Microemulsions

D. LANGEVIN

Laboratoire de Spectroscopie Hertzienne de l'E.N.S., 24, rue Lhomond, 75231 Paris Cedex 05, France

I. Introduction

Microemulsions are dispersions of oil and water made with surfactant molecules.[1] In many respects, they are small-scale versions of emulsions. Indeed, they are frequently droplet type dispersions, either of oil in water (o/w) or of water in oil (w/o) (Figure 1). However, the droplet sizes are very small, typically 100 Å, about 100 times smaller than typical emulsion droplet sizes. For this reason, microemulsions are relatively translucid. They usually behave like Newtonian fluids; their viscosity is comparable to that of water, even at high droplet concentration, probably because of reversible droplet coalescence. Indeed the microstructure evolves constantly due to constituent exchanges. This important feature strongly affects the dynamic properties of microemulsions, which sometimes behave almost as molecular mixtures of their constituents.[2] Also because of the small dispersion size, microemulsions are thermodynamically stable, contrary to emulsions. This may seem at first sight surprising, but it is due to the very low interfacial tensions between oil and water microdomains. When these tensions are below about 10^{-2} dyn/cm, it can be shown that surface energy can be compensated by dispersion entropy, thus minimizing the free energy of the system.[3] Usual surfactants cannot lower the interfacial tensions between oil and water to such ultralow values. A cosurfactant, such as a short-chain alcohol, is frequently necessary. The requirement of an ultralow interfacial tension explains why emulsions are more commonly encountered in practice than microemulsions when oil, water, and surfactants are mixed.

Microemulsions were not recognized as a special kind of colloidal dispersion before the work of Schulman in 1943. They were only named microemulsions in 1958. However, they were probably discovered well before: Australian housewives have used since the beginning of this century water–eucalyptus oil–soap flake–white spirit microemulsions to wash wool.[4] The first commercial microemulsions were probably the liquid waxes discovered by Rodawald in 1928. However, it was not until 1970 that research in the field reached a large scale, when it was recognized that microemulsions could improve oil recovery and when oil prices reached levels where tertiary recovery methods became profit-earning.[5] Nowadays, this is no longer the case, but other microemulsion applications were discovered, e.g., catalysis, preparation of submicron particles, solar energy conversion, liquid–liquid extraction (minerals, proteins, etc.), etc. Together with the classical applications in detergency and lubrication, the field remains sufficiently important to continue to attract a number of scientists.

From the fundamental research point of view, a great deal of progress has been made in the understanding of microemulsion properties.

Droplet microemulsions have been widely studied, and their structure is now reasonably well understood. An interesting phenomenon of percolation was observed in many w/o microemulsions: when the droplet concentration is increased, the electrical conductivity rises steeply above a certain threshold, as if the medium were turning water continuous (Figure 2). A number of

Dr. Langevin is Directeur de Recherche, C.N.R.S., and works at the Physics Laboratory of the Ecole Normale Supérieure, Paris, France. She received here D.Sc. in 1974 from the University of Paris. Her research has concerned light scattering by liquid surfaces and other optical techniques applied to simple fluids, liquid crystals, polymer solutions, and surfactant systems.

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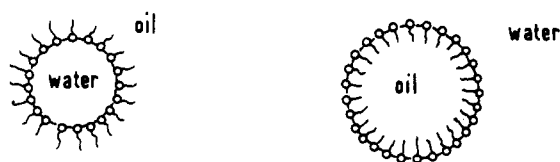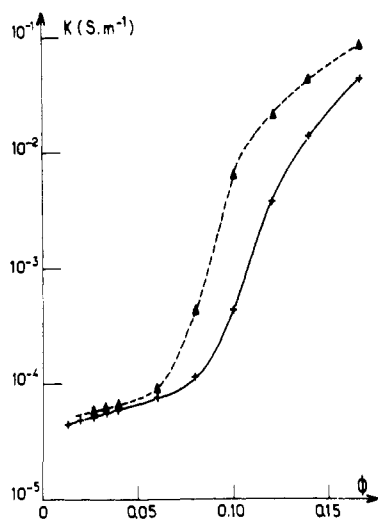
Figure 1. Droplet structures.

Figure 2. Electrical conductivities of w/o microemulsions versus droplet volume fraction. The left curve corresponds to more attractive droplets (R = 82 Å) than the right curve (R = 55 Å). Water–benzene–benzylhexadecyldimethylammonium chloride mixtures.[43]
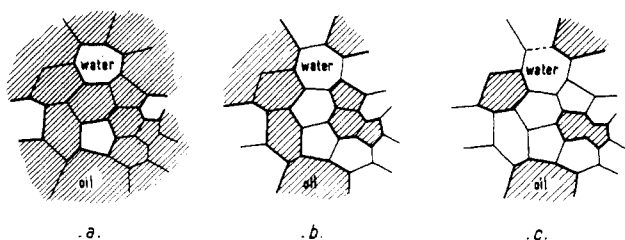

Figure 3. Voronoi polyhedra of the Talmon–Prager model.

experimental and theoretical studies have been devoted to the subject,[6] but many features are still not understood. The phenomenon is frequently followed by a continuous inversion toward o/w structures. Numerous efforts have been made to describe the microemulsion structure in the inversion region. The passage through bicontinuous structures was first suggested by Scriven.[7] A space-filling model (with polyhedra) was proposed by Talmon and Prager allowing an o/w structure to evolve smoothly toward a w/o structure via bicontinuous structures[8] (Figure 3). A simpler space-filling model (with cubes) was subsequently proposed by de Gennes and Taupin.[9] This important step showed that it was possible to describe microemulsions with Ising models and to use the wide theoretical developments of random Ising lattices (spin glasses). Widom showed in particular that within some approximations microemulsions can be related to the ANNNI (anisotropic, next-nearest-neighbor Ising) models.[10]

Meanwhile, experimental evidence of the existence of bicontinuous structures was found, especially in cases where the microemulsions are in equilibrium with both excess oil and water.[11,12] Such systems had already been studied in great detail because they were model systems for oil recovery. The microemulsions are in an inversion region, and the interfacial film between oil and water microdomains has a spontaneous radius of curvature close to zero.[11] The structure is therefore lamellar-like. The reason the system is not macroscopically ordered has been explained by de Gennes and Taupin.[9] The bending elasticity of the surfactant film is small and the thermal fluctuations roughen the film: the lamellar order is rapidly lost. Two-dimensional fluctuations of that kind are also important features in many other fields of physics and chemistry,[13,14] for example, biomembranes, wetting transitions, commensurate–incommensurate phase transitions, and elementary particle physics, fields that are all very active nowadays.

Other types of microemulsion structures were also found or predicted recently: bicontinuous tubular, foam-like, etc., for which novel random type structural descriptions were proposed.[15]

The dynamic properties of microemulsions have also been widely studied, but they are still poorly understood. The problem of constituent exchanges has received great attention and it is now reasonably well understood.[16] However, the link between these exchanges and the other microemulsion properties remains to be properly established. For instance, it has been observed that when the exchange rate in w/o microemulsions increases, attractive forces between droplets become increasingly important.[17] They can eventually lead to phase separation between a droplet-poor microemulsion and a droplet-rich microemulsion, exactly as in a liquid–gas phase transition. Critical points are found close to which the exchanges are anomalously rapid. The origin of the attractive forces is not yet fully understood.[18,19]

Chemical reactivity is also an important area where the role of exchanges is dominant.[20]

In the following we discuss these different aspects of microemulsions in more detail. We begin with some basic concepts for surfactant films, continue with the description of the main microemulsion models, then illustrate the theoretical notions by experiments done with droplet microemulsions, describe droplet aggregation and percolation, and present some data on bicontinuous microemulsions. We will end the discussion with the interfacial aspects of multiphase equilibria.

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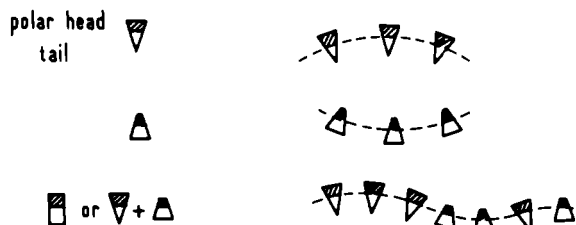
polar head

tail

Figure 4. Variation of the film spontaneous curvature with surfactant shape.

We will not address formulation problems, which are somewhat complex and are well described elsewhere.[1,21]

II. Surfactant Film: Basic Concepts

When a surfactant film is adsorbed at the oil–water interface, it constitutes a two-dimensional system, in which one can define a pressure π.[22] The oil–water interfacial tension γ_{ow} decreases by an amount equal to the surface pressure π: $\gamma = \gamma_{ow} - \pi$. If one minimizes the free energy of the medium with respect to the area Σ per surfactant molecule at a fixed number of surfactant molecules n_s, one finds that the system adopts a well-defined area per surfactant $\Sigma = \Sigma^*$, called the "saturated state", where $\pi(\Gamma^*) = \gamma_{ow}$ and therefore $\gamma = 0$.[9] Such a state may not be reached if the surfactant film collapses or if the critical micellar concentration (cmc) occurs at $\Sigma > \Sigma^*$. Certain authors assume that because of the exchanges between the bulk oil and water and the film, n_s is not fixed and thus γ is nonzero, although very small.[14,23,24] Other authors assume that the film is incompressible so that $\gamma = 0$,[25,26] as for flaccid vesicles.

The surfactant film also possesses bending elasticity. It is usually bent due to the spontaneous curvature C_0 of the film. As in emulsions it bends spontaneously toward the medium where the surfactant molecule is more soluble (Bancroft rule) (Figure 4). This has been rationalized in terms of surfactant molecular geometry by Ninham and Mitchell.[27] The surfactant molecule is replaced by a truncated cone. If the polar part is more bulky than the hydrophobic part, the interface will curve spontaneously toward water and o/w structures will be favored. The spontaneous curvature C_0 is by convention positive. If the polar part is less bulky than the hydrophobic part, the interface will curve in the opposite direction and w/o structures will be favored: $C_0 < 0$. If the surfactant has the shape of a cylinder or if a surfactant for which $C_0 > 0$ and a cosurfactant for which $C_0 > 0$ are mixed, a zero mean spontaneous curvature can be obtained (Figure 4). This explains probably why continuous inversion can be obtained by changing the relative proportions of oil and water in an oil–water–surfactant–alcohol mixture. The alcohol partition coefficient between the surfactant film and oil and water bulk phases can be adjusted to vary C_0 continuously from positive to negative values.

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If the spontaneous curvature is close to zero and if $\gamma = 0$, one can evaluate the effect of thermal undulations of the film. The result is that the film is strongly wrinkled at scales larger than a persistence length ξ_k.[9]

$$\xi_k = a \, \exp(2\pi K/kT) \qquad (1)$$

where a is a molecular length, k the Boltzmann constant, and T the temperature. K is the bending elastic constant of the surfactant layer.[28]

This explains why structural inversion sometimes takes place via lamellar phases, and other times continuously. Indeed if the surfactant film is rigid ($K \sim 10$–$100\ kT$ as for phospholipid bilayers), ξ_k is macroscopic and the surfactant layer is flat over large distances. If the surfactant layers contain short-chain alchols that introduce disorder in the film, K can decrease to about kT and ξ_k to about 100 Å: long-range order is destroyed and the system remains a microemulsion.

III. Microemulsion Models

Space-filling models are helpful to describe microemulsion structures. Talmon and Prager first proposed using Voronoi polyhedra[8] (Figure 3). The polyhedra are filled with either oil or water, and the surfactant film volume is neglected. If the oil volume fraction φ_o is large, water polyhedra are isolated: this represents the w/o structure (case a in Figure 3). If the water volume fraction is large, oil polyhedra are isolated: o/w structure (case c). In the intermediate range $\varphi_p < \varphi_w < 1 - \varphi_p$ a bicontinuous structure is obtained (case b). The volume fraction φ_p at which an infinite path of water polyhedra first appears is the percolation threshold. In this model $\varphi_p = 0.16$.

The model reflects no evidence of a well-defined characteristic size in the medium. As we will see later, experiments show that even in bicontinuous microemulsions a well-defined size is favored. De Gennes and Taupin proposed using instead of polyhedra a simple cubic lattice where the size of the cube is either twice the droplet radius R or the persistence length ξ_k.[9] The free energy F per site is the sum of dispersion entropy, surface energy, and curvature energy. By neglecting the latter, one has

$$F = kT(\varphi_w \ln \varphi_w + \varphi_o \ln \varphi_o) + 6\gamma\xi^2\varphi_o\varphi_w \qquad (2)$$

an expression formally identical with the free energy of a regular binary solution. The problem is well-known. A single-phase system is found for $\gamma \lesssim kT/\xi^2$. Typically without surfactant $\gamma_{ow} \sim kT/a^2 \sim 50\ \text{mN/m}$. If the scale of the dispersion ξ is about 100 times larger than the molecular length a, then $\gamma \lesssim 10^{-4}\gamma_{ow}$. The microemulsion will be thermodynamically stable only if γ is ultralow, as already mentioned.

This model is very crude: it predicts that two-phase systems with symmetrical o/w and w/o microemulsions can coexist. This is never observed in practice, because of preferred curvature requirements. Widom generalized it by including the curvature energy and introducing a cutoff for the cell size ($\xi > a$).[24] He was able to account for the so-called Winsor equilibria: o/w microemulsion in equilibrium with excess oil (Winsor I), w/o microemulsion in equilibrium with excess water (Winsor II), and bicontinuous microemulsion in equi-

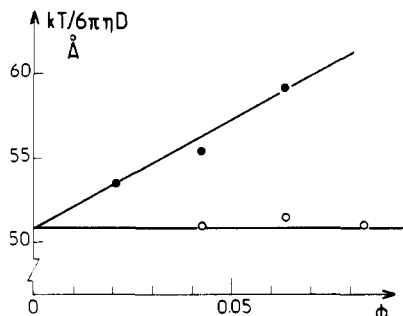(28) Helfrich, W. *Z. Naturforsch.* **1973**, *C28*, 693.

Figure 5. Apparent hydrodynamic radius of w/o microemulsion versus droplet volume fraction: (O) AOT–isooctane–water mixtures; (●) AOT + MPB protein. See ref 35 for details.

librium with both excess oil and water (Winsor III).

A different approach was recently proposed by Safran et al.[26] They assume $\gamma = 0$, but they take into account the renormalization effects on the curvature modulus K. Indeed Helfrich proposed that K should decrease with the length scale due to thermal fluctuations.[29] For $C_0 = 0$, this model leads to $\xi \sim \xi_k$.

Several authors[10,30,31] also attempted to adapt Ising models to microemulsions. This allows one to calculate interfacial profiles and to explain unusual wetting properties,[32] problems that could not be treated with the earlier mean field models.

IV. Droplet Microemulsions

Droplet structures are very frequent in microemulsion systems. Since the interfacial film is mainly incompressible, the area per surfactant molecule is close to or equal to Σ^*. In the following we will suppress the asterisk. The droplet radius can be easily calculated by assuming the surfactant molecules to sit at the droplets' surface. One gets

$$R = 3\varphi_o/C_s\Sigma \qquad (3a)$$

and

$$R = 3\varphi_w/C_s\Sigma \qquad (3b)$$

for, respectively, o/w and w/o droplets. C_s is the number of surfactant molecules per unit volume n_s/V.

A number of determinations of droplet sizes have been made on many different microemulsion systems with neutron, X-ray, or light scattering methods. They are all in good agreement with the above formula. Frequently Σ is independent of the amount of cosurfactant in the interfacial film and is close to the Σ value of the surfactant in simple micellar solutions. For single-chain surfactants $\Sigma \sim 50$ Å^2.[33]

Light scattering techniques can only be used when the microemulsion is dilutable. Dilution is easy with three-component mixtures, where the continuous phase of the droplets is either pure oil or pure water. When a cosurfactant such as an alcohol is used, dilution is more difficult because the continuous phase contains alcohol. A method proposed by Schulman was widely used and generalized.[34]

This allows one to deduce from the experiments information about osmotic virial coefficients and thus about interactions between droplets. Figure 5 shows an example of the kind of information obtained with quasi-elastic light scattering.[35] The lower curve corresponds to a w/o microemulsion made with a single surfactant: aerosol OT (AOT) diluted with oil. Theory predicts that when φ is small ($\varphi \lesssim 0.1$), the measured diffusion coefficient D varies with droplet volume fraction φ as

$$D = D_0(1 + \alpha\varphi)$$

$$D_0 = kT/6\pi\eta R_H$$

where α is the virial coefficient, η the oil viscosity, and R_H the droplets' hydrodynamic radius.For hard spheres $\alpha \simeq 1.5$. If a supplementary attractive potential is present, $\alpha < 1.5$. From the figure it is seen that the AOT droplets behave almost like hard spheres. The upper curve corresponds to the same microemulsion where a protein, the basic myelin protein, has been solubilized. Now α is negative, indicating that the protein induces an attractive between droplets. This was later confirmed by direct force measurements.

Dilution methods become inoperant in some cases, where droplet size changes upon dilution.[36] In these cases X-ray and neutron scattering techniques have to be used, and a model taking into account the shape and the interactions between the droplets is necessary to analyze the data.[37]

Dilution fails mainly when attraction between droplets is important. Attraction is usually much larger than predicted from van der Waals forces alone and can be strong enough to induce phase separation beyond some critical point. Frequently the critical point is a lower consolute point (one phase at low temperature, two phases at high temperature), indicating that the attraction is of entropic character, as for the cloud points of aqueous solutions of nonionic surfactants.[38] There have been many measurements of critical exponents in these systems,[39,40] and many theories have been proposed to explain the differences with classical Ising theories, but the issue is yet far from being solved.

V. Droplet Aggregation: Percolation

When the interaction potential between droplets is sufficiently attractive, an appreciable number of dimers and higher order aggregates can be found. They have been made evident in w/o microemulsions first in neutron scattering experiments[41] and later in more discriminating experiments by transient electrical birefringence and fluorescence photobleaching recovery.[42,43] In o/w and w/o microemulsions, evidence

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of clustering can be inferred from viscosity measurements.[44] The amount of clusters increases when attractive interactions increase, as well as the cluster's lifetime, which is typically of the order of microseconds. When the potential is very attractive, the number of isolated droplets becomes negligible.

When the volume fraction φ of droplets is large enough, an infinite cluster appears: this corresponds to the percolation threshold $\varphi = \varphi_p$. In w/o microemulsions where the potential is attractive, a large increase in electrical conductivity is observed around φ_p[45] (Figure 2). φ_p decreases with increasing attraction.[46] In hard-sphere-like w/o microemulsions such an increase is not observed,[46] probably because the charges cannot move across the insulating surfactant layer. All these features disagree with the Talmon–Prager–de Gennes–Widom models that neglect the role of the surfactant layer and predict the occurrence of bicontinuous structures above $\varphi_p \sim 0.16$. The experimental values of φ_p are usually smaller ($\varphi_p \lesssim 0.1$) excepted for the Winsor microemulsions. They depend on the interaction potential, and the electrical percolation phenomenon disappears for repulsive potentials. All this suggests, as pointed out by Safran et al.,[6] that the percolation is governed by a hopping mechanism which is facilitated by the interpenetration of surfactant layers (associated with attractive forces and flexible and fluid layers). Droplets can remain present even above φ_p as was observed in ternary microemulsions.[47]

The inversion behavior of Figure 3, via bicontinuous structures, is observed in Winsor microemulsions, probably because the surfactant layer is extremely permeable. Self-diffusion measurements indeed show that the constituents' mobilities are similar[48] in bicontinuous microemulsions and in molecular solutions. Such situations can probably be encountered in systems that are not Winsor microemulsions but where the surfactant layer is also very permeable.[46] Up to now, only partial evidence of this has been reported.[49]

VI. Bicontinuous Microemulsions

The Winsor bicontinuous microemulsions have been the more widely studied. Although as mentioned earlier, the transient character of the microstructure is extremely pronounced, the existence of well-defined surfactant layers has been proved with X-ray experiments.[11] When the scattering wave vector q is such as $q\xi \gg 1$, where ξ is the characteristic microdomain size, the flat portions of the oil–water interfaces are seen. Porod predicted that the product of the intensity I scattered by a flat interface times q^4 should be constant and proportional to the ratio of total area to total volume and thus to $C_s\Sigma$. This has been verified in a number of systems, and the area per surfactant molecule determined in this way is consistent with other determinations.[50-53]

Figure 6. Scattered X-ray intensity I versus the squared wave vector q. Water–NaCl–toluene–butanol–dodecyltrimethylammonium bromide (DTAB) mixture; water salinity $S = 2.5$ wt %.[53]

At smaller q a maximum of intensity is generally observed (Figure 6). Although very broad the peak is the evidence that there is a well-defined length scale in the microstructure. This peak has been attributed by some authors to a form factor feature[15,54] and by some others to a structure factor feature (correlations).[55] Empirically $\xi \approx \pi/q_{max}$, where ξ is the cube size in the de Gennes–Taupin model:

$$\xi = 6\varphi_o\varphi_w/C_s\Sigma \qquad (4)$$

This equation is the equivalent of eq 3 for droplets. It is just assumed that the oil–water interfaces are covered with surfactant molecules of area Σ.

As seen from Figure 6, the typical spectra are very broad, about 10 times broader than in lamellar liquid crystalline structures. This means that the microstructures are strongly disordered. Although there are not yet precise predictions for the shape of $I(q)$, it can be qualitatively said that the spectral width is a measure of the range of local order, i.e., according to de Gennes, of the persistence length of the surfactant layer. The width being comparable to q_{max}, it follows that $\xi \sim \xi_K$ as predicted by theory.[26]

Let us finally mention that electron micrographs of bicontinuous ternary microemulsions were recently made,[56] where the oil–water interfaces are clearly visible. Numerous attempts were made previously without success, mainly because the cooling rates were not fast enough to freeze the structure: as already explained, this structure also evolves very rapidly, especially when a cosurfactant is used.

VII. Interfacial Properties

Microemulsions can coexist with many different types of other phases: oil, water, liquid crystals, or other microemulsions. Up to four different phases have been observed in equilibrium, and this number if certainly not a limit.[57] We will restrict ourselves here to the

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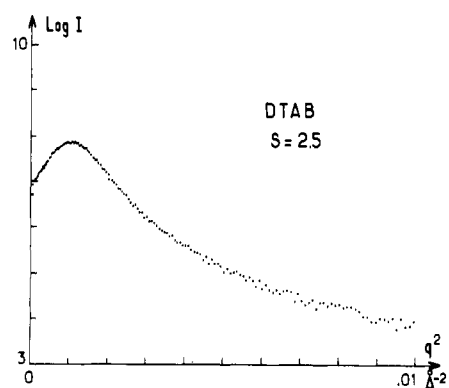(49) Larché, F.; Rouvière, J.; Delord, P.; Brun, B.; Dussossoy, J. L. *J. Phys. Lett.* **1980**, *41*, L-437.

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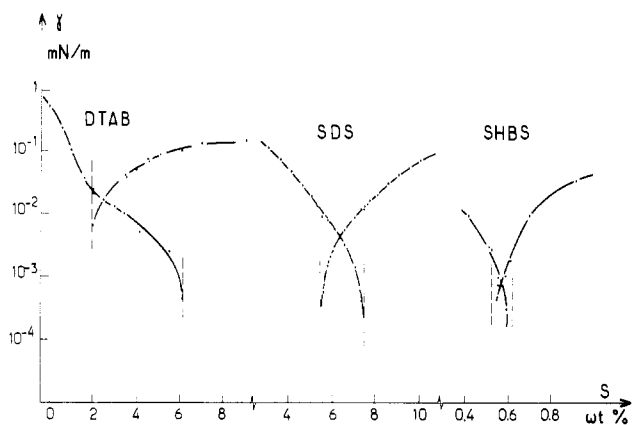
Figure 7. Interfacial tension between microemulsion and excess oil and water phases versus brine salinity for different Winsor systems: brine–toluene–butanol–sodium dodecyl sulfate (SDS); brine–dodecane–butanol–sodium hexadecylbenzenesulfonate (SHBS); brine–toluene–butanol–dodecyltrimethylammonium bromide (DTAB). Data from ref 58, ref 60, and unpublished observations.

more widely studied phase equilibria: Winsor microemulsions with excess oil and/or water, because of their interest in oil recovery.

A particularly important problem was the origin of the ultralow interfacial tensions between the microemulsion and the excess phases (Figure 7). The subject was very controversial, but it is now well established that in most cases the tension γ is low because the surface pressure of the surfactant monolayer at the interface between the microemulsion and the excess phase is high and almost compensates the bare oil–water interfacial tension.[58,59] It was found that in these cases the interfacial tension γ is approximately kT/L^2, where L is either the droplet radius for Winsor I and II microemulsions or ξ in Winsor III microemulsions. This is in qualitative agreement with theories, but some work remains to be done to achieve also quantitative agreement, especially in the Winsor III case, where theories are scarce.[60]

Interfacial structure has been probed with light reflectivity[61] and ellipsometry.[62] The most important feature is the very large roughness of these interfaces. Interfacial tensions being ultralow, thermal fluctuations are very large: their mean square amplitude reaches values up to 1000 Å. The short-wavelength fluctuations probed by ellipsometry have an amplitude that is appreciably dependent on the bending elastic modulus K. It has therefore been possible to deduce the values of K from the experiments.[62] Some examples are given in Table I for bicontinuous microemulsions having equal oil and water volume fractions. The persistence

Table I
Measured and Renormalized Elastic Bending Constants, Measured Dispersion Sizes ξ in Bicontinuous Microemulsions for Which $\varphi_o = \varphi_w$, and Calculated Persistence Lengths[a]

system	K/kT	renormalized K/kT	ξ	ξ_k
DTAB	0.41	0.55	95	63
SDS	0.65	1.00	230	275
SHBS	0.40	0.86	400	175

[a]Systems as in Figure 7. Data from ref 11, 12, 50, and 62 and unpublished observations.

length is also calculated and compared to ξ.

The macroscopic interfaces are therefore very rough like the microscopic ones. They are also structured.[62] A droplet-depletion layer is found in Winsor I and II microemulsions: droplets cannot cross the macroscopic interface. Bicontinuous microemulsions can be separated from the excess phase by a surfactant monolayer: the thickness of the depletion layer is smaller than ξ. The surfactant monolayer can also be disrupted at the macroscopic interface. The corresponding interfacial tensions are then the lowest; the low values have been ascribed to the proximity of critical end points in the phases diagrams.[58] They correspond to the lowest branches of the curves of Figure 7.

VIII. Conclusion

Microemulsion properties are extremely varied. The extreme diversity of their practical applications is one consequence. One of their disadvantages is the large amount of surfactant required to stabilize them because of the small dispersion size. This is, for instance, a problem in biological applications like artificial blood. However, the existence of "giant" microemulsions has just been demonstrated (dispersion sizes ~6000 Å),[63] enlarging the range of possible applications. Very promising applications deal with chemical synthesis in well-controlled microstructural environments, as, for instance, enzymatic reactions.[64]

Although microemulsion properties are beginning to be satisfactorily understood, especially the droplet structure, large research domains remain to be clarified: inversion mechanisms, structures other than droplets, the role of thermal fluctuations, and finally dynamic properties, which are certainly the most poorly understood although often the most important in applications.

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