

The lamellar-to-isotropic transition in ternary amphiphilic systems

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(received 21 June 1996; accepted in final form 29 August 1996)

PACS. 64.70Ja – Liquid-liquid transitions.

PACS. 64.75+g – Solubility, segregation, and mixing.

PACS. 82.70–y – Disperse systems.

Abstract. – We study the dependence of the phase behavior of ternary amphiphilic systems on composition and temperature. Our analysis is based on a curvature elastic model of the amphiphile film with sufficiently large spontaneous curvature c_0 and saddle-splay modulus $\bar{\kappa}$ sufficiently negative that the stable phases are the lamellar phase and a droplet microemulsion. In addition to the curvature energy, we consider the contributions to the free energy of the long-ranged van der Waals interaction and of the undulation modes. We find that for bending rigidities of order $k_B T$, the lamellar phase extends further and further into the water apex of the phase diagram as the phase inversion temperature is approached, in good agreement with experimental results.

Introduction. – The theory of ternary amphiphilic systems has developed rapidly during the last few years [1], [2]. For long-chain amphiphiles the molecular solubility is very small, so that essentially all amphiphilic molecules are located in monolayers at the interface between oil and water. In this long-chain limit, the description of the system by an ensemble of surfaces is justified and used frequently [3]. The monolayer is described by an ideal surface in this approach, with the shape and fluctuations determined by the curvature energy [4]

$$\mathcal{H}_{\text{curv}} = \int dS [2\kappa(H - c_0)^2 + \bar{\kappa}K] , \quad (1)$$

where H and K are the mean and Gaussian curvatures, respectively, and the integral runs over the total interface area. The parameters are the bending rigidity κ , the saddle-splay modulus $\bar{\kappa}$, and the spontaneous curvature c_0 .

Most of the previous theoretical work on the phase behavior of ternary amphiphilic systems has focused on balanced systems with $c_0 = 0$, and on the interplay between the curvature energy, which favors the lamellar phase, and entropy, which favors disordered bicontinuous or

droplet phases [1], [3]. However, in addition to the curvature energy, long-range interactions between the molecules also give an important contribution to the free energy. This is well known for the unbinding of membranes [5], and for wetting transitions in simple fluids [6]. Attractive interactions have also been used to explain the re-entrant phase separation of spherical and (very long and flexible) cylindrical micelles near the water apex of the composition phase diagram [7]. In systems containing non-ionic amphiphiles, or in systems with screened electrostatic interactions, the dominant contribution is the van der Waals interaction [8], [9].

In this paper, we want to study the dependence of phase diagrams on the spontaneous curvature c_0 . We consider systems with c_0 sufficiently large that the isotropic phase is a droplet microemulsion (in order to avoid complications with the bicontinuous phase). It has been shown experimentally that c_0 varies linearly with temperature T over a wide range of T [10]. Using this relation for $c_0(T)$, we can compare our results directly with the temperature dependence of experimental phase diagrams.

It has been shown [11] that, in the zero-temperature limit, the curvature model—together with the constraints of fixed volume fractions ϕ_s of the amphiphile and ϕ_o of the interior phase—predicts for $-0.5 < \bar{\kappa}/\kappa < 0$ with increasing $c_0 \phi_o/\phi_s$ the progression from a lamellar phase via a phase of infinitely long cylindrical micelles to a phase of spherical micelles, while for $\bar{\kappa}/\kappa < -0.5$ the phase of cylindrical micelles is absent. This model has been extended to include both thermal fluctuations and long-range interactions in ref. [12]. However, with the interactions described phenomenologically, and no explicit temperature dependence, this model yields highly schematic phase diagrams, which cannot be compared easily with experiment.

The model. — We consider the coexistence of a lamellar phase L_α and an oil-in-water microemulsion phase L_1 . We assume that $\bar{\kappa}$ is sufficiently negative that a hexagonal phase of cylindrical micelles is suppressed [11]. The L_α -phase is a stack of oil and water layers of thickness d and l , respectively. All lengths are measured in units of the amphiphile length, so that the repeat distance in the lamellar phase is given by $L = d + l + 2$. The radius of the neutral surface of the oil droplets is denoted by R , so that the radius of the oil core is $R - 1/2$, while the outer radius of the micelle is $R + 1/2$ (for equal lengths of heads and tails). The number density of droplets is ρ .

We write the free-energy density, f , of the lamellar and the droplet phases as a sum of three contributions,

$$f = f_{\text{curv}} + f_{\text{therm}} + f_{\text{vdW}}. \quad (2)$$

The curvature-energy density, f_{curv} , is given by

$$f_{\text{curv}} = \begin{cases} 4\kappa c_0^2/L, & \text{for } L_\alpha, \\ 4\pi\rho(2\kappa(1 - c_0 R)^2 + \bar{\kappa}), & \text{for } L_1. \end{cases} \quad (3)$$

Thermal fluctuations in the lamellar phase lead to a steric (repulsive) interaction, as first proposed by Helfrich [13]. When the size of the amphiphile is used as an ultraviolet cut-off for the wavelengths of the undulation modes, the steric-interaction density of pairs of monolayers, which are separated by a water film of thickness l , is found to be

$$f_{\text{steric,w}}(l) = \frac{k_B T}{8\pi L} \left(q_c^2 \ln[1 + (q_c \xi_{\parallel})^{-4}] + \frac{2}{\xi_{\parallel}^2} \arctan[(q_c \xi_{\parallel})^2] \right), \quad (4)$$

where $q_c = 2\pi$, and $\xi_{\parallel} = (8\kappa\mu/k_B T)^{1/2} l$ is the parallel correlation length. The parameter μ has been determined by Monte Carlo simulations to be $\mu \simeq 0.135$ [14], [15]. Note that eq. (4) reduces to the familiar l^{-2} -form of the steric interaction of *two* monolayers [13] for $q_c \xi_{\parallel} \gg 1$.

It has been pointed out recently that for an *asymmetric* lamellar phase, the steric interaction of two monolayers is a function of *both* the thickness of the oil and of the water films [16]. This is obvious in the case of vanishing oil concentration, where the interacting surfaces are amphiphilic bilayers with an effective bending rigidity $\kappa_{\text{eff}} = 2\kappa$. In ref. [16], Monte Carlo simulations have been used to extract the expression

$$\kappa_{\text{eff}}(l; d)/\kappa = 2 - (d/l)^\nu / [(d/l)^\nu + x_0^\nu] \quad (5)$$

with $\nu = 3/2$ and $x_0 = 0.3$. The steric interaction, $f_{\text{steric,o}}(d)$, of two monolayers through an oil film is obtained from eqs. (4) and (5) by interchanging l and d . Thus, the total entropic part of the free-energy density of the lamellar phase is $f_{\text{therm}}(l, d) = f_{\text{steric,w}}(l) + f_{\text{steric,o}}(d)$.

To calculate the entropy of the droplet phase, we assume that the swollen micelles behave as hard spheres of radius $R + 1/2$. The free-energy density is then very well approximated by the Carnahan-Starling form [17]

$$f_{\text{HS}}(R, \rho) = k_{\text{B}} T \rho \left(\ln \Lambda^3 \rho - 1 + \frac{4 - 3\eta}{(1 - \eta)^2} \eta \right), \quad (6)$$

where $\eta = (4\pi/3)\rho(R + 1/2)^3$ is the packing fraction, and Λ a microscopic length scale, which in the following is taken to be equal to the amphiphile length. Undulation modes on microemulsion droplets give an additional contribution to the free energy, which in the limit $R \ll c_0^{-1}$ has the form [18]

$$f_{\text{drop}}(R, \rho) = \rho \frac{8}{3} k_{\text{B}} T \ln(R^2). \quad (7)$$

Such a term becomes important for large droplet radii, and disfavors the droplet microemulsion in this regime. The entropic part of the free-energy density of droplets then reads $f_{\text{therm}}(R, \rho) = f_{\text{HS}}(R, \rho) + f_{\text{drop}}(R, \rho)$.

Finally, we have to calculate the contribution of the van der Waals interaction to the free energy. This is done within the Hamaker approach, where a pairwise form of the interaction is assumed [8], [9]. The dielectric properties of the amphiphile tails (heads) are assumed to be identical to those of the oil (water) molecules. We subtract the free energy of the pure-water phase, so that only the interaction between oil molecules (and amphiphile tails) has to be taken into account. For a molecular fluid, the interaction free-energy density is given by [17]

$$f_{\text{vdW}} = \frac{1}{V} \int_V d^3 r_1 \int_V d^3 r_2 w(|\mathbf{r}_1 - \mathbf{r}_2|) g(|\mathbf{r}_1 - \mathbf{r}_2|), \quad (8)$$

where $w(r)$ is the interaction potential, which consists of a long-ranged attractive and a short-ranged repulsive part, and $g(r)$ is the normalized density-density correlation function, which approaches unity for large distances and vanishes for short ones. We approximate the product of these two functions by

$$w(r)g(r) = \phi(r) \equiv \frac{A}{\pi^2} \left[\frac{\epsilon^2}{(r^2 + \epsilon^2)^4} - \frac{1}{(r^2 + \epsilon^2)^3} \right], \quad (9)$$

where A is the Hamaker constant. The parameter ϵ in eq. (9) determines at which length scale (in units of the amphiphile length) the repulsion becomes dominant.

The calculation of the free-energy density, f_{intra} , of the van der Waals interaction of the oil molecules within one aggregate is straightforward in both the droplet and lamellar phases (compare ref. [8]). This also holds for the inter-aggregate part of the free-energy density, f_{inter} ,

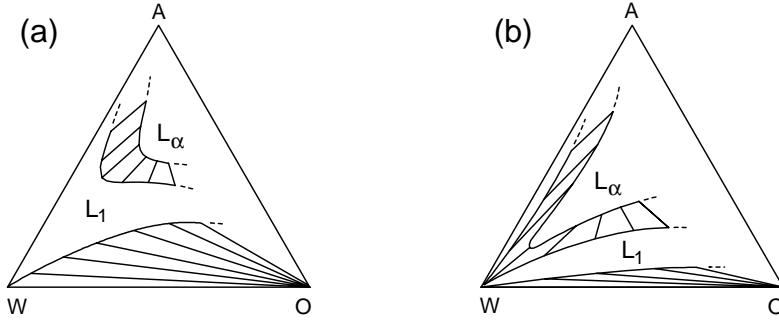


Fig. 1. – Ternary composition phase diagrams for low bending rigidity and a) $T = 293$ K and b) $T = 310$ K. The parameters of the model are $\kappa/k_B T_1 = 1.0$, $\bar{\kappa}/\kappa = -0.5$, $c_0(T_1) = 1/6$, $\epsilon = 0.7$, $T_1 = 293$ K and $T_2 = 321$ K. Each Gibbs triangle contains two coexistence regions: for higher amphiphile concentrations the lamellar phase L_α coexists with the droplet phase L_1 , for lower amphiphile concentration the droplet phase coexists with an excess oil phase (emulsification failure).

in the lamellar phase. In the (disordered) droplet phase, the inter-aggregate part is taken to be

$$f_{\text{inter,drop}} = \frac{\rho^2}{2} \int_{r>2R+1} d^3r W_R(r), \quad (10)$$

where $W_R(r)$ is the interaction energy of two spheres of radius R with distance r between their centers. To obtain eq. (10), we have replaced the two-particle distribution function for hard spheres of radius $R + 1/2$ by a step function [19]. It is important to note that with the choice (9) for the interaction potential, all interaction integrals can be carried out analytically. However, the results are rather lengthy and cannot therefore be given here.

Phase diagrams. – In order to calculate phase diagrams, we add chemical-potential terms to the free energy, and minimize with respect to l and d , or R and ρ , respectively. Since the functional form of $\kappa_{\text{eff}}(l; d)$ was determined self-consistently in ref. [16], we have to use the same procedure here. The free energies in our model depend on the parameters κ , $\bar{\kappa}$, c_0 , and A . The value of the Hamaker constant is well known experimentally to be $A = (0.28 \text{ T}/300 \text{ K} + 0.17)10^{-20}$ J for the interaction of hydrocarbon across water [9]. For $T = 300$ K one therefore has $A \simeq 1k_B T$. For the spontaneous curvature, we assume a linear temperature dependence of the form $c_0(T) = c_0(T_1)(T_2 - T)/(T_2 - T_1)$, where T_2 denotes the phase-inversion temperature.

A typical sequence of phase diagrams with decreasing spontaneous curvature c_0 is shown in fig. 1 for bending rigidities of the order of $1k_B T$. The parameters are chosen such as to allow a comparison with the experimentally well-studied oil-water- C_{12}E_5 system. In addition to the two-phase coexistence region of lamellar and droplet phase, we also show the two-phase coexistence of the droplet microemulsion with a pure oil-phase (emulsification failure). We can follow the two-phase coexistence curves in the L_1 -phase only to a minimum water concentration of about 30%, where the oil-filled micelles become close-packed. The most prominent feature of the phase diagrams shown in fig. 1 is that, with decreasing spontaneous curvature, the lamellar phase extends further and further into the water apex of the Gibbs triangle. This behavior is in excellent agreement with experimental observations [20], [21].

Phase diagrams for larger bending rigidities are shown in fig. 2. For $\kappa/k_B T \simeq 3$, the re-entrant behavior of the droplet phase disappears, and the lamellar phase is found to be always stable for small oil content. Finally, for $\kappa/k_B T \simeq 10$, the lamellar phase (with low oil

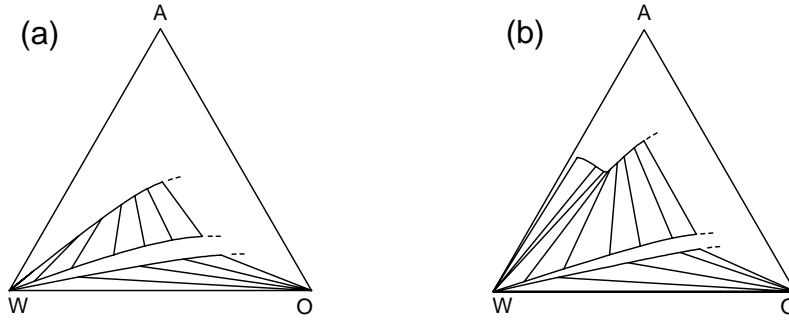


Fig. 2. – Ternary composition phase diagrams for *a*) intermediate and *b*) high bending rigidity. The parameters are $c_0^{-1} = 15.3$, $\bar{\kappa}/\kappa = -0.5$, $\epsilon = 0.7$, and $\kappa/k_B T = 2.8$ and $\kappa/k_B T = 9.5$, respectively.

content) can no longer be swollen to large intermembrane separations, but coexists with an almost pure-water phase.

Discussion. – The extension of the lamellar phase into the water apex of the Gibbs phase triangle for $\kappa/k_B T \simeq 1$ can be understood as follows. Consider a path in the Gibbs triangle of fig. 1 *b*) of constant amphiphile concentration, for which the system is in the droplet phase for equal oil and water concentrations. With decreasing oil content, the droplet size decreases, so that the bending energy cost for droplets increases, and ultimately leads to a transition into the lamellar phase. This is the effect considered in ref. [11]. With further decreasing oil content, the steric interaction of the monolayers across the oil films increases, and leads to a (re-entrant) transition to the droplet phase.

When the bending rigidity is increased to $\kappa/k_B T \simeq 3$, the lamellar phase can be swollen by a very large amount by adding water. Thus, the repulsive interaction dominates in the lamellar phase for $\kappa/k_B T \lesssim 3$. Only when the bending rigidity is increased to $\kappa/k_B T > 3$ does the attractive interaction begin to affect the phase behavior, and unbinding transitions [5] can be observed (compare ref. [22] for a discussion of unbinding transitions in the binary water-amphiphile system). The first-order character of the phase transitions for $\kappa/k_B T \lesssim 3$ discussed above should therefore hold beyond the superposition approach (2).

It is also interesting to note that the van der Waals interaction is *not* strong enough to produce a two-phase coexistence between two droplet microemulsion, in agreement with recent calculations for colloidal systems [19]. This result may change when the deformability of the oil droplets is taken into account, which allows a larger contact area of two adhering droplets and thereby increases the interaction energy [23].

Our work can be extended in several directions; it would be interesting, for example, to investigate the stability of the hexagonal phase of cylindrical micelles. A more detailed comparison with experiment requires the systematic measurement of ternary phase diagrams with larger bending rigidities.

We thank J. GOOS, H. LÖWEN and R. STREY for stimulating discussions.

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