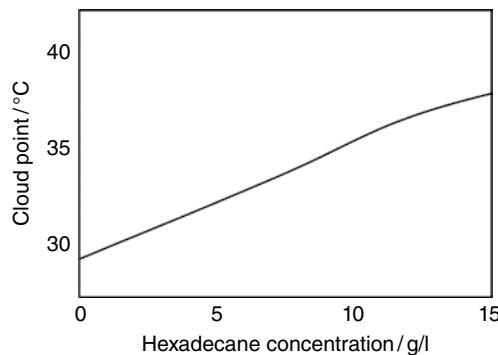


Figure 25.8 Effect on the cloud point of a nonionic surfactant of the addition of a high molecular weight hydrocarbon, hexadecane

liquid crystalline phase in water. For removal of oils of a chain length smaller than that of the surfactant tail, washing should be done at a temperature below the surfactant cloud point.

In the discussion above, temperature has been used as the variable to obtain maximum oil solubilization. The other parameter that can be used to optimize cleaning efficiency is the choice of surfactant. Particularly in the case of fatty alcohol ethoxylates, the surfactant can be fine-tuned to meet a specific need. The two parameters, temperature and choice of surfactant, are, of course, interrelated. Washing at 40 and 60°C requires different surfactants for optimum results.

In the real situation, the oil, that is, the dirt, is not a variable (unless the cleaning formulation contains hydrocarbon, in which case we have a microemulsion cleaning formulation; page 458). In a model experiment one may, however, vary the oil while keeping temperature and choice of surfactant constant. Figure 25.9 shows that a distinct minimum in the oil–water interfacial tension is obtained for a specific oil molecular weight. For that specific oil, the temperature used in the experiments corresponds to the PIT of the system (compare with Figure 25.18).

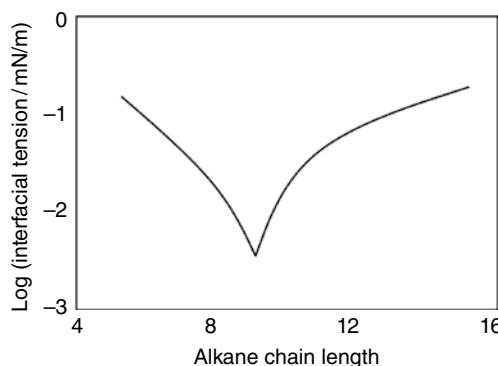


Figure 25.9 Effect of hydrocarbon chain length on the oil–water interfacial tension for a system based on a nonionic surfactant

Oil Solubilization around the PIT Leads to the Formation of a Microemulsion

Solubilization of an oil at a temperature close to the PIT of an oil–water–surfactant mixture usually gives a three-phase system in which a microemulsion is in equilibrium with excess oil and water. (If enough surfactant is present, the whole mixture will be transformed into a microemulsion, but such high surfactant concentrations are not used in normal textile cleaning.) The middle-phase microemulsion, which invariably has a bicontinuous structure (Chapter 17), exhibits an extremely low interfacial tension toward both oil and water. Once formed through oil solubilization, such a system is, therefore, very efficient in solubilizing more oil. Formation of a middle-phase microemulsion in oily soil removal can be directly observed by video microscopy. As is often the case with microemulsions, a lamellar liquid crystalline phase may coexist with the microemulsion. Also this four-phase system—excess oil, microemulsion, liquid crystalline phase and water—can be observed by using the video technique. It can be seen how the two intermediate phases grow rapidly by solubilization of the oil.

If the washing temperature is considerably below the PIT, no three-phase system with a middle-phase microemulsion will be formed. Instead, an oil-in-water microemulsion in equilibrium with excess oil will be obtained. Such a microemulsion will have higher interfacial tension toward oil and the rate and capacity of oil solubilization will not be as good as for the bicontinuous middle-phase microemulsion.

If, on the other hand, washing is performed well above the PIT, a water-in-oil microemulsion in equilibrium with excess water will form. Such conditions often give poor detergency, since the surfactant is now highly oil soluble and may dissolve into the oil rather than acting to remove it from the fabric. When the surfactant partitions into the oil it brings water along in the form of small droplets. In the video microscopy experiments this can be seen as a swelling of the oil phase. Moreover, when washing is made far above the PIT, redeposition of the dirt, in the form of a water-in-oil emulsion or microemulsion, is often a problem.

A more detailed discussion about microemulsion phase behavior is given in Chapter 17, and Figure 17.3 shows the phase behavior of a system based on nonionic surfactant at temperatures below, at and above the PIT. The PIT is where the system is completely balanced, that is, where there is a middle-phase microemulsion that is in equilibrium with equally large oil and water phases (assuming that the system contains equal volumes of oil and water). Figure 25.10 illustrates the importance of a well-balanced system for oily soil removal. For the two nonionic surfactants, $C_{12}E_4$ and $C_{12}E_5$, optimum detergency occurs at the temperature at which the ternary system surfactant–hydrocarbon soil–water forms a three-phase system.

In determining the PIT for the surfactant–oily soil–water system a very high surfactant-to-oil ratio should be used in order to mimic the washing situation. It should also be taken into account that salts, including the detergent builders, normally decrease the PIT.

Polar Components in the Soil Affect Phase Behavior

In the discussion above, only pure hydrocarbon soil has been considered. In the real situation the soil is seldom entirely nonpolar, however. Polar, but still water-insoluble, components of various types, for example, fatty acids, fatty alcohols, and alkyl phenols, are common

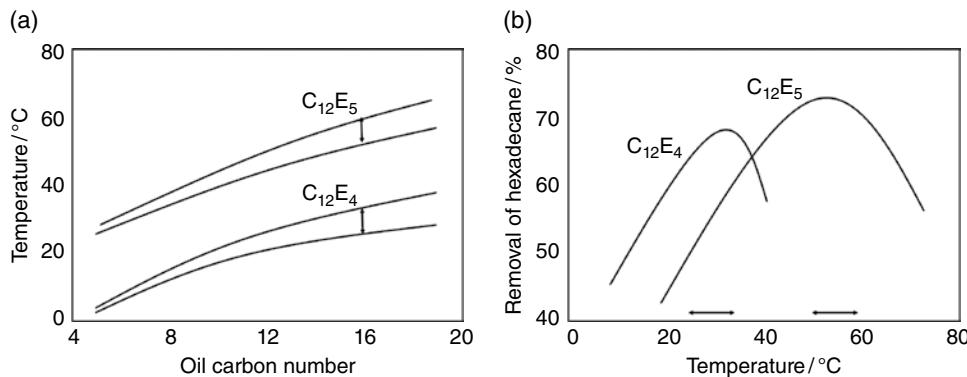


Figure 25.10 (a) The phase behavior of the systems $C_{12}E_5$ -hydrocarbon-water and $C_{12}E_4$ -hydrocarbon-water corresponds well with the efficiency in removing oily soil. The regions between the lines for the two surfactant systems are the temperature intervals where a middle-phase microemulsion exists. (b) The cleaning results relate to hexadecane removal but similar good correlations are obtained also for other hydrocarbons. (With permission from Stickdorn, K., Schwuger, M.J. and Schomaecker, R. (1994) Microemulsions for technical applications. Tenside Surfactants, Detergents, **31**, 4–12. Copyright 1994, Carl Hanser Verlag GmbH & Co. KG.)

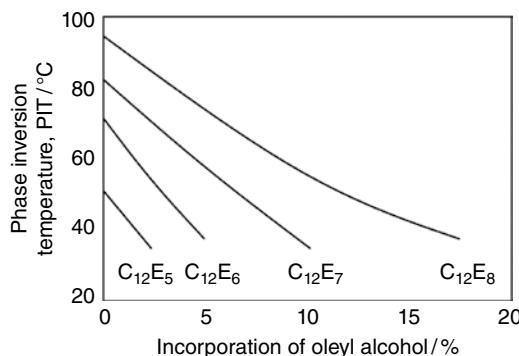


Figure 25.11 Effect of addition of oleyl alcohol to $C_{12}E_n$ -hexadecane-water systems on the PIT of the system. The percentage of oleyl alcohol given is the percentage in the soil (hexadecane). The surfactant-to-hexadecane ratio is kept constant at 0.05. (With permission from Raney, K.H. and Benson, H.L. (1990) The effect of polar soil components on the phase inversion temperature and optimum detergency conditions. Journal of the American Oil Chemists' Society, **67**, 722–729. Copyright © 1990, Springer.)

ingredients in many oily soils. Such polar substances will form mixed assemblies with the surfactants in the systems and, in doing so, they will increase the CPP value of the mixture. This will lead to a reduction in the PIT. The effect on PIT can be considerable if the amount of polar component is large, as is seen in Figure 25.11.

In practice, the soil is seldom uniform. Different spots of oily soil may have different PITs, which means that different washing temperatures are best for the different soil spots. The

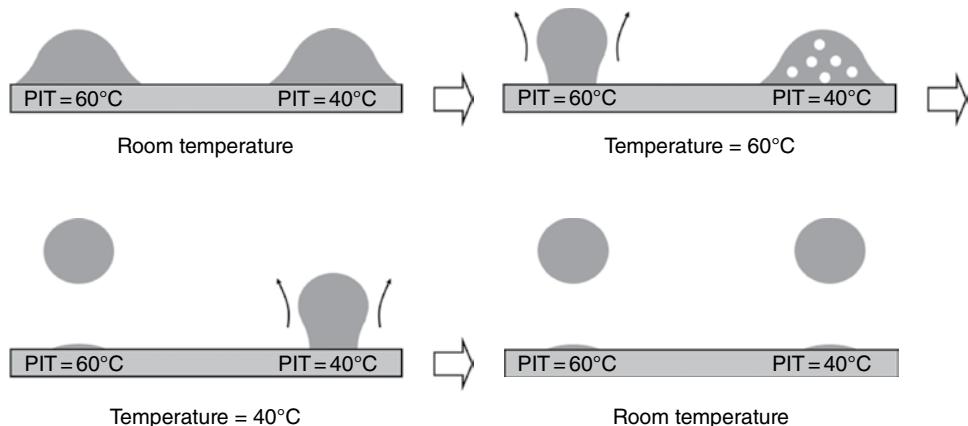


Figure 25.12 Removal of two oil spots that have different PITs. See text for discussion

situation is illustrated in Figure 25.12. In this figure there are two oil spots, one with a PIT of 40°C and one with a PIT of 60°C. If washing is first made at 60°C the spot with matching PIT may be efficiently removed but the other spot may grow in size because of incorporation of water in the form of small droplets. The surfactant that gives a PIT of 40°C is much too hydrophobic at 60°C and prefers to go into the oil where a w/o microemulsion is generated. This is equivalent to formation of a Winsor II system (Figure 17.2). If the temperature is subsequently reduced to 40°C, also the spot that has a PIT of this temperature will be removed.

Removal of Triglyceride Soil is Difficult

Triglycerides are generally much more difficult than hydrocarbons to remove by surfactant action. The reason for the poor detergency with triglyceride soil may partly be related to specific interactions between the slightly polar oil and the fabric surface, but the main reason is undoubtedly related to the fact that triglycerides are not readily solubilized. It is generally difficult to obtain microemulsions with large and slightly polar oil components, such as triglycerides. With normal nonionic surfactants of the fatty alcohol ethoxylate type almost no microemulsion regions can be found. Instead, lamellar and sponge phases appear (Chapter 6), both of which solubilize only small amounts of oil. The interfacial tensions between these phases and either oil or water are not very low.

One way to facilitate the formation of microemulsions of triglyceride oils is to add a medium-chain alcohol as cosurfactant. With such formulations microemulsions can be obtained as long as the concentrations of both the surfactant and the cosurfactant are relatively high. In practice, however, such high loading of a volatile alcohol to a washing formulation is not feasible.

Addition of a cosurfactant improves solubilization partly by increasing the CPP value and partly by disturbing the ordering of the surfactant hydrocarbon tails at the oil–water interface. Another way to attain this dual effect is to use a branched-chain surfactant instead of the usual straight-chain compound. With branched-tail nonionics, such as secondary alcohol ethoxylates, a moderately large microemulsion region can be obtained. This leads

to effective triglyceride soil removal, most certainly by an emulsification–solubilization mechanism, provided that a composition is chosen so that washing occurs close to the PIT of the system. Triglycerides generally give PITs far above the cloud point of nonionic surfactants, which means that in this respect they behave as large hydrocarbon oils, such as hexadecane (Figure 25.8). As an example, the PIT for the system $C_{12}E_5$ –triolein–water is around 65°C and the cloud point for $C_{12}E_5$ is around 30°C.

Fortunately, under real washing conditions triglyceride soil removal is facilitated by the action of other detergent components. As mentioned in the first section of this chapter, the triglycerides are hydrolyzed during the washing process, either by saponification due to the high pH of the washing solution or by the action of lipases. The generated mono- and diglycerides, as well as the fatty acid soap formed, are polar lipids, which are easily removed and which may assist in solubilizing remaining triglycerides.

Mixtures of Surfactants are Often Used

The discussion above has focused on nonionic surfactants. However, the same principles can be applied to other surfactant types, although for ionic surfactants the phase behavior is adjusted by variation of the electrolyte concentration rather than by temperature. Most of the common anionics tend to be too hydrophilic, that is, have too small a CPP value, to give efficient soil removal by the emulsification–solubilization mechanisms. However, by combining them with a hydrophobic fatty alcohol ethoxylate, or even a fatty alcohol, or by washing at high salt concentrations, excellent detergent action can be obtained.

The observation that a mixture of two surfactants often gives better detergency than either of the two used alone is sometimes referred to as a synergistic effect. However, it need not be that the mixture has a lower CMC than either of the two individual surfactants, which, as was discussed in Chapter 13, is the definition of synergism of a surfactant mixture. In most cases, as with a combination of a hydrophilic anionic surfactant and a hydrophobic nonionic surfactant, it is merely the result of the mixture having a CPP value close to one and the individual components either being too hydrophilic, that is, having too low a CPP, or too hydrophobic, that is, having too high a CPP.

Monitoring Soil Removal

The traditional methods to study soil removal under controlled conditions include reflectance measurements (“whiteness”) by the use of a launderometer, radioactive determinations of remaining soil and direct optical probing of the amount of surface-adsorbed soil. More recently other surface analysis techniques have become important in laboratory experiments. By ellipsometry, which is an optical technique that records the dielectric properties of thin films at surfaces, it is possible to measure *in situ* the amount of soil at a surface with a submolecular resolution. This technique is useful for monitoring the amount of soil remaining on a solid surface as a function of time of exposure to a surfactant solution. Quartz crystal microbalance (QCM) is another useful technique for the purpose. QCM is a gravimetric method, that is, it monitors the weight and the change of the weight, of adsorbed material on a surface. This means that with QCM one detects also the water incorporated in a surface film. This is very useful for monitoring events of the type discussed in relation to Figure 25.12. Additional information comes from

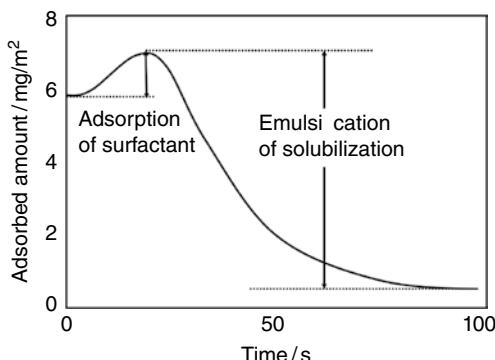


Figure 25.13 Monitoring the soil removal process by ellipsometry or QCM

including dissipation monitoring in the measurements (QCM-D). The dissipation gives information about the viscoelastic properties of the adsorbed soil at the surface.

Figure 25.13 shows an example of a soil removal experiment performed with ellipsometry or QCM. The starting surface is one with an adsorbed layer of oily soil. Initially, there is a slight increase in the amount of substance on the surface, corresponding roughly to adsorption of a surfactant monolayer. As emulsification and/or solubilization proceeds, the total amount of material on the surface gradually decreases. Eventually a surfactant monolayer may be obtained at the surface. Extensive rinsing will give a totally clean surface.

Microemulsion-Based Cleaning Formulations are Efficient

So far, this chapter has dealt with *in situ* formation of a microemulsion during the washing process. This relates to the process that occurs in a normal washing machine and the oily soil constitutes the oil component of the microemulsion that is generated. However, a cleaning formulation may also be a ready-made microemulsion. Microemulsions, being microheterogeneous mixtures of oil, water, and surfactant, are excellent solvents for nonpolar organic compounds as well as for inorganic salts. The capability of microemulsions to solubilize a broad spectrum of substances in a one-phase formulation has been found useful for cleaning of hard surfaces—dirt is often a complex mixture of hydrophilic and hydrophobic components. Of particular interest from a practical point of view is the possibility of replacing formulations based on halogenated or aromatic hydrocarbons with microemulsions containing nontoxic aliphatic hydrocarbons. A typical example is given in Figure 25.14.

Microemulsions, mainly based on nonionic surfactants, have an established position in industrial and institutional cleaning of hard surfaces. They are usually sold as concentrated mixtures, which are to be diluted with water before use. Hence, the isotropic domain should preferably extend to the water corner. A typical example of a suitable model system is that of $C_{12}E_6$ –decane–water, employed at 30°C, as shown in Figure 25.15. Nonionics are suitable surfactants in these formulations as they can be formulated with ionic builders such as phosphate or citrate. Such systems suffer from the drawback of considerable temperature sensitivity, however, as is also illustrated in Figure 25.15. One way to increase the temperature interval is to use a mixture of nonionics, for example, a blend of fatty alcohol

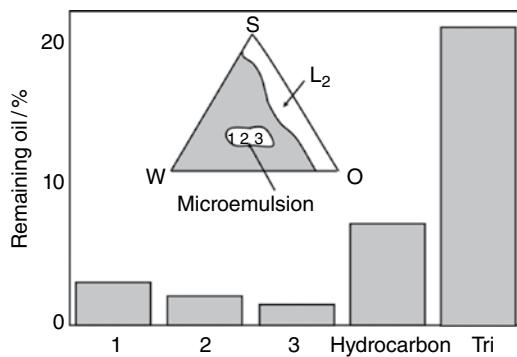


Figure 25.14 Removal of a lubricating oil from a surface by three formulations, all lying within a bicontinuous microemulsion phase, indicated in the triangular phase diagram. (L_2 denotes a reversed micellar phase.) The surfactant component (S) is a mixture of two fatty alcohol ethoxylates with a combined hydrophilic–lipophilic balance value of 10.7 while the hydrocarbon used as oil component is an aliphatic distillation fraction with a boiling point of 190–240°C. Oil removal with only the hydrocarbon used as oil component in the microemulsion and with trichloroethylene (tri) is shown for reference

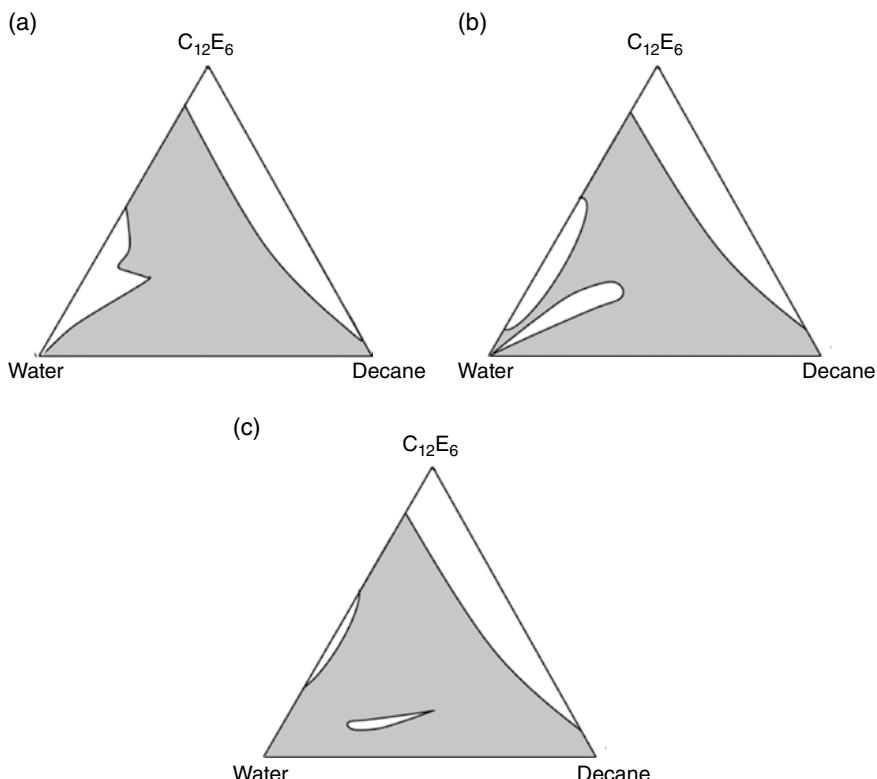


Figure 25.15 Phase diagrams for the $C_{12}E_6$ –decane–water system at (a) 30, (b) 40 and (c) 50°C. At 50°C, two small isotropic phase regions exist in the water-rich region. At 40°C, these have grown larger but are still not connected. At 30°C, one larger isotropic phase region is present in the water corner

ethoxylates with polyoxyethylene chain lengths below and above that of the optimum compound. Commercial ethoxylates have a very broad homologue distribution by themselves and give microemulsions with broader temperature regions than homologue-pure model compounds.

***In Situ* Generated Microemulsions are of Interest for Enhanced Oil Recovery**

Oil fields consist of porous rock, usually limestone or sandstone, in which the pores are filled with petroleum and brine. The porous rock formation is surrounded by impermeable rock. The permeability depends on the pore size, which is typically 50–1000 nm. In a normal oil field, 10–25% of the pore volume is occupied by brine, 55–80% by oil, and the rest is void volume. The pressure in the reservoir is normally high and the temperature is typically in the range 60–110°C.

When the first wells are dug, oil comes out under its own pressure. This spontaneous production is later supplemented by pumping action. Together, these two processes are referred to as the primary recovery. On average this stage leads to a recovery of 15–20% of the oil in place. In the next stage, the secondary recovery, water is used to sweep out additional oil. Water is pumped down the injection well and moves outwards in a piston-like fashion, thus displacing the oil. The mobilized oil is recovered via production holes, as shown in Figure 25.16. The so-called sweep efficiency is sometimes not very good, however, particularly when the oil is of higher viscosity than the displacing water. The primary and secondary recovery together often manage to recover considerably less than half of the total amount of petroleum in the reservoir.

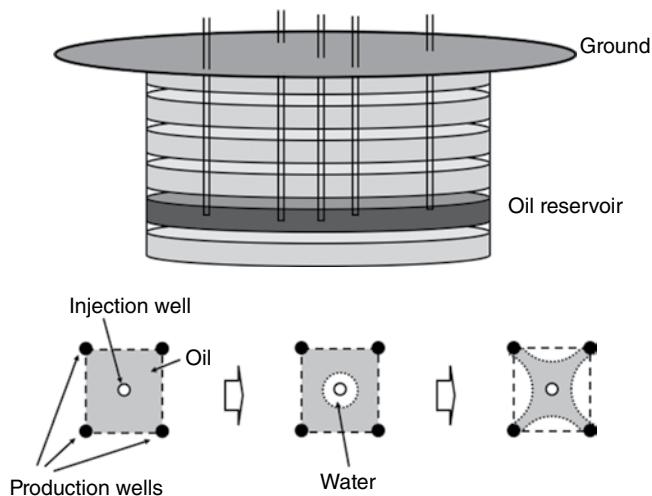


Figure 25.16 Schematic illustration of oil production

The poor yield often obtained after the water flooding step may be caused by poor wetting of the reservoir rock. Maximum oil recovery usually takes place at slightly water wet conditions. One way to adjust the wetting is to optimize the ion composition in the injected water. For example, in chalk fields water with a high content of divalent ions (Ca^{2+} , Mg^{2+} , SO_4^{2-}) is useful. For off-shore fields sea water is often the natural choice of injection water and sea water is rich in these ions. More recently it has been found that sea water depleted in NaCl but spiked with Na_2SO_4 , “smart water,” gives higher recovery after water flooding than natural sea water. Thus, the types and concentrations of ions in the injection water is a parameter of importance for the recovery.

Any oil recovery process following water flooding is referred to as EOR or tertiary oil recovery. Surfactant flooding, sometimes called microemulsion flooding, is the technique of relevance to us here. The interest in microemulsions for this purpose derives from their ability to reduce the oil–water interfacial tension to ultra-low values. During the 1970s and 1980s, very large efforts were put into the development of surfactant flooding and that research contributed very much to the general understanding of phase behavior of oil–water–surfactant systems. Since oil prices did not develop as they had been predicted to do, the interest in surfactant flooding declined from the beginning of the 1990s. In more recent years, from around 2010, the interest among the oil companies seems to have come back and there is now considerable activity in the area again.

One main reason for the inefficiency of water flooding through the reservoir rock is that oil is trapped by capillary action in the form of disconnected droplets. Figure 25.17 shows two different mechanisms for capillary trapping of oil, a snap-off process that traps oil in the wider sections of a pore and a bypass process, caused by competition of flow between pores. Snap-off occurs in pores with a large ratio between the pore body and pore throat. The wetting phase (water in Figure 25.17) forms a collar around the nonwetting phase (oil), which eventually breaks at the narrow throats. Bypassing, on the other hand, is caused by differences in pore size. Viscous forces make the fluid flow faster in the larger channels, whereas capillary forces draw the displacing phase into the smaller pores. Thus, under conditions when the flow is an imbibition process, that is, at low injection rates and low viscosity of the displacing phase, oil in the large pores will be trapped.

The amount of oil retained in the reservoir after water flooding will depend on the ratio between viscous forces trying to displace the oil and capillary forces trapping the oil in pores. A dimensionless number, the capillary number (N_c) is often used to describe the relationship between viscous and capillary forces, according to the expression:

$$N_c = \eta v / \gamma_{ow} \quad (25.1)$$

where η is the viscosity and v the velocity of the displacing fluid.

It has been experimentally shown that the residual oil saturation in the reservoir is constant below a certain value of N_c , typically in the range 10^{-4} – 10^{-5} . Normal water flooding yields N_c values below that number. Above a critical N_c the residual saturation after flooding decreases almost linearly with $\log N_c$.

Thus, the key to obtain good oil recovery is to attain a high enough N_c . In principle, an increase in N_c can be attained by (i) increasing the viscous forces (viscosity and/or velocity of the water flood), (ii) decreasing the capillary forces, or (iii) a combination of (i) and (ii). In practice, there is a limit to the increase of the viscous forces that can be employed: a high

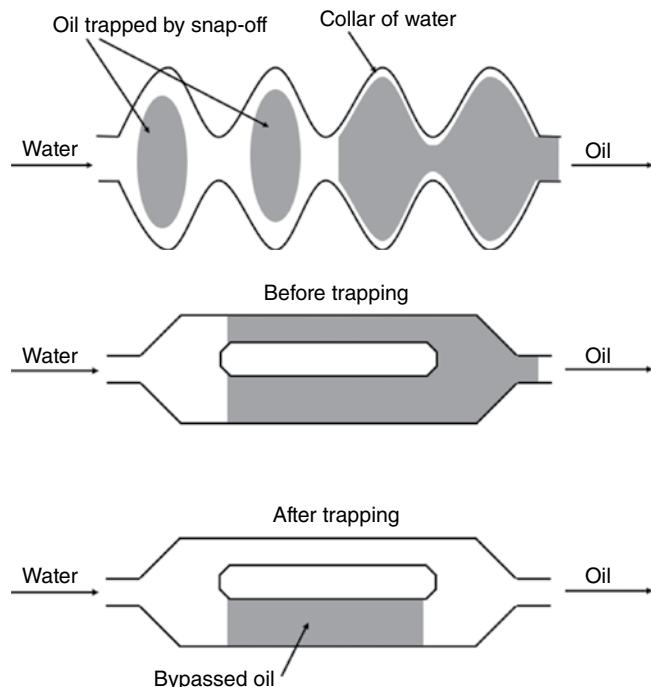


Figure 25.17 Oil trapping by a snap-off mechanism (top) and by by-passing (bottom)

water pressure will fracture the reservoir rock and large fractures cause a considerable decrease in sweep efficiency. Thus, the remaining variable is the oil–water interfacial tension ($\gamma_{o/w}$), which needs to be reduced to very low values. It can be shown that, at least in water-wet rocks, reduction of the interfacial tension to values of the order of 10^{-3} mN/m or lower is needed in order to obtain substantial mobilization and recovery of oil.

Ultra-Low Oil–Water Interfacial Tension is Needed

The phase behavior of oil–water–surfactant systems was discussed earlier in Chapter 5 and the phase behavior that specifically relates to microemulsions was treated in Chapter 17. It was demonstrated that on increasing surfactant hydrophobicity a transition occurs from a two-phase system consisting of an o/w microemulsion in equilibrium with excess oil (Winsor I), via a system comprising a microemulsion coexisting with both oil and water (Winsor III) to a two-phase system consisting of a w/o microemulsion in equilibrium with excess water (Winsor II) (Figure 17.2). It has been found that the oil–water interfacial tension has a deep minimum in the three-phase region, that is, $\gamma_{o/w}$ has a minimum in the middle of the Winsor III region and increases as it moves toward the Winsor I and the Winsor II regimes (Figure 25.18). (The Winsor I>III>II transition can be achieved by raising the temperature for a system based on a nonionic surfactant and by increasing the salinity for a system based on an ionic surfactant.) While the PIT is the condition at which the system is balanced for nonionic surfactants, for ionic surfactants this state is

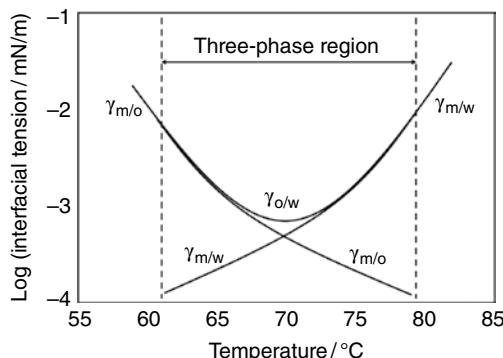


Figure 25.18 Interfacial tensions as a function of temperature for an oil–water–nonionic surfactant system. The symbols $\gamma_{o/w}$, $\gamma_{m/o}$ and $\gamma_{m/w}$ are the interfacial tensions between the phases excess oil–excess water, middle-phase microemulsion–excess oil and middle-phase microemulsion–excess water, respectively. The system is balanced at 70°C

often referred to as optimal salinity. At this point there is equal volumetric solubilization of oil and water in the middle-phase microemulsion and the interfacial tension is at minimum.

It has been demonstrated in laboratory flooding experiments that surfactant formulations capable of forming Winsor III microemulsions with the specific oil and brine present in the rock at the specific temperature of the reservoir could give a remarkable yield of recovered oil.

Cosurfactant-Free Formulations are Required

Since, particularly in offshore reservoirs, the distances between the injection and the production holes are long, the formulations used should preferably contain as few surface active components as possible. Mixtures of different surfactants or surfactant–cosurfactant combinations are less suitable, as they are likely to separate during their way through the porous rock. In this respect the rock can be expected to act like a long chromatography column. Therefore, surfactants have been sought that display the following properties:

1. Form Winsor III systems with the specific reservoir oil and brine at the reservoir temperature.
2. Are hydrolytically stable for an extended period of time under reservoir conditions.
3. Do not precipitate in hard water.
4. Do not adsorb extensively at the surfaces of the reservoir.

In addition to the above requirements, “trivial” aspects such as cost, toxicity, and biodegradability need to be taken into account. Several laboratories have come up with branched ether sulfonates as a suitable choice of surfactant type. Ether sulfates are a less expensive alternative but, as discussed on pages 15 and 30, the sulfuric ester bond in these surfactants is not a very stable one, so the use of sulfate surfactants for EOR is limited to low temperature reservoirs. Two representative compounds are shown schematically in Figure 25.19.

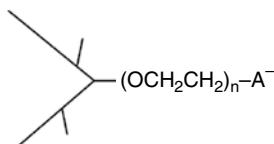


Figure 25.19 Branched-chain ether sulfonate ($A=SO_3^-$) or ether sulfate ($A=OSO_3^-$) surfactants suitable for use in EOR. n is typically 2 or 3

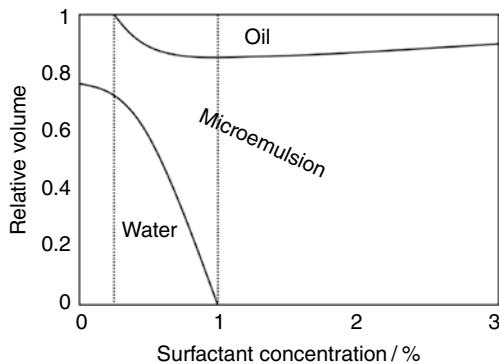


Figure 25.20 Relative phase volumes as a function of surfactant concentration for a branched-tail ether sulfonate at a water-to-oil ratio of four. Above 1% and below 0.25% surfactant, two phases form, that is, an o/w microemulsion in equilibrium with excess oil and a w/o microemulsion in equilibrium with excess water, respectively. In the range 1–0.25% surfactant, a three-phase system appears, consisting of a bicontinuous microemulsion in equilibrium with excess oil and excess water

Figure 25.20 shows relative phase volumes as a function of surfactant concentration for a system containing a branched-tail ether sulfonate of the general structure shown in Figure 25.19, designed for specific reservoir conditions. Note that there is a Winsor I>Winsor III>Winsor II transition on dilution of the surfactant, which must be taken into account in the optimization of the surfactant. The system shown in Figure 25.20 goes from Winsor I to Winsor III at 1.0% surfactant and from Winsor III to Winsor II at around 0.25% surfactant. A very high displacement efficiency was obtained in core flooding experiments with reservoir oil as the oil phase.

The Winsor I>Winsor III>Winsor II transition that often occurs on dilution may be counterbalanced by the use of a salinity gradient. The surfactant system is then optimized for a salinity that is slightly higher than the salinity of the formation water. During the flooding process the surfactant will experience a gradually reduced salinity, which tends to favor a transition in the opposite direction.

An extension of the surfactant flooding technology is to use a combination of an anionic surfactant and a water-soluble polymer in the displacing fluid. This concept, known as “low-tension polymer flooding” or, better, “polymer-assisted surfactant flooding,” can generate an ultra-low interfacial tension with a reduced amount of surfactant compared to surfactant flooding without added polymer in the displacement fluid. The mechanism

behind this effect is not clear. In Chapter 17 it was shown that the middle phase of a three-phase microemulsion can swell considerably if a polymer is added that associates with the surfactant film (Figure 17.11). However, the polymers that have been found to work best for polymer-assisted surfactant flooding are those that do not associate with the typical EOR surfactants, which all have an anionic head group (Figure 25.19). Polysaccharides, such as xanthan and scleroglucan, and synthetic polymers, such as sulfonated polyacrylamide, have been found useful for the purpose and they are used in very low concentrations. It has been proposed that the polymer displaces the surfactant from the bulk aqueous phase, thus promoting its accumulation at interfaces. The demands on the surfactant are the same as in normal surfactant flooding, that is, it should form a microemulsion without any cosurfactant, and so on. Similar to normal surfactant flooding, the displacing fluid is pushed forward by a viscous plug containing a polymer, which may, or may not, be the same as the one used together with the surfactant.

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