Microemulsions

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Water and oil can be made completely miscible by adding a sufficient amount of an amphiphilic compound, such as soap or a detergent. For historical reasons, such stable homogeneous solutions are called "microemulsions." In this article the term microemulsion is used in a more restrictive manner; at low concentrations of the amphiphile, mixtures of water, nonpolar solvents, and amphiphiles may separate into three coexisting liquid layers, namely, an aqueous phase, an amphiphile-rich phase, and an oil-rich phase. In the amphiphile-rich phase, which is the microemulsion in the narrower sense, one finds for thermodynamic reasons a maximum of the mutual solubility between water and oil, combined with a minimum of the interfacial tension between the aqueous and the oil-rich phase, properties that are of interest for both theory and application. The present state of art in this rapidly growing field of science is reviewed.

IN THIS ARTICLE ON SO-CALLED "MICROEMULSIONS," THREE questions are addressed:

Who invented the term "microemulsion?";

What are they good for?;

What is known about them?

Everybody knows from experience that water and oil are practically insoluble in each other, but that their mutual solubility can be increased by adding an amphiphilic compound such as soap or a detergent. Amphiphiles are organic molecules that consist of a hydrophilic, that is, water-friendly, head group, and an oleophilic, that is, oil-friendly, hydrocarbon chain. Amphiphiles are thus compounds that can dissolve in both water and oil and which therefore try to surround themselves with molecules of both liquids. If offered an interface between water and oil, they will concentrate at that interface, with their hydrophilic heads anchored in the water, and their oleophilic tails anchored in the less polar liquid. If the hydrophilic heads consist of charged groups with counterions of opposite charge that dissociate in water, this will give rise to an electric double layer at the interface. This effect must have triggered an idea in the mind of the British chemist Schulman: since equal charges repel each other, why not cover oil droplets with a layer of an ionic amphiphile and disperse them in water? This should keep them from coarsening and thus produce a stable emulsion of oil droplets in water. The experiment failed. Instead of a stable emulsion, Schulman obtained a viscous glue. It is now well known that this glue was a so-called liquid crystal. Now, what does a chemist do if he has a viscous glue? He dilutes it with an organic solvent such as a short-chain alcohol. And indeed, after having added a sufficient amount of alcohol, Schulman obtained a stable, slightly turbid homogeneous solution. Having his goal in mind, namely to produce a colloidal emulsion of oil droplets in water, he called this solution a "micro emulsion" (*1*). Actually it had been known since the end of the last century (*2*) that adding a third compound to two immiscible compounds increases their mutual solubility if that compound is equally well soluble in the other two and that, in particular, simple nonionic amphiphiles like short-chain alcohols increase the mutual solubility between water and oil even in the absence of electric charges. At 25°C, 10 g of water and 10 g of toluene, for instance, can be made completely miscible by adding about 30 g of propanol. This amount, however, is much too large to be of use in any practical application. Since the amount of propanol needed for completely "solubilizing" water and toluene varies with temperature, one is interested either in determining that temperature at which propanol is most efficient, or in finding another amphiphile that is much more efficient than propanol at 25°C. Both goals can be reached by searching for that temperature at which the mixture of water, oil, and amphiphile separates into three liquid layers.

This leads to the second of the above questions: what are microemulsions good for? The answer is that the increase of the mutual solubility between water and oil by amphiphiles is the basis for the washing process as well as for producing stable homogeneous solutions of water and hydrophobic compounds. Although soaps have been known for at least 3000 years, the washing process is still not fully understood. How do a few amphiphilic molecules manage to make water and oil completely miscible? Why does a particular amphiphile reach its highest efficiency only at a particular temperature that depends sensitively but systematically on the chemical nature of both the amphiphile and the oil? In a particular application, the temperature, the chemical nature of the oil, and the salt concentration of the water are given. The problem is to find that amphiphile that is most efficient in solubilizing these components at the given temperature. If such amphiphiles could be found, detergents could be "tailored" with respect to their application. Detergents could be synthesized that wash at ambient temperatures as efficiently as today's detergents at 60°C, nontoxic amphiphiles could be applied for dissolving drugs in blood at body temperatures, or inexpensive detergents could be produced for the "chemical flooding" of exhausted oil fields. About 50% of the crude oil is left in oil fields after pumping. It is for these reasons that so many groups in the United States, Europe, Japan, and Australia are presently working on microemulsions.

What is known about microemulsions? The above statement that amphiphiles are equally well soluble in water and oil is incorrect. Consider nonionic (uncharged) amphiphiles at this point. At low temperatures, such amphiphiles are more soluble in water than in oil; at elevated temperatures the reverse is true. This rather dramatic change of the distribution between water and oil with rising temperature is one of the most fascinating properties of nonionic amphiphiles and is only qualitatively understood. Conceptually,

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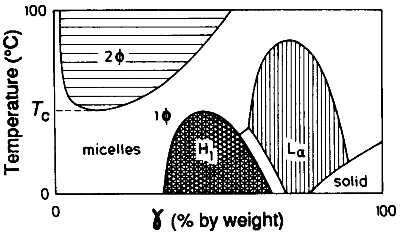


Fig. 1. Schematic phase diagram of a mixture of water and a nonionic amphiphile of mass fraction γ. On the right-hand side one can see the hexagonal (H_I) and the lamellar (L_α) mesophases, and at elevated temperatures the miscibility gap with its lower critical temperature T_c.

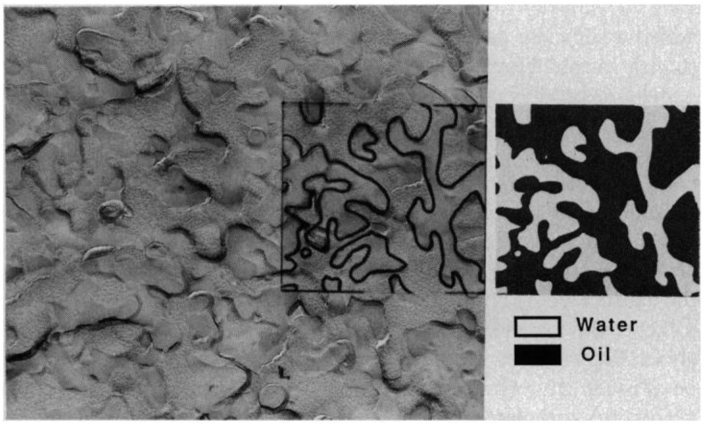


Fig. 2. Electron micrograph of a microemulsion of water, *n*-octane, and a long chain *n*-alkyl polyglycolether at equal volumes of water and oil and 5% by weight of the nonionic amphiphile.

amphiphilic molecules can be viewed as "chemical dipoles" with the hydrophilic and the oleophilic groups as opposite "charges." They differ from electric dipoles insofar as their charges can be changed independently of each other and that, furthermore, equal charges attract each other.

Amphiphiles in Water

At ambient temperatures, the hydrophilic head groups form hydrogen bonds with water. In pure water the hydrophobic tails try to escape the aqueous environment by pulling the amphiphilic molecules to the water surface, for which reason amphiphiles are referred to as surface-active substances or "surfactants." It is well known that the accumulation of amphiphiles at the water surface leads to a strong decrease of the surface tension of the solution, which is one of the properties used in application. If one increases the amphiphile concentration, the water surface will eventually become completely covered by a monolayer of the amphiphile. At a so-called "critical micelle concentration," the amphiphiles start to form submicroscopic "association colloids" in the bulk solution. These "micelles" are spherical aggregates with a mean aggregation number of about 100 molecules per micelle. The hydrophilic heads of the molecules are turned toward the aqueous environment, protecting the hydrophobic tails in the interior of the micelle. As one increases the concentration further, the micelles become cylindrical until, at rather high concentrations, the molecules first form hexagonal (H_I) and then lamellar liquid crystals (L_α), as shown schematically on Fig. 1.

The higher the "dipole moment" of the molecules, that is, the stronger their amphiphilicity, the stronger the tendency to form such structures. The micelles as well as the liquid crystals readily dissolve oils that are insoluble in pure water. This solubilization of hydrophobic compounds by aqueous solutions of detergents is essentially the basis of the washing process.

If the temperature is raised, the hydrogen bonds between the hydrophilic groups and water break. This lowers the solubility of the amphiphile in water so that, at elevated temperatures aqueous solutions of (nonionic) amphiphiles separate into two isotropic liquid phases (2ϕ), namely, a water-rich phase and an amphiphile-rich phase. As one raises the temperature further, the miscibility gap first widens, and then shrinks, until at sufficiently high temperatures—in general above the boiling point of the solution—water and amphiphiles become completely miscible again. Walker and Vause have recently considered such "reappearing phases" (*3*), showing that the reason for this behavior lies in the interplay between energy and entropy.

Amphiphiles in Water-Oil Mixtures

The solubilization capacity of micellar solutions is limited. If too much oil is added, it is expelled to form a bulk phase on top of the aqueous solution. In applications, however, one is frequently confronted with the problem of how to prepare a homogeneous solution of mixtures of water and oil with rather high volume fractions of the oil. Therefore one needs to consider ternary mixtures of water, oil, and nonionic amphiphiles with comparable masses of water and oil. If dissolved in such a mixture, the hydrophilic and the oleophilic groups of the amphiphilic molecules enter a "rope-pulling" contest. At ambient temperatures, the hydrophilic groups, supported by the hydrogen bonds with water, pull the oleophilic groups into the aqueous phase, although the latter are strongly hydrophobic. At elevated temperatures, the hydrogen bonds break, and the oleophilic groups pull the hydrophilic groups into the oil-rich phase in spite of their oleophobicity. As a consequence of this change of distribution, there must be an intermediate temperature at which the amphiphile is equally soluble in water and oil. At this temperature the amphiphile prefers to be in the interface between the two liquids instead of being dissolved in either one of the bulk phases. Accordingly, the interfacial area is increased to provide a more favorable environment for the amphiphile by dividing the water and oil bulk phases into a large number of microscopically small water and oil domains that are separated by a monolayer of the amphiphile. The hydrophilic head groups are anchored in the water domains and the oleophilic tails are anchored in the oil domains. The macroscopically homogeneous mixture of water, oil, and amphiphile is thus microscopically heterogeneous. It has a sponge-like structure that has the appearance of very many irregular "honeycombs." Some of the honeycombs are filled with water and the others with oil, whereas the walls between the combs consist of a flexible monolayer of the amphiphile. This structure is strongly fluctuating, with the water and oil domains rapidly changing their size and shape and the amphiphile molecules rapidly changing their position in the monolayer. This motion is a consequence of a rather subtle balance between the opposite solvation tendency of the hydrophilic and oleophilic groups, thermal energy, and gravity. Figure 2 shows an electron micrograph of such a structure, taken by Jahn and Strey in 1987 (*4*). The surfaces that look like a "leopard fur" are those of the oil domains, and the other areas are those of the water domains; the monolayer interface cannot be seen at this scale.

The surplus of water and oil that cannot be absorbed by the sponge is expelled to form a lower aqueous bulk phase and an upper oil-rich bulk phase, respectively. Near the temperature at which the amphiphile changes from being hydrophilic to being oleophilic, the mixture thus separates into three liquid phases, namely, a lower aqueous layer, a middle amphiphile-rich phase (the microemulsion),

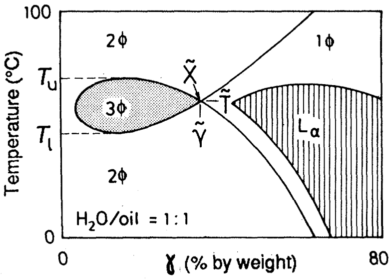


Fig. 3. Schematic phase diagram of a mixture of water, an oil, and a nonionic amphiphile for equal masses of water and oil but varying mass fraction γ of the nonionic amphiphile. On the left-hand side one can see the two-phase regions (2ϕ) with the three-phase region (3ϕ) at intermediate temperatures. On the right-hand side one can see the homogeneous solution (1ϕ) with the lamellar mesophase (L_α).

and an upper oil-rich layer. If more amphiphile is added, that is, if the absorbency of the sponge is increased, the water and oil layers shrink until both eventually disappear. The separation into three liquid phases takes place only within a well-defined temperature interval that depends sensitively on the chemical nature of both the oil and the amphiphile. Below and above that temperature interval, the mixture separates into two liquid phases only. For demonstrating this "phase behavior," one may prepare mixtures of equal masses of water and oil, then add various amounts of the amphiphile and observe the number of phases with rising temperature. The result is demonstrated schematically in Fig. 3, which shows such a quasibinary phase diagram.

In the absence of an amphiphile ($\gamma = 0$ in the phase diagram), water and oil separate into two phases at all temperatures between the melting and boiling points of the mixture. If some amphiphile is added, one finds at ambient temperatures two liquid phases (2ϕ) with the amphiphile mainly dissolved in the lower phase. At a certain temperature, the lower phase separates into a water-rich phase and a microemulsion with a high water content, so that one now observes three liquid layers (3ϕ) with the oil-rich phase floating on top. As one raises the temperature further, the microemulsion gradually takes up more oil until it and the upper oil-rich phase eventually merge, so that above a certain temperature one finds again two liquid phases, except that the amphiphile is now mainly dissolved in the upper phase. If one repeats this experiment for gradually increasing mass fraction γ of the amphiphile, one finds the three-phase temperature interval first to widen and then to shrink again until, at a certain γ, the three-phase region disappears altogether. If one increases the concentration of the amphiphile further, one finds at ambient temperatures two phases, at intermediate temperatures a homogeneous solution (1ϕ) of all three components, and at elevated temperatures two phases again. The extensions of the three-phase region at a fixed ratio between water and oil can be characterized by three properties: its three-phase temperature interval,

$$\Delta T \equiv T_u - T_l$$

its position on the temperature scale defined by its mean temperature,

$$\bar{T} \equiv (T_l + T_u)/2$$

and the coordinates of point $\tilde{X}$, that is, the point at which the three-phase region touches the homogeneous mixture. $\tilde{X}$ represents that point in this quasibinary phase diagram at which one finds a macroscopically homogeneous solution of the three components with the lowest amount of the amphiphile. At a fixed ratio between water and oil, point $\tilde{X}$ is unambiguously defined by the coordinates $\tilde{T}$ and $\tilde{\gamma}$. $\tilde{T}$ is a measure for the mean temperature $\bar{T}$ of the three-phase interval, whereas $\tilde{\gamma}$ is a measure for the "efficiency" of the amphiphile. The lower the value of $\tilde{\gamma}$, the higher its efficiency. If one adds more amphiphile than is needed for completely solubilizing the water and oil and thus offers more interfacial area, the mean size of the water and oil domains will gradually decrease until the sponge-like structure is replaced by a lamellar liquid crystal (L_α), that is, a viscous anisotropic sandwichlike structure of alternating layers of water or oil that are separated by monolayers of the amphiphile. This lamellar mesophase points at $\tilde{X}$ like an arrow, being separated from the lower and upper two-phase region by narrow channels of isotropic homogeneous solutions.

A comparison between Fig. 1 and Fig. 3 demonstrates that both phase diagrams are apparently related, although the binary mixture of water and the amphiphile (Fig. 1) "has never heard of oil": the lower temperature T_l of the three-phase interval in Fig. 3 lies near the (lower) critical temperature T_c of the miscibility gap in Fig. 1, and the L_α extends from the binary mixture deep into the ternary mixture. The upper temperature T_u of the three-phase interval, on the other hand, is related to the (upper) critical temperature of the miscibility gap in the phase diagram of the binary mixture of oil and amphiphile that "has never heard of water." The essential properties of the amphiphiles thus exhibit themselves in the miscibility gaps of these two binary mixtures, the interplay of which enforces the formation of a three-phase region in the multicomponent mixture. This demonstrates that a quantitative understanding of the phase diagrams of these two binary mixtures is a prerequisite for understanding the phase diagrams of the more complex mixtures.

The ability of an amphiphile to create such structures, and thus its efficiency, depends on the strength of its hydrophilic and oleophilic groups. The stronger the hydrophilic and oleophilic groups, the stronger will each group be anchored in the water and oil domains, respectively, and, accordingly, the stronger the monolayer and the larger the mean domain size. The difference between strong and weak amphiphiles is thus a quantitative but not a qualitative one. The sponge-like structure of the microemulsion exhibits itself in the scattering of visible light, x-rays, or neutrons. The scattering peak, which is a measure of the mean domain size, decreases smoothly with decreasing efficiency of the amphiphiles, until it becomes hardly detectable in mixtures with weak amphiphiles. However, recently published experimental results have shown that even mixtures with very weak amphiphiles show indications of an ordering into very finely dispersed water and oil domains (*5*).

The separation of multicomponent mixtures into three coexisting condensed phases is not a particular property of mixtures with amphiphiles (*6*). Even the fact that, at point $\tilde{X}$ of the three-phase region, the mutual solubility between water and oil reaches a maximum is not a particular property, but rather is an inevitable consequence of the laws of thermodynamics. What makes mixtures with amphiphiles particular is that this maximum is so pronounced. Even with rather simple nonionic amphiphiles, ten molecules may completely solubilize hundreds of water and oil molecules.

Another fascinating property of the three-phase region is that the maximum of the mutual solubility between water and oil is combined with a pronounced minimum of the interfacial tension between the aqueous and the oil-rich phase, again for thermodynamic reasons (*7*). The interfacial tension between pure water and oil is comparable with that between water and air. In a three-phase region, however, the interfacial tension between the lower aqueous and the upper oil-rich phase may lie three orders of magnitude lower. The magnitude of this interfacial tension again depends on the efficiency of the amphiphile. The lower the value of $\tilde{\gamma}$, the lower the interfacial tension between the aqueous and the oil-rich phase. The interfacial tensions between the various liquid phases are related to those tensions between these phases and solids (including textiles), the so-called wetting behavior, which is of great importance in washing and flooding processes. Both properties of the three-phase regions, the pronounced maximum of the mutual solubility between water and oil and the pronounced minimum of the interfacial tensions, make searching for three-phase regions so important for both research and applications, because at temperatures below or above the three-phase regions, the efficiency of the amphiphile is much lower and the interfacial tension between the aqueous and the oil-rich phase is much higher. Experiments have actually shown that the efficiency of an amphiphile in a washing process reaches its maximum at a temperature near the mean temperature of the corresponding three-phase interval.

As already mentioned, the temperature at which an amphiphile changes from being hydrophilic to being oleophilic, and thus, the mean temperature $\overline{T}$ of the three-phase interval, depends sensitively but systematically on the chemical nature of the oil and the amphiphile, as well as on the salt concentration of the aqueous solution, the so-called "brine." Since the temperature of application, the nature of the oil, and the brine concentration are usually given, the problem is to find that amphiphile that is most efficient under these conditions. The temperature, the oil, and the brine concentration vary considerably from case to case. (Consider the various oil fields around the world which are at temperatures ranging from ambient temperatures to above 100°C, and that contain oils with varying fractions of aromatic oils and alkanes, not to mention the other components, and with brine concentrations varying between weakly concentrated and saturated solutions.) Thus there can be no "universal" detergent that works equally well in all oil fields. The same considerations hold for the solubilization of drugs that vary considerably in their composition.

General Patterns

Research has concentrated on two problems: (i) to empirically clarify the dependence of the positions and extensions of the three-phase regions on the nature of the components and (ii) to find a deeper theoretical insight into the physics of such multicomponent mixtures. The first problem can be considered to be solved (*8*). The dependence of the properties of the three-phase regions on the nature of the components follows general patterns. The detailed knowledge of these patterns permits the prediction of the temperature at which a three-phase region is to be found and the efficiency of the amphiphile to be expected. In view of the above qualitative considerations, the following patterns for nonionic amphiphiles generally hold:

1) The stronger the oleophilic group in comparison with the hydrophilic group, the lower the mean temperature $\overline{T}$ of the three-phase interval.

2) The more hydrophobic the oil, that is, the greater the number of its carbon atoms, the harder it is for the oleophilic group to pull the hydrophilic head group into the oil, that is, the higher the mean temperature of the three-phase interval.

3) The addition of an inorganic electrolyte like NaCl lowers the mean temperature of the three-phase interval, as if the salt makes the hydrophilic group of the amphiphile effectively weaker, which is presumably caused by the competition between the ions and the hydrophilic groups in binding the water molecules. In principle, this effect was discovered already in 1888 (*9*), but unfortunately has not yet attracted sufficient attention from theorists.

If one replaces nonionic by ionic amphiphiles, these patterns are in every respect reverse (*10*): with "ionics," the mean temperature of the three-phase interval rises with increasing strength of the oleophilic group, drops with increasing carbon number of the oil, and rises with increasing brine concentration. Furthermore, ionic amphiphiles are oleophilic at low temperatures, but are hydrophilic at elevated temperatures. Accordingly, if one determines a phase diagram with an ionic instead of a nonionic amphiphile, one finds the upper phase to separate into an oil-rich phase and a microemulsion as one raises the temperature. With further increases in temperature, the microemulsion gradually accommodates more water until it eventually merges with the lower aqueous phase. The origin of this reverse phase behavior is not as transparent as with "nonionics." We shall, therefore, refrain from discussing it in more detail in this article. In principle, however, the phase diagrams look similar, although the phase behavior is reversed. This raises the question with respect to the phase behavior of mixtures of nonionic and ionic amphiphiles. The answer is of considerable importance, because usually mixtures of both classes of amphiphiles are used in applications. The reason is that only a few ionic amphiphiles show a three-phase region in the temperature range between the melting and boiling points of the mixture. With standard single-tailed ionics like sodium dodecyl sulfate (SDS), the three-phase regions lie below the melting point, whereas with more oleophilic double-tailed ionics, they lie in general above the boiling point. When studying the phase behavior of mixtures of appropriately chosen nonionic and ionic amphiphiles (amphiphiles that both show a three-phase region with the same oil between melting and boiling point), one finds, as one would expect, nonionic patterns for low fractions of the ionic amphiphile, but ionic patterns for high fractions. At a certain fraction that depends on the relative strength of the two amphiphiles as well as on the nature of the oil, the three-phase region emerging from the mixture with the purely nonionic amphiphile and that emerging from the mixture with the purely ionic amphiphile overlap, the reverse patterns compensating each other. As a consequence, one finds a microemulsion that exists almost over the entire temperature range between the melting and boiling points. Although this microemulsion is insensitive to temperature variations, it is rather sensitive to changes of the ratio between nonionic and ionic amphiphile and also to changes of the brine concentration. The knowledge of these general patterns provides guidelines for searching for an appropriate mixture of amphiphiles to solve a particular problem if the temperature of an application, the nature of the oil, and the brine concentration are given.

Tricritical Points

Another fascinating aspect of the general patterns is the fact that the three-phase regions appear to evolve from so-called tricritical points. Thermodynamics requires that the two phases of a partially miscible binary mixture become identical at a sufficiently high temperature. The point in the binary phase diagram at which they become identical is called the critical point of the mixture. As has been discussed above, two immiscible compounds may also be made completely miscible by adding an appropriate third compound at constant temperature. The point in an isothermal ternary phase diagram at which the two phases become identical is called the plait point of that mixture at that particular temperature. Thermodynamics predicts, however, that there should exist particular plait points at which the homogeneous mixture separates into three instead of two phases if the three components, the temperature, and the pressure are appropriately chosen. Such points are called tricritical points (*11*). When studying the phase behavior of ternary mixtures systematically by changing one of the components within a homologue series, one finds that the relation between the mean temperature $\overline{T}$ and the three-phase temperature interval ΔT of the three-phase bodies resembles that of near-tricritical mixtures (*12*). For such mixtures theory predicts (*13*)

$$\Delta T \sim (\overline{T} - T_{\mathrm{tcp}})^{3/2}$$

where T_{tcp} denotes the temperature of the tricritical point at a particular pressure and composition.

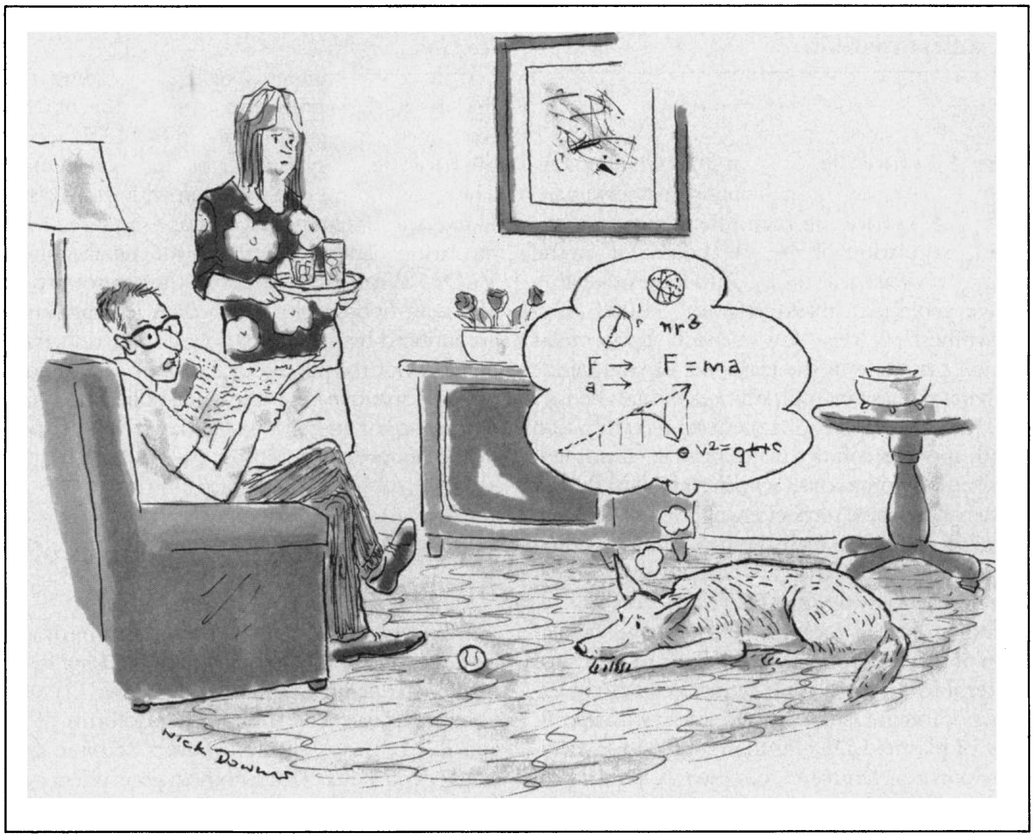
At atmospheric pressure, it would be purely accidental to find a tricritical point in a ternary mixture. But since thermodynamics states that the effect of pressure may be replaced by the effect of an appropriately chosen fourth component, one may search for tricritical points by adding either an inorganic electrolyte or an ionic amphiphile. Lang and Widom (*14*) actually succeeded in determining the coordinates of a tricritical point in the quaternary mixture H_2O-benzene-ethanol-$(NH_4)_2SO_4$ at atmospheric pressure, ethanol being a (very) weak nonionic amphiphile. This result encourages the search for tricritical points in mixtures with medium and long chain amphiphiles. A success would be of importance for both research and application. In research it would permit comparing the results of experimental studies on near-tricritical mixtures with the predictions of theory, in particular, with the predicted "universal scaling laws," and in applications it would permit describing the phase behavior of such mixtures semiquantitatively on the basis of these scaling laws.

The first attempt to phenomenologically describe microemulsions was made by Talmon and Prager in 1978 (*15*). In their and all subsequent models (*16*), the ternary mixture is considered as an essentially binary mixture of water and oil with the amphiphilic layer between the domains being treated as a flexible membrane with a bending energy that contributes to the Gibbs free energy of the mixture. This approach can explain the existence of three-phase regions with a sponge-like structure of the microemulsion, but—at least until now—cannot explain the dependence of the position and extensions of the three-phase regions on the nature of the oil, the amphiphile, and the brine concentration. Since this dependence is strongly related to the features of the phase diagrams of the binary mixtures, water-amphiphile and oil-amphiphile, respectively, the properties of the membrane must furthermore exhibit themselves in the features of these two binary phase diagrams. Finally, the dependence of the properties of the membrane on temperature, pressure, and nature of the components must be such that the phase behavior of the mixtures resembles that of mixtures evolving from tricritical points.

Soap-boilers were able to produce efficient soaps long before scientists entered the field. In the meantime, however, science has caught up a little, so that both research and industry may benefit from a more intense exchange of knowledge and experience in the future.

REFERENCES AND NOTES

1. J. H. Schulman, W. Stoeckenius, L. M. Prince, *J. Phys. Chem.* **63**, 1677 (1959).
2. W. D. Bancroft, *ibid.* **1**, 414, 647 (1896).
3. J. S. Walker and Ch. A. Vause, *Sci. Am.* **256**, 90 (May 1987).
4. W. Jahn and R. Strey, *J. Phys. Chem.*, in press.
5. P. K. Kilpatrick, H. T. Davis, L. E. Scriven, W. G. Miller, *J. Colloid Interface Sci.* **118**, 270 (1987).
6. F. A. H. Schreinemakers, *Die heterogenen Gleichgewichte* (Vieweg, Braunschweig, 1913), vol. 3, p. 2. For an example of a more recently published monograph in English, see A. Prince, *Alloy Phase Equilibria* (Elsevier, Amsterdam 1966).
7. See, for example, B. Widom, *Langmuir* **3**, 12 (1987).
8. For a review, see, for example, M. Kahlweit *et al.*, *ibid.*, in press.
9. This effect referred to here is the so-called "Hofmeister series." See, for example, P. Firman, D. Haase, J. Jen, M. Kahlweit, R. Strey, *Langmuir* **1**, 718 (1985).
10. M. Kahlweit and R. Strey, *J. Phys. Chem.*, in press.
11. See, for example, B. Widom, *ibid.* **77**, 2196 (1973).
12. M. Kahlweit, R. Strey, P. Firman, *ibid.* **90**, 671 (1986).
13. See, for example, J. L. Creek, Ch. M. Knobler, R. L. Scott, *J. Chem. Phys.* **74**, 3489 (1981).
14. J. C. Lang and B. Widom, *Physica A* **81**, 190 (1975).
15. Y. Talmon and S. Prager, *J. Chem. Phys.* **69**, 2984 (1978).
16. For a review, for example, see D. Andelman, M. E. Coates, D. Roux, S. A. Safran, *ibid.* **87**, 7229 (1987).



"All he thinks about is that stupid ball."