Origin of Middle-Phase Microemulsions

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A simple model is used to calculate the phase behavior of microemulsions. The surfactant film at the oil-water interface is treated as an incompressible layer whose bending constant is renormalized by thermal fluctuations. Two- and three-phase equilibria involving upper-, lower-, and middle-phase microemulsions are found. The structure of the middle phase is characterized by the persistence length of the film, beyond which the bending constant is renormalized to smaller values.

Microemulsions[1] are multicomponent solutions which are characterized by domains of water and oil with a surfactant monolayer at the interface. For small amounts of oil in water or water in oil, the structure is often that of globules whose colloidlike properties are well understood.[2,3] However, when the volume fractions of water and oil are comparable, a description in terms of random (possibly bicontinuous[1]) domains is necessary.[4-7] By use of special surfactants, or by changes in temperature, salinity, or the amount of cosurfactant, a microemulsion phase (known as the middle phase) can be made[8] that coexists with both water and oil. Such "balanced" systems are important in many applications since the middle-phase microemulsion shows extremely low interfacial tension ($\sim 10^{-3}$ dyn/cm) with both oil and water.[8]

The first thermodynamic model of a bicontinuous microemulsion was given by Talmon and Prager[4] who considered a random partitioning of space into oil and water domains. However, this model considered only the entropy of mixing and did not correctly account for the curvature energy of the surfactant film.[9] de Gennes and co-workers[5,6] modified the Talmon-Prager model by including the bending energy of the surfactant. The domains of oil and water composed a lattice whose lattice constant was equal to the persistence length[5] ξ_K, which characterizes the rigidity of the interface and is found by calculation of the undulation modes of a surfactant film.[5] However, this model did not predict three-phase equilibrium.

Widom[7] made an important advance in the theory by allowing the cell size to vary and then determining it self-consistently at each point of the phase diagram. He obtained two- and three-phase equilibria by introducing a microscopic cutoff, and by allowing the area per surfactant in the interfacial film to vary. This degree of freedom was crucial to the phase equilibria he found, which depended strongly on the bare oil-water interfacial tension and only weakly on the bending properties of the surfactant film (in the limit of a large bending constant). Thus, in contradiction to the previous models,[5,6] the characteristic length scale predict-

ed for the middle-phase microemulsion was unrelated to the persistence length ξ_K. Moreover, Widom's theory does not explain the sensitivity of the experimental phase diagrams to the properties of the surfactant film (surfactant, cosurfactant, salinity, temperature).

In this paper, we study a simple model which results in a middle-phase microemulsion characterized by the persistence length ξ_K. Along the two-phase coexistence curves, the length scale in the microemulsion varies from ξ_K to a molecular size. The persistence length ξ_K enters the model through the *effective* bending constant of the surfactant layer; this bending constant is length-scale dependent because of thermal fluctuations of the film.[10,11] Both two- and three-phase equilibria can then be found quite simply by a search for coexistence of the microemulsion with phases consisting of small amounts of surfactant in water or oil.

Our model is based on the following assumptions: (i) All the surfactant in the microemulsion phase is at the water-oil interface; the surfactant film is modeled as an *incompressible liquid*.[4] This assumption is consistent with experiments on globular[12] and bicontinuous[13] microemulsions. (ii) Following Refs. 6 and 7, we divide space into cubes of size ξ; the characteristic size ξ is to be determined in Eq. (3) below. (iii) A random-mixing approximation accounts for the entropy of the interface at length scales larger than the cell size ξ. Undulations of the interface at smaller length scales are also taken into account through the renormalization of the bending constant.[10,11] This turns out to be essential to our results.

With these assumptions, the free energy per unit volume of the microemulsion phase is

$$f = \frac{1}{\xi^3}\left[TS(\phi) + 8\pi P(\phi)K(\xi)\left(1 - \frac{2\xi(1-2\phi)}{\rho_0}\right)\right].$$

(1)

The first term in Eq. (1) represents the entropy of mixing of the water and oil domains, where T is the

temperature. $S(\phi) = \phi \ln\phi + (1 - \phi) \ln(1 - \phi)$, where $\phi = \phi_w + \phi_s/2$, with ϕ_w and ϕ_s the water and surfactant volume fractions, respectively. The oil volume fraction is $\phi_o = 1 - \phi_w - \phi_s$. We have arbitrarily assigned half the surfactant volume to the oil and half to the water domains. This does not affect the properties of the microemulsion phase where $\phi_s \ll \phi_w, \phi_o$.

The second term in Eq. (1) is the bending energy of the surfactant film at the water-oil interface.[9] The factor $P(\phi)$ accounts for the total area of oil-water interface. In a random-mixing approximation we have $P(\phi) = \phi(1 - \phi)$. The effective bending constant $K(\xi)$ depends explicitly on the length scale ξ. Using perturbation theory, Helfrich[10] and Peliti and Leibler[11] have shown that $K(\xi)$ is reduced from its bare value K_0 by the thermal undulations of the film. For a finite sheet of size ξ, which we identify with the cell size, these authors find

$$K(\xi) = K_0[1 - \tau \ln(\xi/a)]. \tag{2}$$

In Eq. (2), a is a molecular distance comparable to the in-plane spacing of two surfactant molecules. The amplitude of thermal fluctuations is determined[10,11] by $\tau = \alpha T/4\pi K_0$. The value of α depends on the details of the calculation; Helfrich[10] finds that $\alpha = 1$, while Peliti and Leibler[11] have $\alpha = 3$. Clearly Eq. (2) is not valid for $\xi \geq \xi_K = ae^{1/\tau}$, since $K(\xi)$ cannot be negative.[14] However, for all the phases considered here, $K(\xi)$ turns out to be positive (of order kT or greater), so that the use of the perturbation theory result, Eq. (2), is appropriate. The term $1 - 2\xi(1 - 2\phi)/\rho_0$ in Eq. (1) accounts for the spontaneous radius of curvature, ρ_0, which reflects the tendency of the surfactant layer to bend towards either water or oil regions.[3,15,16] The factor of $1 - 2\phi$ in this term was introduced phenomenologically by Jouffroy, Levinson, and de Gennes,[6] and by Widom.[7] Like $P(\phi)$, this factor can be derived from the lattice model and is only accurate at the simplest level of random mixing.

Since we assume that the area per molecule of the surfactant film is fixed, the lattice constant ξ in Eq. (1) is determined by the volume fractions of surfactant, water, and oil.[4] In the random-mixing approximation, we have

$$\xi/a = z[\phi(1 - \phi)/\phi_s], \tag{3}$$

where for convenience we have chosen the length of the surfactant molecule equal to a as defined under Eq. (2) above; z is the coordination number in the lattice model.

Equations (1)–(3) complete the specification of our model. The free energy is a function of two independent variables, such as ϕ and ϕ_s. A typical phase diagram for $\rho_0 \to \infty$, calculated numerically by a double-tangent plane construction,[7] is shown in Fig. 1. The resulting three-phase region consists of a middle-phase

microemulsion which coexists with very dilute phases of surfactant in oil and surfactant in water.

The length scale ξ in the middle phase is comparable to ξ_K over a wide range of temperatures. (For the parameters chosen in Fig. 1, $\xi = 0.23\xi_K$.) Moreover, ξ remains comparable to ξ_K along the two-phase boundaries except for small regions near $\phi = 0$ and $\phi = 1$, where it falls rapidly to the molecular size, a.

Of course, we do not expect our free energy to be accurate at $\xi \sim a$. Consequently, the detailed structure in the corners of the phase diagram (see the inset in Fig. 1) would be altered in a more realistic treatment of the dilute phases. However, much of the remaining phase behavior can be understood quite simply by our noting that the characteristic three-phase equilibrium results from the presence of deep minima in the free energy, Eq. (1), in the dilute limit where $\xi \sim a$ and $\phi_w = 0$ or $\phi_o = 0$. For example, when $\phi_o \to 0$, Eq. (1) reduces to $f \approx f_w^* \propto [\kappa_w\phi + \phi(\ln\phi - 1)]/a^3$, where $\phi = \phi_s/2$ and $\kappa_w = 2/\tau$. The minimum of f_w^* is located at $\phi_s = \phi_s^* \sim \exp(-\kappa_w)$. Since $f_w^*(\phi_s^*) \sim -\exp(-\kappa_w)$ is much lower than the free energy, f, of the microemulsion phase $f \sim -\exp(-3\kappa_w/2)$, the coexistence curve by equilibrium with a water-rich, dilute phase is determined approximately[17] by

$$f + (1 - \phi) \partial f/\partial\phi - \phi_s \partial f/\partial\phi_s \approx f_w^*(\phi_s^*). \tag{4}$$

This simplified procedure gives a phase diagram which is almost indistinguishable from Fig. 1 (except for the region shown in the inset).

Equation (4) leads us to an important generalization of our model. We can regard κ_w (and hence f_w^*) as a
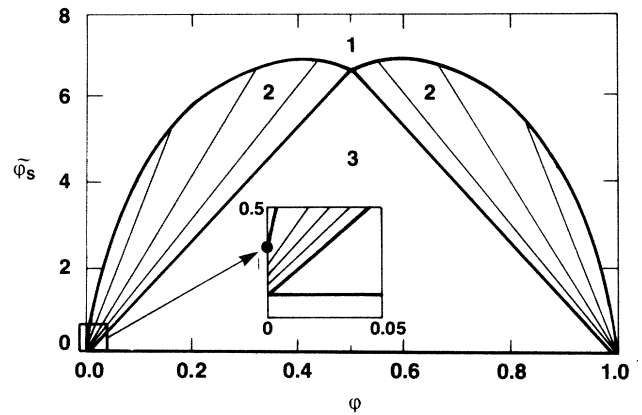

FIG. 1. Phase diagram of a microemulsion with no spontaneous curvature $(\rho_0 \to \infty)$. The volume fraction $\tilde{\phi}_s = \phi_s/\phi_m$, where ϕ_s is the volume fraction of surfactant, and $\phi_m = e^{-1/\tau}$. The water volume fraction is ϕ_w and $\phi = \phi_w + \phi_s/2$. The numbers indicate the number of coexisting phases and the tie lines in the two-phase region are shown. Inset: The details of the tie lines at small volume fractions. The filled circle in the inset is a critical point. Values of $\tau = 0.2$ and $\alpha = 1$ were used in these calculations.

purely phenomenological parameter which characterizes the solubility of the surfactant in the dilute phase. The equations for the equilibrium of the microemulsion phase with a dilute oil-continuous phase are obtained from those given above by letting $\phi \rightarrow (1-\phi)$ and $\kappa_w \rightarrow \kappa_o$. In general, we do not assume $\kappa_w = \kappa_o$.

Figure 2 shows the phase diagram for $\rho_0 \rightarrow \infty$ and $f_w^* \neq f_o^*$. Note that the phase diagram is asymmetric, although there is no spontaneous curvature of the surfactant film. For extremely large differences between f_w^* and f_o^*, the three-phase region can entirely disappear. Thus the phase equilibria are sensitive not only to the properties of the microemulsion phase, but also to the solubility of the surfactant in the dilute phases. The phase diagrams of Figs. 1 and 2 are in agreement with recent experiments[18] on three-component systems with nonionic surfactants.

When the spontaneous radius of curvature, ρ_0, is finite, we also find asymmetry in the phase diagram.[6,7] For values of $\rho_0 \ll \xi_K$, the three-phase region vanishes; the microemulsion phase is then characterized by "globules" of size $\xi \sim \rho_0$. We identify the remaining two-phase region as the emulsification-failure[3] instability where these globules coexist with excess water or oil.[19]

The results summarized above for the middle phase are markedly different in their physical origin and consequences from those of Widom.[7] In his model, the phase behavior is determined by the finite compressibility of the surfactant layers and the *bare oil-water interfacial tension, γ*. For the symmetric case $(\rho_o \rightarrow \infty)$, in the limit of large K_0/T, his prediction for ϕ_s in the middle phase is an exponential function of the surface tension and has only a weak dependence on the bending energy $[\phi_s \sim (e^{-\gamma}/K_0)^{1/3}]$; it should therefore be fairly insensitive to changes in K_0. In the present work, the renormalization of the *bending constant* by thermal undulations of the film is responsible for the stability of the middle phase. The volume fraction of surfactant in the middle phase is $\phi_s \sim \exp[-4\pi K_0/\alpha T]$, which may explain why microemulsions are so sensitive to changes in K_0 induced by the presence of cosurfactants or alcohol.

In addition, the intuitively appealing relationship between ξ and the persistence length[5] ξ_K arises naturally in our treatment: Near the middle phase, the scale of ξ is ξ_K. Another important prediction of our model is the sensitivity of the three-phase coexistence to the solubility of the surfactant (or surfactant micelles) in the dilute phases. (We note, however, that these details influence only the phase equilibria; they have *no* influence on the structure of the microemulsion phase itself.) Very asymmetric phase diagrams can result if the solubility in oil and water are very different. In order to get a middle phase not only must ρ_0 be large, but also f_w^* and f_o^* must be approximately equal (and
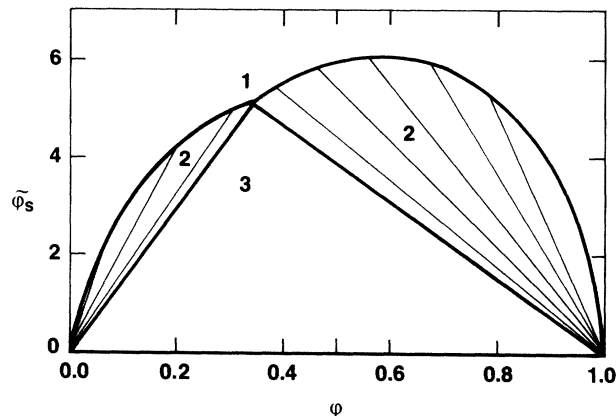

FIG. 2. Phase diagram as in Fig. 1, for $f_w^* = -15T/\xi_K^3$ and $f_o^* = -15T/2\xi_K^3$.

less than or comparable to the energy of the microemulsion phase). This may explain why one generally needs two degrees of freedom (such as salinity and cosurfactant concentration) to obtain a middle-phase microemulsion experimentally.

While these results indicate that middle-phase microemulsions can be understood in simple terms, there are still several unresolved issues. The first of these concerns deviations from the random-mixing approximation in the treatment of the entropy and the bending energy. In addition, the renormalization of the bending energy, Eq. (2), has been computed perturbatively only to first order by Helfrich[10] and by Peliti and Leibler.[11] The fact that this renormalization appears to be responsible for the middle phase and for the small value of ϕ_s in that phase should motivate more detailed calculations of the effective bending constant. Future studies will treat the equilibria with ordered phases[20] (e.g., lamellar, cylindrical[3]) which can compete with the random, bicontinuous, middle phase considered here.[17]

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[16]Both the value of ρ_0 and the interfacial area per cell are renormalized by thermal fluctuations (see Refs. 10 and 11). However, for $\xi \leq \xi_K$, we expect these renormalizations to contribute numerical factors of order unity.

[17]These details, as well as a treatment of the lamellar phase, will be published elsewhere. (The phase equilibria for the case $f_w^* \approx f_o^* \approx 0$ are more complicated and involve the coexistence of several microemulsion phases.)

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