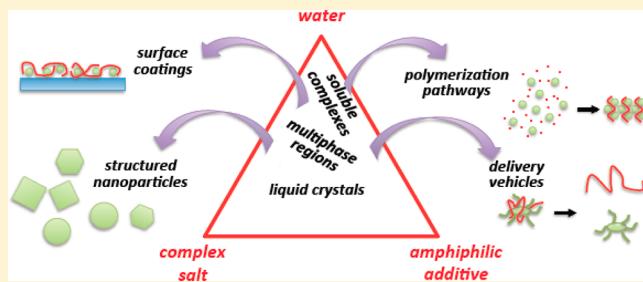


Understanding and Exploiting the Phase Behavior of Mixtures of Oppositely Charged Polymers and Surfactants in Water

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ABSTRACT: Complexes of oppositely charged polymers and surfactants (OCPS) in water come in many varieties, including liquid-crystalline materials, soluble complexes, structured nanoparticles, and water-insoluble surface layers. The range of available structures and properties increases even further with the addition of other amphiphilic substances that may enter, or even dissolve, the complexes, depending on the nature of the additive. Simple operations may change the properties of OCPS systems dramatically. For instance, dilution with water can induce a phase separation in an initially stable OCPS solution. More complicated processes, involving chemical reactions, can be used to either create or disintegrate OCPS particles or surface layers. The richness of their properties has made OCPS mixtures ubiquitous in everyday household products, such as shampoos and laundry detergents, and also attractive ingredients in the design of new types of responsive particles, surfaces, and delivery agents of potential use in future applications. A challenge for the rational design of an OCPS system is, however, to obtain a good fundamental understanding of how to select molecular shapes and sizes and how to tune the hydrophobic and electrostatic interactions such that the desired properties are obtained. Recent studies of OCPS phase equilibria, using a strategy where the minimum number of components is always used to address a particular question, have brought out general rules and trends that can be used for such a rational design. Those fundamental studies are reviewed here, together with more application-oriented studies where fundamental learning has been put to use.



1. MOTIVATION AND SCOPE

Self-assembled aggregates of surfactant ions (SI) typically associate strongly with oppositely charged polymers (PI) when mixed in an aqueous environment. Depending on a number of factors, such as the charge density of the PI, the hydrophobic/hydrophilic balance of the PI, the SI/PI charge ratio, and the presence of other added components, this association can result in macroscopic phase separation, a stable dispersion of colloidal particles, or a true solution of soluble complexes. In all cases, the complexes formed contain surfactant aggregates that can harbor hydrophobic guest molecules. When concentrated phases or colloidal particles are formed, these may or may not display long-range liquid-crystalline order of variable structure. Phase separation of initially soluble PI-SI complexes can often be induced by simple operations such as dilution with water or a change in pH or by more complicated processes such as a chemical reaction involving the PI or the SI. Because of this richness in possibilities, combinations of oppositely charged polymers and surfactants (OCPS) are attractive as ingredients in a wide range of contexts where internally structured soft materials, particles, or surface layers are desired. Research on such systems is therefore very active, as evidenced by several recent reviews.^{1–5} However, to be able to design OCPS materials in a rational manner, we would like to have detailed answers to the following very basic questions: How can we control the solubility of PI-SI complexes and the properties of soluble complexes? How can we control the structure and the

maximum water uptake of the concentrated phases that separate out from water? These questions are closely related to the question, what are the key similarities and differences between ionic surfactants that are neutralized by monomeric or polymeric counterions?

To approach the above questions in a systematic way, a method of choice is to map out the phase behavior of OCPS systems. An experimental difficulty with this strategy is, however, that the number of components in OCPS systems is typically large. Even the simplest of the traditionally studied mixtures contain a polyelectrolyte (PI + monovalent counterion) and an ionic surfactant (SI + monovalent counterion) mixed in water. Given the constraint of electroneutrality of all equilibrium phases, a mixture of water and four different ionic species corresponds to a four-component system for which a full isothermal-isobaric phase diagram requires three dimensions, as in a tetragonal pyramid.⁶ To simplify systematic studies of OCPS systems, our group introduced, a little over a decade ago, an alternative approach where the minimum number of components is always used to address a particular question.⁷ The key to this approach is first to produce the stoichiometric complex salt, which is a neutral salt that consists of only SI and PI, and always use the complex salt as one of the components in the phase studies. Pure complex salts may be

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obtained by a number of methods, such as titrating a polyacid with the hydroxide form of a cationic surfactant,⁷ diluting (washing) a phase-separated mixture with pure water,^{8,9} and extracting the phase-separated aqueous complex into an organic solvent.¹⁰ To the binary complex salt/water mixtures any of a variety of substances can be added as a third component. Over the past decade, researchers in our laboratory and others have used this approach successfully to clarify a number of important trends and relationships between conventional surfactant phases, on one hand, and those formed by complex salts and their mixtures, on the other hand. Our early work has been summarized in two reviews.^{11,12}

In addition to systematic studies of highly idealized model systems based on complex salts, our group is also involved in research aimed at solving problems in current applications. Furthermore, we work on the design of new responsive or evolving OCPS systems that we hope can find use in future applications. In our work aimed at applications, the knowledge gained from fundamental studies is being put into practice. Hence, the purpose of the present Feature Article is twofold: to summarize the most recent progress in our fundamental studies of aqueous OCPS systems using the systematic complex-salt approach and to illustrate how the insights and trends that emerge from such fundamental work may be used as guides for our thinking about more complex multicomponent systems, with a bearing on present and future applications. I will restrict myself to effects of changing the compositions of the systems; temperature effects, which could be more or less important, depending on the system, are outside the scope of this short review.

The work in our group has mostly been concerned with highly flexible synthetic polyions. By contrast, Bilalov and co-workers have recently adopted the complex-salt strategy to study complexes of double-helical DNA with cationic surfactants in mixtures with water and various additives. Their systematic work has very recently been reviewed, and one important conclusion that emerged is that the rigidity of DNA imposes severe restrictions on the possible structures of concentrated phases containing DNA–surfactant complex salts.¹³ The focus of the present review will be on complex salts containing flexible polyions, but occasional comparisons will be made in cases where systems containing rigid DNA have been shown to be notably different.

2. UNDERSTANDING PHASE BEHAVIOR AND SOLUBLE COMPLEXES

In this section, I will discuss properties of complex salts mixed with water, with a particular emphasis on the effects of adding a third, low-molecular weight, amphiphilic component. The third component may be a conventional ionic surfactant, an alcohol, or a nonionic surfactant. The phase behavior of the corresponding ternary mixture of complex salt/additive/water will illustrate to what extent the added component affects the structure and/or the maximum water uptake of the mixture, which are two very important properties of OCPS materials and formulations. In addition, I will discuss various strategies to obtain soluble PI–SI complexes.

2.1. Surfactant Ion Aggregates with Mixed Monomeric and Polymeric Counterions. Let us first consider the case where a conventional ionic surfactant (SI + monovalent counterion) is added to a mixture of water with a complex salt that contains the same SI as the surfactant. This is a conceptually simple ternary system that can be thought of as

an aqueous surfactant ion that is neutralized by mixed polymeric and monomeric counterions in all proportions.

2.1.1. Simplest Case with Only Charge–Charge Attractions. As the simplest conceivable “baseline” case, we will first consider mixtures where the polyion is a hydrophilic homopolymer that interacts with surfactant aggregates purely by Coulombic charge–charge attractions. Experimental studies indicate that mixtures of anionic polyacrylate (PA^-) with cationic alkyltrimethylammonium surfactant ions (C_nTA^+ , where n is the number of carbons in the alkyl chain) represent such a case because the association between PA^- and C_nTA^+ micelles can be effectively broken by added simple salt.^{14,15} Furthermore, to eliminate possible effects of chemical specificity, the monovalent counterion of the surfactants should be chemically similar to the repeat unit of the polyion. For that purpose, we have chosen the acetate (Ac^-) anion. In Figure 1a,b, we compare two recently established phase diagrams for aqueous mixtures of C_{12}TAAc with two $\text{C}_{12}\text{TAPA}_p$ complex salts that differ widely in the number of repeat units, p , of the polyion (25 or 6000 units, respectively).¹⁶ Note the simplicity of these two phase diagrams, which both contain only three phases: a disordered micellar solution, a cubic phase of small discrete micelles, and a hexagonal phase of rodlike surfactant aggregates. The concentrated liquid-crystalline (cubic or hexagonal) phases both extend all the way from the binary $\text{C}_{12}\text{TAPA}_p$ /water axis to the binary C_{12}TAAc /water axis. The transition from cubic to hexagonal (i.e., the lower boundary of the cubic phase) occurs at a practically constant water content of ca. 40% in all cases, irrespectively of the nature of the anion (long or short PA^- or monovalent Ac^-). This immediately tells us that the concentrated aqueous systems are quite insensitive to the monomeric or polymeric nature of the counterion to the SI, at least when the polyion is highly charged and flexible. (We will look at other situations below.) At high concentrations, the structure is determined by the spontaneous local curvature of the SI aggregate, together with the strong interaggregate repulsion that results from a low water content.

In water-rich mixtures, however, striking differences appear in the mixtures with $\text{C}_{12}\text{TAPA}_{25}$ or $\text{C}_{12}\text{TAPA}_{6000}$, respectively. Above ca. 50% water, we see the following important effects of changing the PA^- chain length: (1) Although both of the pure complex salts are virtually insoluble in water, the maximally water-swollen cubic phase in equilibrium with excess water contains more water for $\text{C}_{12}\text{TAPA}_{25}$ than for $\text{C}_{12}\text{TAPA}_{6000}$. (2) The aqueous complex salts respond quite differently to added surfactant. When C_{12}TAAc is added to a biphasic mixture of $\text{C}_{12}\text{TAPA}_{25}$ in water, a disordered micellar solution soon develops that extends all the way to the water corner. By contrast, the corresponding region for $\text{C}_{12}\text{TAPA}_{6000}$ contains phase-separated systems for all proportions of added C_{12}TAAc . The latter biphasic systems contain a water-rich disordered micellar phase of pure C_{12}TAAc in equilibrium with a concentrated cubic phase with mixed Ac^- and PA^- counterions with the C_{12}TA^+ aggregates. We can say that when the complex contains short polyions, excess conventional surfactant eventually redissolves the phase-separated PI–SI complex into a micellar solution. By contrast, no such surfactant redissolution occurs at any excess of the surfactant when the polyions are long.

To gain additional physical insight into the diagrams in Figure 1a,b, dos Santos et al. revisited a very simple Flory–Huggins (FH) lattice model for polyelectrolytes.¹⁶ In the model employed,¹⁷ the polyion, P^- , and the surfactant aggregate, S^+ ,

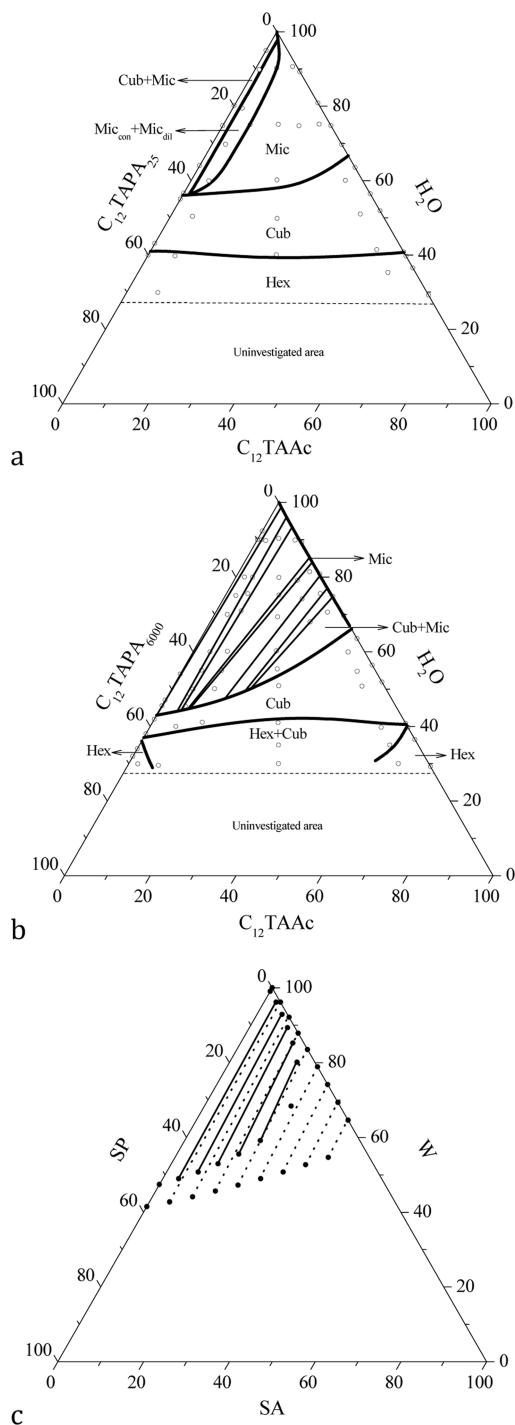


Figure 1. Experimental and theoretical phase diagrams for a complex salt mixed with excess surfactant and water.¹⁶ (a) $\text{C}_{12}\text{TAPA}_{25}/\text{C}_{12}\text{TAAc}/\text{H}_2\text{O}$ and (b) $\text{C}_{12}\text{TAPA}_{6000}/\text{C}_{12}\text{TAAc}/\text{H}_2\text{O}$ phase diagrams at 25 °C featuring disordered micellar (Mic), micellar cubic (Cub), and hexagonal (Hex) phases. Estimated phase boundaries (thick lines) and tie lines (thin, straight lines) are indicated. (c) Phase diagrams produced by FH model calculations describing mixtures of a complex salt (SP) with an ionic surfactant (SA) in water (W). Model parameters: $\chi_{\text{SP}} = \chi_{\text{SA}} = -3.5$, $\chi_{\text{AW}} = \chi_{\text{SW}} = \chi_{\text{PW}} = \chi_{\text{PA}} = 0$, $r_{\text{W}} = r_{\text{A}} = 1$, $r_{\text{S}} = 60$, and $r_{\text{S}} = 15$ (solid tie lines) or $r_{\text{S}} = 3000$ (dotted tie lines), where χ_{ij} are Flory–Huggins interaction parameters and r_i is the number of repeat units of component i . Reprinted with permission from *Langmuir* 2011, 27, 592–603. Copyright 2011 American Chemical Society.

are both treated as flexible polymers, whereas the monovalent ion, A^- , is treated as a small molecule, just like the solvent, W . To each ionic species is assigned a charge number (-1 for A^- and for a repeat unit of P^- , $+1$ for a repeat unit of S^+), and an additional constraint in the calculations is the condition of electroneutrality: each equilibrium phase must contain equal numbers of positive and negative charges. As in the real experimental system, the electroneutrality condition ensures that the mixture of three ionic species + solvent becomes a three-component mixture. The attraction between positive and negative charges is described by a single, strongly negative FH interaction parameter; no other preferential interactions have been introduced because the aim was to make the model maximally simple. Figure 1c shows the calculated phase diagrams for short and long P^- polyions. (See the legend for detailed parameter choices.) Indeed, this simple model manages to reproduce the qualitative features of the experimental phase diagrams in Figure 1a,b remarkably well, including (1) a larger maximum solvent uptake for the pure complex salt with the shorter polyion, (2) a gradual surfactant redissolution of the complex salt with the short polyion, contrasted by a total lack of surfactant redissolution of the salt with the long polyion, and (3) tie lines that run more or less parallel to the binary complex salt/water axis, showing that the surfactant concentration is almost the same in the two coexisting phases.

The beauty of the simple FH model is that the physical mechanisms that operate are readily identifiable: the phase behavior is totally determined by the balance between preferential attractions and the entropy of mixing of the various species. As is well understood, the entropy of mixing of a species becomes increasingly large when its degree of polymerization decreases because the number of particles in the system then increases. Hence, the unbiased partitioning of the surfactant component between the two phases that is seen in Figure 1c (tie lines parallel to the SP/W axis) should be a result of maximizing the entropy of mixing for the numerous A^- ions, which are part of the SA component. By contrast, for the long polyions, the gain in entropy of mixing that would result from a partial transfer to the dilute phase never outweighs the larger number of attractive interactions per particle experienced in the concentrated phase. Therefore, the long polyions always remain quantitatively in the concentrated phase. The unequal solvent content in the two phases can still be maintained because the increase in the osmotic pressure of either phase, concentrated or dilute, is determined essentially by the concentration of the numerous A^- ions, which as we saw are uniformly distributed in the system. For short polyions, the situation is intermediate. The larger entropy of mixing of the more numerous short polyions compared to that of the long polyions is also seen for the pure complex salt, which exhibits a larger amount of swelling in excess pure solvent. And as more and more surfactant is added, the increasing concentration of surfactant ion aggregates in the dilute phase makes the latter phase an increasingly better environment for the short polyions, resulting in an increasing concentration in the dilute phase. Eventually, a critical point is reached, and the concentrated and dilute phases merge into a single mixed phase.

We propose that the generic physical mechanisms identified from the simple FH model above are indeed also the dominating ones for the real experimental phase diagrams in Figure 1a,b. Further support for this conclusion comes from the observation that ion-specific effects, which result from changing the surfactant counterion from acetate to bromide, also emerge

in a qualitatively correct way from the model simply by letting the A^- ion be even more strongly attracted to the S^+ species.¹⁶ In fact, because the FH model describes both the S^+ and the P^- species as flexible polymers, we believe that the general features and trends of the phase diagrams in Figure 1 should also be valid at equilibrium for complex salts based on oppositely charged polyions (so-called polyelectrolyte complexes, including polyelectrolyte multilayers at surfaces) in cases where only nonspecific electrostatic interactions dominate and additional hydrophobic attractions may be neglected.

2.1.2. More Complex Case with Additional Hydrophobic Interactions. Recently, Sitar et al. made a very detailed study of the phase behavior of complex salt $\text{C}_{16}\text{TAPSS}_{340}$ (PSS^- = poly(styrene sulfonate)) mixed with either C_{16}TACl or NaPSS_{340} in water.¹⁸ Conventional mixtures of poly(styrene sulfonate) and alkyl ammonium surfactants are widely studied, and it is well established that PSS^- , unlike PA^- , also experiences a strong hydrophobic interaction with cationic surfactants.^{5,15,19–22} In fact, an NMR study of dilute aqueous solutions has shown that the hydrophobic portion of PSS^- takes part in aggregate formation with the cationic surfactant.²⁰ Differences in the phase behavior of NaPSS and NaPA mixed with conventional cationic surfactants in water have been highlighted previously and were ascribed to the additional hydrophobic interaction with PSS^- .¹⁵

Figure 2 shows the phase diagram for the system $\text{C}_{16}\text{TAPSS}_{340}/\text{C}_{16}\text{TACl}/\text{water}$, reproduced from the work of

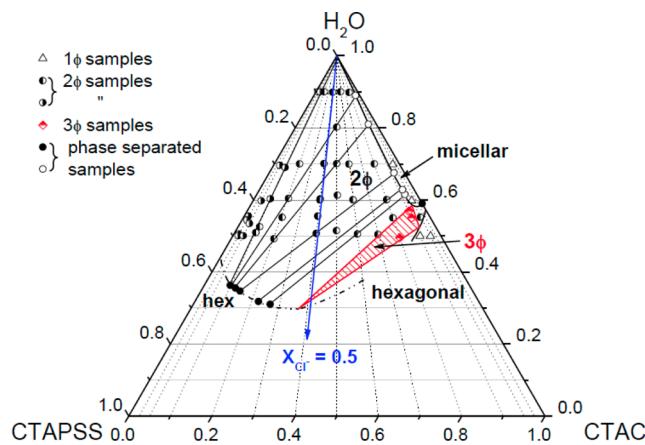


Figure 2. $\text{C}_{16}\text{TAPSS}/\text{C}_{16}\text{TACl}/\text{H}_2\text{O}$ phase diagram at 25 °C.¹⁸ The blue arrow indicates global compositions where the concentrations of chloride ions and styrene sulfonate repeat units are equal. Reprinted with permission from *J. Phys. Chem. B* 2012, 116, 4634–4645. Copyright 2012 American Chemical Society.

Sitar et al.¹⁸ The large region of phase separation, which separates surfactant-rich liquid-crystalline phases from complex-salt-rich phases, is a feature that the phase diagram in Figure 2 shares with that for the $\text{C}_{12}\text{TAPA}_{6000}/\text{C}_{12}\text{TAAc}/\text{water}$ system (Figure 1b) and also with a previously published phase diagram for the $\text{C}_{16}\text{TAPA}_{6000}/\text{C}_{16}\text{TAAc}/\text{water}$ system.²³ An additional similarity between the PA-based and the PSS-based systems is that the hexagonal phase seems to extend continuously across the phase diagram. However, there are also important differences. One concerns the disordered micellar solution phase: for the $\text{C}_{16}\text{TAPSS}_{340}/\text{C}_{16}\text{TACl}/\text{water}$ system, the micellar phase can incorporate a finite concentration of complex salt and thus extends into the three-component triangle along the $\text{C}_{16}\text{TACl}/\text{water}$ axis; see Figure 2. This

means that complex salts containing long-chain PSS^- as opposed to those containing long-chain PA^- can be redissolved by excess cationic surfactant, although a large global excess of surfactant ions (≥ 13 surfactant ions per PSS charge)¹⁸ is required. The formation of a hydrophobically associated PI-SI aggregate is not considered in the simple FH analysis (Figure 1c), and it seems likely that the formation of discrete, soluble, nonstoichiometric complexes is responsible for the observed redissolution behavior.

Also in the concentrated region there are differences between the PA-based and PSS-based systems. In the $\text{C}_{16}\text{TAPSS}_{340}/\text{C}_{16}\text{TACl}/\text{water}$ system, the region of phase separation extends to very low water contents. Expressed alternatively, the concentrated hexagonal phase has a very limited maximum water uptake, which could be a result of the hydrophobicity of the complex. Moreover, a wide three-phase region appears in the lower-right part of the phase-separation region, where one disordered phase coexists with two hexagonal phases of widely different compositions. This three-phase area seems to be a consequence of a combination of two features of the micellar–hexagonal two-phase region, namely, the direction of the tie lines at high surfactant contents, together with the pronounced minimum in the water content of the hexagonal phase close to the 1:1 charge ratio between chloride and poly(styrene sulfonate) ions.

2.2. Mixtures with *n*-Alcohols of Varying Length: From Cosurfactants to Cosolvents. Above we noted that when excess ionic surfactant is added to an aqueous complex salt containing the same SI neutralized by a highly charged flexible PI it mixes into the concentrated liquid-crystalline phase(s) of the complex salt without changing the structure (micellar cubic or hexagonal, in the cases investigated). We will now see that effects of added alcohols are totally different. Alcohols are uncharged and amphiphilic and may be miscible with water, depending on their chain length.

Bernardes et al. systematically investigated the phase behavior of ternary mixtures of $\text{C}_{16}\text{TAPA}_{30}$ or $\text{C}_{16}\text{TAPA}_{6000}$ with water and each of the *n*-alcohols ethanol, butanol, hexanol, octanol, and decanol.²⁴ Three of the corresponding phase diagrams for $\text{C}_{16}\text{TAPA}_{30}$ are shown in Figure 3. Long-chain alcohols, which are water-insoluble, enter the surfactant aggregates quantitatively as cosurfactants, resulting in a change in the curvature of the aggregate surface and hence a change in the structure of the concentrated phase. A particularly rich sequence of structures is observed for mixtures with octanol (Figure 3a). As the content of octanol in the concentrated phase containing $\text{C}_{16}\text{TAPA}_{30}$ is varied, the structure changes in the sequence micellar cubic (C) → normal hexagonal (H) → lamellar (L) → reverse hexagonal (H_2) → disordered alcohol-rich solution (L_2). Because both octanol (at room temperature)²⁵ and the complex salt are effectively insoluble in water, this means that all of these ordered structures can exist as stable, concentrated phases in an environment of excess pure water.

Short-chain alcohols are more or less miscible with water and therefore partition between the surfactant aggregates and the surrounding aqueous domain. As demonstrated by Antonietti and co-workers,^{10,26} neat short-chain alcohols are also potent solvents for polyion–surfactant ion complex salts, presumably because small molecules mix well with the surfactant hydrocarbon chains that make up the palisade layer of reverse surfactant aggregates.²⁷ The phase diagrams in Figure 3b,c illustrate that both ethanol and butanol can dissolve large

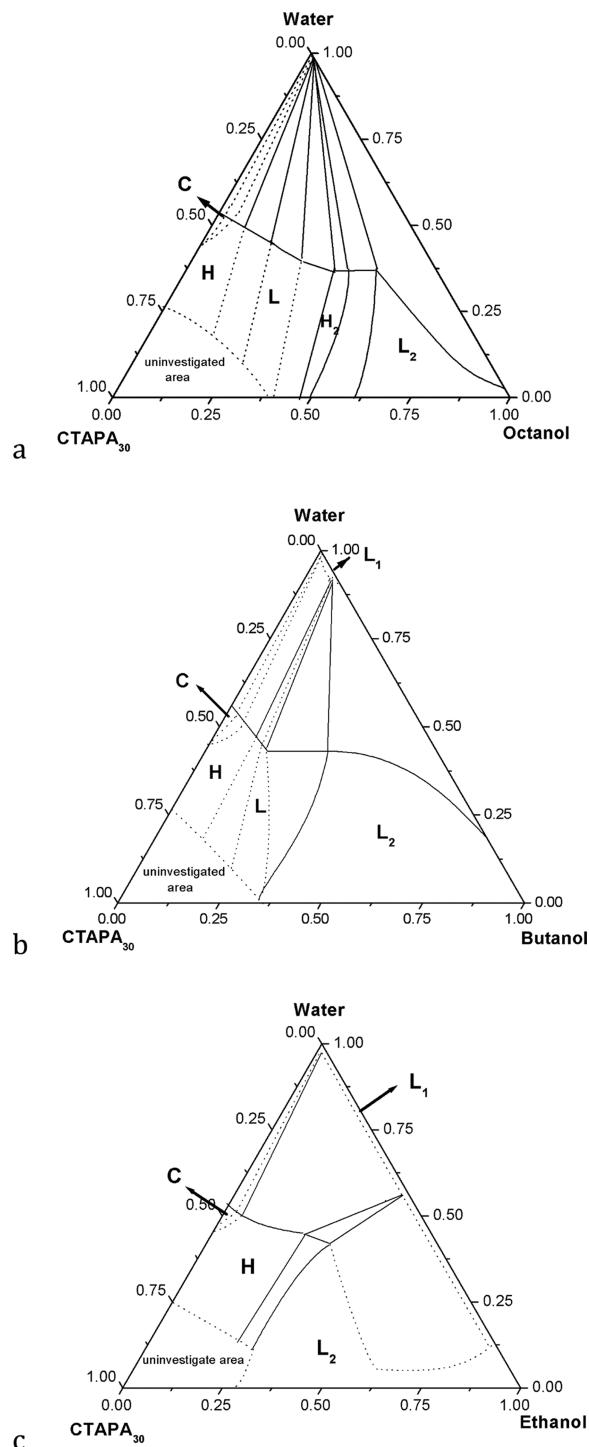


Figure 3. Phase diagrams at 25 °C for C₁₆TAPA₃₀ mixed with water and *n*-alcohol (a) octanol, (b) butanol or (c) ethanol.²⁴ The various phases encountered are an aqueous solution (L₁), micellar cubic (C), normal hexagonal (H), lamellar (L), reverse hexagonal (H₂), and a disordered alcohol-rich solution (L₂). Reprinted with permission from *J. Phys. Chem. B* 2011, 115, 9050–9058. Copyright 2011 American Chemical Society.

proportions of dry C₁₆TAPA₃₀, and large solubility in these two alcohols was also found for C₁₆TAPA₆₀₀₀.²⁴ Octanol seems to be a borderline case because it can dissolve large proportions of C₁₆TAPA₃₀ (Figure 3a) whereas the solubility of C₁₆TAPA₆₀₀₀ in octanol was found to be rather low.²⁴ An interesting feature of the phase diagram with ethanol (Figure 3c) is that when

even small proportions of water are added to an ethanolic solution of a complex salt the complex salt separates out in a concentrated phase. This is because water is fully miscible with ethanol, and when the water content increases, the mixed solvent rapidly becomes a poor solvent for the complex salt. By contrast, solutions of complex salt in butanol (Figure 3b) can incorporate large proportions of water without giving rise to phase separation; this is because here the water is mainly incorporated into the interior of the reverse complex-salt aggregates without substantially entering and worsening the solvent properties of the continuous phase.

An extensive investigation by small-angle X-ray scattering (SAXS) and NMR diffusometry and rheology of the L₂ phases of C₁₆TAPA₃₀ and C₁₆TAPA₆₀₀₀ mixed with water and butanol, hexanol, or octanol was conducted by Bernardes et al.²⁸ It was concluded that the complex salts dissolve in these alcohols as “reverse micelles with spines”; that is, each dissolved aggregate contains one polyion and water surrounded by a palisade layer of mixed surfactant ions and alcohol molecules with their headgroups facing the aqueous micellar interior. As a result of this morphology, highly viscoelastic solutions were obtained in concentrated alcohol solutions of the complex salt with the C₁₆TAPA₆₀₀₀ complex, whereas the C₁₆TAPA₃₀ complex gave low-viscosity solutions.

It is illuminating to compare the complex salt/alcohol/water systems to the corresponding ternary mixtures for a conventional cationic surfactant. Fontell et al. made extensive phase studies of ternary systems of C₁₆TABr, water, and each of the *n*-alcohols decanol, octanol, hexanol, butanol, ethanol, and methanol.²⁹ Interestingly, the water-poor regions show many similarities between the C₁₆TABr-based mixtures and those based on C₁₆TAPA. Thus, when increasing amounts of *n*-alcohol are added to a binary C₁₆TABr/water mixture containing 60 wt % CTABr, the sequence of phases observed is H → L → H₂ → L₂ for octanol, H → L → L₂ for butanol, and H → L₂ for ethanol;²⁹ the same sequences are indeed observed for 60 wt % complex salts in Figure 3. Once more we conclude that concentrated phases are not very sensitive to the nature (monomeric or polymeric) of the counterion to the ionic surfactant. The major differences again show up at high water contents, where the complex salt systems show limited swelling, whereas many of the phases in the C₁₆TABr-based mixtures can take up large (sometimes infinite) proportions of water.

A further interesting comparison can be made with the ternary mixtures of C₁₂TADNA with water and *n*-alcohols of varying chain lengths, whose phase behavior was studied by Leal et al.³⁰ Like C_nTAPA_p (Figure 3), C₁₂TADNA was found to be quite miscible with *n*-alcohols in the binary mixtures and the miscibility increased with the decreasing length of the alcohol alkyl chain. However, in the C₁₂TADNA/*n*-alcohol/water mixtures, the single-phase regions were generally found to be quite narrow. For instance, and in contrast to the results shown in Figure 3, not much water could be taken up in the L₂ phases for any of the studied C₁₂TADNA/*n*-alcohol mixtures. The conditions required for the simultaneous incorporation of significant proportions of all the three components C₁₂TADNA, water, and alcohol in the same structure are evidently quite restrictive, presumably because of the rigidity of the DNA polyion.

2.3. Mixtures with Nonionic Surfactants. Above we saw how added water-insoluble long-chain alcohols act as cosurfactants and affect the properties of aqueous complex

salts. We may then wonder what happens if, instead of an alcohol, we add a water-soluble nonionic surfactant with a hydrophilic oligo(ethylene oxide) headgroup. Unlike long-chain alcohols, nonionic surfactants with sufficiently long ethylene oxide (EO) headgroups are totally miscible with water at room temperature and form various liquid-crystalline phases in their highly concentrated aqueous mixtures (ca. 50 wt % and above).³¹ Because aqueous complex salts also form liquid-crystalline phases, it is interesting to see to what extent mixed aggregates are formed and what liquid-crystalline structures such mixed aggregates may form.

Janiak et al. addressed this problem by establishing equilibrium phase diagrams for aqueous mixtures of complex salts $C_{16}\text{TAPA}_{25}$ and $C_{16}\text{TAPA}_{6000}$ with added nonionic surfactant $C_{12}\text{EO}_5$ or $C_{12}\text{EO}_8$.³² Three of these diagrams are reproduced in Figure 4. The simplest case of those investigated is the $C_{16}\text{TAPA}_{25}/C_{12}\text{EO}_8/\text{water}$ system (Figure 4a). Here the most water-rich liquid-crystalline phase is a hexagonal phase

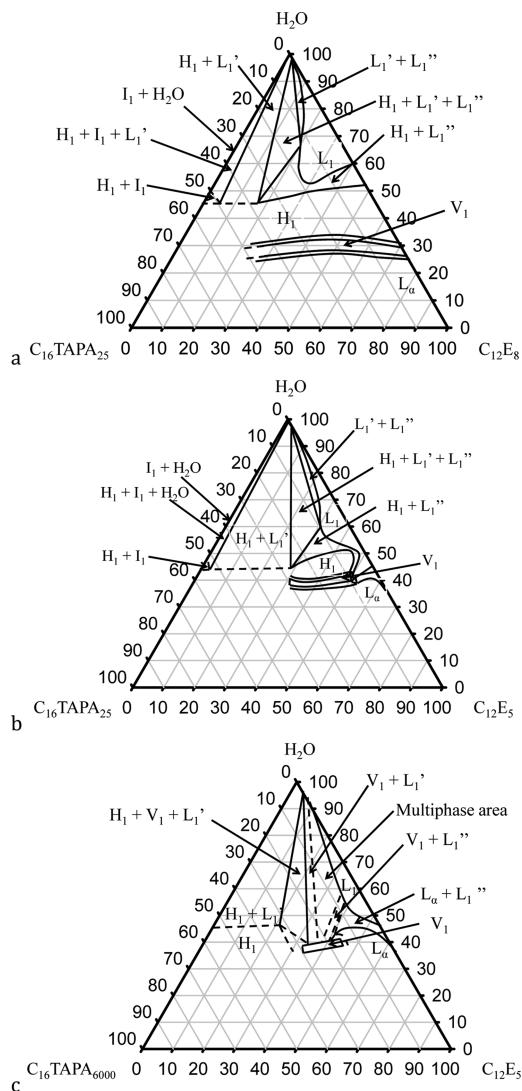


Figure 4. Phase diagrams at 25 °C for mixtures in water of $C_{16}\text{TAPA}_{25}$ with (a) $C_{12}\text{E}_8$ or (b) $C_{12}\text{E}_5$ and (c) $C_{16}\text{TAPA}_{6000}$ mixed with $C_{12}\text{E}_5$.³² The micellar and bicontinuous cubic phases are denoted I_1 and V_1 , respectively, and the lamellar phase is denoted L_a ; other notations are the same as in Figure 3. Adapted from *Phys. Chem. Chem. Phys.* **2011**, *13*, 3126–3138 by permission of the PCCP Owner Societies.

that extends across all proportions of the complex salt and nonionic surfactant, from the $C_{16}\text{TAPA}_{25}/\text{water}$ axis to the $C_{12}\text{EO}_8/\text{water}$ axis. Investigations by SAXS show that the repeat distance between the cylindrical aggregates in the hexagonal phase is almost constant.³² Thus, it is possible to vary the proportions of the nonionic/complex salt freely without changing the structure. Even more interestingly, the bicontinuous cubic phase (V_1), which forms in a narrow concentration region above 70 wt % $C_{12}\text{EO}_8$ in pure water, is found to persist and at a nearly constant water content, even when more than half of the nonionic surfactant is replaced by $C_{16}\text{TAPA}_{25}$. Remarkably, this is also true for complex salt $C_{16}\text{TAPA}_{6000}$, which contains a very long polyion (not shown).³² There seems to be close matching of the curvatures of the complex-salt aggregates and the $C_{12}\text{EO}_8$ aggregates, resulting in nearly composition-invariant mixed aggregates. This structural compatibility between $C_{16}\text{TAPA}_p$ and $C_{12}\text{EO}_8$ is in striking contrast to the results found by Leal et al. for mixtures of $C_{12}\text{TADNA}$ with $C_{12}\text{EO}_8$ in water.³³ In the latter system, the complex salt based on the rigid DNA polyion could essentially not be incorporated at all in the structures formed by $C_{12}\text{EO}_8$ and water.

In mixtures of $C_{16}\text{TAPA}_{25}$ with $C_{12}\text{EO}_5$, which has a shorter hydrophilic headgroup than $C_{12}\text{EO}_8$, the situation becomes more complex (Figure 4b). At room temperature in pure water, $C_{12}\text{EO}_5$ forms neither a hexagonal nor a bicontinuous cubic phase. However, both of the latter phases appear when a rather low fraction of $C_{12}\text{EO}_5$ is replaced by $C_{16}\text{TAPA}_{25}$. Interestingly, the same transitions of the concentrated micellar phase into a hexagonal phase or, at higher concentrations, a bicontinuous cubic phase occur when the temperature of the $C_{12}\text{EO}_5/\text{water}$ system is lowered.³¹ The temperature effect is a result of an increased curvature of the surfactant aggregate as water becomes a better solvent for the headgroup.³¹ Because the $C_{16}\text{TAPA}$ complex salt has a stronger aggregate curvature than $C_{12}\text{EO}_5$ in water at room temperature, an increasing fraction of $C_{16}\text{TAPA}$ in the mixed aggregates also gives rise to increasing curvature and hence a similar change in the liquid-crystalline structure as a temperature decrease.³²

In the water-rich parts of the phase diagrams, we can see that both nonionic surfactants have the capacity to solubilize both complex salts based on flexible polyacrylate. (For $C_{12}\text{TADNA}$, only a very small proportion of complex salt could be solubilized by nonionic micelles.³³) For each of the four investigated systems, there is a disordered micellar phase that extends into the phase triangle from the $C_{12}\text{EO}_m/\text{water}$ axis. As expected, the extension of this region increases with increasing length m of the nonionic headgroup and with decreasing degree of polymerization p of the polyion (Figure 4a–c). Note, however, that even the least efficient nonionic compound, $C_{12}\text{EO}_5$, eventually solubilizes even the most difficult complex salt, $C_{16}\text{TAPA}_{6000}$ (Figure 4c). This is in contrast to the situation for added ionic surfactant; we recall (Figure 1b) that $C_{16}\text{TAAc}$ cannot redissolve $C_{16}\text{TAPA}_{6000}$ at any excess. Another interesting comparison between added $C_{16}\text{TAAc}$ and added $C_{12}\text{EO}_m$ concerns the directions of the tie lines in the wide biphasic areas in the top left parts of the phase diagrams. We saw above that added $C_{16}\text{TAAc}$ partitions almost equally between the concentrated and the dilute phases. By contrast, added nonionic surfactant is clearly enriched in the concentrated phase. Two differences should contribute to this effect. The nonionic micelles have no associated small counterions, hence, the entropic penalty for an uneven

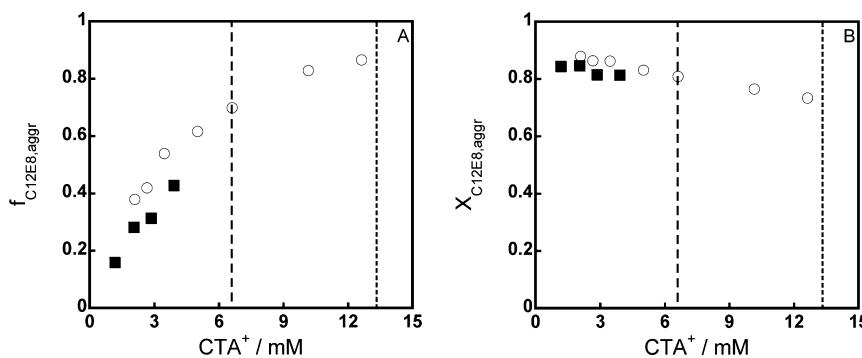


Figure 5. Fraction of C₁₂EO₈ that is included in complex salt aggregates, $f_{C_{12}EO_8,agr}$ (left graph), and the mole fraction of C₁₂EO₈, $X_{C_{12}EO_8,aggr}$ in the mixed C₁₆TA⁺/C₁₂EO₈ micelles of the complex salt aggregates (right graph) for C₁₆TAPA₂₅/C₁₂EO₈ mixtures (open circles) or C₁₆TAPA₆₀₀₀/C₁₂EO₈ mixtures (filled squares) plotted vs the concentration of complex salt in solutions containing a constant concentration of 40 mM C₁₂EO₈. Vertical lines represent approximate limits of the one-phase solution regions for C₁₆TAPA₆₀₀₀/C₁₂EO₈ mixtures (dashed lines) and C₁₆TAPA₂₅/C₁₂EO₈ mixtures (dotted lines), respectively. Adapted from ref 34.

distribution is much less. However, there is an entropy of mixing to be gained in mixing the nonionic surfactant with the surfactant ions inside an aggregate. The latter entropy of mixing is absent for mixtures of a complex salt with an ionic surfactant that contains the same SI.

As we have seen repeatedly, one effect of increasing the length of the polyion in the complex salt is a decrease in the maximum water uptake of the concentrated phases bordering the miscibility gap. This is one way of explaining the differences above 40 wt % water in the phase diagrams in Figure 4b,c. The hexagonal phase that exists above the bicontinuous cubic phase in Figure 4b for mixtures of C₁₂EO₅ with C₁₆TAPA₂₅ has vanished in the corresponding mixtures with C₁₆TAPA₆₀₀₀. As a consequence, one can in the latter system obtain a concentrated bicontinuous structure in equilibrium with a dilute nonionic surfactant solution. We will return to this observation below.

Janiak et al. made a detailed investigation by NMR self-diffusion and dynamic light scattering in order to characterize the soluble aggregates in the disordered micellar phases (the L₁ regions in the diagrams of Figure 4) for C₁₆TAPA₂₅ or C₁₆TAPA₆₀₀₀ mixed with C₁₂EO₈ in water.³⁴ For each complex salt, a series of solutions was prepared with a constant concentration (40 mM) of C₁₂EO₈ and a concentration of complex salt that was varied within the boundaries of the one-phase region. Some illuminating results emerging from the analysis of the NMR experiments are reproduced in Figure 5. Here the fraction of the total C₁₂EO₈ that is incorporated in mixed micelles and the mole fraction of C₁₂EO₈ within the mixed C₁₆TA⁺/C₁₂EO₈ micelles are plotted as functions of the global concentration of complex salt. At small additions of complex salt, most aggregates in the solution must necessarily be pure C₁₂EO₈ micelles, but even at the maximum content of complex salt before the system reaches phase separation there still remains a sizable fraction of pure C₁₂EO₈ micelles (Figure 5, left). This is especially true for the complex salt with the long polyion. This means that the true stoichiometry of the mixed micelles never equals the global ratio of SI/nonionic surfactant. The mixed micelles (Figure 5, right) are always dominated by the nonionic surfactant at a stoichiometry that is relatively independent of both the length of the polyion and the global ratio of nonionic surfactant to surfactant ions. We note that the mixed micelles contain a minimum fraction of ca. 15 mol % surfactant ions even at very low complex salt concentrations. This is certainly a consequence of the fact that the negative

counterions are connected in polyions; the SI will therefore also be grouped together in the limited number of mixed micelles that can fit close to the polyions in the mixed aggregates. The primary NMR diffusion data (not shown) indicate a significant growth of the mixed complex salt/nonionic surfactant aggregates with increasing concentration of complex salt.³⁴ A clustering of polyions and mixed micelles into larger aggregates is a likely scenario as the system approaches phase separation.

Dubin and co-workers have conducted numerous studies on the complexation of mixed nonionic–ionic surfactant micelles with oppositely charged polyions. See two recent reviews.^{35,36} In their studies, the mixed micelle has been viewed as a model colloid with a charge density that can be varied by varying the relative proportions of ionic/nonionic surfactant, and a central objective has been to establish critical conditions for complex formation to occur in terms of parameters such as the mean charge density of the mixed micelles, the linear charge density of the polyion, and the ionic strength of the solution. Indeed, a simple power-law relationship connecting these parameters could be established.³⁷ It is instructive to consider the differences in solution conditions between the studies of Dubin et al. and those of Janiak et al. In the former studies, conditions were tuned (for instance, by added salt) so as to ensure weak interactions between the polyions and the mixed micelles. Under such circumstances, the central assumption that there is a monomodal population of mixed micelles, with a uniform surface charge density and a composition corresponding to the global average, seems justified. In the latter studies, however, the electrostatic interactions are maximally strong (no simple ions are present) and the mixtures are clearly quite different. As demonstrated in Figure 5, soluble complexes of a stoichiometry that depends only weakly on the global nonionic/ionic surfactant ratio are found to coexist with pure nonionic micelles.

2.4. Complex Salts Based on Random Copolymers. An obvious strategy for changing the properties of aqueous complex salts is to vary the chemistry of the polyion. Both the hydrophobic/hydrophilic balance and the charge density of the polyion can be varied by copolymerization.

2.4.1. Mixing Ionic Comonomers along the Chain. Perceboom et al. have studied complex salts based on a random copolymer containing equimolar amounts of styrene sulfonic acid and maleic acid repeat units.³⁸ By titrating this polymer to varying degrees with C₁₆TAOH, they obtained complex salts

where half or all of the carboxylic acid groups were neutralized with the base. These complex salts were studied in their aqueous mixtures with *n*-butanol and *n*-decanol, essentially confirming the trends described in section 2.2. In the present context, I will discuss only the binary mixture with water for the complex containing the fully charged polyion. The corresponding phase diagram is shown in Figure 6, which also includes a

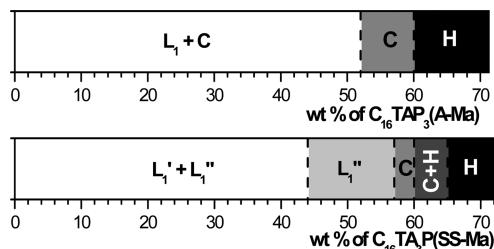


Figure 6. Binary phase diagrams of complex salts (top) $C_{16}TA_3P(A\text{-Ma})$ and (bottom) $C_{16}TA_3P(SS\text{-Ma})$ in water at 25 °C.³⁸ Dashed lines represent estimated boundaries. The notation is the same as in Figures 3 and 4. Reprinted with permission from *J. Phys. Chem. B* 2012, 116, 2376–2384. Copyright 2012 American Chemical Society.

phase diagram for a complex salt based on a random 1:1 copolyion of acrylate and maleate repeat units. Note that the charge density is the same for both copolyions, but whereas the charges on the maleate-*co*-acrylate copolyion are only hydrophilic carboxylate groups, a third of the charges on the maleate-*co*-styrene sulfonate polyion are situated on hydrophobic phenyl groups. Figure 6 shows that for the complex salt based on the latter copolyion the most water-rich concentrated phase is a disordered micellar solution. By contrast, the complex salt with the maleate-*co*-acrylate copolyion features an ordered liquid-crystalline phase in equilibrium with excess water, similar to what has consistently been found for complex salts of highly charged homopolyions PA^- and PSS^- .^{7,16,18} From this, we infer that even highly charged random copolyions can give rise to disordered complex salt structures if they contain a mixture of charged groups with very different hydrophobicity.

2.4.2. Introducing Uncharged, Slightly Hydrophobic Comonomers in the Chain. Some years ago, Norrman et al. studied complex salts consisting of $C_{16}TA^+$ and various copolyions, which contained charged acrylate monomers combined with uncharged comonomer dimethylacrylamide (DAM), *N*-isopropylacrylamide (NIPAM), or acrylic acid.³⁹ It was found that an increasing fraction of uncharged comonomers led to a decreasing aggregation number for the $C_{16}TA^+$ micelles (an increasing curvature of the aggregate) and, eventually, both a loss of liquid-crystalline order and an increased maximum water uptake in the concentrated complex salt phases. Impressively, these features were later predicted semiquantitatively by a simple thermodynamic model for complex salts in water, developed by Hansson.⁴⁰ However, because the focus of the present article is on very recent results, I will not discuss these previous studies in detail here. In the present context, it is sufficient to underline the observation that a copolyion with a large fraction of neutral comonomers does indeed change the structure, compared to that of a simple surfactant, of very concentrated phases. With this observation, we can make the trend, noted above, more precise: polymeric counterions that are both highly charged and flexible produce

the same liquid-crystalline structures in concentrated systems as do conventional monomeric counterions.

Common household products, such as shampoos and laundry detergents, utilize combinations of PI and SI that are insoluble in water as the stoichiometric complex salts but redissolve as overcharged complexes on addition of excess surfactant ions. We will return to such formulations and their use in section 3.2. As described in section 2.1.1, it has been found that C_nTAPAp complexes, which are formed essentially by electrostatic attractions alone, do not redissolve in any excess of the trimethyl alkyl ammonium surfactant if p is large. By contrast, Figure 2 shows that a complex salt containing hydrophobic PSS^- does redissolve with added $C_{16}TACl$, although a very large excess of the cationic surfactant is required. Previous work on polyelectrolyte gels has shown that copolyions of ionic monomers and slightly hydrophobic neutral comonomers give complex salts that are more readily redissolved by excess surfactant, indicating that the additional hydrophobic attraction favors the enhanced binding of SI to the PI above the charge stoichiometry.⁴¹

Recently, Santos et al. made systematic studies of the surfactant redissolution phenomenon by investigating the results of adding surfactant sodium dodecyl sulfate, $NaC_{12}SO_4$, to dilute solutions of a series of cationic copolymers that all had similar charge densities but a varying hydrophobicity of the neutral comonomer (Figure 7).⁴² In these experiments, the onset of phase separation is signaled by an increase in turbidity whereas a subsequent decrease in turbidity reflects the onset of surfactant redissolution. After complete redissolution, there is a constant low level of turbidity. Figure 7 clearly shows that the redissolution by $NaC_{12}SO_4$ becomes increasingly efficient (occurs at a lower concentration of added surfactant) with the increasing hydrophobicity of the neutral comonomer.

Obviously, full phase studies provide much more information on the surfactant redissolution of copolyion complex salts. For that purpose, dos Santos et al. established ternary phase diagrams for a number of complex salts based on random copolyions of acrylate and DAM or NIPAM mixed with water and excess cationic surfactant.¹⁶ It was found that an increase in the content of either DAM or NIPAM gave rise to an increased maximum swelling of the concentrated phase containing added surfactant and eventually, at sufficiently high contents of the neutral comonomer, a sharp redissolution of the complex salt. Figure 8a shows the phase diagram for a complex salt based on a very weakly charged polyion, containing 82 mol % NIPAM and 18 mol % acrylate comonomers, and a $C_{12}TA^+$ surfactant ion. We note the following features, which are quite different from those found for complex salts containing highly charged homopolyions (Figures 1 and 2): (1) The wide biphasic area is surrounded by a continuous disordered micellar phase that extends all the way to the binary complex salt/water axis. (2) In the water-rich region, the phase boundary to the disordered micellar phase is essentially a straight line with a well-defined intercept at the binary surfactant/water axis. The surfactant concentration at the intercept was found to decrease with an increasing content of slightly hydrophobic comonomers.¹⁶ For the system in Figure 8a, the intercept concentration is very close to the critical micelle concentration ($cmc = 30 \text{ mM}$) of $C_{12}TAAc$.⁴³ In other cases, however, the surfactant concentration required for the redissolution of highly dilute systems has been found to be either substantially higher¹⁶ or lower⁴² than the cmc of the surfactant.

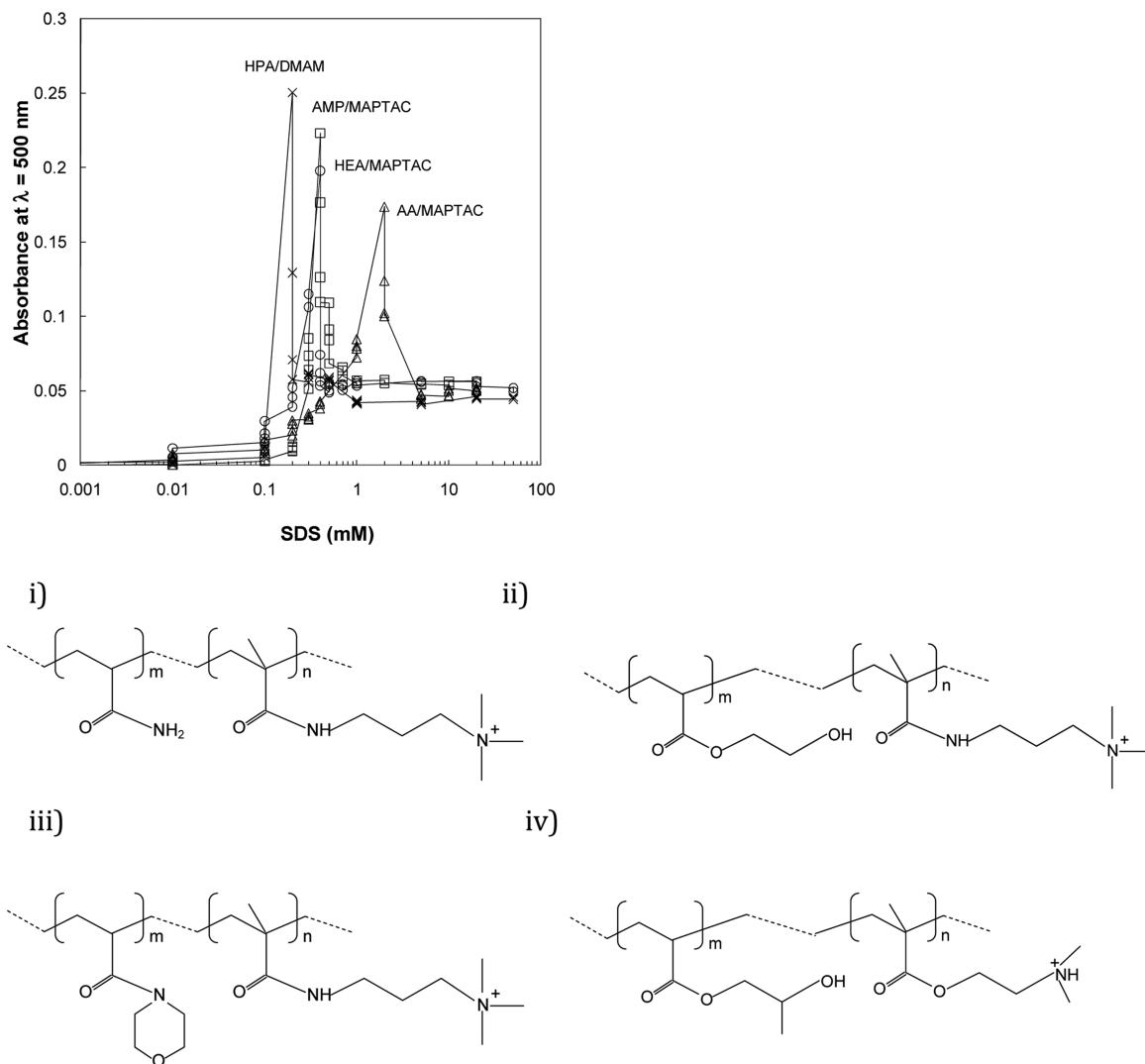


Figure 7. Variation of solution turbidity with added $\text{NaCl}_{12}\text{SO}_4$ for 100 ppm solutions of polyions (i) AA/MAPTAC, (ii) HEA/MAPTAC, (iii) AMP/MAPTAC, and (iv) HPA/DMAM.⁴² Reprinted with permission from *Langmuir* 2010, 26, 9357–9367. Copyright 2010 American Chemical Society.

We conclude this section by noting that the phase diagram in Figure 8a is strikingly similar to that in Figure 8b,⁹ which was established earlier for a chemically very different system where $\text{NaCl}_{12}\text{SO}_4$ was mixed in water with a complex salt that had cationic hydroxyethyl cellulose (cat-HEC) as the polyion and $\text{C}_{12}\text{SO}_4^-$ as the surfactant ion. This suggests that a very general mechanism, insensitive to chemical detail underlies the type of phase behavior seen in Figure 8a,b. We have proposed that this mechanism involves an additional cooperative SI binding step caused by hydrophobic PI-SI interactions, resulting in an “overcharged” and eventually soluble PI-SI complex.^{18,41}

2.4.3. Attaching Blocks of Neutral Comonomers to the Polyion. If soluble complex salts are also desired at charge stoichiometry, when the complexes are net neutral, an obvious strategy is to attach chains of hydrophilic neutral comonomers to the polyions. Early on, Kabanov and co-workers showed that soluble complexes in the 100 nm size range formed when a diblock copolymer, consisting of one neutral hydrophilic block and one ionic block, was mixed with an oppositely charged surfactant.⁴⁴ Each complex was stabilized by a corona of the neutral blocks. A considerable amount of work has since been performed on aggregates of linear neutral–ionic diblock

copolymers with surfactants; a good source of references to the literature is a recent comprehensive review of so-called complex coacervate core micelles.⁴⁵ Detailed scattering studies by Berret et al. have shown that a core of the net neutral aggregates that are formed by this type of system consists of some hundreds of densely packed surfactant micelles, surrounded by polyions and water,⁴⁶ similar to the bulk concentrated phases formed by the corresponding homopolyion complex salts (section 2.1).

Less work has been performed on complexes where the charged polyions contain neutral hydrophilic blocks in the form of grafted side chains. The groups of Kabanov, Maiti, and Bokias have looked at various systems of this type, all using a similar approach.^{47–49} Surfactant was added to a dilute solution of the polyelectrolyte, and measurements were performed in order to gain information on the onset of surfactant self-assembly at the polyions, the presence/absence of macroscopic phase separation, and the size and zeta potential of the dispersed aggregates that were formed in the absence of macroscopic phase separation. It was generally observed that for a sufficiently high fraction of hydrophilic side chains on the polyions well-dispersed aggregates with sizes in the range of

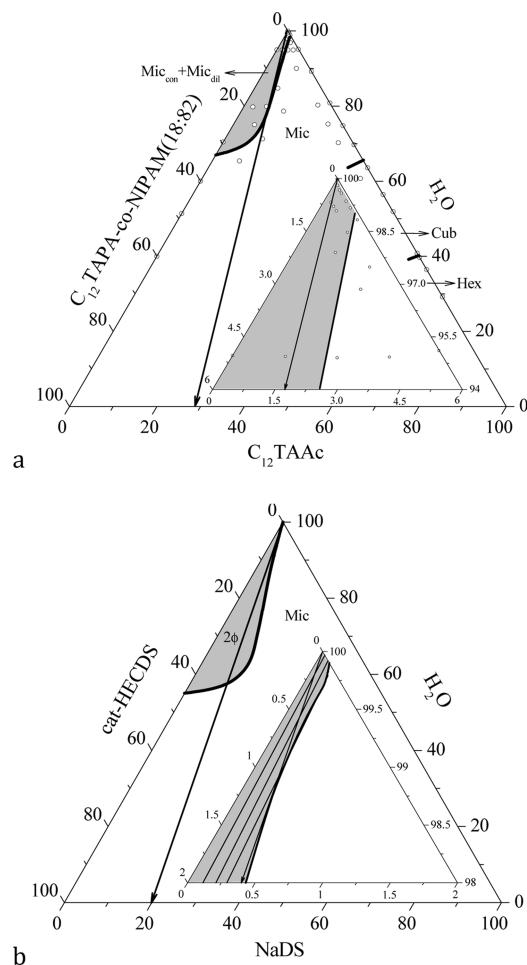


Figure 8. Strikingly similar phase diagrams are found for chemically quite different complex salts based on slightly hydrophobic polyions when excess surfactant is added. $C_{12}\text{TAPA}-\text{co-NIPAM}(18:82)/C_{12}\text{TAAC}/\text{H}_2\text{O}$ (a, from ref 16) and cat-HECDS/ $\text{NaC}_{12}\text{SO}_4/\text{H}_2\text{O}$ (b, redrawn from ref 9) at 25 °C. cat-HEC is a cationically modified hydroxy(ethyl) cellulose. (Insets) Dilute regions of the phase diagrams. Reprinted with permission from *Langmuir* 2011, 27, 592–603. Copyright 2011 American Chemical Society.

30–120 nm were formed even under conditions when the aggregates had no net charge. Recently, Perceboom et al. studied this type of soluble complex using the complex salt approach.^{50,51} A set of copolymers of methacrylic acid with ethoxylated methacrylate were synthesized, and the corresponding complex salts, in which all methacrylate units were charged and neutralized by $C_{16}\text{TA}^+$, were produced and studied over a very wide concentration range in their binary mixtures with water. When the polyion contained a sufficiently large proportion of EO groups, the complex salts became totally miscible with water at room temperature. This was the case for complex salts $C_{16}\text{TAP}(\text{MA-MAEO}_5)36:64$ and $C_{16}\text{TAP}(\text{MA-MAEO}_{24})69:31$ based on polyions containing 64 or 31 mol % neutral side chains with 5 or 24 EO groups, respectively (Figure 9). A disordered L_1 phase dominates the accessible region of the phase diagram (up to 80% complex salt) for both complex salts, but an ordered hexagonal phase was found at high concentrations for the complex containing the most highly charged polyion. Both $C_{16}\text{TAP}(\text{MA-MAEO}_5)36:64$ and $C_{16}\text{TAP}(\text{MA-MAEO}_{24})69:31$ were found to phase separate

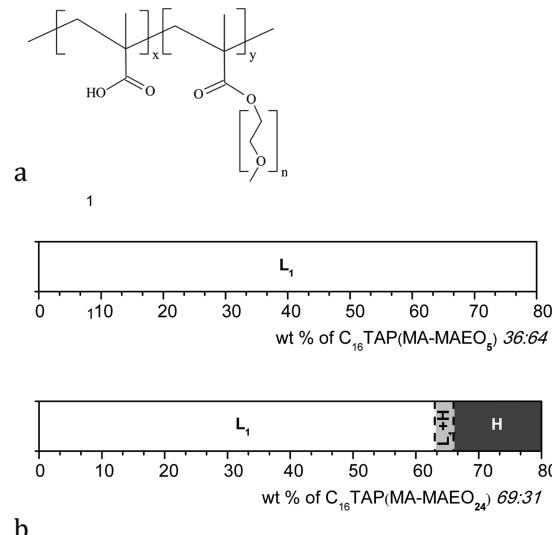


Figure 9. (a) General formula for random copolymers of methacrylic acid and ethoxylated methacrylate and (b) phase behavior of two corresponding soluble complex salts, where all of the methacrylate groups of the copolymers are charged and neutralized by $C_{16}\text{TA}^+$ surfactant ions in their binary mixtures with water. Adapted from ref 50.

from water at higher temperatures; clouding was observed above 50 and 60 °C, respectively.

As would be expected, a smaller proportion of neutral comonomers in the copolyions were required to achieve water solubility if the EO side chains were long. It is interesting to compare the requirements for water solubility of this type of soluble complex salt with a complex salt obtained by incorporating nonionic surfactant in a complex based on a homopolyion (section 2.3). We recall (Figure 5b) that soluble complexes formed by $C_{16}\text{TAP}_p$ when mixed with nonionic surfactant $C_{12}\text{EO}_8$ were found to contain ca. four $C_{12}\text{EO}_8$ surfactant molecules per charged repeat unit of the polyion. Fewer EO groups are thus required to achieve a soluble complex when EO side chains are covalently incorporated into the polyions, compared to when they are added as nonionic surfactants in mixed micelles.

Detailed studies were performed on dilute aqueous solutions of $C_{16}\text{TAP}(\text{MA-MAEO}_5)36:64$ and $C_{16}\text{TAP}(\text{MA-MAEO}_{24})69:31$. Interestingly, surface tension measurements (Figure 10) showed that both of these complexes form micelles at a well-defined cmc of the surfactant ion. This is the first time that the cooperative micellization of surfactant ions in a complex salt has been observed to occur as a consequence of increasing the complex salt concentration in pure water. At concentrations below the cmc, these complex salt solutions should be analogous to ordinary dilute polyelectrolyte solutions, where the counterions (here, nonaggregated surfactant ions) are distributed in an ionic atmosphere around the polyions. The cmc's of the complex salts were much lower than those of common surfactants $C_{16}\text{TABr}$ and $C_{16}\text{TACl}$, which are on the order of 1 mM. Studies by NMR and light scattering at concentrations well above the cmc showed the existence of polydisperse aggregates with an average hydrodynamic radius of ca. 10 nm. The size distribution of these complexes at 25 °C was the same before and after heating a sample to above the phase-separation temperature and cooling back again, suggesting that the aggregates were equilibrium structures. The size of

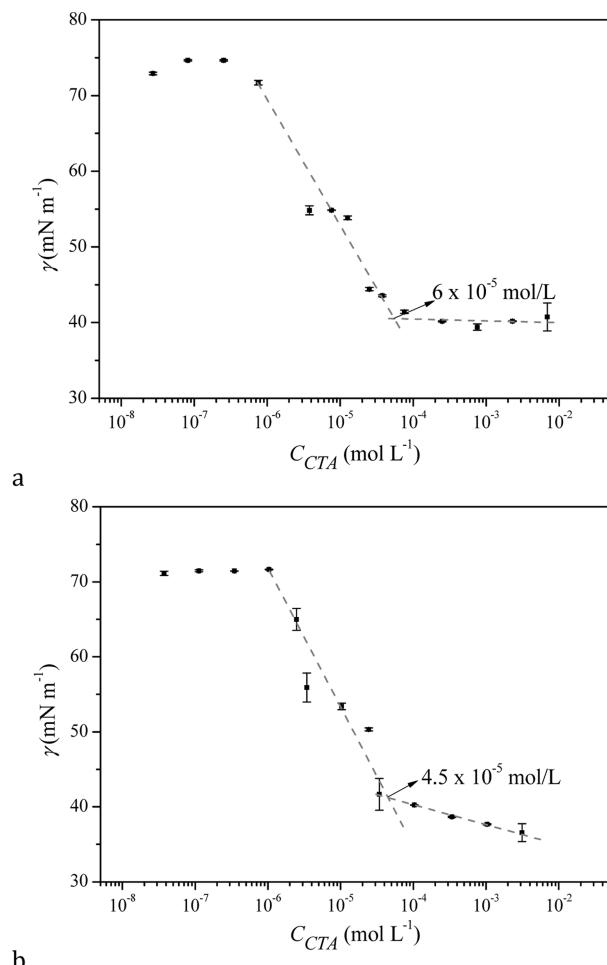


Figure 10. Surface tension measurements of aqueous solutions of (a) $C_{16}\text{TAP}(\text{MA-MAEO}_5)36:64$ and (b) $C_{16}\text{TAP}(\text{MA-MAEO}_{24})69:31$ evidencing cooperative micelle formation at the indicated concentrations of the surfactant ion.⁵¹ Reproduced from *Soft Matter* 2013, 9, S15–S26 by permission of The Royal Society of Chemistry.

a soluble aggregate was found to be consistent with a “hairy micelle” structure, where each average aggregate contains one surfactant ion micelle with an average aggregation number of

ca. 200 neutralized by one copolyion chain with its PEO side chains extending like hairs into the aqueous solution.

3. UTILIZING PHASE BEHAVIOR

The phase diagrams and solution studies summarized above are not only of fundamental interest but also can be used as guides for designing applied formulations and soft materials with the desired structures and properties. This will be illustrated in the present section. We note that in applications both soluble and phase-separated systems may be very relevant. For instance, it may be essential to obtain a concentrated structured material that is stable in the presence of excess dilute solution or pure water. Another very useful aspect of phase diagrams that will be highlighted here is that they actually predict the outcome of processes, such as a simple dilution with water or a chemical reaction.

3.1. Stable Dispersions of Particles with Internal Structure.

Several of the complex salt phase diagrams shown above feature wide biphasic areas where a concentrated phase, often structured, exists in equilibrium with pure water or a dilute solution of excess surfactant. If the structured phase can be dispersed as particles in the dilute solution, which is typically found to be the case, especially in a global excess of either the surfactant or the polyelectrolyte, then one obtains a dispersion of structured particles that can be used as containers or vehicles for the delivery of other substances. Another option is to produce the concentrated phase in the form of a thin surface layer; one may thus obtain a surface film with a controllable structure in contact with a dilute aqueous solution or pure water.

Nizri et al. have shown that stable dispersions of internally structured OCPS particles in the 10–100 nm size range can be produced by simply mixing dilute solutions of a polyelectrolyte and an oppositely charged surfactant if an off-stoichiometric mixing ratio is used to produce the mixtures.^{52,53} One of these studies was on mixtures of NaPA and $C_n\text{TABr}$, which gave particles of a predominantly hexagonal internal structure for long-chain surfactants. This structure agrees with what has been found for the concentrated phase that separates out macroscopically from dilute mixtures of NaPA and $C_{16}\text{TABr}$.⁸ It is then interesting to note that our recent phase diagrams for mixtures with long-chain alcohols and nonionic surfactants (sections 2.2 and 2.3) point to possibilities to obtain phases

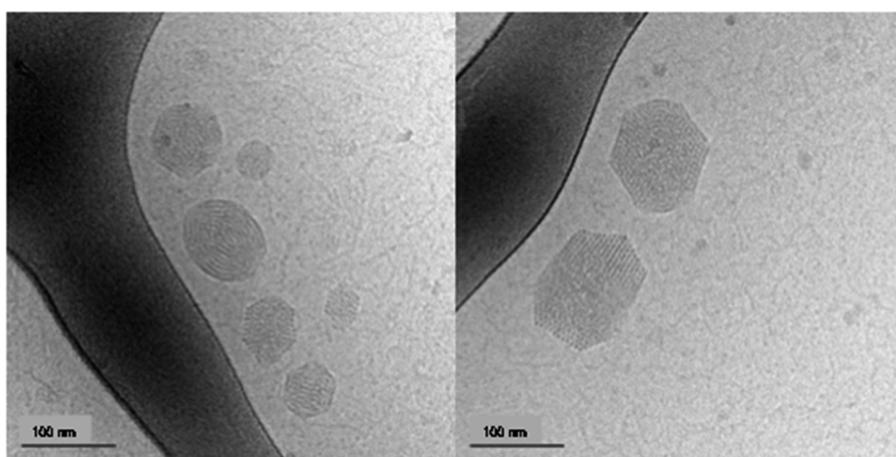


Figure 11. Cryo-TEM images of internally structured nanoparticles composed of $C_{16}\text{TAPA}_{6000}$ and $C_{12}\text{EO}_5$. From ref 54. Reprinted with permission from *Langmuir* 2011, 27, 592–603. Copyright 2011 American Chemical Society.

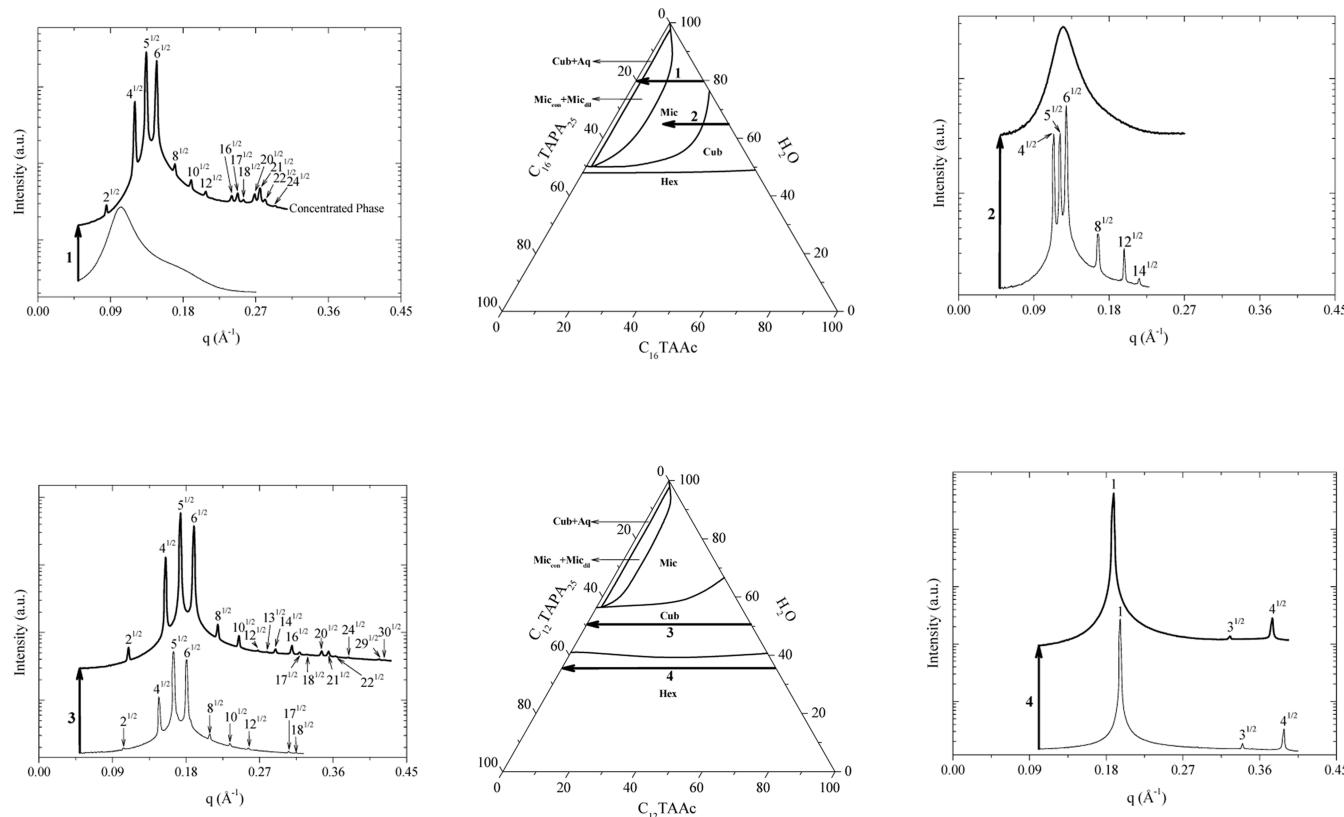


Figure 12. Phase diagrams help us understand how to create, destroy, or preserve structured surfactant phases by polymerizing the counterions. SAXS patterns on the sides show the results of polymerizing acrylate counterions; in each panel, the bottom patterns are before and the top patterns are after polymerization.⁶¹ The horizontal arrows in the central phase diagrams show the changes in composition of the various systems. Reproduced from *Soft Matter* 2011, 7, 1830–1839 by permission of The Royal Society of Chemistry.

with a range of other internal structures. For octanol in particular, particles or surface layers with cubic, hexagonal, lamellar, or inverse hexagonal structures should be possible to achieve in equilibrium with dilute aqueous solutions, according to the results in Figure 3a. Similarly, the phase diagram in Figure 4c above suggests that if $C_{12}EO_5$ is mixed in water with a $C_{16}TAPA_p$ complex salt where p is large then particles with bicontinuous structure could be obtained. Janiak et al. explored the latter possibility, and they were indeed able to make very stable dispersions of particles with a size of ca. 100 nm that, according to SAXS evidence, had a bicontinuous internal structure.⁵⁴ Figure 11 shows cryo-TEM images of some of these dispersions.

3.2. Phase Separation by Dilution. One very useful aspect of a phase diagram is that it predicts the outcome of processes where the composition of the system is changed. For an aqueous formulation, a very common way to change the composition is simply to dilute with water. This corresponds to following a linear path in the phase diagram, starting at the original composition and progressing toward the water corner until the final global composition is reached. For relevance to many applications, we may consider the phase diagram in Figure 8b, which describes the behavior of a complex salt that is insoluble in water but redissolves on addition of excess surfactant. The diagram shows that any single-phase micellar solution of complex salt and excess surfactant will, upon dilution with water, eventually enter the two-phase region and phase separate into one dilute and one concentrated phase. This property of certain oppositely charged polymer–surfactant formulations is used extensively in, for instance, hair-care

formulations.⁵⁵ The aim is that the dilution-induced phase separation should result in the deposition of a layer of the concentrated phase on some target surface, which could be hair but also textiles in laundry applications. A series of studies from our laboratory in collaboration with Procter & Gamble, Cincinnati has shown that this indeed is the case: surface deposition from an OCPS formulation is most efficient under conditions when there is phase separation.^{42,56–58} However, fine-tuning of the phase behavior of the polymer–surfactant combination still becomes an issue. First, one needs a polyion–surfactant ion combination of the type illustrated in Figure 8, where a one-phase formulation can be achieved at a small excess of surfactant. Our accumulated knowledge suggests that some hydrophobicity of the polyion is required for this to be the case (section 2.4.1). However, the surfactant redissolution should not be too efficient. If the two-phase area is too narrow along the complex salt/water binary axis (Figure 8), then a very extensive dilution might be required in order to reach the area of phase separation. The danger is that, at that stage, the system is so dilute that very little surface deposition actually occurs. The results in Figure 7 above then suggest that the polyion should not be too hydrophobic because it will redissolve too readily. Indeed, ellipsometry experiments by Santos et al., where the dilution-induced surface depositions of various formulations containing the polyions in Figure 7 mixed with $NaC_{12}SO_4$ were compared, confirmed this hypothesis: when diluted from formulations at a fixed surfactant concentration, the least hydrophobic polyion in Figure 7 gave the largest amount of surface deposition.⁴² Similar patterns were found

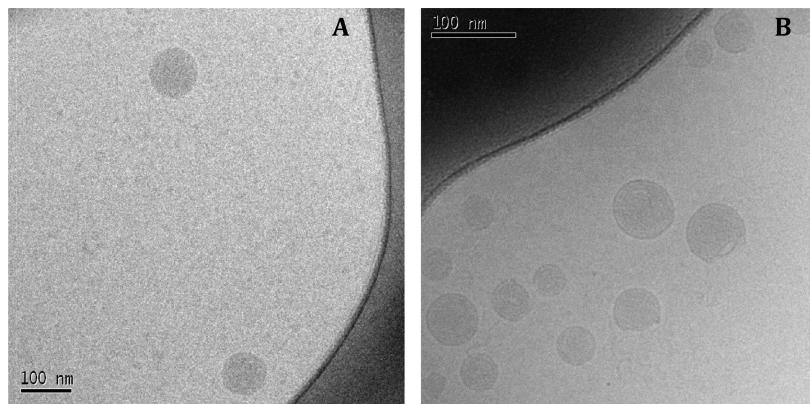


Figure 13. Cryo-TEM images showing the time evolution of particles produced by simply mixing dilute solutions of NaPA with DeBCl, as (A) freshly prepared and (B) after 17 days.⁶⁶ Reproduced from *Soft Matter* 2011, 7, 5540–5544 by permission of the Royal Society of Chemistry.

earlier when comparing polyions based on natural polysaccharides guar and cellulose.⁵⁷

A further challenge for shampoo and laundry applications is that often a codeposition of some dispersed particles on a target surface is desired, together with the deposition of the PI–SI complex. For a conditioning shampoo, emulsified silicone oil droplets are an example of such a desired “codeposant”.⁵⁹ Our studies have shown that the codeposition of silicone oil droplets from OCPS formulations indeed occurs and that the same rules apply here: the codeposition is most efficient if the composition of the original OCPS formulation is not too far from phase separation.^{57,58} The correlation between bulk phase separation and enhanced surface deposition is thus robust; moreover, it applies to both hydrophobic and hydrophilic target surfaces.⁵⁸

The phase diagrams in sections 2.2 and 2.3 above indicate that less conventional mixtures, where components other than excess surfactant are added to the complex salt formulation, also offer possibilities of achieving phase separation by dilution. Thus, it is clear from the phase diagrams in Figure 4 that a dilution of any mixed micellar solution of a complex salt and a nonionic surfactant should eventually lead to phase separation. For some systems, such as the C₁₆TAPA₆₀₀₀/C₁₂EO₅/water system in Figure 4c, the concentrated phase that separates out should also undergo a sequence of transitions between different liquid-crystalline structures on progressive dilution of the system, a feature that implies a responsiveness of the material to the external conditions.

The phase diagram for a mixture with ethanol in Figure 3c presents another interesting case. Complex salts are found to be soluble in ethanol, but if water is added to the ethanol solution, then this should quickly result in the separation of a phase that is concentrated in a complex salt. At sufficient dilution, a liquid-crystalline phase (initially a hexagonal phase for the system in Figure 3c) develops. This is reminiscent of the behavior of certain lipids that are soluble in ethanol but separate out as liquid-crystalline structures on addition of water. For such mixtures, dilution by water is an established method of producing structured nanoparticles.⁶⁰

3.3. Predicting Results of Counterion Polymerization in Ionic Surfactant Systems. Other potentially useful pathways through phase diagrams are those that describe the replacement of one component by another one. Such a replacement may seem difficult to achieve in a real process, but it does in fact occur in a system that undergoes a chemical reaction. For a specific example, the phase diagrams in Figure 1

can be used to predict the results of polymerization reactions, where an originally monomeric surfactant counterion reacts to produce a polymeric counterion. Such a process corresponds to a pathway starting from an original composition along the surfactant/water binary axis and then progressing along a horizontal line to the left across the phase diagram. Complete polymerization would result in a final point on the binary complex salt/water axis, whereas incomplete polymerization gives a final composition with mixed polymeric and monomeric counterions. A recent systematic study by dos Santos et al. confirms these ideas.⁶¹ There it was found that, depending on the choice of concentrations and reactants, polymerization could preserve a pre-existing structure, create structured particles, or even destroy a pre-existing structure. These apparently confusing results could all be readily understood as pathways through phase diagrams. Some examples are shown in Figure 12. The polymerization experiments again illustrate a general feature of complex salt–surfactant mixtures that was noted in sections 2.1 and 2.2: the phase structure is sensitive to the polymerization of the counterion only at high water contents (here above ca. 50 wt %).

The study in ref 61 showed that in some cases particles were produced as a result of the polymerization. Thus, a polymerization process is not only a way to produce bulk materials; one can also produce colloidal particles and polymerized surface layers.

To conclude this section, we note that the production of mesoporous inorganic materials typically involves the polymerization of an inorganic precursor in the presence of a self-assembling amphiphilic molecule, which can be a surfactant with a charge opposite to that of the inorganic material.⁶² The inorganic systems are much more complex than those that we have discussed here for at least two reasons: the reaction baths contain many components, and the structure that evolves does not necessarily represent an equilibrium state because the 3D inorganic polymerization at some point results in the arrest of the structure formed. Nevertheless, general principles and trends that emerge from phase studies of idealized model systems, such as those shown here, are very useful as guides for our thinking on mesoporous systems.

3.4. Systems that Respond or Evolve through Surfactant Hydrolysis. Surfactant ions can undergo interesting and useful chemical reactions. Lundberg and co-workers have demonstrated that degradable betaine ester surfactants can be used to produce systems that evolve with time and/or

respond to changes in pH in a medium.^{63,64} Long-chain betaine esters are cationic surfactants with properties similar to those of alkyltrimethylammonium surfactants with two carbons less in the alkyl tail. Thus, decyl betainate ($C_{10}B^+$) behaves similarly to $C_{12}TA^+$. The betaine esters are especially prone to alkaline hydrolysis, and the hydrolysis results in the production of the zwitterionic betaine and a long-chain alcohol. To understand the consequences of the hydrolysis of betaine, we note that the process can be described as replacing a positively charged surfactant ion with an alcohol and a proton. Although the real system contains more components, insights into the effect of such a process can be gained from phase diagrams of the type shown in Figure 3 above. For the degradation of $C_{10}BPA$, the most relevant phase diagram is that for mixtures of $C_{12}TAPA$ with decanol,⁶⁵ which shows that as the decanol content increases, the structures of the concentrated phase evolve in the sequence cubic \rightarrow hexagonal \rightarrow lamellar. Because acid is produced on hydrolysis, the pH decreases and the system can be designed to be self-quenching so that the hydrolysis effectively stops before all of the betaine ester has been consumed. Another way of ensuring that some ionic surfactant is left after the reaction is, of course, to include some nonreactive surfactant in the reaction mixture. By using these strategies, dos Santos et al. demonstrated that systems with different final structures could be produced by betaine ester hydrolysis.⁶⁶ As an example, Figure 13 illustrates that particles with an internal structure that changes with time can be made using decylbetainate complex salts. When dilute solutions of NaPA and $C_{10}BCl$ were mixed, particles in the 100 nm size range formed spontaneously, in agreement with the findings of Nizri et al. for analogous nonreactive systems.⁵³ However, with time, the particles based on $C_{10}BCl$ evolved to produce a multilamellar onionlike internal structure.

One consequence of the $C_{10}B^+$ degradation is that the content of ionic surfactant decreases. Ultimately, this must result in a disintegration of the PI–SI complexes. This opens up the possibility to design complex salt particles that release their polyions. To demonstrate this possibility, Janiak et al. made solutions of soluble mixed complexes of ca. 10 mM $C_{10}BPA_p$ and ca. 40 mM $C_{12}EO_8$.⁶⁷ Those solution compositions were selected on the basis of the phase diagram in Figure 4a and the subsequent detailed studies of the corresponding micellar solutions in Figure 5. The mixed $C_{10}BPA_p/C_{12}EO_8$ solutions were then degraded by alkali to various degrees and were subsequently studied by NMR diffusometry. Figure 14 reproduces the results for aggregates containing short polyacrylate ($p = 25$) polyions. Figure 14a shows how the self-diffusion coefficients of the nonionic surfactant and the polyion vary with the extent of $C_{10}B^+$ hydrolysis. The nonionic surfactant mostly resides in micellar aggregates, and its diffusion coefficient changes only slightly with degradation, indicating that small mixed micelles dominate throughout. Initially, the mixed micelles contain ionic and nonionic surfactant, but after the complete hydrolysis of $C_{10}B^+$, they should contain nonionic surfactant and decanol. By contrast, the diffusion coefficient of the polyion increases with increasing degradation, demonstrating the release of the polyions from the mixed micellar aggregates. Figure 14b shows how the fraction of released PA^- increases with increasing hydrolysis of $C_{10}B^+$ on the basis of a detailed analysis of the NMR data.⁶⁷

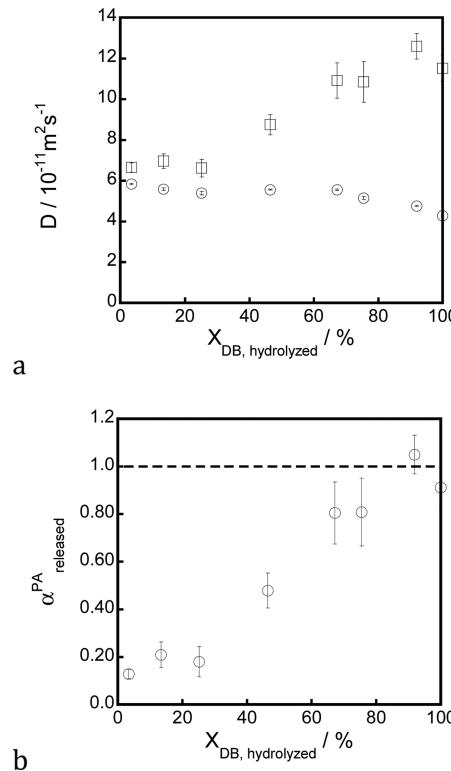


Figure 14. (a) Self-diffusion coefficients of PA^- (□) and $C_{12}EO_8$ (○) at increasing degrees of hydrolysis of $C_{10}B^+$ in mixed aggregates. (b) Fraction of PA^- released from the mixed surfactant aggregates.⁶⁷ Adapted from *Soft Matter* 2013, 9, 4103–4112 by permission of the Royal Society of Chemistry.

4. CONCLUDING REMARKS AND OUTLOOK

Aqueous ionic surfactants are truly versatile systems whose self-assembly properties can be tuned to yield a great variety of aggregate shapes. Additional features appear when polyions are used as the surfactant counterions because the polyions will generally influence the interactions between the surfactant aggregates and sometimes also their shape, hence the great interest in OCPS systems. In water-rich systems, polyions can thus be used to collect surfactant aggregates into anything and everything from finite soluble particles to macroscopic concentrated phases, with or without a liquid-crystalline structure. Mixtures with other low-molecular-weight amphiphilic compounds, such as alcohols or low-molecular-weight surfactants, introduce additional possibilities.

All of the above-mentioned points are generally appreciated by scientists working on OCPS systems and are also widely exploited in applications. However, owing to the complexity of the systems, there is still a lack of systematic knowledge on how to tune the phase behavior of OCPS systems. One of the main purposes of this article is therefore to show that the complex-salt approach can effectively bring out general trends and rules governing OCPS phase behavior and make the underlying molecular mechanisms understandable simply because the minimum number of components is always used to address a specific question. It is my experience that the power of this approach is also quite apparent to industrial scientists whose daily work involves much more complex multicomponent systems. Through the efforts of our group and others, a library of phase studies is now emerging where one can compare not only the effects of altering the PI and SI components but also

the similarities and differences in the effects of different amphiphilic additives.

The other main point of this article is that a phase diagram, like any map of a multidimensional reality, is not merely a description of the features of the landscape around a certain set of coordinates. A map, to someone who knows how to read it, also suggests interesting pathways through the landscape. With the proper imagination, one can thus use an isothermal phase diagram to predict the results of realistic processes where the composition is changed. Obvious processes are those that involve a change in the water content by dilution or drying. A less commonly exploited process in OCPS systems is a change in solvent, and above we have seen how such a process can be understood as a pathway through a phase diagram. Although chemical reactions in OCPS systems are commonly performed, to my knowledge these are rarely analyzed as pathways through phase diagrams. Our work has shown that such an analysis is both possible and powerful; what is required is a phase diagram whose components include both the reactant and the product.

The last point I have attempted to illustrate is that a good fundamental understanding of phase behavior can help us to understand and optimize processes already in use in applications, and it also points to new and interesting possibilities. I am convinced that much remains to be done here. Research on oppositely charged polymer–surfactant systems is not only alive and well but is thriving.

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Notes

The authors declare no competing financial interest.

Biography



Lennart Piculell received his Ph.D. in 1985 at the Division of Physical Chemistry, Lund University, where he now holds a position as professor and the head of the division. After finishing his Ph.D. on the dynamics of water molecules in colloidal systems, he started to study coil–helix transitions and the gelation of carrageenans, a family of charged polysaccharides. His current research deals mainly with polymer–surfactant interactions in the bulk and at surfaces, where he combines studies of carefully chosen idealized model systems with work on considerably more complex formulations that are relevant to industrial applications.

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