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Enhancing Solubilization in Microemulsions—State of the Art and Current Trends

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ABSTRACT: Along a formulation scan, solubilization is maximal when a bicontinuous microemulsion is in equilibrium with both oil and water excess phases in a so-called Winsor III system. The logical way to enhance solubilization is to increase the interaction of the surfactant for both the oil and water phases, which can be easily attained by increasing the size of both the head and tail groups. However, this approach is limited by solubility constraints. Additional solubilization enhancement can be attained by introducing a molecule(s) that bridge the bulk phase and the adsorbed surfactant layer; this can be accomplished by using the so-called lipophilic and hydrophilic “linker effect” or by using block copolymer additives. In either case, the goal is to modify an extended zone in the oil and water domains close to their boundary. The intramolecular grafting of a linker group between the hydrophilic and lipophilic moieties in a surfactant results in a so-called “extended” surfactant structure, which produces enhanced solubilization, as does the surfactant/linker combination, but with the added benefit that the self-contained extended surfactant structure does not undergo selective partitioning. We conclude that an improvement in solubilization is directly related to the presence of a smooth, blurred, and expanded transition across the interfacial region from polar to apolar bulk phases.

KEY WORDS: Extended surfactants, future trends, interfacial tension, lipophilic and hydrophilic linkers, microemulsions, solubilization, state of the art.

MICROEMULSIONS

Microemulsions are thermodynamically stable mixtures of oil and water that are stabilized by surfactants. Although several books have been written on the subject (1–7), they are not al-

ways advisable as introductory reading for the uninitiated researcher because they are symposium proceedings or assemblages of articles with a variety of authors on a variety of concepts that are not always well integrated. The exception is the contribution of Bourrel and Schechter (8), which was written in a pedagogical manner for practitioners, although it might be too complex as a first reading on microemulsions. Several review papers with a pedagogical approach are more convenient for a first contact with the topic, although the presentation approach varies from author to author (9–12). The present monograph seeks to provide such an introductory treatment of the microemulsion as a high-solubilization medium.

Interest in the application of microemulsions continues to grow. Figure 1A presents the number of publications per year on microemulsions, beginning with the original paper by Hoar and Schulman in 1943 (13) and continuing through 2003 (14). Figure 1A shows that microemulsions attracted only limited attention from 1940 to 1970, but that in the mid-1970s, a greater interest in microemulsions emerged because of their potential use in enhanced oil recovery (EOR). Although microemulsion-based EOR proved to be technically feasible, declining oil prices in the late 1980s discouraged its use for economical reasons. However, intensive surfactant research greatly improved our understanding of microemulsion systems, which in turn helped promote their use in a wide variety of applications. Figure 1B illustrates the range of applications that were made possible by advances resulting from the earlier EOR research.

It is worth pointing out that the term “microemulsion” is a misnomer, since, with the exception of some borderline cases, microemulsions cannot be considered tiny droplets dispersed in a continuous phase (15), i.e., a microemulsion is not really a “special case” of a regular emulsion or macroemulsion. In fact, regular emulsions and microemulsions are fundamentally different. Unfortunately, the well-entrenched terminology of “macroemulsions” and “microemulsions” emphasizes similarities that do not really exist. The most fundamental difference between them is that microemulsions exist in a state of thermodynamic equilibrium. In contrast, macroemulsions are metastable two-phase systems in which the coalesced state is the actual state

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Abbreviations: ACN, alkane carbon number; EO, ethylene oxide; EON, ethylene oxide number; EOR, enhanced oil recovery; HLB, hydrophilic-lipophilic balance; HLD, hydrophilic-lipophilic deviation; LC, liquid crystals; OW, oil/water; S+A, surfactant + alcohol; SAD, surface affinity difference; SAOW, surfactant–alcohol–oil–water; SOW, surfactant–oil–water; WOR, water-to-oil ratio.

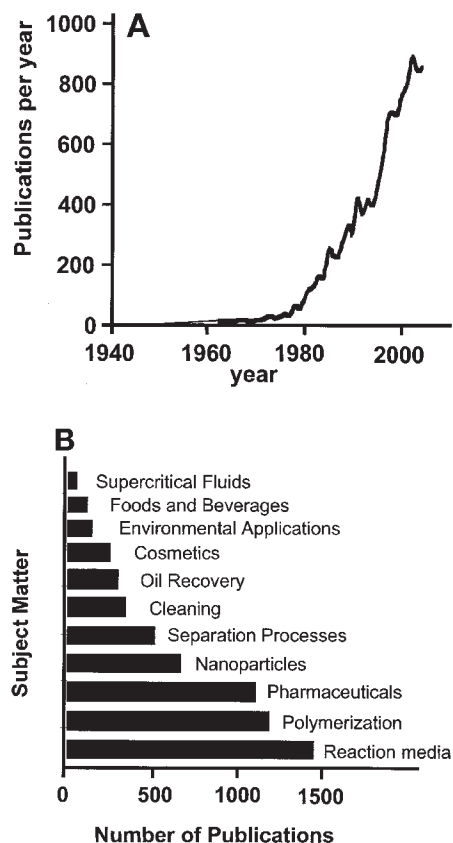


FIG. 1. Publications classified with the key word "microemulsion." (A) Number of publications per year; (B) subject matter or application.

of equilibrium. Macroemulsions are only kinetically stable, meaning that the kinetics of coalescence is slowed by the presence of a film of surface-active materials at the oil/water (OW) interface.

Although microemulsions and macroemulsions are fundamentally different, this does not mean that they are unrelated. In fact, there is a direct correlation between microemulsion type (water continuous vs. oil continuous vs. bicontinuous) and the corresponding type of macroemulsion that is formed by mechanical mixing of a microemulsion and the excess oil and/or water phases. As observed by Bourrel and Schechter (8), when a microemulsion and its excess phase are mixed, the microemulsion becomes the continuous phase of the macroemulsion, in keeping with Bancroft's rule for macroemulsions.

The relationship between microemulsions and macroemulsions goes beyond even this observation, however, in that the conditions leading to a transition from one microemulsion type to another type (for example, the transition from water continuous to bicontinuous) are precisely the conditions that alter the stability of the corresponding macroemulsions. Thus, those having some familiarity with macroemulsions are in a good position to understand microemulsions, the focus of this paper.

Microemulsions are typically classified into three main categories, or Winsor-type systems (16). Winsor's Type I micro-

emulsions consist of oil-swollen micelles in a water continuum, whereas a Type II system consists of water-swollen reverse micelles in an oil continuum. Type III microemulsion systems can be understood as an accumulation of swollen micelles so numerous that they touch one another, forming either some kind of percolated dispersion or a perfectly bicontinuous structure (17,18) in which all water domains are connected and all oil domains are likewise connected. Because microemulsions are not dispersions, the boundary between the oil and water domains does not exhibit a strong curvature. In fact, as far as solubilization is concerned, the best microemulsions are found to have a zero net-curvature condition for the surfactant layer between the oil and water domains. Although a zero net-curvature can be attained by plane geometry, in this case a liquid crystal (LC) of the lamellar type is produced instead of a microemulsion. More desirable are folded but zero net-curvature geometries such as the surfaces depicted in Figure 2 (17,19); these geometries can match the disorder, flexibility, and relatively low viscosity found in microemulsions (20). Such microemulsion systems are typically found in the center of a surfactant-oil-water (SOW) ternary-phase diagram of the Winsor Type III (to be discussed later), which corresponds to a physicochemical formulation in which the affinity of the surfactant for the oil phase exactly matches its affinity for the water phase. This peculiar situation, described by Winsor 50 years ago (16), has been referred to as the "optimum formulation" by people involved in the 1970s EOR research, since it is associated with the ultralow interfacial tension required to displace petroleum from the reservoir after waterflooding (21). The Winsor Type III diagram contains a region exhibiting a three-phase behavior, the occurrence of which is not limited to surfactant systems, and detailed descriptions of whose underlying thermodynamics can be found in the literature, both from the theoretical and the experimental point of view (22). For the purpose of this review, it is enough to quickly analyze the basic concepts of the physicochemical formulation of SOW systems and the so-called formulation scan technique, which will be used to detect the variations of solubilization. Additional details can be found elsewhere (8,11,23).

FORMULATION CONCEPTS

In the past 50 years, several attempts have been made to partially or totally quantify the physicochemical formulation of SOW systems (24). Such attempts include the hydrophilic-lipophilic balance (HLB) (25), the phase-inversion temperature (26,27), the cohesive energy ratio (28), and last, the interaction energy ratio R , which was introduced by Winsor as a handy way to interpret the phase behavior of SOW systems (16). Winsor's approach is actually the conceptual framework underlying the current understanding of formulation and microemulsions, and it will be reviewed briefly here.

In Figure 3, the phase behavior of a SOW ternary system is symbolized according to Winsor's early work. Although ternary-phase diagrams of the type used by Winsor are not often used in modern microemulsion work, they are very

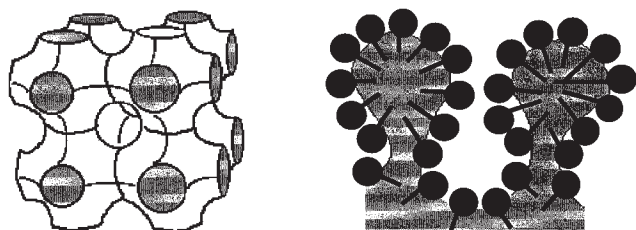


FIG. 2. Models for bicontinuous microemulsion structures exhibiting an average zero curvature (adapted from Refs. 17 and 18).

helpful in understanding the role of the surfactant in microemulsion systems. In a ternary-phase diagram, each of the vertices corresponds to a pure component (surfactant, oil, and water), and the composition of a particular mixture of the three components is represented as a point inside the triangle. In the case of the Type I and Type II microemulsion systems shown in Figure 3, the dome in the lower part of the triangle represents a two-phase (polyphasic) region. A SOW mixture inside the dome will separate into two phases, as indicated by the tie lines shown in Figure 3. In the case of Type I microemulsions, the separation occurs in such a way that an excess oil phase is produced along with a surfactant-rich aqueous phase; the composition of each phase can be determined by locating where the tie line intersects with the dome frontier, i.e., the so-called binodal curve. The intersection point of the tie line and binodal curve closest to the water vertex is the surfactant-rich water phase, whereas the other intersection point is the excess oil phase. This phase behavior is referred to as $\bar{2}$ in Figure 3, a useful mnemonic notation (29) to indicate that the surfactant-rich microemulsion is the lower (generally more dense) aqueous phase. Conversely, in a Winsor Type II two-phase behavior region, the tie-line slope is in the opposite direction, and a surfactant-rich microemulsion (oil) phase is in equilibrium with an excess aqueous

phase, a situation symbolized by the symbol $\bar{2}$. A Winsor Type III system contains a region in which three phases are in equilibrium: a surfactant-rich microemulsion, a so-called middle phase because of its intermediate location in the test tube, and two excess phases (oil and water). For the simplest Type III systems, the three phases can be represented by a tie triangle (excess oil, excess water, and a bicontinuous microemulsion), and any point in the triangle will separate into three phases, as represented by the vertices of the triangle (see the lower ternary diagram in Fig. 3). Although the composition of the three phases is independent of where the system plots within the tie triangle, the relative volumes of the three phases are directly proportional to the proximity of the overall composition to each corner of the tie triangle.

To interpret the different cases of phase behavior, Winsor introduced the following ratio of interactions (R) between the surfactant, oil, and water phases:

$$R = \frac{A_{CO}}{A_{CW}} \quad [1]$$

where A_{CO} indicates the interaction between the surfactant adsorbed at the interface and the oil phase per unit area of interface, and where A_{CW} does likewise for the water phase. Figure 4 shows a schematic for these interactions at the OW interface. In this simplified form, the Winsor R ratio is a handy tool to interpret the phase behavior changes. By definition, $R = 1$ when a middle-phase microemulsion contains equal volumes of oil and water (the tie triangle shown in Fig. 3). When the physicochemical formulation changes, either because of a change in the nature of one of the three components or because of a change in temperature, salinity, or pressure, at least one of the interactions is likely to change. For instance, if the aqueous-phase salinity (electrolyte concentration) increases, the interaction A_{CW} will decrease and R will increase, resulting in an uptake of oil by the middle

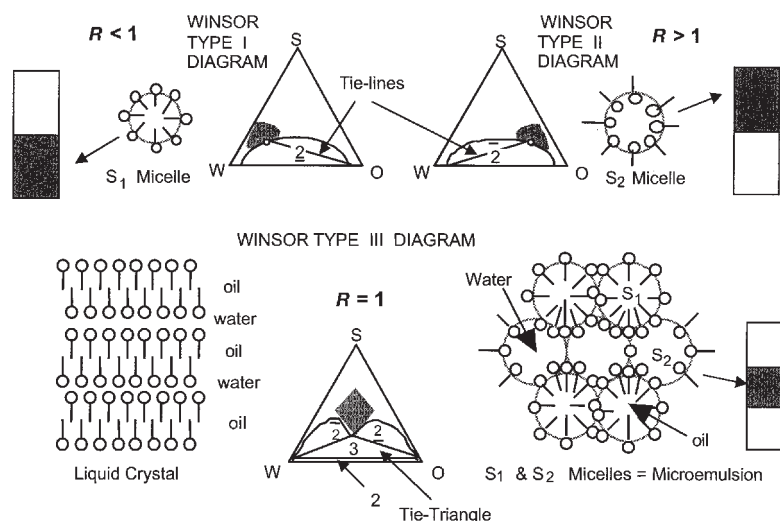


FIG. 3. The three types of phase behavior for surfactant (S)–oil (O)–water (W) systems according to Winsor (adapted from Ref. 16). Shading indicates the surfactant-rich phase.

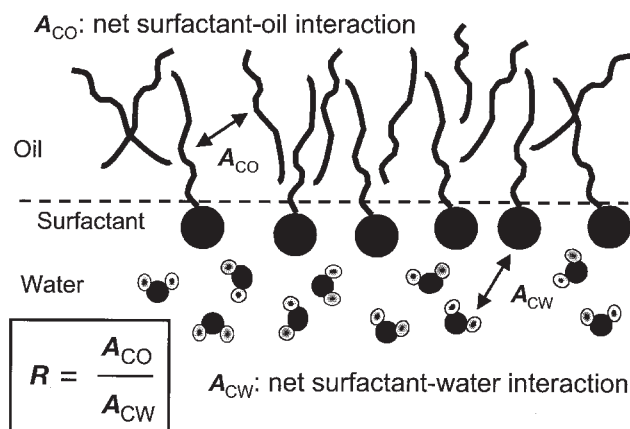


FIG. 4. Adsorbed surfactant interactions with oil and water according to Winsor.

phase. Hence, a change in R from $R < 1$ to $R > 1$, or vice versa, will produce a change in diagram type, which is easily detectable through a change in the phase behavior.

Figure 5 illustrates this transition by a series of test tubes in which the SOW systems have a constant composition of surfactant, oil, and water, as indicated by the square dot in the ternary diagrams, but in which the salinity of the aqueous phase varies from one system to the next (increasing from left to right). The surfactant-rich phase is indicated as the shaded phase in the test tubes. Provided that the composition of the systems is properly selected to be located in the multiphase region, observing the phase behavior in the test tube allows one to deduce the type of Winsor diagram that applies to the system.

Such a series of systems, in which a single formulation variable such as salinity is varied in a continuous way, is called a formulation scan. Most often, changing the formulation variable produces a $I \rightarrow III \rightarrow II$ transition of the phase behavior if the change increases R , or vice versa. The formulation scan is the basic technique to pinpoint experimentally the case in which $R = 1$, a very special situation in which extraordinary phenomena take place (30). Specifically, the interfacial tension goes

through a very low minimum and the solubilization reaches a maximum when $R = 1$. For this reason, the formulation with equal oil and water uptake is known as the optimum formulation, as first designated by EOR researchers. As R approaches but is still less than unity, a three-phase system appears that has more water than oil in the middle phase. This is a “under-optimum” system, e.g., where $S = 2.0$ in Figure 5, one that exhibits a tie triangle slanted to the left (toward the water corner) and a middle phase (shaded) region in the test tube that is centered below the original OW interface. Likewise if R is just greater than unity, e.g., case $S = 4$ in Figure 5, the tie triangle slants toward the oil corner and the center of the shaded area of the test tube moves just above the original OW interface. As described before, for the optimum system both the tie triangle and the shaded region of the test tube are centered, and the interaction of the surfactant with oil and water is exactly balanced ($A_{CO} = A_{CW}$ and $R = 1$).

Winsor’s research pointed out that there are only three basic types of diagrams in a true SOW system and that the type of diagram, and thus the type of multiphase region, depends solely on the interaction ratio (R). Thus, in a single parameter, the R ratio provides a unique yardstick to describe the formulation. This was quite an enlightening revelation because most formulators were struggling with dozens of variables to define their systems.

However, in Winsor’s time, and even much later, the individual interaction energies (A_{xx}) could not be estimated with accuracy. Hence, this formulation yardstick had to be quantified in some other way, which was a major focus of the EOR research frenzy. As reported extensively in Bourrel and Schechter’s book (8), thousands of formulation scans were carried out, and the effect of every imaginable variable was studied. Since the R ratio can be altered by many different variables, there are many different ways to make it unity, and from there to change it to $R > 1$ or $R < 1$.

For relatively simple systems, multivariate three-phase behavior correlations were provided as a linear relationship between the formulation variables for anionic (31), cationic (32), and nonionic surfactant systems (33). These expressions were later found to be related to the free energy of transfer of a surfactant molecule from the water to the oil phase ($\Delta G[w \rightarrow o]$), also called the surfactant affinity difference (SAD), where the affinity is taken as the negative of the standard chemical potential:

$$SAD = -\mu_o^* - (-\mu_w^*) = \mu_w^* - \mu_o^* = \Delta G(w \rightarrow o) = RT \ln(C_o/C_w) \quad [2]$$

where μ_w^* and μ_o^* are the chemical potential of the surfactant in the water and oil phase, respectively; R in this case corresponds to the ideal gas constant; T is the temperature; and C_o and C_w are the concentrations of surfactant in the oil and water phases, respectively.

The dimensionless SAD value (SAD/RT) was called the hydrophilic-lipophilic deviation, or HLD (from an optimum formulation situation), i.e., some kind of global HLB not far from a clever early suggestion (34), identified by the correlations for

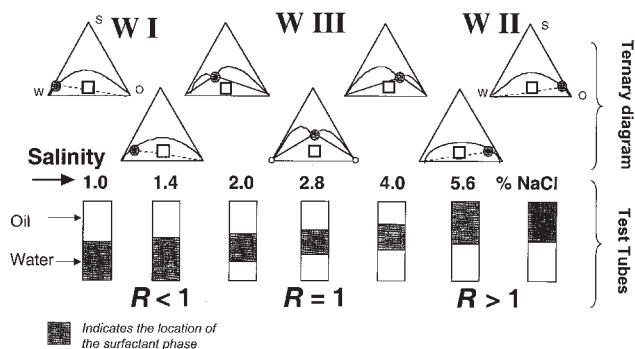


FIG. 5. Phase behavior along a salinity scan: test tube aspect and phase diagrams.

three-phase behavior, with some slight reference adjustments for the sake of thermodynamic correctness (35). By definition $R = 1$ when $HLD = 0$. Both concepts are defined as “optimum” conditions, i.e., where the middle phase or Winsor Type III microemulsion contains equal volumes of oil and water. Since the partition coefficient of the surfactant (36,37) is attainable by measuring surfactant concentrations in the excess phases of a three-phase system, the unknown data in the HLD expression can be measured.

The generalized formulation can be rendered by the following expressions:

$$HLD = SAD/RT = \ln S - K(ACN) - f(A) + \sigma - a_T(\Delta T) \quad [3]$$

(ionic systems)

$$HLD = SAD/RT = \alpha - EON + bS - k(ACN) - \phi(A) + c_T(\Delta T) \quad [4]$$

(nonionic systems)

where S is the salinity in wt% of NaCl; ACN is the alkane carbon number, which is a characteristic parameter of the oil phase equal to the number of carbon atoms per molecule for alkanes, $f(A)$ and $\phi(A)$ are functions of the alcohol type and concentration, respectively; σ and α are parameters characteristic of the surfactant structure; and EON is the average number of ethylene oxide groups per molecule for a polyethoxylated nonionic surfactant. ΔT is the temperature deviation measured from a certain reference (25°C); and k , K , a_T , and c_T are empirical constants that depend on the type of system (12,15,38,39).

These expressions encompass the same concept as the Winsor R ratio in providing a unique generalized formulation variable, but this time in a more quantifiable way, with the equivalence between $R = 1$ and $HLD = 0$, $R > 1$ and $HLD > 0$, and vice versa. The signs in the numerical expression indicate the way in which each variable alters the formulation, and the coefficient values allow one to evaluate the relative effect of the different variables. Nonoptimum formulations can also be compared according to their HLD values.

Not only is the HLD concept useful in formulating microemulsions, but it has also been used to model aggregate sizes, solubilization, phase volumes, phase transitions, and interfacial tension of microemulsion systems (Types I, II, and III). This has recently been done by using the HLD concept in a critical scaling/statistical modeling approach to microemulsions, and is known as the net-average curvature model (40).

SOLUBILIZATION IN MICROEMULSIONS

Solubilization, not to be confused with solubility, refers to the increase in equilibrium coexistence of oil and water (i.e., in a single-phase system), which results from the addition of a third component. Miscibility can be reached above a critical point, but this is not considered here because of the required extreme pressure and temperature conditions in the case of oil and water. Miscibility of oil and water also can be attained

by adding solvents such as C_2 – C_5 alcohols (41), ketones, or the like [e.g., butoxyethanol (42–44), which is not referred to as a “real” surfactant but as an amphiphile (45,46)]. This approach, sometimes referred to as co-solvency, requires a very high amphiphile concentration, e.g., 50% or more. Such systems result in a random molecular mixture, i.e., a true solution, and thus rely on solubility rather than solubilization.

Solubilization results from the presence of highly efficient sheltering structures, such as swollen micelles that contain a core phase immiscible with the solvent phase, which is hidden or encapsulated somehow by the presence of the surfactant. Hence, solubilization is related to the presence of surfactants that are able to produce micelles. Since micelles are aggregates with 100 or so molecules, they are relatively large; as such, a small amount of surfactant, say, 10% or less, is sufficient to solubilize large amounts of both oil and water, one outside the micelles (or inverse micelles) and the other one inside them (47).

In any case, the amount of oil solubilized inside the micelle is proportional to the volume or the cube of the radius, whereas the amount of surfactant required to form the micellar “skin” is proportional to the micellar surface area, i.e., to the square of the radius (if micelles are assumed to be spherical). Hence, the solubilization parameter, which is the amount of a phase solubilized in the core of the swollen micelles per unit mass of surfactant, is proportional to the volume (amount solubilized) divided by the surface area (surfactant) and is thus roughly proportional to the radius or micellar size. Therefore, as the micellar size increases (as the curvature decreases, as the Winsor R ratio approaches a value of 1 or the HLD tends toward 0), the solubilization improves. When micelles are numerous enough to touch each other and percolate, they form a microemulsion structure that, according to Winsor, looks like a mixture of micelles and inverse micelles, whose cores are connected and whose boundary curvature changes from place to place and from time to time. This is essentially the kind of bicontinuous structure discussed earlier. In such a case, it can be said that the solubilization parameter is roughly proportional to the characteristic length of the domains in the bicontinuous structure.

From a practical point of view, solubilization can be measured in two ways. First, it can be measured through the solubilization parameter SP_o (or, respectively, SP_w), which is defined as the maximum amount of oil (respectively, water) solubilized in the microemulsion (m) per unit amount of surfactant (S) ($SP_o = V_{oil}/m_S$ and $SP_w = V_{water}/m_S$) (23). The word “maximum” implies an excess of this phase, and is hence a multiphase system.

Another way to measure solubilization is to measure the minimum amount of surfactant necessary to produce a single phase in an SOW system (i.e., the oil, water, and surfactant coexist all as one phase). This concept can easily be observed in a ternary diagram representing the phase behavior since it corresponds to the height of the polyphasic zone located near the OW side. In most cases, and to avoid giving a preference to one of the phases, the solubilization is measured

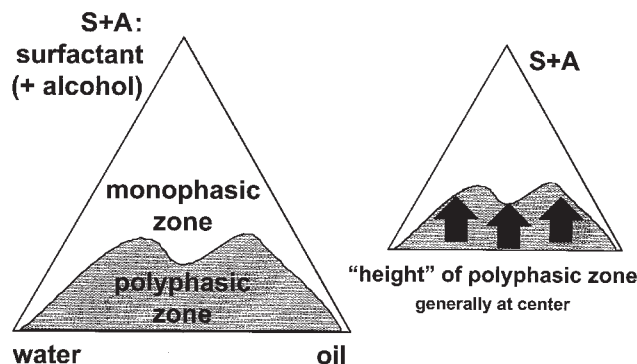


FIG. 6. Quality of a formulation as the minimum amount of surfactant (S) and alcohol co-surfactant (A) to attain the single-phase-behavior region in a ternary diagram.

at the center of the diagram, i.e., as the height of the polyphasic zone along the median of the OW side (see Fig. 6). This height is often referred to as S+A (%) to indicate that it is the amount of total amphiphile, including both surfactant and alcohol, in which the alcohol is often present to avoid the formation of LC.

When the S+A% required to attain the single-phase region for a certain water-to-oil ratio (say, unit WOR) is plotted against a formulation variable (e.g., any of the variables able to alter the SAD), a minimum is found at the so-called optimum formulation, as indicated in Figure 7 (bottom-left graph). In this figure, which is often called a gamma phase diagram, the S+A requirement to obtain the single-phase region (1ϕ) passes through a minimum at a so-called “tricritical point,” indicated as a cross. Below this point, a three-phase region (3ϕ) indicates that a microemulsion coexists with ex-

cess oil and excess water. An equivalent plot (Fig. 7, bottom-right graph) is often found in studies with ethoxylated non-ionic surfactants, in which the temperature is the formulation variable but in this case is plotted as the ordinate. In fact, it is the same diagram as before but rotated 90° , and because of its shape, it is referred to as a “fish” diagram by some researchers.

In practice, a three-phase system is sufficient to estimate solubilization (by the measurement of phase volumes) since the amount of surfactant in the excess phases is extremely small and can be neglected. This is true for many systems, although not necessarily for nonionic surfactants that can partition into the oil phase at high concentrations without producing micelles (48).

In the presence of a mixture of surfactants, or of a surfactant and alcohol, the two amphiphiles can fractionate differently between the phases; hence, the composition of the interface might depend on the overall concentration of amphiphile and on the WOR (49–51). As a consequence, the formulation (in particular, the optimum formulation) depends on this concentration. In this case, the gamma or fish diagram exhibits an optimum concentration that depends on S+A%. In practice, this means that the center line of the three-phase region is not at a constant formulation or temperature but is more or less slanted, as indicated in Figure 8. The slanting can be one way or the other, depending on the amphiphile. In the case of a surfactant and an alcohol, the alcohol generally leads the formulation change with S+A total concentration at a constant alcohol/surfactant ratio. In other words, if the alcohol is more lipophilic than the surfactant (usually the case for *n*-butanol and higher alcohols), an increase in S+A concentration produces an increase in lipophilicity of the interfacial S+A

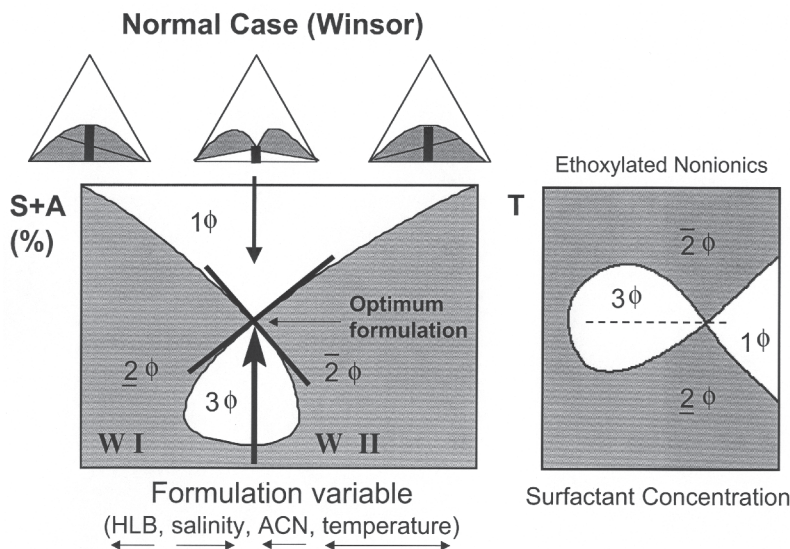


FIG. 7. Phase behavior of a surfactant–alcohol–water–oil system at a constant water-to-oil ratio. Amount of surfactant and co-surfactant to attain the single-phase behavior as a function of formulation or temperature (T) in the case of the collective behavior of the surfactant and co-surfactant. HLB, hydrophilic-lipophilic balance; ACN, alkane carbon number; for other abbreviation see Figure 6.

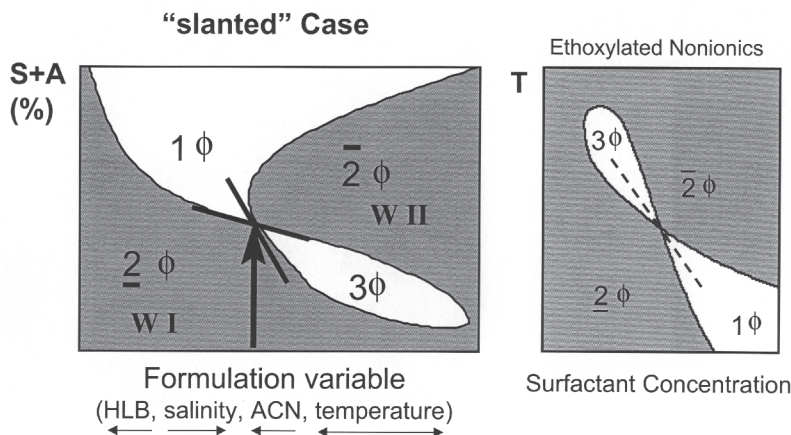


FIG. 8. Phase behavior of a surfactant–alcohol–water–oil system at a constant water-to-oil ratio. The amount of surfactant and co-surfactant to attain the single-phase behavior as a function of formulation or temperature (T) in the case of partitioning behavior of the surfactant and co-surfactant. For abbreviations see Figures 6 and 7.

mixture that has to be compensated for somehow, e.g., by a decrease in salinity (Fig. 8 left) or, with ethoxylated nonionic surfactants, a decrease in temperature (Fig. 8 right) or an increase in EON. With very short-chain alcohols, the slanting is in the opposite direction but is often not as dramatic (52). The best solubilization is attained at the tricritical point in this case as well, occurring at a given amount of S+A and at a precise formulation or temperature. Hence, three-phase systems with lower S+A might indicate a different optimum formulation.

An alternative representation is the variation of solubilization parameters with respect to the formulation variable at a constant system composition (surfactant concentration and WOR), as shown in Figure 9. When far from the optimum formulation, the solubilization parameters are low and essentially correspond to micellar solubilization. As the optimum formulation is approached from either side, the solubiliza-

tion increases as the micellar size increases and the curvature decreases. In the three-phase region, both solubilization parameters exist and at some point they are equal. This crossing point at which $SP_o = SP_w$ is often referred to as the optimum solubilization and is designated as SP^* (23). It essentially coincides with an optimum formulation in which the interfacial tension (γ) undergoes a deep minimum. This correlation between the variation of the interfacial tension and solubilization parameter has generally been found to be valid and is expressed in the following relationship, sometimes referred to as the Chun Huh relationship: $SP^* \gamma = \text{constant}$ (53,54).

Hence, at an optimum formulation the interfacial tension passes through a minimum (γ_{\min}), whereas the solubilization parameter reaches a maximum (SP^*). These values define the “quality” of an optimum system and allow one to

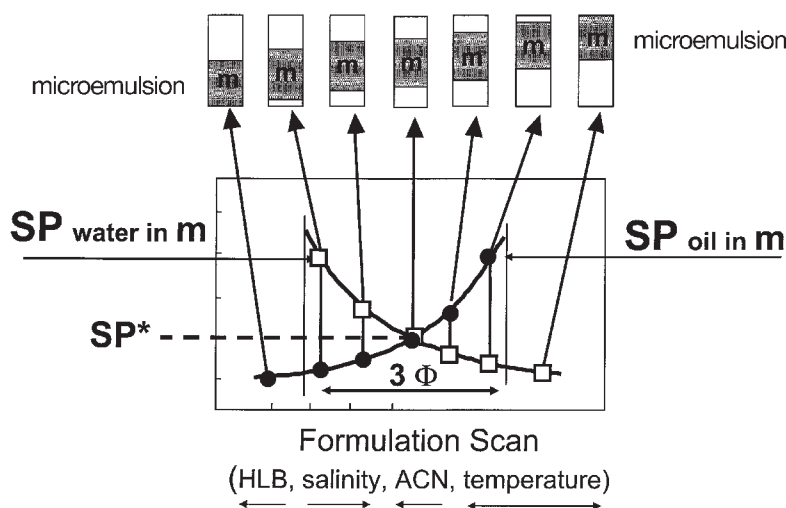


FIG. 9. Solubilization variation along a formulation scan, expressed as solubilization parameters (SP). m, microemulsion; for other abbreviations see Figure 7.

compare systems from a global or topological point of view (55). It is worth noting that any comparison of solubilization must be made between an optimum formulation and another optimum formulation (along different scans, but always at $HLD = 0$); if not, the variation of solubilization with HLD will blur the comparison and thus the conclusion. As indicated earlier, the variation in solubilization vs. the formulation near the optimum has been studied, showing that the variation in the correlation length along a formulation scan is directly related to the deviation from an optimum formulation, as measured with a generalized parameter such as HLD , a numerical value that accounts for a free energy deviation from the optimum formulation situation (40). Whatever the shape of the structure, lower interfacial tension or increased solubilization implies a more solubilized phase (i.e., volume) per solubilizing surfactant (i.e., surface), that is, a larger structure domain or larger correlation length (40,56), and hence increased light-matter interactions and a corresponding increase in opacity. This actually means that a good microemulsion, i.e., one with high solubilization, is not completely transparent at all, contrary to the definition found in many early, and some even not-so-early, publications of a microemulsion as a transparent system. An SP^* value larger than 5 g of water or oil per gram of surfactant produces a translucent bluish microemulsion, characteristic of a Tyndall diffusion, whereas an SP^* value larger than 20 definitely corresponds to an opaque microemulsion, which can be similar in appearance to a macroemulsion. It should be noted that when $SP^* = 20$, 1 g of surfactant is able to cosolubilize 20 g of water and 20 g of oil in a single phase. This means that, in this case, the $S+A$ value at optimum is 2.5%, an extremely slim diphasic zone in a ternary diagram, hence showing very good solubilization. Although at these levels of solubilization, microemulsions and macroemulsions can have similar OW -to-surfactant ratios, the interfacial tensions experienced by the microemulsion systems range between 10^{-4} and 10^{-5} mN/m, which is consistent with the Chun Huh expression (53,57). In addition, microemulsions are equilibrium systems. Once again, the term microemulsion could be misleading to the uninitiated, as it fails to emphasize the equilibrium nature of these SOW systems.

SOLUBILIZATION ENHANCEMENT WITH A SINGLE AMPHIPHILIC SPECIES

Solubilization depends on more than the surfactant; it also depends on the nature of all the additives as well as on temperature (and probably pressure). Since a comparison of microemulsions has to be carried out between two optimum formulations, the effect always depends on a change of at least two formulation variables: one change to move away from the first optimum formulation (at which $HLD = 0$), and a second change to again attain an optimum formulation (i.e., to return to $HLD = 0$). It is thus impossible to isolate the effect of a single formulation variable.

The trends of the dual changes found in the exhaustive studies carried out by Bourrel and co-workers (52,58,59) indicate that an increase in solubilization is produced in ionic surfactant systems by the following compensating changes: (i) a decrease in both oil ACN and salinity; (ii) a decrease in salinity and an increase in surfactant alkyl chain length (23); or (iii) a decrease in oil ACN and a decrease in branching in alkyl benzene sulfonates (60).

In ethoxylated nonionic surfactant systems an increase in solubilization is produced by similar compensating changes (61): (i) a decrease in temperature and a decrease in EON ; (ii) a decrease in temperature and an increase in alkyl chain length; (iii) a decrease in temperature and an increase in salinity; (iv) a decrease in temperature and a decrease in oil ACN (62); or (v) an increase in both the alkyl chain length and EON (63).

With ethoxylated Guerbet alcohol sulfates, an increase in solubilization is attained by decreasing the temperature and either increasing the salinity (for a high degree of ethoxylation) or decreasing it (for a low degree of ethoxylation) (64).

In a number of cases, a minimum in interfacial tension (hence, a maximum in solubilization) seems to take place for a specific formulation, probably as a combination of opposite trends (58,65,66). For instance, in Figure 10, an intermediate degree of branching (isomer 5 ϕ) results in the lowest value of the minimum in interfacial tension (67), noted as $(\gamma_{min})_{min}$. It has also been reported that in a $\ln S - ACN$ compensated variation, the width of the three-phase region, either as ΔS or ΔACN , is inversely related to the value of solubilization (63). On the other hand, other compensating changes—for instance, (i) an increase in oil ACN and surfactant alkyl chain length (68,69) or (ii) an increase in EON and an increase in salinity (59)—seem not to affect the solubilization in a significant way.

The data in Figure 10 not only indicate that branching influences solubilization but also demonstrate another concept helpful in understanding microemulsion phase transition: the surfactant critical packing factor (68). The surfactant packing factor is expressed as $v/(a^*l)$, where v is the volume of the surfactant tail, a is the surfactant area per molecule, and l is the length of the surfactant hydrophobe. Critical packing factors of 1:3 suggest spherical micelles (Type I), whereas packing factors near 1 suggest that the surfactant molecule has the tendency to form zero-curvature surfactant membranes (Type III). Critical packing factors much larger than 1 form negatively curved (Type II) microemulsions (70). Thus, increasing the critical packing factor by decreasing the area per head group (e.g., increasing salinity, shielding the ionically charged head groups) or increasing the volume of the tail group (e.g., using branched surfactants) predicts a transition from Type I to Type III to Type II, in keeping with the formulation experience.

The importance of a balanced surfactant system is consistent with a suggestion made by Winsor 50 years ago, i.e., that increased interactions on both sides of the interface would enhance the affinity of the surfactant for both phases, and

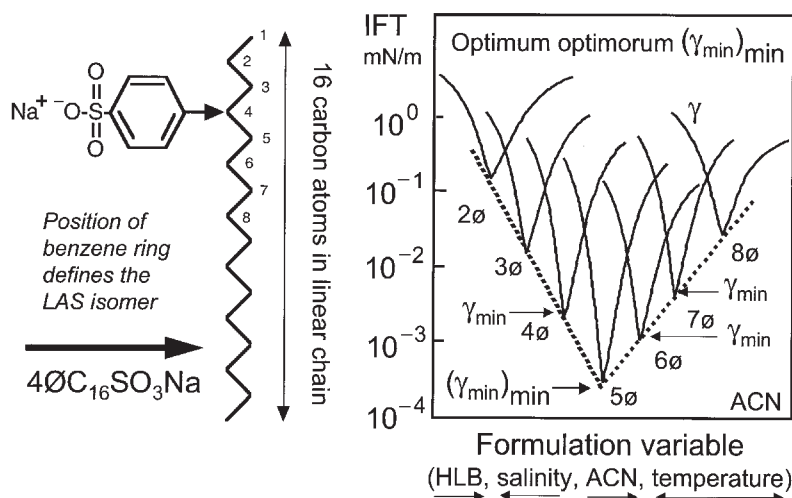


FIG. 10. Variation of interfacial tension (IFT) along a formulation scan for different *n*-hexadecyl benzene sulfonate isomers. An envelope of minimum tension values (γ_{\min}) indicates an optimum of IFT for the $5\text{ØC}_{16}\text{LAS}$ isomer (adapted from Ref. 67). LAS, linear alkylbenzenesulfonate; for other abbreviations see Figure 7.

would thus improve the solubilization while maintaining optimum behavior. Since the maximum solubilization of a scan takes place when the interactions are equal, i.e., when $R = 1$, it was a matter of comparing various ways to attain $R = 1$, e.g., $R = 2:2$ or $5:5$, or to reach $\text{HLD} = 0$, e.g., $\text{HLD} = 2 - 2$ or $5 - 5$.

Bourrel and Chambu (71) used the dual-variation technique for microemulsion optimization (12), whereby one starts at an optimum formulation, then changes a first formulation variable to place the system off optimum, and finally brings the system back to yet another optimum formulation by changing a second formulation variable. They showed definitively that, for compensating changes, when the first occurs on one side of the interface and the second on the other side, and thus the return to $R = 1$ implies an increase in both the numerator (N) and denominator (D), an increase in solubilization results. On the contrary, when the compensating changes are both on the same side of the interface, hence the return to $R = 1$ does not produce corresponding changes in N and D , no change in solubilization is observed (71).

The simplest way to improve solubilization at optimum is thus to increase the interaction of both the polar head group with water and the apolar tail group with oil. This can be achieved by using bigger or longer groups while keeping the same optimum formulation [e.g., passing from $\text{C}_{12}\text{--OSO}_3\text{Na}$ to $\text{C}_{18}\text{--CH}(\text{COONa})\text{--NH--OCH}_3$, which has exactly the same hydrophilicity and hydrophobicity (71)]. This is particularly easy to do with ethoxylated nonionic surfactants in which the hydrophilicity can be varied continuously by changing the average EON of a mixture (72). For instance, a nonyl phenol with 5.1 ethylene oxide (EO) groups has the same hydrophilicity as a dodecylphenol with 8.3 EO groups, but the second one produces twice as much solubilization of octane and water. However, increasing both groups in order to boost solubilization has a limit. For example, apolar tails longer

than C_{18} are highly susceptible to precipitation, either because the conditions are below the Krafft temperature or above the cloud point, or because a mesophase is formed. So the challenge is how to achieve increased values in N and D within the limitations of surfactant solubility, as discussed in the next section.

SOLUBILIZATION ENHANCEMENT WITH MULTIPLE AMPHIHILIC SPECIES

In many microemulsions, the surfactant is accompanied by a so-called co-surfactant, e.g., a smaller amphiphile with a reduced head and tail size compared with the surfactant. It can be an amine, an acid, or a phenol, but in most cases it is an alcohol in the $\text{C}_3\text{--C}_6$ range, sometimes longer. For this reason it is labeled "A" in this paper (also known as an S+A mixture). Co-surfactants appear to play three different roles, two of which we will refer to as the "conventional" ones, which have been known since the days of EOR research. Here we also introduce a third more recently recognized role, which is referred to as the "linker effect."

Role of the co-surfactant as a formulation modifier. The first of the conventional roles of a co-surfactant is to adsorb at the OW interface and become a part of the S+A amphiphilic mixture. As such, it modifies interactions on the interfacial layer with oil and water and thus alters the formulation. Short-chain alcohols (methanol and ethanol) slightly increase the hydrophilicity, whereas C_5 alcohols and higher tend to increase the lipophilicity (73), requiring opposite compensations in salinity, temperature, and so on to remain at optimum formulation. The effect, measured by the $f(A)$ and $\phi(A)$ functions in correlation Equations 3 and 4, respectively, is positive for the hydrophilic alcohols and negative for the lipophilic ones; at low concentrations, it can be approximately

expressed as a linear function of the alcohol concentration, with a proportionality coefficient that increases with the alcohol chain length (12). In practice, it means that introducing a certain amount of pentanol in an SOW system tends to increase the HLD value, but by less than adding the same amount of hexanol. The value of $f(A)$ or $\phi(A)$ actually depends on the partitioning of the alcohol between the phases. Hence, the alcohol that does not produce any change in formulation, i.e., the one with $f(A)$ or $\phi(A) = 0$, slightly depends on the oil and water, but not by very much. For instance, shifting from *n*-propanol to *n*-butanol helps compensate for a change in the oil phase from hexane to octadecane and for an aqueous phase that is pure water. If the water contains some electrolytes, the range is shifted slightly toward shorter-chain alcohols (71).

As a rule of thumb, it can be said that the $f(A)/\phi(A) = 0$ alcohol is approximately a mixture of *n*-propanol and *n*-butanol, say, a $C_{3.5}$ alcohol (essentially equivalent to *sec*-butanol) for the middle-of-the-road system in which the oil is decane and the water a 2% brine (slightly shorter for higher salinity; slightly longer for a longer alkane).

The co-surfactant as a source of disorder. The second conventional role of the co-surfactant, which is crucial in EOR, is to keep the viscosity low by avoiding the formation of gel phases, i.e., LC. LC form because of the self-association interactions that take place between surfactant molecules, particularly for ionic species. LC can be "melted" by introducing disorder, either thermotropic or lyotropic, or by introducing geometric disorder, i.e., by mixing different amphiphilic species so that they do not fit together well enough to generate an organized structure such as LC. Because of their amphiphilic character, co-surfactant molecules are driven to the surfactant molecules and are able to produce a disordered S+A mixture. At interfaces, they adsorb and push the surfactant molecules apart, hence reducing the surfactant-surfactant interactions as well as the interactions of the interfacial layer with oil and water, thus reducing the solubilization (74). The same happens with other short amphiphiles such as amines, amides, or carboxylic acids (75) or other additives that have been proposed, such as butoxy-random EO-propylene oxide polyethers (76,77). These compounds might be called co-solvents, as in the case of some intermediate alcohols (*sec*- and *tert*-butanol, *tert*-pentanol), since their main role seems to be to reduce the antagonism of the OW binary mixture by making the water less polar and the oil more polar (78).

In general, it can be said that long- and straight-chain surfactants, particularly ionic surfactants, exhibit a high solubilization but tend to produce LC and gel phases, whereas mid-chain and branched and mixed surfactants do not produce as high a solubilization but do not produce gel phases. A mixture of both kinds has been found both to disrupt gel formation and to achieve fair solubilization (79). In this case, there is no co-surfactant but the principle is the same, i.e., two different amphiphiles result in sufficient disorder to reduce the formation of LC. Recently, the use of branched surfactants has been successful in formulating alcohol-free microemulsions with mixtures of anionic and cationic surfactants (80).

Nonionic surfactants of the polyethoxylated type are mixtures of oligomers, and in many cases are able to produce a microemulsion in the absence of a co-surfactant such as alcohol. As expected from the degree of disorder resulting from the mixture, their solubilization ability is generally lower than with equivalent ionic surfactants, which generally contain fewer isomers. In effect, one can calculate that the HLD change due to an additional EO unit in the head group is equivalent to a reduction of 3 methylene groups in the tail. Polyethoxylated oligomers bearing differences such as 5–6 EO groups are common in commercial nonionic surfactants. This would be equivalent to differences in 15–18 methylene groups in the tail of ionic surfactants such as alkylarylsulfonates or alkyl ammoniums, a very unlikely fluctuation. Hence, ionic surfactants can be considered more uniform than ethoxylated nonionics.

This discussion leaves us with a dilemma. On the one hand, a higher solubilization ability is associated with larger surfactant molecules. On the other hand, these larger surfactants tend to generate precipitates and mesophases. In a later section we discuss ways to balance these competing factors.

Representation of surfactant-alcohol-oil-water (SAOW) systems. The phase behavior of SAOW systems can be represented in a quaternary diagram, the thermodynamics of which have been described in simple cases (22,81,82). These diagrams allow the interpretation of more complex systems.

In practice, solubilization is studied with SAOW systems as it is in SOW ones, i.e., by mapping the phase behavior as a function of composition, but the dimensionality of the system (four composition variables, three dimensions) is not easy to handle, and the studies are carried out in general as pseudoternary cuts that can be represented in two dimensions. The classical cut with an amphiphile pseudocomponent S+A at a constant S/A ratio (Fig. 11A) is quite logical but does not produce a good result if the S and A substances do not exhibit the same hydrophilicity, with a strong departure from the classical Winsor diagrams. In such a case, a cut at a constant WOR generates a phase diagram (Fig. 11B) that is very similar to the gamma or fish diagrams, provided that the S/A ratio accounts for the change in formulation.

In this case, the gamma or fish 3ϕ region is slanted, i.e., the optimum formulation depends on the amount of S+A (see Fig. 8). This is consistent with the change in phase behavior in a pseudoternary diagram at S/A constant, with an increasingly dominant alcohol effect as the S+A amount increases at constant S/A (Fig. 11A) (83).

Interpretation of solubilization beyond Winsor's premise. The full complexity of the effect of the alcohol was unveiled 20 years ago in the S+A vs. formulation diagram schematically reproduced in Figure 12 (71). This figure gathers the gamma diagrams (each represented only as the cross shown around the tricritical point in Figs. 7 and 8) for systems containing ethoxylated nonylphenols whose average EON is the formulation variable, with octane and brine (1 wt% NaCl) at unit WOR, and with different *n*-alcohols at a constant S/A ratio (72:28 in wt).

The number beside each cross (intersection of two lines) refers to the number of carbon atoms of the *n*-alcohol in a

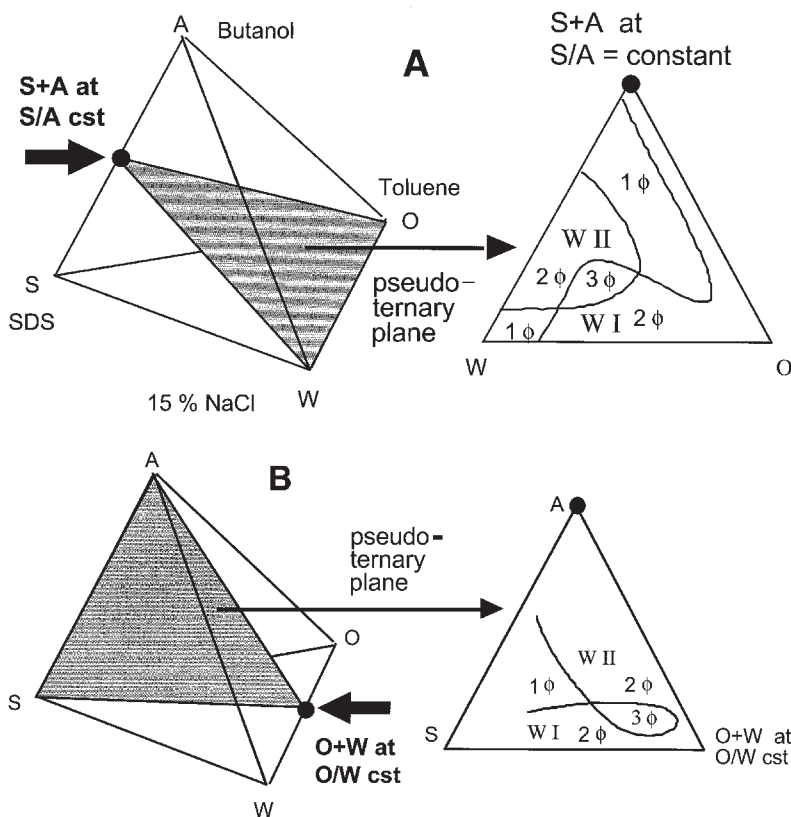


FIG. 11. Pseudoternary cuts of a surfactant (S)–alcohol (A)–water (W)–oil (O) quaternary diagram (A) at a constant (cst) S/A ratio, and (B) at a constant W/O ratio. For other abbreviations see Figure 6.

given case. Zero refers to a system without alcohol, and 3.5 to an equimolar mixture of *n*-propanol and *n*-butanol. For each case, a formulation scan is carried out by varying the EON of the surfactant. Hence, the effect of the alcohol type (i.e., the number of carbon atoms in an *n*-alcohol), is compensated for by the surfactant EON at the tricritical point. The location of this point and its change from one case to the next provide information on the formulation change in the abscissa and the solubilization change in the ordinate. Since everything else remains constant (oil, brine, temperature), the interfacial S+A formulation is constant, and the change in surfactant EON is opposite and compensates for the effect of the change in alcohol.

As a consequence, a shift to a lower (respectively, higher) EON, i.e., a more lipophilic (respectively, hydrophilic) surfactant means that the alcohol contribution is hydrophilic (respectively, lipophilic). On the other hand, an increase in S+A at the tricritical point denotes a decrease in solubilization (more surfactant is required to achieve the Winsor Type IV microemulsion in which all of the oil and water are solubilized), and vice versa.

Figure 12 shows that as the alcohol chain length increases, the following changes take place in four successive stages, which are denoted by (a) to (d) and identified by arrows in Figure 12:

(a) From no alcohol to ethanol, arrow (a) indicates that the optimum EON decreases, i.e., the surfactant required to equilibrate the affinity of S+A at the interface becomes less hydrophilic; thus, the alcohol contribution as a co-surfactant is hydrophilic. On the other hand, the amount of S+A at the tricritical point increases, denoting a decrease in solubilization, which is explained by the replacement of surfactant molecules by alcohol molecules at the interface, realizing that alcohol molecules are less efficient as far as interactions with oil and water are concerned. For this range of alcohols $R = 1$ and $HLD = 0$ are maintained at the cost of lower solubilization (more surfactant required means a less efficient surfactant system).

(b) From ethanol to an equimolar mixture of propanol and butanol, the alcohol becomes less hydrophilic, hence the shift of optimum EON toward the right. On the other hand, the S+A value increases, again denoting a decrease in solubilization.

(c) As the alcohol becomes more lipophilic, the shift toward the right continues in the (c) arrow path. The amount of S+A decreases in the (c) arrow path; thus, the maximum S+A required to form a single-phase microemulsion is found at an equimolar mixture of propanol and butanol. In this system, the alcohol mixture is neither hydrophilic nor lipophilic but just balanced, as corroborated by the fact that the formulation (EON) is essentially identical to the formulation in the

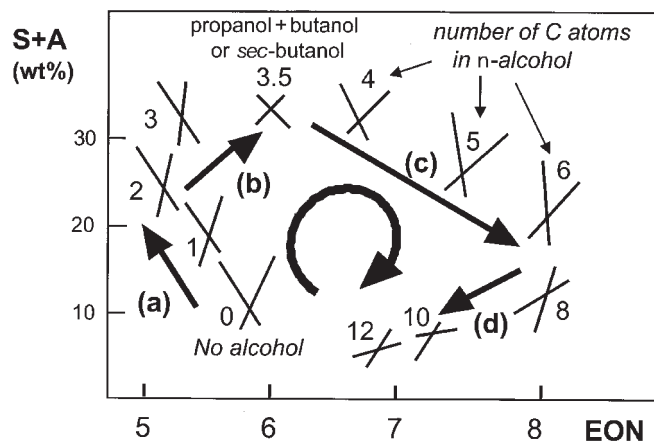


FIG. 12. Tricritical point position in the amphiphile concentration/formulation map (according to Figs. 7 and 8) as a function of the length of the *n*-alcohol cosurfactant. The effect of alcohol is compensated for by changing the degree of ethoxylation (EON, ethylene oxide number) of the nonionic surfactant (adapted from Ref. 71). For other abbreviation see Figure 6.

absence of alcohol. This mixture (or equivalent *sec*-butanol) is the one that exhibits the highest affinity for the interface; hence, it displaces the highest proportion of surfactant molecules, thereby yielding the lowest solubilization. It is worth noting that the “worst” alcohol actually depends on the aqueous and oil phases, but it is always somewhere between propanol and butanol since the first one is significantly hydrophilic and the second one is soluble in most oil phases. This alcohol mixture is roughly equivalent to *sec*-butanol as far as the balanced hydrophilicity–lipophilicity is concerned. This is the reason *sec*-butanol is often used as a co-surfactant, because it does not significantly shift the formulation and prevents the formation of LC.

(d) In the last stage, for alcohols longer than octanol, the optimum EON diminishes, indicating a reduction in the lipophilic effect of the alcohol. The lipophilic effect of the alcohol turns out to be the combination of two effects: first, the effect inherent to the species, which increases with the alkyl chain length, and second, a decrease in the proportion of alcohol molecules present between the surfactant head groups. As the alkyl chain increases, the affinity of the alcohol for the oil phase increases, thereby shifting the alcohol toward the oil side of the interface and placing it between the surfactant tails rather than between the surfactant head groups. Because less alcohol is present between the surfactant head groups, and since the alcohol can partition between the tails without holding the surfactant heads apart, the amount of surfactant at the interface increases and the optimum S+A diminishes all along the (c) and (d) arrows.

In looking at systems along the (d) arrow, an explanation is needed for the fact that the optimum formulation for C_{10} – C_{12} alcohols does not coincide with the no-alcohol case.

In fact, the asymptotic position as the number of carbon atoms in the alcohol increases, located close to the C_{12} system, is anomalous for two reasons. First, it is located at an EON that is significantly higher than the one exhibited in the absence of alcohol. This means that the interaction between the amphiphiles and the oil is higher than expected (which must be compensated for by a higher interaction on the water side, i.e., a higher EON). Since this cannot be due to a lipophilic effect of the S+A mixture, it is probably due to some change in the oil. The second puzzling fact is that the solubilization with a C_{10} – C_{12} alcohol is notably improved relative to the no-alcohol case (the cross in Fig. 12 occurs at a lower value of S+A). This cannot be explained by Winsor interaction concepts, since the surfactant density at the interface cannot be higher with a very small amount of a C_{10} – C_{12} alcohol than in the total absence of alcohol.

From these data, it was clear that stage (d) was due to a new phenomenon, produced by very lipophilic alcohols; however, the Winsor premise was so firmly anchored at that time that it took about a decade to elucidate the rationale behind this effect.

The linker concept. The first serious evidence of this phenomenon appeared when it was discovered that among the additives, the less hydrophilic, i.e., those less adsorbed at the interface, were more efficient in increasing solubilization. It meant that the increase in solubility was not due to something happening at the interface but rather in the oil phase; for this reason, the effect was called “lipophilic linking” (84) and was interpreted as the positioning of slightly polar oil molecules close to the interface so that they would extend the reach of the surfactant tail in the oil phase and thus increase interactions with the oil phase over a thicker “ordered” zone (Fig. 13) (85). A very small amount of lipophilic linker in oil (say, 1%) can more than duplicate the solubilization with very little compensation change on the water side of the interface. Very lipophilic amphiphiles, which are generally referred to as polar oils, were found to behave as lipophilic

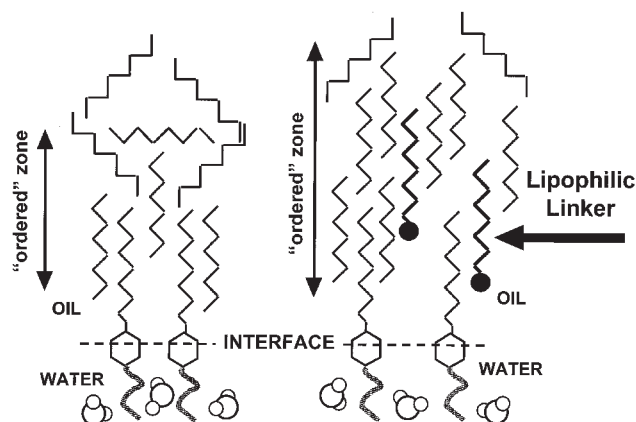


FIG. 13. How a so-called polar oil “lipophilic linker” tends to organize a thicker layer of oil molecules near the interface.

linkers: long chain ($>C_{10}$) *n*-alcohols, phenols, fatty esters, and the like (86). It is worth noting that such molecules may occur naturally in an oil phase, as “polar” impurities at the 1% level.

An analysis of the efficiency of the linking effect showed that the most efficient lipophilic linker was the one with a lipophilic chain intermediate between its surfactant and oil counterparts, regardless of the polar group, a result which corroborated that the interaction depended essentially on the lipophilic chain, as its name indicates (87). The fundamental finding of all these studies was that the most polar oil molecules tended to accumulate in the region close to the interface with water, probably because of a long-range attraction on the weak polar group. This so-called interfacial segregation of the most polar molecules (88) increases solubilization essentially because it produces a more continuous change from bulk oil to bulk water, as they are better “hidden” from each other. It is worth noting that this shielding effect, or blurring of the interface, is exactly how the surfactant is able to lower the tension in the first place, and it is no wonder that a better shielding results in a lower tension and a higher solubilization.

Following this approach, other substances have been tested to improve the continuity of the change from water to oil. First, a so-called hydrophilic linker effect was found, this time on the water side of the interface, by introducing an amphiphilic molecule whose behavior was between that of a hydrotrope and a co-surfactant. Hydrophilic linker molecules are hydrophobic enough to segregate or co-adsorb with the surfactant at the OW interface while avoiding a strong interaction with the oil phase typical of a co-surfactant (89,90). Three sodium naphthalene sulfonate derivatives were tested as linkers on the water side of the interface to enhance the interaction of the surfactant (dihexyl sulfosuccinate) with the water. The best enhancement was not attained with the more surface-active additive (dibutyl naphthalene sulfonate—the most lipophilic of the three molecules, although much less so than the surfactant) nor with the hydrotrope (naphthalene sulfonate—the most hydrophilic and located mainly in the bulk water), but rather with the in-between mono-/di-methyl naphthalene sulfonate (90).

An earlier observation of the lipophilic linker phenomenon revealed that the solubilization enhancement provided by the addition of these molecules was marginal at relatively high lipophilic linker concentrations (89). This marginal efficiency at high lipophilic linker concentrations could be due to the limited number of potential segregation sites. The addition of the hydrophilic linker molecules was proposed as a way to create an additional interfacial area and number of sites for the lipophilic linker to segregate (89,90).

Co-added hydrophilic and lipophilic linkers have been demonstrated to behave like an “assembled” surfactant at the OW interface, which is partially able to replace the main surfactant at the OW interface. In this way, the combination produces an even higher solubilization capacity than the main surfactant alone, as observed for a variety of oils, ranging

from polar chlorinated hydrocarbons up to more hydrophobic oils such as motor oil and squalene; it also allows microemulsions to be formulated with biocompatible surfactants such as lecithins (14,57,91,92). Biocompatible microemulsions formulated using soybean lecithin as the surfactant, hexyl glucoside as the hydrophilic linker, and sorbitan monooleate as the lipophilic linker also have shown the ability to form microemulsion systems with a wide range of oils at low electrolyte concentrations and with higher solubilization capacities than linker-based anionic surfactant formulations (92).

The resulting combination produces a very smooth and continuous variation of the polarity from the water to the oil bulk phases (Fig. 14A), which is believed to be the key to ultralow interfacial tension and high solubilization. The combination of the two effects was shown to produce increased solubilization without sacrificing kinetic performance. In particular, the addition of a lipophilic linker alone produced a

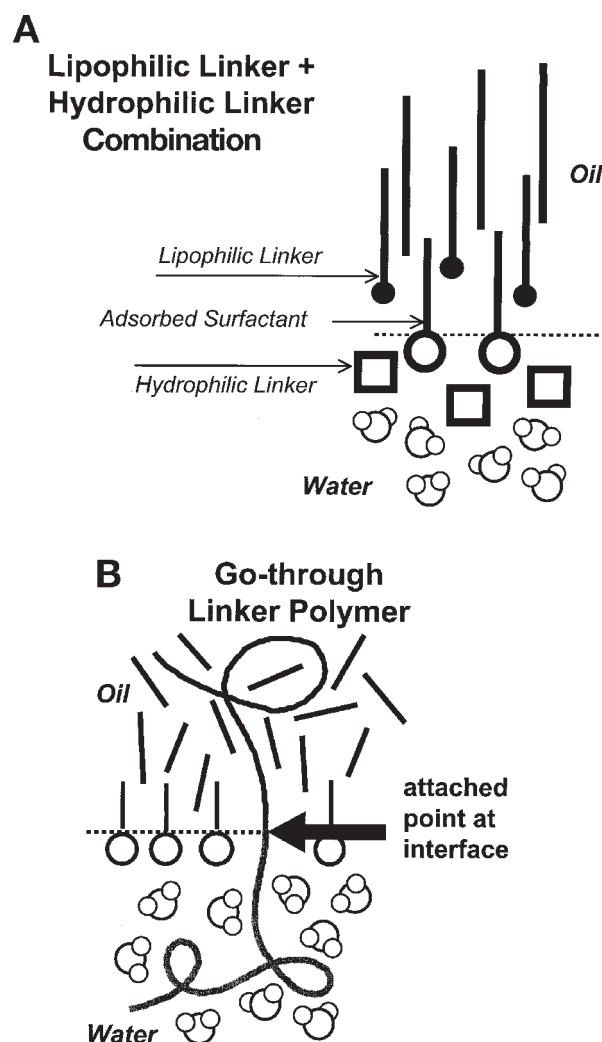


FIG. 14. An increase in solubilization by extending the reach of the surfactant into the oil and water phases: (A) a lipophilic-hydrophilic linker combination, and (B) a go-through linker polymer.

crowded packing of the surfactant tails, which led to an increased stiffness of the surfactant membrane; this also produced slower coalescence of the microemulsions formed upon shaking of the bicontinuous microemulsions and excess oil and water phases. The addition of a hydrophilic linker increased the space between surfactant molecules, thus allowing for more a flexible surfactant membrane, which translates into faster coalescence and solubilization kinetics. The co-addition of hydrophilic and lipophilic linkers offers an intermediate kinetic response similar to that of the surfactant alone (93). However, it is worth noting that these specific effects might be associated with the structure, particularly the overall shape, of the linker molecules used in the reported studies.

The idea of mixing different molecules at or near the interface was dealt with in another fashion, i.e., by adding to the conventional surfactant a small amount of the extra-large “best-candidate solubilizer” according to Winsor’s premise. It was recently found that the introduction of a small amount of block copolymer, such as poly(propylene-ethylene)[10]-polyethyleneoxide[20], could considerably improve the solubilization (94,95). These macromolecules, which may be called “go-through” linkers, have a relatively low molecular weight (5–10 times greater than the surfactant) and are used at low concentrations to avoid precipitation. They are believed to increase the interactions of the amphiphilic layer with both the water and oil phases according to Winsor’s premise (Fig. 14B) but without precipitating, as would be expected for a surfactant of this molecular size, simply because they are too diluted at the interface to self-associate. Thus, their role is also to “thicken” the region of interfacial transition between the water and oil bulk phases.

USE OF A SINGLE SPECIES REVISITED

The addition of multiple amphiphilic substances in SOW systems often causes a major inconvenience, i.e., the potential for selective partitioning of the additives, resulting in a change in formulation and loss of some species that do not go where they should go, e.g., on dilution. As a consequence, the introduction of the continuous transition-at-the-interface feature described previously into a single molecule is well worth considering, provided its precipitation can be avoided.

The first so-called “extended” surfactants (Fig. 15A) have a structure mimicking the hydrophilic/lipophilic linker combination (Fig. 14A), but now the surfactant is stretched out to increase its reach in both the oil phase and the water phase and to provide a smooth transition between the oil and water bulk phases without the loss in solubility associated with longer alkyl chains. In addition, the elongation is provided by an intermediate polarity extension located in the middle of the molecule, so that a continuous gradation of polarity takes place from end to end. The first generation of extended surfactants of the type alkyl-polypropyleneoxide(6-14)-polyethyleneoxide(2)-sulfate sodium salt was found to produce a high solubilization with long hydrocarbons and polar oils

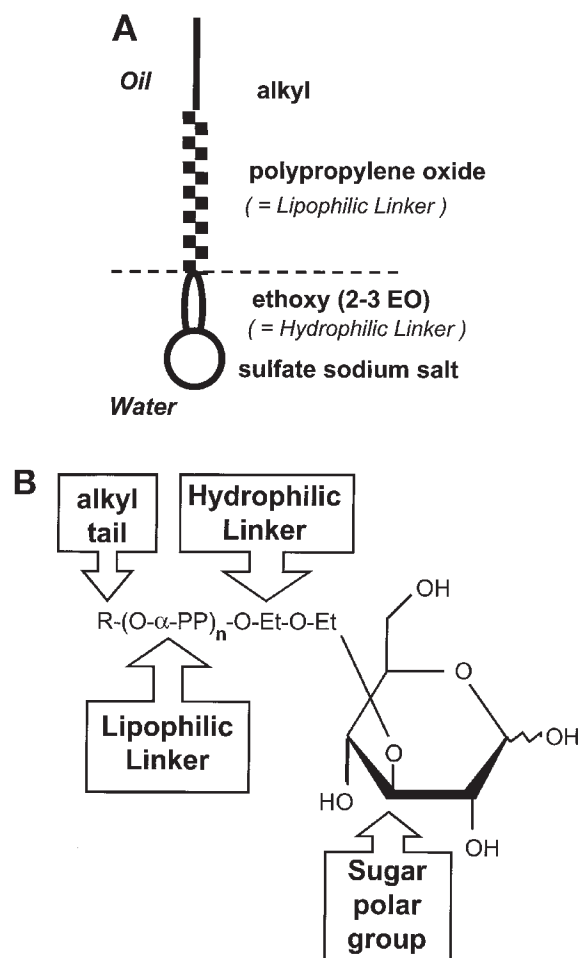


FIG. 15. An increase in solubilization by stretching the surfactant interior to increase the penetration into the oil and water phases. (A) First generation: anionic–nonionic extended surfactant; (B) second generation: sugar-based extended surfactant. EO, ethylene oxide.

($SP^* = 30\text{--}40\text{ mL/g}$), including an outstanding performance ($SP^* = 15\text{ mL}$) with natural triglycerides such as soy oil (96,97).

Extended surfactants also have been found to mix well with conventional surfactants, just as the go-through linker does, with a solubilization performance that depends on the amount of extended surfactant, but with a formulation that is adjustable, thanks to the conventional surfactant species (a nice feature for the formulator) (98). Some propoxylated Guerbet alcohol sulfates show some of the features of extended surfactants due to their similar molecular structures (64,99).

Since the solubilization of natural oils has been essentially impossible with conventional surfactants up to now, it seems reasonable to suppose that the main target of these new, extended surfactants in the near future would be the solubilization of oils and fats in natural products and in biological or biomedical applications. Hence, the second generation of extended surfactants has to exhibit a higher biocompatibility than did the first generation. As a consequence, the new com-

pounds that have recently been synthesized have been designed with biofriendly polar groups such as glucose, galactose, xylitol, carboxylate (see Fig. 15B), or their combinations (100–106).

The potential applications of such systems to biocompatible and edible oils are numerous. Many oil-soluble prescription drugs could be injected into the blood stream directly in a microemulsion containing natural oil. The *in situ* dissolution of a bladder stone might be possible by a microemulsion containing an ethylene diamine tetraacetic acid (EDTA) aqueous solution to dissolve calcium rubinate crystals and cholesterol. Cleaning equipment soiled by edible oil and fat products in the food industry, or in domestic detergency and dishwashing, could be handled with a solubilizing microemulsion, e.g., through a mechanism involving a soak, with no need for scrubbing or mechanical energy. Petroleum operations such as waste treatment, spill remediation, or drilling, particularly offshore, might also benefit from the introduction of environmentally compatible surfactants with ultrahigh solubilization and ultralow interfacial tensions. We propose that these potential benefits may fuel microemulsion research and development efforts in the years to come.

PAST AND FUTURE TRENDS

The authors believe that with the turn of the century, the microemulsion story is poised to enter an exciting new phase. When introduced to the world a half century ago by the work of Winsor, the microemulsion was little more than a scientific curiosity, although certainly an intriguing one. For decades there was little interest in microemulsions, beyond an occasional academic study. This situation changed dramatically in the decade of the 1970s, when the energy crisis, and the burst of enthusiasm for EOR, demonstrated that ultralow interfacial tensions could be achieved through microemulsions; the ensuing research greatly advanced the industrial and economic importance of microemulsions. In retrospect, however, although the research of the 1970s consolidated our understanding of the phenomenon of microemulsions, and certainly dramatically improved our ability to quantify them, the follow-on academic publications of the 1980s still thought of the microemulsion in much the same way as Winsor. In fact, our microemulsion formulations were still fundamentally the same as Winsor's.

From the late 1980s through the early 1990s, however, microemulsions were explored for use in new and emerging areas. Microemulsions were used to produce nanoparticles and deliver therapeutic agents and to remediate contaminated aquifers. The unique needs of these new technologies pushed researchers to look for ways to reduce their requirement for high surfactant/co-surfactant levels and to eliminate the persistent tendency to include low molecular weight alcohols in the formulation. As alternative strategies developed, it finally became evident that the microemulsion differs from the macroemulsion in much more fundamental ways than particle size. In fact, the oil/surfactant ratio in highly efficient microemulsions can be as high as that in a macroemulsion—and the domain size will subsequently be as high as the drop size in a macroemulsion, albeit in an equilibrium state.

With the discovery of the lipophilic linker effect, it became clear that the efficiency of a microemulsion was not solely controlled by the surfactant and only fine-tuned by other additives. Rather, the efficiency of a microemulsion could be greatly enhanced by using molecules that would extend the interaction of the surfactant “membrane” (interface) further into the oil and water phases, respectively, thereby further blurring the interface and decreasing the interfacial tension. Fast upon the heels of the publication of the lipophilic linker effect, the corresponding effect was discovered for the water side of the membrane, the hydrophilic linker effect, along with the mixed linker effect. And most recently, the novel concept of the extended surfactant has been developed, which incorporates the linkers into the design of the surfactant itself, thereby eliminating concerns of differential partitioning and loss of the combined linker effect.

When looking at the concept of the surfactant membrane that has dominated our view of the microemulsion since the work of Winsor, and the concepts of the lipophilic linker, the hydrophilic linker, mixed linker formulations, and extended surfactants that have emerged of late, it is interesting to note how this series of concepts unifies this approach. For example, it is easy to see how these concepts are consistent with Gibbs' idea of a dividing surface or region, where every component at a higher concentration in the dividing region (surfactant membrane) than in the bulk alters the nature of the interface. By using either linkers or extended surfactants, one is swelling the original interface (or inter-“phase”) or dividing region; and by applying the Gibbs equation, the second law of thermodynamics, and the Chung Huh relationship, we expect lower interfacial tensions and higher solubilization parameters. These concepts, along with that of the curvature of the surfactant membrane, which can be altered using the critical packing factor, can go a long way in explaining and guiding microemulsion formulation. From this perspective, then, and based on views that have been around for decades to a century, the utility of linkers and extended surfactants in a microemulsion formulation is not only understandable but also expected.

Consequently, at the beginning of the 21st century, both the colloid scientist and the technologist discover that the potential impact of microemulsions is greater than ever. With the possibility of applying advanced microemulsion concepts in cleaning products, in medicine, in environmental remediation, in the formulation of environmentally friendly solvent substitutes, and in exciting new fields such as nanotechnology, it seems that the true potential of microemulsions is yet to be realized. And with this continued research emphasis, we can anticipate additional insights and breakthroughs that will only serve to advance microemulsion technology further.

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