

Phase Diagrams for Microemulsions

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A phenomenological mean-field model of globules for a three-component microemulsion is presented and typical phase diagrams are obtained. Two types of two-phase coexistence are found as well as a three-phase equilibrium. The topology of the phase diagram is determined by the ratio of the critical globule radius to the natural bending radius and by the radius dependence of the attractive interactions.

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Recent experimental interest has focused on the phase-separation critical behavior of oil-water-surfactant mixtures ("microemulsions"). The equilibrium, three-component microemulsion is characterized by a globular or domainlike ($\sim 100 \text{ \AA}$) arrangement of oil and water regions with surfactant molecules, which have hydrophilic polar heads and hydrophobic hydrocarbon tails, at the interfaces.¹ For some low-density systems, neutron scattering indicates that the microemulsion consists of a single phase of monodisperse spherical globules of one component (e.g., water) coated with a surfactant layer, immersed in a sea of the other component (e.g., oil).^{2,3} As either the concentration or the temperature is varied, this single phase of globules separates into two coexisting phases. Light scattering experiments have identified a critical point associated with this phase separation, with correlation-length exponents appropriate to a binary mixture.⁴⁻⁶ In addition, measurements of the second virial coefficient in the single-phase region indicate that those systems possessing a critical point are characterized by large attractive interactions between globules.^{6,7}

Most previous theoretical studies of phase separation in microemulsions have concentrated on the coexistence of the globular phase with a phase of excess fluid (e.g., water, for water globules in an oil-continuous medium).^{8,9} The observation of a critical point for phase separation is inconsistent with this type of two-phase behavior and implies the coexistence of two globular phases with the same continuous component. Ruckenstein and Chi¹⁰ have presented numerical calculations of the free energy for microemulsions, but have neither analyzed the critical point for phase separation, nor presented a general picture of the phase diagram. Jouffroy, Levinson, and de Gennes¹¹ have used a model proposed by Talmon and Prager¹²

to examine phase equilibria. However, they neglect attractive interactions between globules and only generate a single type of two-phase equilibrium, in distinction to the experiments which indicate the existence of two types of two-phase equilibria as well as a three-phase region.^{4-6,13}

This paper analyzes a phenomenological mean-field model for the free energy of a microemulsion in the limit of small globule concentration. It is shown that there exist two types of two-phase equilibria: (i) globules coexisting with an excess phase, (ii) two phases (high and low density) of globules—with a critical point at which both phases become identical. The first type of phase separation is driven by the bending energy of a single globule, while the second is driven by the interactions between globules. The possibility of both types of phase separation gives rise to a three-phase region in the phase diagram.

The free energy (per unit volume) used in these calculations has an intraglobular contribution from the bending energy F_b of the globules, and an interglobular contribution from the entropy of mixing S_m of the globules and the background fluid and from the attractive interaction F_i between the globules.

The bending energy reflects the tendency of the surfactant interface to bend locally towards either the oil or water region through the "natural" bending radius ρ_1 of the globules. The remaining discussion will consider water-in-oil systems, where ρ_1 will be defined to be positive; oil-in-water microemulsions can be treated by reversing the sign of ρ_1 . For a single phase of n identical, spherical globules per unit volume, the bending energy is¹⁴

$$F_b = 16\pi nK(1 - \rho/\rho_1)^2, \quad (1)$$

where ρ is the actual radius of the globule. For $\rho_1^{-1} = 0$, Eq. (1) reduces to the splay energy for a

single layer of a smectic liquid crystal where typically $K \sim 0.1$ eV, although a lower value of K is expected for microemulsions or micelles.¹¹ The radius ρ and the volume fraction x of spheres are related to the volume fractions v_w and v_s of water and surfactant by

$$x = v_w + \frac{1}{2}v_s = \frac{4}{3}\pi n\rho^3, \quad (2)$$

$$\frac{1}{2}v_s = x[1 - (1 - \delta/\rho)^3]. \quad (3)$$

In Eqs. (2) and (3), the volume of surfactant has been divided between the water and oil phases; δ is a typical surfactant length (~ 10 Å). We later use the scaled globule radius $r = \rho/\delta$. Fluctuations in the shape and size of the globules¹⁴ are negligible in the region of the phase diagram that is examined in the following calculations.

The entropy of mixing is calculated from the virial expansion for hard spheres and takes the form¹⁵

$$S_m = -n_0k[x(\ln x - 1) + 4x^2 + 5x^3 + \gamma x^4 + \beta x^5], \quad (4)$$

where n_0^{-1} is the volume of a water globule and where $\gamma \approx 6.12$ and $\beta \approx 7.06$. The attractive interaction between globules is phenomenologically written as

$$F_i = -\frac{1}{2}n_0kTA(\rho, T)x^2, \quad (5)$$

where $A(\rho, T)$ is a dimensionless function of both the radius of the globules and the temperature.¹⁶

The single phase of spherical globules is unstable with respect to phase separation into a two-phase equilibrium of water-in-oil globules and excess water when $\partial F/\partial x = 0$ (at fixed ρ), where the chemical potential of the excess water has been set equal to zero. In the limit that the bending energy is much larger than the temperature¹⁷ or the interaction energy, this phase separation occurs whenever $\rho \gtrsim \rho_1$. The physical origin of this phase separation lies in the bending energy being minimized for $\rho \sim \rho_1$. For small water concentrations, droplets of radii $\rho < \rho_1$ are formed. As water is added, the droplets grow in radius. When ρ reaches ρ_1 , the bending energy can be minimized by constraining all droplets to have this optimum size, and expelling the excess water into a separate phase. This equilibrium has previously been considered.^{8-10, 13}

In addition to this emulsification failure instability, the single phase can separate into two phases of globules with the same continuous component. In the limit that the bending energy is much larger than the temperature or the inter-

actions, it can be shown that the two coexisting phases of spheres have identical radii.¹⁷ This phase separation is thus analogous to that of a binary mixture; the two phases consist of a high and low density of globules. It is to be noted that the radius of the globules enters via the interaction term. Equating the chemical potentials and requiring total volume conservation in the two-phase region yields a critical volume fraction $x_c \approx 0.13$ and a critical interaction strength $A_c \approx 21$. We define the critical globule radius r_c by $A(r = r_c) = A_c$ and $\epsilon(r) = [A_c - A(r)]/A_c$. For $\epsilon > 0$, the single phase is stable, while for $\epsilon < 0$, we obtain two coexisting phases. For $\epsilon \leq 0$, the difference in volume fractions between the two phases is made proportional to $\sqrt{|\epsilon|}$ in our mean-field approximation.

The coexistence curve for x as a function of $\epsilon(r)$ is shown in Fig. 1. The tie lines connecting the two coexisting phases are lines of constant ϵ and hence constant radius. For $\epsilon > 0$, the single phase of interacting spheres is stable with respect to this type of phase separation. However, the ultimate stability of the one-phase region is determined by the phase separation into globules coexisting with an excess phase which is driven by the bending energy for $r > r_1 = \rho_1/\delta$. Since it is assumed that the bending energy is larger than

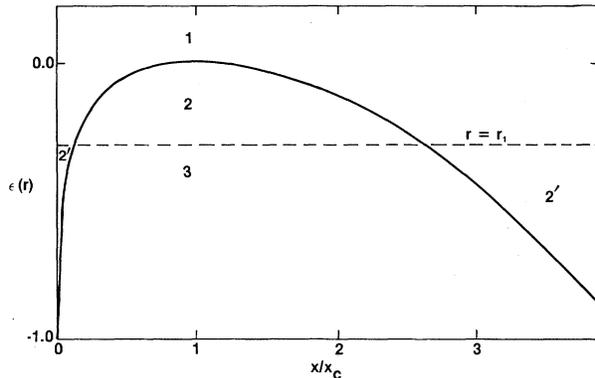


FIG. 1. Scaled coexistence curves as a function of the volume fraction x and $\epsilon = [A_c - A(r)]/A_c$. The case where ϵ decreases with increasing globule radius is shown. The region marked 1 is a single phase of spheres, 2 is a two-phase region with two phases of globules, and 3 denotes a three-phase region. In the three-phase region, excess water coexists with the low-density ("oillike") and high-density ("middle") globular phases located at the intersection between the dashed and solid lines. The phase marked 2' refers to the coexistence of an excess-water phase and a globular phase.

either the temperature or the interactions, the latter phase separation precludes the separation into two phases of globules for $r_1 < r_c$. On the other hand, if $r_1 > r_c$, as shown in Fig. 1, a more complicated phase diagram arises. For radii $r < r_c$, the single phase (1) of spheres is stable, while for $r_c < r < r_1$, two phases of spheres (2) coexist, with values of x given on the coexistence curve. For $r > r_1$, the phase separation into globules and an excess phase dominates and the regions marked 2' denote regions of coexistence of water-in-oil globules and excess water. However, the phase of globules with $r = r_1$ which coexists with the excess water is itself unstable to phase separation into two phases, each with $r = r_1$ but with different volume fractions of spheres. This gives rise to a three-phase region consisting of the two globular phases with values of x on the coexistence curve at $\epsilon(r_1)$, in equilibrium with the excess-water phase.

A more conventional representation of the phase diagram in terms of the water and surfactant volume fractions is shown in Fig. 2. The dependence of the interaction energy on the radius is parametrized¹⁸ by writing $\epsilon = \alpha(r_c - r)$. We first consider the case $r_1 > r_c$ and $\alpha > 0$ which

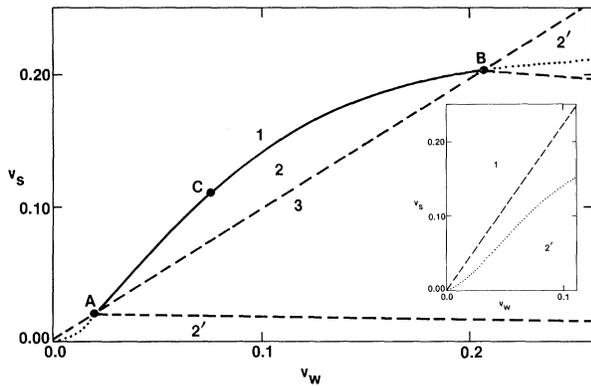


FIG. 2. Phase diagram calculated from Fig. 1 for $r_c = 6$, $\alpha = 0.1$ and $r_1 > r_c$. The notations 1, 2, 2', and 3 are defined in the caption of Fig. 1. The point C is the critical point for the type-ii phase separation. The three-phase region, bounded by the dashed lines, consists of excess water in equilibrium with globular phases whose concentrations are those at points A—the “oillike”—and B—the “middle” phases. The dotted line is the continuation of the coexistence curve into the 2' region, where it is no longer a phase boundary. The region near point A has been exaggerated for clarity. The inset shows the phase diagram for $r_1 < r_c$, for the same values of α and r_c .

implies the accessibility of the critical point and the three-phase region. The labeling of the regions in Fig. 2 follows that of Fig. 1 and the critical point is labeled by C. In Fig. 2, the points labeled A and B are the concentrations of the two globular phases which coexist with the excess-water phase in the three-phase region. Since a very small volume fraction of globules exists at A, it can be termed the “oil” phase which coexists with both the excess-water and the globular phase B, which is termed the “middle phase.”¹⁹ Although phase B has a relatively small volume fraction of globules for the calculation presented here, this is merely a limitation of the simple form assumed for the dependence of ϵ on the radius. The inset to Fig. 2 shows the phase diagram for $r_1 < r_c$, where only the phases 1 and 2' are stable and there is no longer a critical point.

Figure 3 shows the qualitatively different phase diagrams that result for the case $\alpha < 0$. For $r_1 < r_c$ [Fig. 3(a)], a three-phase region exists, but without a critical point. For $r_1 > r_c$ [Fig. 3(b)], we recover the critical point, but there is no three-phase region. Thus, the observation of both a critical point and a three-phase region would imply $\alpha > 0$.

In summary, we have analyzed a phenomenological free energy containing both the bending energy and the interactions between spherical microemulsion globules. In the limit of large bending energies, the model admits an emulsification failure phase separation into a globular and an excess phase as well as a phase separation into two globular phases. A three-phase

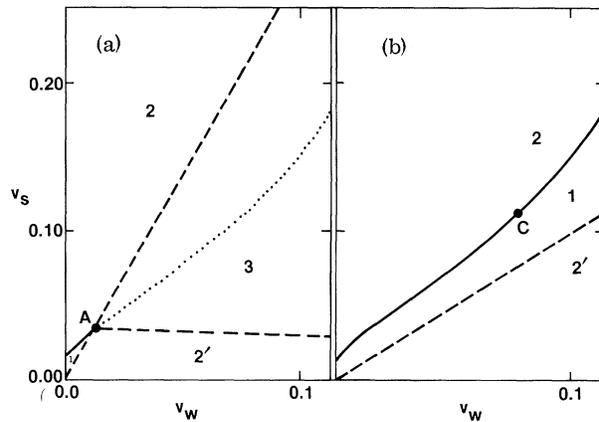


FIG. 3. Phase diagram for $\alpha = -0.1$ for (a) $r_1 < r_c$ and (b) $r_1 > r_c$. The notation is the same as in Figs. 1 and 2.

equilibrium is predicted as well. The topology of the phase diagram is determined by the ratio r_1/r_c and, through the sign of α , by the dependence of the attractive interactions on the globule radius near r_c . We believe the AOT-water-decane system of Refs. 3 and 4 to conform to the phase diagram of Fig. 2.¹⁹ Experimental determinations of the nature of the phases in simple microemulsion systems will further test the qualitative predictions of this model phase diagram. Finally, measurements of the radius dependence of the second virial coefficient will enable a better understanding of the interaction terms.

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¹⁶In a cluster expansion, the second virial coefficient is $A \sim \int d^3r \{\exp[-U(\vec{r})/kT] - 1\}$ where $U(\vec{r})$ is the attractive interaction between globules. Since $U(\vec{r})$ depends, in general, on the globule size ρ (e.g., van der Waals interactions between colloidal particles), A will acquire ρ dependence. For the microscopics of microemulsion interactions, see B. Lemaire, P. Bothorel, and D. Roux, *J. Phys. Chem.* **87**, 1023 (1983).

¹⁷The bending energy of a sphere is $16\pi K \gg kT$. Within this approximation, the entropy and interaction terms provide small corrections to the phase boundaries calculated in this paper.

¹⁸ $\alpha > 0$ ($\alpha < 0$) expresses a decrease (increase) in the free energy F_i with increasing radius. The interaction energy is expected to increase with increasing radius.

¹⁹J. S. Huang, private communication.