MICROEMULSIONS

1. Introduction

Although there is no universally accepted definition of what constitutes a microemulsion, most researchers now agree that a microemulsion is a thermodynamically stable, fluid dispersion of two or more ordinarily immiscible liquids, such as water and oil, stabilized by at least one amphiphile. During the years from ~1975–1980 the term microemulsion ascended from obscurity to ubiquity. By the end of 1996, there were 13 widely available English-language books (1–9) with the word "Microemulsion" in their titles (10) (Table 1). Many more books on surfactants are in print, and those on industrial applications (9,11–18) and environmental effects (19–21) are of particular interest here.

The concept of microemulsions now holds a central role within the field of surfactant technology. Perhaps the most fundamental fact captured by the term is that, contrary to a popular saying, oil and water can mix.

2. Definition of a Microemulsion

The term microemulsion was introduced by Schulman, as early as 1943 (22). At that time it was widely accepted that "oil and water do not mix," but instead may

Table 1. **Growth in Microemulsion Publications**

Year	Number[a] of publications
1970	12
1975	29
1980	123
1985	237
1990	410

[a] In *Chemical Abstracts*.

form emulsions. Emulsions are typically opaque thermodynamically unstable dispersion of one liquid in the other, often "kinetically" stabilized against coalescence, which eventually separate into constituent phases. Schulman understood that an emulsion scatters light because it contains droplets whose diameters are large compared to the wavelength of light (see EMULSIONS). The term *micro* emulsion implies a system that (like an emulsion) contains droplets of oil or water, but in which the droplets are too small to scatter light.

Microemulsions are distinct from emulsions in another key way. Unlike emulsions, microemulsions are true, thermodynamically stable, liquids. Most common microemulsion contain water, oil, at least one amphiphile, and may also contain one or more inorganic salts. Typically the oil is a mineral oil or hydrocarbon, but it may be almost any nonpolar compound. The oil and the amphiphile may be single, pure components; or (as in most commercial formulations), the oil, amphiphile, or both may contain an indefinitely large number of compounds. In practice, most microemulsions contain at least one true surfactant (eg, an amphiphile that forms liquid crystalline phases and has a well-defined critical micelle concentration). Many widely used microemulsions furthermore contain both a true surfactant and a cosurfactant (sometimes called a cosolvent), ie, an amphiphile whose molecular weight is too small for it to be a true surfactant. However, some members of a homologous series of amphiphiles may be surfactants and others not, depending only on their molecular weight. For example, depending on the values of m and n, the amphiphile $C_mH_{2m+2}(OC_2H_4)_n$ OH may be an alcohol, a cosolvent, or a true surfactant. Moreover, many microemulsion properties change only incrementally when a small change is made in the molecular weight of the amphiphile. Therefore, some researchers consider that almost any amphiphile–oil–water solution may be fairly called a microemulsion.

In addition, many solutions of common nonionic surfactants and water separate into two phases when heated above a certain temperature (the cloud point), and some investigators call the phase of greater surfactant concentration, a microemulsion. Thus, there is not even universal agreement that a microemulsion must contain oil.

3. Microemulsions and Phase Diagrams

Viewed in a simplified way, microemulsions form when the amphiphile adsorbs at the oil–water interface to lower the interfacial tension between two immiscible

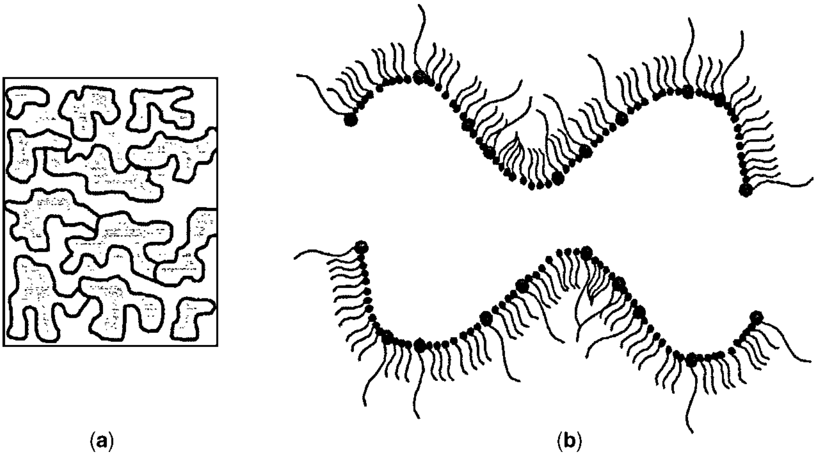

Fig. 1. Simplified representation of microemulsions showing (**a**) fluctuating domains of oil and water and (**b**) surfactant and cosurfactant molecules adsorbed at the oil and water interface.

liquids (eg, oil and water) to ultralow values (often <0.001 dynes/cm) allowing random thermal motions to spontaneously disperse the two immiscible liquids into each other (23). Unlike conventional emulsions, microemulsion domains may fluctuate in size and shape and undergo spontaneous coalescence and breakup (24,25). Microemulsions typically contain discrete domain microstructure that can be described as a continuum of possible topologies ranging from "water" continous, to bicontinous, and "oil" continuous (recognizing that the "water" and "oil" subphases may contain small amounts of additional dissolved components). These subphase domains typically range in size from 100 to 1000 Å and are illustrated qualitatively in Figure 1.

From the very beginning (22), researchers recognized that microemulsion formation depends not only on the presence of certain classes of compounds (ie, components), but also on the concentrations of these components. The number of phases present and their compositions, when presented in graphical form, constitute a phase diagram or (eg, when the amphiphile contains multiple species) a pseudoternary phase diagram (26). Moreover, as specified by Gibbs' phase rule, amphiphile–oil–water phase diagrams form characteristic patterns that change in qualitatively similar ways when the temperature, pressure, concentrations, or molecular structures of the components are changed. Thus, phase diagrams offer not only another way to define microemulsions, but also a rigorous way to clarify differences in terminology and usage.

Figure 2 (27) illustrates the phase diagram of a model amphiphile–oil–water system (28) such as $C_4H_9OC_2H_4OH$ (C4E1)–decane–water (29) or C_6H_{12}–$(OC_2H_4)_2OH$ (C_6E_2)–tetradecane–water (30). For a real surfactant, such as $C_{12}E_4$, the diagram may be more complicated, because of the occurrence of liquid crystalline phases (31). By the most general definition, every phase described by Figure 2 would be a microemulsion. But, to avoid confustion, when two or more phases are simultaneously present, only the compositions between the two plait points (points on upper curved phase boundaries) are

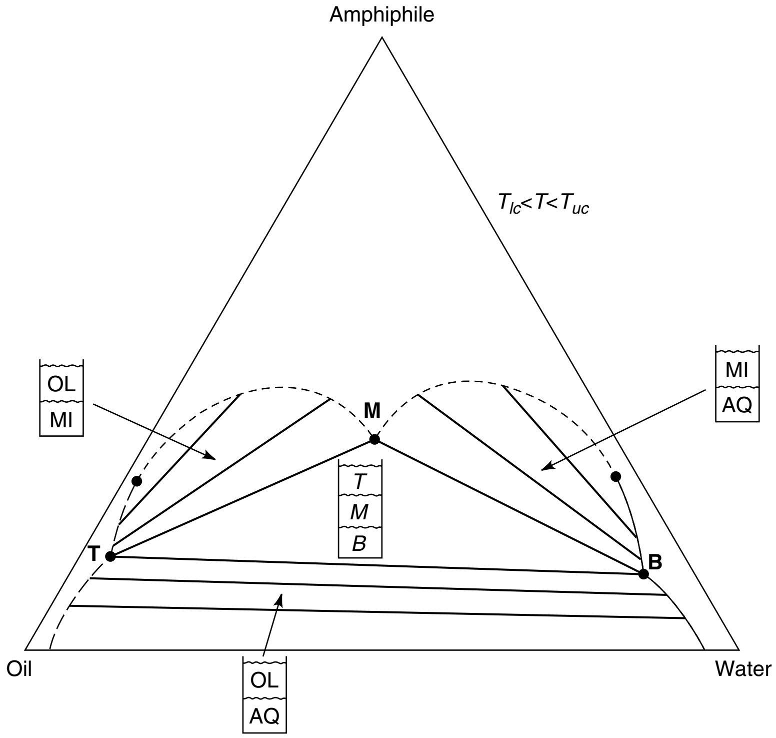

Fig. 2. Phase diagram of an amphiphile–oil–water system that forms a middle-phase microemulsion, and illustration of the pairs (and triad) of phases formed in the various multiphase regions of the diagram. Boundaries: (—), aqueous (AQ); (– –), oleic (OL); (——), limiting microemulsion (MI).

termed microemulsions. Other conjugate phases are called oleic phases or aqueous phases, respectively, depending on whether their main component is oil or water. (Oleic phases and aqueous phases are ubiquitously called oil and water, even in scientific journals. This practice should be rigorously avoided, because it produces unnecessary confusion between components, at the corners of the phase diagrams, and phases, which always contain at least minute concentrations of all components present in the system.)

In the lower portion of the phase diagram, the surfactant concentration is insufficient to efficiently form a microemulsion and the system splits into only oleic and aqueous phases. Samples whose compositions fall within the "tietriangle" of Figure 2 form three liquid phases, of compositions, T, M, and B (corners of the tietriangle). Moving compositions within this tie triangle changes the proportions of the phases, but typically not the compositions. Adjacent to the tie triangle, compositions form two conjugate phases in equilibrium with each other; each such pair of phases is connected by a tieline that terminates at "binodal curve". Compositions of the conjugate phases can become closer and their connecting tielines shorter, until the phase compositions and the end points of the tielines become identical at a plait point.

Compositions outside of the tietriangle and the binodal curves (at higher surfactant concentrations) typically form only a single liquid microemulsion phase. On the amphiphile–water edge of the phase diagram, these single phases contain only amphiphile and water (no oil); on the amphiphile–oil edge of the phase diagram these single phases contain only amphiphile and oil (no water). Since most real systems contain many more than three single components, the phase diagram is usually only an approximate representation of their behavior. For example, in multicomponent systems, phase compositions may in fact change somewhat within the two and three phase regions, and more complex multiphase behavior may be encountered.

In Figure 2, the pairs (or triad) of phases that form in the various multiphase regions of the diagram are further illustrated by the corresponding test tube diagrams. Except in rare cases, the oleic phase densities are less than the conjugate microemulsion densities and the microemulsion densities are less than the conjugate aqueous-phase densities. Accordingly, compositions lying within the three-phase triangle contain a top oleic phase, *T*, a middle microemulsion phase, *M*, and a bottom aqueous phase, *B*. Similarly, compositions lying within the oleic phase-microemulsion binodal, contain an upper oleic phase and a lower microemulsion phase. Compositions within the aqueous phase-microemulsion binodal, contain an upper layer microemulsion and a lower layer aqueous phase. Compositions with amphiphile concentrations too low for formation of a middle phase, simply form an upper layer oleic phase (oil) and a lower layer aqueous phase (water). Commonly, microemulsions in equilibrium with an oleic phase are “water continuous”, those in equilibrium with aqueous phases are “oil continuous”, and those in equilibrium with both are “bicontinuous”, as determined by microscopy and transport properties (25).

Microemulsions that occur in equilibrium with one or two other phases are sometimes called “limiting microemulsions”, because they occur at the limits of the single-phase region. Rigorous and useful as it is, the definition of limiting microemulsions does not specify which compositions in the single-phase region should also be called microemulsions. Furthermore, in Figure 2 there is a critical micelle concentration point for formation of normal micelles on the amphiphile–water side of the phase diagram and an inverse critical micelle concentration point for formation of inverted micelles on the amphiphile–oil side of the diagram (32). (Depending on the compounds and temperature, these CMC points may be easily detected, or exist only in a formal sense.) Geometrically, each of the two CMC points can be connected by a line to a nearby plait point. These lines serve to separate the single-phase area of the diagram formally into (nonlimiting) microemulsion, aqueous, and oleic regions.

Often the identities (aqueous, oleic, or microemulsion) of the layers can be deduced reliably by systematic changes of composition. Thus, without knowing the actual compositions for some amphiphile and oil of points *T*, *M*, and *B* in Figure 2, an experimentalist might prepare a series of samples of constant amphiphile concentration and different oil/water ratios, then find that these samples formed the series (*1*) one phase, (*2*) two phases, (*3*) three phases, (*4*) two phases, (*5*) one phase as the oil/water ratio increased. As illustrated by Figure 2, it is likely that this sequence of samples constituted (*1*) a “water-continuous” microemulsion (of normal micelles with solubilized oil), (*2*) an upper-phase microemulsion in equilibrium with an excess aqueous phase, (*3*) a middle-phase microemulsion with conjugate top and bottom phases, (*4*) a lower-phase microemulsion in equilibrium with excess oleic phase, and (*5*) an oil-continuous microemulsion (perhaps containing inverted micelles with water cores).

4. Perturbing Variable Scans

Microemulsion structure and phase properties are determined both by the component ratios and the interactions between the aqueous and oleic domains and amphiphile(s). Increasing water content biases microemulsion structure toward “water continuous”, while increasing oil content biases the microemulsion structure toward “oil continuous”.

In addition, the affinity of the amphiphile for oil and water can strongly influence the microemulsion structure and nature of the phase diagram. Many authors describe surfactants in terms of their “amphiphile strength”, a measure of the surfactant molecule affinity for residing at an oil–water interface. “Strong” amphiphiles are more efficient at producing microemulsions, and may require only low surfactant levels to produce a single microemulsion phase (point M in Fig. 2 is low). In contrast “weak” amphiphiles such as depicted in Figure 2 form microemulsions at higher amphiphile concentrations. (25,33). Common oxygenated solvents such as glycol ethers represent interfacially active molecules with low amphiphile strength, while conventioanl surfactants such as alkyl benzene sulfonates are characterized as having high amphiphile strength (33,34).

A host of molecular parameters, compositional parameters and field variables, can influence amphiphile strength and microemulsion structure. These perturbing variables include length and structure of the surfactant tail, structure, length and charge of the surfactant “head”, solvent structure and composition, aqueous-phase composition (especially electrolyte content) as well as temperature and pressure. As a result, the, locations of the tietriangle and binodal curves in the phase diagram depend on all of these variables (35,36), because all of these factors can influence the amphiphile–oil–water interaction.

It is quite common to change either the temperature of one or more samples of fixed composition, or the electrolyte concentration in a series of samples of fixed amphiphile/oil/water ratio. The former constitutes a temperature scan; the latter experiment is widely known as a salinity scan. When the temperature of an amphiphile–oil–water system is varied, the phase diagram can be plotted as a triangular prism (because temperature is an intensive or field variable). When a fourth component (eg, NaCl) is added at constant temperature, tetrahedral coordinates are appropriate (conjugate phases have different salinities, and the planes of different tietriangles are no longer parallel).

Changes of temperature or salinity cause the phase diagram to evolve through the sequence illustrated by Figure 3. In systems containing ethoxylated amphiphiles (such as in Fig. 3), decreasing the temperature results in an increase in surfactant–water attraction. Increasing the water–surfactant affinity (or decreasing the oil tail affinity) drives the microemulsion toward a more “water-continous” structure. As a result, as the temperature is decreased

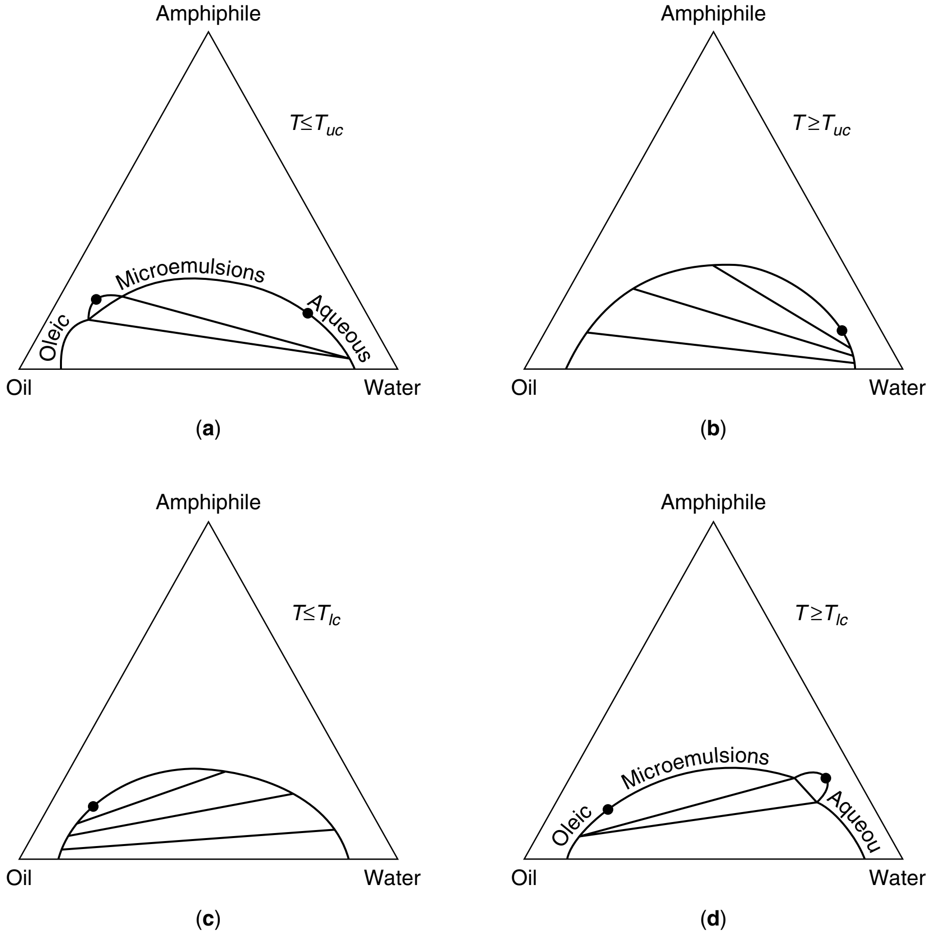

Fig. 3. Typical nonionic amphiphile–oil–water temperature phase diagram.

from some temperature between T_{lc} and T_{uc}, in Figure 3, the microemulsion becomes more "water continuous" and the aqueous phase-microemulsion binodal shrinks until it becomes a single point, the lower critical endpoint. Simultaneously, the tietriangle shrinks in height, becoming a lower critical tieline of zero height at $T = T_{lc}$. Conversely, when the temperature is raised, the oleic phase-microemulsion binodal shrinks, until it becomes an upper critical end point at T_{uc}. Below T_{lc} and above T_{uc} the respective binodal curves and plait points disappear, leaving only a single two-phase region.

Figure 3 also shows the phase diagrams of a nonionic amphiphile–oil–water system at $T < T_{lc}$ and $T > T_{uc}$, respectively. Because of the relative densities of the phases, for $T < T_{lc}$ the system is sometimes said to contain an upper phase microemulsion in equilibrium with an aqueous phase, whereas for $T > T_{uc}$ the system may be said to contain a lower-phase microemulsion in equilibrium with an oleic phase. However, if the existence of middle-phase microemulsions at intermediate temperatures is unknown, the respective phase pairs are likely to be called simply oil and water.

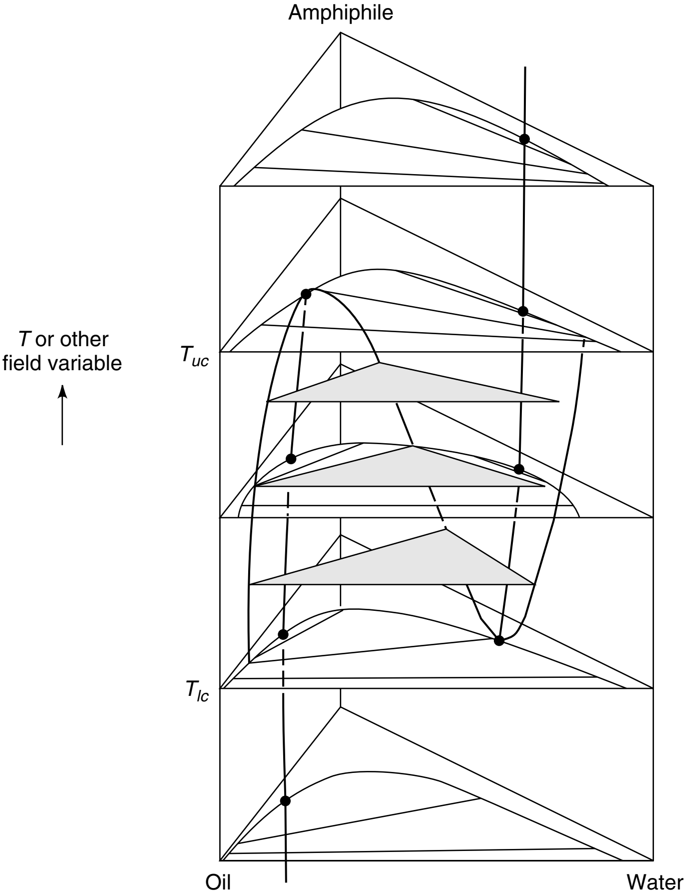

Fig. 4. The phase diagrams and terminology of a microemulsion system close to its two critical end points, where the middle phase and one of the binodals disappear.

Of all the characteristic points in the phase diagram, the composition of the middle phase is most sensitive to temperature. Point M moves in an arc between the composition of the bottom phase (point B) at T_{lc} and the composition of the top phase (point T) at T_{uc}, reaching its maximum surfactant concentration near $T=(T_{lc}+T_{uc})/2$. (Points B and T move by much smaller amounts.) The individual nonionic-amphiphile–oil–water phase diagrams illustrated at several temperatures by Figure 4, showing the evolution of structure with temperature near the lower and upper critical end points; along with the lower and upper critical tielines (at T_{lc} and T_{uc}, respectively).

A simplified way to represent and screen the complex behavior of the phase prism in Figure 4 is to construct a “fish diagram”. The fish diagram is simply a two-dimensional (2D) transect of the phase prism, where the “water/oil” ratio is maintained at a constant value (eg, 1:1), and the phase behavior is plotted as a function of amphiphile level versus perturbing variable(such as temperature). A representative “fish diagram” is shown in Figure 5. Here, decreasing solvent strength is equivalent to increasing temperature. The behavior of this ternary

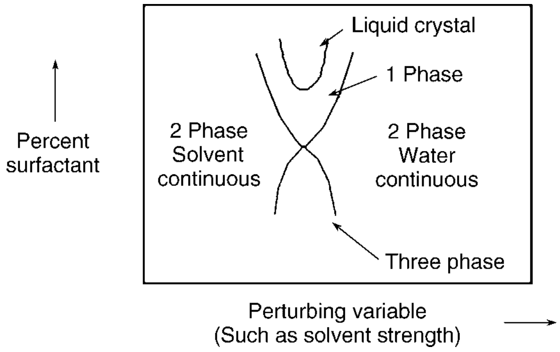

Fig. 5. Typical "fish diagram" used for determining the effect of perturbing variable on microemulsion phase behavior.

diagram "middle slice" can be used to infer the likely appearance of the rest of the phase diagram and allows for a rapid peliminary screening of the effects of perturbing variables on formulation structure. Fish diagrams are particularly useful in identifying effiency a surfactant has in generating a microemulsion.

Figure 6 illustrates the analogous (to Fig. 3) quaternary amphiphile–oil–water–electrolyte phase diagram, including a representative tietriangle, the S-shaped curve of *T*, *M*, and *B* compositions, the lower and upper critical end points (*R* and *Q*, respectively), and the lower (PR) and upper (QS) critical tielines (37). For clarity, the two-phase regions on each side of the stack of tietriangles

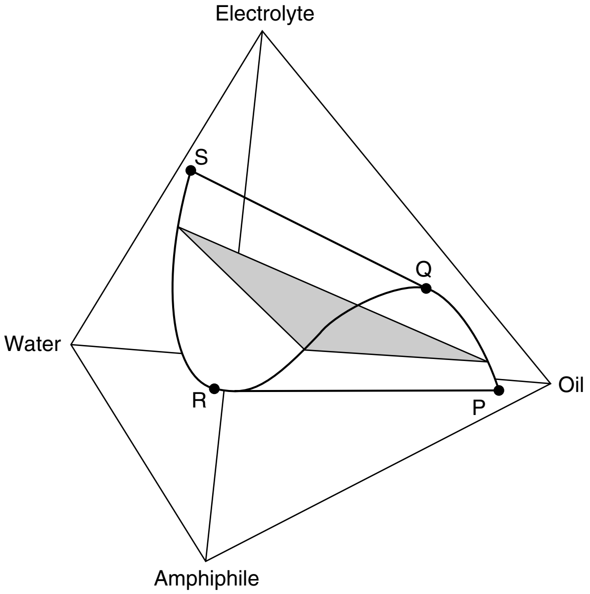

Fig. 6. Typical amphiphile–oil–water–electrolyte phase diagram, illustrating the S-shaped curve of *T*, *M* and *B* compositions, the lower and upper critical end points (R and Q, respectively), and the lower (PR) and upper (QS) critical tielines (31).

have been omitted; the effects of salinity on the binodals are analogous to the temperature effects illustrated by Figure 3.

Microemulsions based on ethoxylated nonionic surfactants are usually very temperature-sensitive, due to temperature-dependent hydration of oligoethylene oxide headgroups, while the effects of inorganic electrolytes are small. Conversly, microemulsions based on ionic surfactants are not very temperature sensitive, but effects of inorganic electrolytes can be large. Most common electrolytes (eg, NaCl) screen electrostatic interactions between surfactant head groups and "salt out" ionic surfactants, making them less soluble in water and moving *M* from *B* to *T*. However, a few electrolytes "salt in" ionic surfactants, and have the opposite effect (38).

When the phase behavior of the amphiphile–oil–water–electrolyte system of Figure 6 is measured at different temperatures (37), the resulting phase diagram has four dimensions. Figure 7 (39) illustrates the effect of temperature on the positions of the critical tielines, which mark the limits of existence of middle-phase microemulsion, within the tetrahedral diagram. Also plotted in Figure 7 is the temperature versus the salt concentrations (of the midpoints) of the critical tielines. For this particular system, as the temperature of the phase-diagram measurements is increased, the lower and upper salinity limits of existence of the middle phase both decrease, but the two critical tielines meet at a cusp (in this example, at a physically unrealizable negative salinity). This is called a tricritical point, because at it the tietriangle of phases *T*, *M*, and *B* shrinks

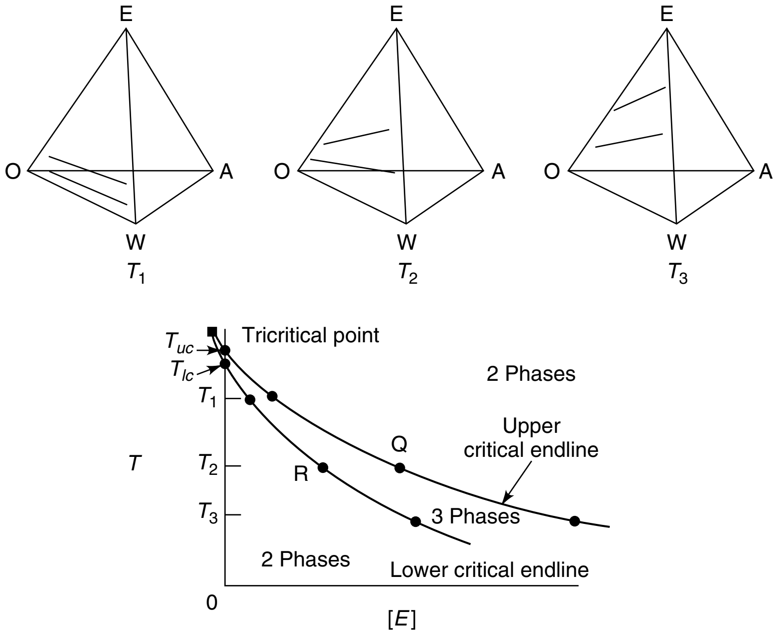

Fig. 7. Lower and upper critical tielines in a quaternary system at different temperatures; and a plot of the critical end point salinities versus temperature, illustrating lower critical endline, upper critical endline, optimal line, and tricritical point for four-dimensional (4D) amphiphile–oil–water–electrolyte temperature phase diagram (39).

to a single point (40). Tricritical points are the thermodynamic origin of ultralow interfacial tensions, which are exploited in micellar-polymer enhanced oil recovery (EOR) and it surfactant-enhanced aquifer remediation (SEAR) analogue.

It is important to note that practical microemulsions can contain many components, potentially simultaneously including ionic surfactants, nonionic surfactant or amphiphile, and inorganic electrolyte. Their phase behavior and thermodynamics are generally similar to the simple nonionic surfactant–oil–water–electrolyte phase diagrams described above except for an additional degree of freedom due to the extra component. Hence, diagrams similar to Figure 6 can be measured, in which inorganic electrolyte is replaced by organic electrolyte. The resulting phase diagrams have five dimensions (four fractional concentrations and temperature), not just four; hence, instead of a single tricritical point, they have a line of tricritical points. The dimensionality of such systems makes them more difficult to understand and study, but the extra degree of freedom can be used, when needed, as an additional variable to tune the system and its physical properties to meet the engineering requirements of an application (39).

5. Applications

The current or potential industrial applications of microemulsions include enhanced oil recovery from underground reservoirs (41), consumer and industrial cleaning formulations (42,43), metal working, catalysis, advanced ceramics processing media, production of nanostructured materials (see NANOTECHNOLOGY), dyeing, agrochemicals, cosmetics, foods, pharmaceuticals [including controlled delivery (44)], coating formulations (45) and biotechnology (including separation applications) (9,12–18). Environmental and human-safety aspects of surfactants have also begun to receive considerable attention (19–21).

Microemulsions became particularly well known from ~1975–1980 because of their use in "micellar-polymer" enhanced oil recovery (EOR) (46). This technology exploits the ultralow interfacial tensions mat exist among top, microemulsion, and bottom phases to remove large amounts of petroleum from porous rocks, that would be unrecoverable by conventional technologies (47,48). Since ~1990, interest in the use of this property of microemulsions has shifted to the recovery of solvents from shallow aquifers. The latter application (15) is sometimes called surfactant-enhanced aquifer remediation (SEAR).

Figure 8 illustrates how the three tensions among the top, middle, and bottom phases depend on temperature for system of nonionic surfactant–oil–water (49), or on salinity for a representative system of anionic surfactant–cosurfactant–oil–water and electrolyte (50). As T approaches T_{uc} from lower temperatures, the composition of M approaches the composition of T, and the interfacial tension between them σ_{MT}, goes to zero at $T = T_{uc}$. Similarly, as T approaches T_{lc} from higher temperatures, the composition of M approaches the composition of B, and the interfacial tension between them, σ_{MB}, goes to zero at $T = T_{lc}$. If Antonov's rule is obeyed (it is virtually always an excellent approximation for applied work) (51,52), the tension between the nonmicroemulsion

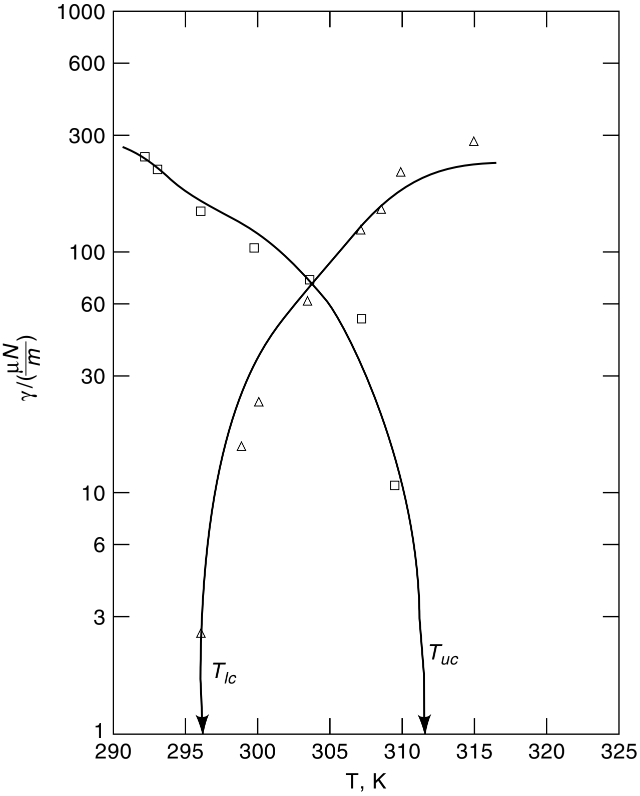

Fig. 8. Interfacial tensions among microemulsion, top, and bottom phases.

pair of phases is given by

$$\sigma_{BT} = \sigma_{MB} + \sigma_{MT} \tag{1}$$

The temperature (or salinity) at which $\sigma_{MB} = \sigma_{MT}$ is called the optimal temperature (or optimal salinity), because at that temperature (or salinity) the oil–water interfacial tension is a minimum, which is optimum for oil recovery. For historical reasons, the optimal temperature is also known as the HLB (hydrophilic–lipophilic balance) temperature (53,54) or phase inversion temperature (PIT) (55). For most systems, all three tensions are very low for $T_{lc} < T < T_{uc}$, and the tensions of the middle-phase microemulsion with the other two phases can be in the range 10^{-5}–10^{-7} N/m. These values are about three orders of magnitude smaller than the interfacial tensions produced by nonmicroemulsion surfactant solutions near the critical micelle concentration. Indeed, it is this huge reduction of interfacial tension which makes micellar-polymer EOR and its SEAR counterpart physically possible.

Additional examples of practical microemulsions abound. For example, microemulsion based cleaning formulations can provide oustanding performance, and solvent-continuous microemulsions with excellent oily soil cleaning and practical microemulsions employed in the preparation of fabric pretreaters were recently reported (56–58). Microemulsions also facilitate and control heterogeneous chemical reactions. Examples include, hypochlorination reactions of water insoluble liquid reactants in microemulsion reaction media produced industrially useful epoxides and epoxide derivatives in high yields (59). Many other microemulsion based reaction systems were described by Hager (60), including Bioorganic reactions in microemulsions (61), metal nanoparticle synthesis in water-in-oil microemulsion (62), as well as polymerization within microemulsions and other self-organized media (63).

6. Physical Description of Microemulsions

A variety of thermodynamic models qualitatively capture the central equilibrium and dynamic features of microemulsion behavior (64–68). These range from phenomenological models, which treat the oil–water interface as a fluctuating membranes to lattice models which describes discrete surfactants interacting with oil and water. Membrane models range from simple cubic lattice descriptions to fluctuating film models that include curvature dependent bending elasticity to prescribe lower limits on domain size. Lattice models seek to describe microemulsion structural domains down to the near-molecular level. These include models of amphiphilicity, imposed by mean field attractive and repulsive interactions applied to simplified “diatomic” or oligomeric amphiphiles, oil and water. Recent versions of these models include “bending energy” contributions for surfactants meeting at angles to approximate realistic molecular features and accurately capture microemulsion phase diagram. In all cases, microemulsion phase behavior is most accuratly captured when the models consider key physical attributes (either explicitely or implicitely), including the balance between entropic (which tend to disperse oil–water into ever finer domains) and interfacial (which drive phase separation and place limits on domain curvature) contributions.

Modern scaling theory is also a powerful theoretical tool (applicable to liquid crystals, magnets, etc) that has been well established for several decades and has proven to be particularly useful for multiphase microemulsion systems (69). Scaling theory relies on the hypothesis that diverse physical systems exhibit large compositional and density fluctuations and essentially behave the same near their critical points. Hence, the only factors that determine their critical properties are the dimensionality of the space and dimensionality of the order parameter. For example, the shape of the σ_{MB} and σ_{MT} curves is theoretically well established by critical scaling theory. The temperature dependence is given by

$$\sigma_{MJ} = \sigma_{TJ}\left|\frac{T - T_C}{T_C}\right|^{\gamma} \tag{2a}$$

and at constant temperature the composition dependence is

$$\sigma_{MJ} = \sigma_{CJ}\left|\frac{C - C_C}{C_C}\right|^{2v/(1-\alpha)} \tag{2b}$$

Here $\sigma_{T,\ J}$ and σ_{CJ} are nonuniversal parameters, whose values must be measured for each chemical system. However, exponents such as α, β, γ, and ν are universal parameters, whose values are known from theory to be $\alpha = 0.89$, $\beta = 0.345$, $\gamma = 1.29$, and $\nu = 0.64$ for all systems (70). Here J is B or T,T_C is the appropriate critical end point temperature, in K, and C_C is the critical point concentration. Scaling theory describes not just interfacial tensions, but virtually any thermodynamic or physical property of a microemulsion system that is reasonably close to a critical point. For example, the compositions of a microemulsion and its conjugate phase are described by equations of the form:

$$|C_J - C_I| = C_1\left|\frac{\mu - \mu_C}{\mu_C}\right|^{\beta} \tag{3a}$$

$$|C_J + C_I| = C_2\left|\frac{\mu - \mu_C}{\mu_C}\right|^{1-\alpha} \tag{3b}$$

where μ is the chemical potential and C_1, and C_2 depend on the combination of components. Equations 2 and 3 each contain one or more nonuniversal parameters, whose values depend on the compounds and must be measured, and universal exponents, whose values are the same for all systems and are known. These equations provide two principal practical advantages for fitting experimental data: (*1*) unlike empirical equations, the forms of the equations already are known and have a theoretical basis; (*2*) the values of the exponents in the equations are accurately known, and this reduces the number of fitting parameters. [The values of the exponents for ordinary critical points or bicritical points (where two phases become identical) are called nonclassical, because (unlike the exponents in van der Waals and other classical equations) they are not multiples of 0.5.]

Scaling theory can be used to design microemulsions for important applications such as enhanced oil recovery. The salinities of brines in oil reservoirs range from potable to saturated at elevated temperature and pressure. When a reservoir of high salinity has been flooded previously with fresh water, the brine salinity can also vary greatly within the reservoir. To find a suitable surfactant requires a laborious search for a formulation with the correct optimal salinity for each reservoir. Thus (see Fig. 8), there has been a desire to find a surfactant that would form three phases over the broadest range of salinities and have ultralow interfacial tensions for those phases at the same time. However, there are thermodynamic limits on the extent to which these goals can be simultaneously met.

Scaling theory (70,71) also shows that there is a simple, universal, thermodynamic relationship between the width of the three-phase region, the composition (ie, amount of solubilized oil or brine) of the middle-phase microemulsion at optimum, and the optimal tensions. The results show that, except for small exceptions the goals of simultaneously lowering the tensions and increasing the width of the three-phase region are mutually contradictory. As in the design of heat engines, thermodynamics can save some work in the design of microemulsion formulations (39).

7. Microemulsions and Macroemulsions

Operationally, it is not always easy to determine whether a given sample is a microemulsion or macroemulsion. Close to a critical point, a microemulsion may not be transparent, and may be confused with a macroemulsion. An extremely stable macroemulsion may require a long time to separate into bulk layers, and thus, appear to be a microemulsion, but it is nevertheless a (macro) emulsion. Such experimental problems added to the early difficulties of developing the microemulsion concept. When the number of components is so large that determination of the phase diagram is impractical, advanced techniques such as quasielastic light scattering, small-angle X-ray or neutron diffraction, or nuclear magnetic resonance (nmr) may be used to determine if the sample is a microemulsion by characterization of its structure (2). However, the formal differences between microemulsions and macroemulsions are well defined. A microemulsion is a single, thermodynamically stable, equilibrium phase; a macroemulsion is a dispersion of droplets or particles that contains two or more phases, which are liquids or liquid crystals (72).

Nevertheless, possibilities for confusion abound. Until recently (73), it was thought that all nonmultiple emulsions were either oil-in-water (O/W) or water-in-oil (W/O). However, from the definitions of microemulsions and macroemulsions and from Figure 2, it follows that in many macroemulsions one of the two or three phases is a microemulsion. The phase diagram of Figure 2 makes clear that there are six possible nonmultiple, two-phase morphologies, of which four contain a microemulsion phase. These six two-phase morphologies are oleic-in-aqueous (OL/AQ, or O/W) and aqueous-in-oleic (AQ/OL, or W/O), but also, oleic-in-microemulsion (OL/MI), microemulsion-in-oleic (MI/OL), aqueous-in-microemulsion (AQ/MI), and microemulsion-in-aqueous (MI/AQ) (73). [Although they have not yet all been reported, theoretically there are 12 three-phase emulsion morphologies formed by the top, microemulsion (ie, middle), and bottom phases (74,75) of three-phase microemulsion systems.]

Just as phase diagrams clarify what constitutes a microemulsion, emulsion morphology diagrams (76–78) provide maps that clarify the relationships among microemulsions and the various emulsion morphologies in which these microemulsions can appear. The emulsion morphology diagram of Figure 9 illustrates each of the six two-phase emulsion morphology regions and, for the various regions within the tietriangle, shows which phase is the continuous phase. Separating the different morphology regions (eg, OL/MI and MI/OL) are narrow hysteresis regions, within which, depending on its history, the emulsion may be in either (eg, OL/MI or MI/OL) morphology. For two-phase microemulsion emulsions, the hysteresis region forms a cusp that terminates at a plait point. For the T-continuous, B-continuous, and M-continuous regions the morphology (nonengulfing, partially engulfing, or totally engulfing) of the dispersed phases is believed (74,79) to depend on the wettability condition (80) among the three phases.

In practice, the excess oleic or aqueous phase usually emulsifies into the conjugate microemulsion phase upon agitation. The reason is that the surfactant-rich continuous microemulsion phase resists coalescence of the surfactant-poor excess phase, presumably because surfactant depletion in the thinning

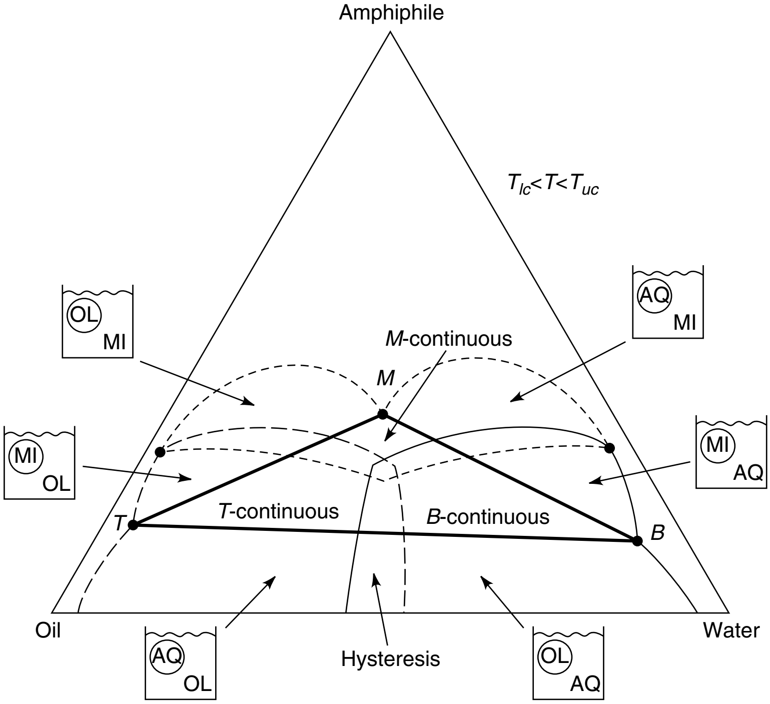

Fig. 9. Emulsion morphology diagram, illustrating where the microemulsion in various macroemulsion morphologies is a continuous phase or dispersed phase. Morphology boundaries: (–), aqueous, continuous; (– –), oleic, continuous; (- - -), microemulsion, continuous.

microemulsion phase is counteracted by surfactant diffusion to restore uniform chemical potential (Gibbs Marangoni stability). In addition, macroemulsions formed from three-phase microemulsion systems tend to coalesce very rapidly back to the three-phase system, while those formed from two-phase conjugate systems tend to coalesce more slowly due to the high degree of deformability of the excess phase domains that arise from ultralow interfacial tensions encountered in three-phase systems.

8. Economic Aspects

There are no specific statistics available for microemulsion products or their annual values, but data for the surfactant industry can be taken as a guide. Annually updated lists of commercial surfactants and their suppliers are available from several sources (81,82). For example, *Chemical &* Engineering News annually publishes a feature article on "Soaps and Detergents". The market for surfactants is very large. According to a recent report (83) North American estimated surfactant consumption in consumer products alone topped 4.3 billion lb in 2002 with an estimated market value of \$3.6 billion. Important markets for surfactants include laundry detergents, with liquids growing rapidly, followed by hard surface cleaners, industrial, and institutional markets (eg, floor waxes, paint strippers, and many other formulated products). Surfactants are also used in cleaning and personal care products such as wipes, emollients, soap bars, formulated skin care products, hair and body care formulations. In the household product category, surfactants are used in dishwashing formulations among others.

The patent literature describes microemulsion or microemulsifiable concentrate forms for all of these surfactant applications. Microemulsifiable concentrates are surfactant-based compositions that undergo rapid microemulsification upon dilution in water into a clear, stable formulation. Microemulsions or microemulsifiable concentrate formulations help maximize performance by minimizing interfacial tension, maximizing wetting, delivering active ingredients such as solvents to substrates and providing for routes to optimize surfactant concentrations (see SURFACTANTS).

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