Temperature-dependent phase transitions in water-oil-surfactant mixtures: Experiment and theory

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We investigate temperature induced phase transitions in mixtures of water, oil, and a nonionic surfactant. By microcalorimetric measurements it is shown that the droplet-lamellar transition shows hysteresis so that it is strongly first order. The position of this transition and of the emulsification boundary are quantitatively described by an interfacial model which considers solely the temperature dependence of the spontaneous curvature. There is no fit parameter in the model. Remarkably, the positions of both boundaries do not depend on the bending moduli. [S1063-651X(96)01208-1]

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Mixtures of water, oil, and surfactant exhibit a variety of thermodynamically stable phases [1–3]. This structural diversity is related to a large number of possibilities to divide space into water and oil regions, where the domains are separated by a monolayer of surfactant molecules. Within a large composition and temperature range oil droplets in water (L_1), water droplets in oil (L_2), and lamellar structures (L_α) are formed [4–7]. Any of these phases can be in equilibrium with an oil- (2ϕ) or a water-rich ($\overline{2\phi}$) phase. The phase formed has to minimize the free energy, which depends on composition and on properties of the interface, i.e., on the interaction of the surfactant molecules with oil and water. These interactions are modeled by a spontaneous curvature c_0 and the bending moduli $\kappa, \overline{\kappa}$ of the interface [8–12], leading to the commonly discussed bending free energy density

$$f^b = \frac{\kappa}{2}[c_1 + c_2 - 2c_0(T)]^2 + \overline{\kappa}c_1 c_2, \qquad (1)$$

where $(c_1 + c_2)/2$ is the mean, and $c_1 c_2$ the Gaussian curvature of the interface.

There are indications in the literature [8,10,13] that some temperature induced phase transitions can be described by considering the temperature dependence of c_0. However this idea has not been worked out, in particular, because the temperature dependence of c_0 has only been determined recently [14]. In the present paper we argue that the temperature dependence of c_0 is sufficient to explain significant parts of the phase behavior. This will be demonstrated for the model system $H_2O - n\text{-octane} - C_{12}E_5$ (n-dodecyl pentaneethylenglycole ether). For this system all parameters in the free energy density (1) have been determined experimentally [14–16] so that the corresponding phase behavior can be calculated without fitting any parameters. Furthermore, the interaction of the surfactant with oil and water, respectively, is compa-

rable, leading to a nearly symmetric phase diagram for equal volume fractions of oil and water.

Microcalorimetry. The specific heat of the solutions is measured with a differential scanning microcalorimeter (Setaram Micro-DSC II). Thermograms are obtained at a scan speed of 7 K/h. A heating curve is shown in Fig. 1 (solid line) for a mixture of $H_2O/n\text{-octane}/C_{12}E_5$ of equal volume fraction of water and oil $\phi_w = \phi_{oil} = 0.41$, and a volume fraction of surfactant $\phi_s = 0.18$. There are two nearly 2 K broad peaks. The width and the height of the peaks are comparable, whereas the shape of the peaks differs slightly. From the phase diagram Fig. 3(b) one verifies that the first peak belongs to the transition $L_1 \rightarrow L_\alpha$, and the second one to the transition $L_\alpha \rightarrow L_2$. For scan speeds up to about 30 deg/h the width and the height of the peaks do not change. The width constitutes a measure of the extent of the coexistence range of a lamellar and a microemulsion phase [1] (not indicated in the phase diagram), and the area a measure of the latent heat connected to the transition. A slight increase of the temperature within the temperature interval of coex-
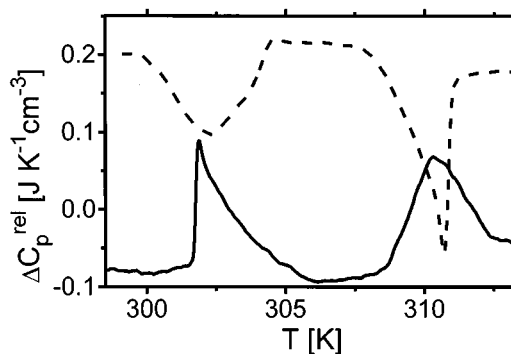

FIG. 1. Temperature dependent variation of the specific heat $\Delta C(T)$ for $\phi_s = 0.18$ and $\phi_{oil} = \phi_w = 0.41$. A thermogram of a heating curve is given by the solid line and the dashed line shows a cooling curve on the same solution. After heating the solution was tempered for 1 hour at 313 K. It was not stirred between the measurements. To prevent phase separation the presented thermograms are aborted before entering the two-phase regions.

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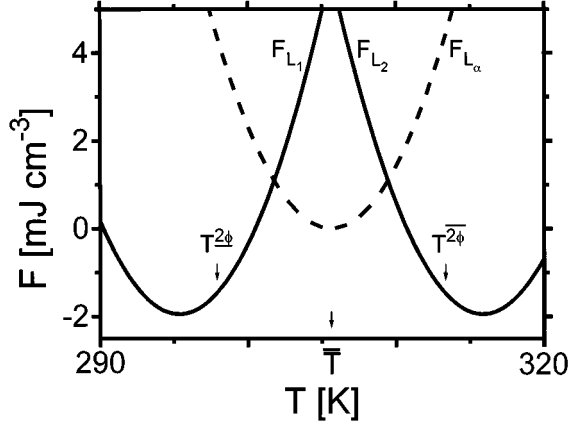
FIG. 2. Bending free energies for a microemulsion phase of oil droplets in water $F_{L_1}^b$, water droplets in oil $F_{L_2}^b$, and a lamellar phase $F_{L_\alpha}^b$ as function of temperature. The emulsification boundaries $T^{2\phi}$ and $T^{\overline{2\phi}}$ are marked by arrows. Sample composition is given by: $\phi_s = 0.18$ and $\phi_{oil} = \phi_w = 0.41$.

istence leads to changes of the relative amount of micro-emulsion and lamellar phase. Since these changes occur continuously the related heat changes remain finite, even though the transitions $L_1 \rightarrow L_\alpha$ and $L_\alpha \rightarrow L_2$ are first order phase transitions because the transition show hysteresis. This can be seen (Fig. 1) from heating curves (solid line) and cooling curves (dashed line) recorded on the same sample. Also in the down scan two peaks of comparable width are visible. The peak positions are close to those of the corresponding heating curve, but the onset of the peaks is shifted towards lower temperatures than the end of the corresponding peak in the heating curve. The peaks in the up as well as in the down scans all have about the same size. The areas under the peak $\Delta Q \equiv \int \Delta C(T) dT$ correspond to the latent heat of the phase transition $L_1 \rightarrow L_\alpha$ and $L_\alpha \rightarrow L_2$, respectively. Within the error margins (cf. Table I) its values coincide for all transitions.

Theory. In the following we check how far these findings for the latent heat can be understood from the free energy (1). We assume that the surfactant molecules are constrained to the water-oil interface and are divided equally between the oil and water domains. In our approach the symmetry of the phase diagram at equal volume fraction of water and oil follows immediately from the bending free energy (1). We start our considerations by reviewing the parameters in f^b. All of them have previously been determined experimentally. Based on measurements for shorter chain homologues [17] one expects κ values of the order of or somewhat smaller than $k_B T$. In [16] it is argued on the basis of calorimetric measurements that $\bar{\kappa} \approx -\kappa/2 = -0.4 k_B \overline{T}$. In Ref. [14] it has been pointed out that to first order the spontaneous curvature depends linearly on $\overline{T} - T$

$$c_0(T) = a(\overline{T} - T)\left(1 + \frac{\bar{\kappa}}{2\kappa}\right), \qquad (2)$$

where $a = 1.2 \times 10^5 \ \text{K}^{-1} \ \text{cm}^{-1}$. The linear dependence of c_0 on T is compatible with the symmetry of the free energy; $\overline{T}$ corresponds to the symmetry line in the symmetric phase

TABLE I. Latent heat. Values for the latent heat ΔQ determined from the calorimetric measurements. The values of the first column yield the heat changes accompanying the transition $L_1 \rightarrow L_\alpha$ and $L_\alpha \rightarrow L_2$ and those of the second row to the transitions $L_\alpha \rightarrow L_1$ and $L_2 \rightarrow L_\alpha$. The errors are due to uncertainties in determining a baseline. Sample composition is given by: $\phi_s = 0.18$ and $\phi_{oil} = \phi_w = 0.41$.

ΔQ	Increasing T	Decreasing T
$L_1 \rightarrow L_\alpha$	0.23 ± 0.03 J/cm	-0.22 ± 0.05 J/cm
$L_\alpha \rightarrow L_2$	0.24 ± 0.04 J/cm	-0.28 ± 0.05 J/cm

diagram and takes the value 305.6 K for the present system [Fig. 3(b)]. Since $c_0(T)$ is an asymmetric function in $\overline{T} - T$, the free energy is invariant under changing the temperature $T \rightarrow 2\overline{T} - T$ and exchanging simultaneously oil and water. On account of the sign of the spontaneous curvature the radius of the droplets is positive for oil droplets in water $R_{oil} \approx 3 l_s(\phi_{oil} + \phi_s/2)/\phi_s$, and negative for water droplets in oil $R_w \approx -3 l_s(\phi_w + \phi_s/2)/\phi_s$, where l_s is the length of the surfactant molecules which is taken to be $(1.3 \pm 0.2) 10^{-7}$ cm according to Ref. [15].

Having fixed all free parameters in (1), we now calculate the elastic free energies for droplet phase microemulsion and for a lamellar phase as a function of temperature. Evaluating the bending energy (1) for a microemulsion phase of monodisperse oil ($F_{L_1}^b$) or water droplets ($F_{L_2}^b$), and for a lamellar phase without any undulations ($F_{L_\alpha}^b$) one finds for the free energy per unit volume

$$F_{L_1}^b(T) = 2\frac{\kappa \phi_s}{l_s R_{oil}^2}\left\{[1 - R_{oil} c_0(T)]^2 + \frac{\bar{\kappa}}{2\kappa}\right\}, \qquad (3a)$$

$$F_{L_2}^b(T) = 2\frac{\kappa \phi_s}{l_s R_w^2}\left\{[1 - R_w c_0(T)]^2 + \frac{\bar{\kappa}}{2\kappa}\right\}, \qquad (3b)$$

$$F_{L_\alpha}^b(T) = \frac{2\kappa \phi_s}{l_s} c_0(T)^2. \qquad (3c)$$

In Fig. 2, $F_{L_1}^b(T)$, $F_{L_\alpha}^b(T)$, and $F_{L_2}^b(T)$ are plotted for $\phi_{oil} = \phi_w = 0.41$ and $\phi_s = 0.18$. $F_{L_\alpha}^b(T)$ (dotted line) is a parabolic positive definite function that is symmetric with respect to $T = \overline{T}$. The free energies for droplet phase microemulsions, $F_{L_1}^b(T)$ and $F_{L_2}^b(T)$ are also parabolic functions. For $\phi_{oil} = \phi_w$ they are mirror images with respect to $\overline{T}$ due to the symmetry of the free energy.

The values for the latent heat of the transitions are given by the difference of the slope of the free energy at the transition temperature [18]

$$T\Delta S_{L_i \rightarrow L_j} \approx -T\left(\frac{\partial F_j^b}{\partial T} - \frac{\partial F_i^b}{\partial T}\right) = \frac{-2\kappa T}{3 l_s^2}\phi_s^2\frac{\partial c_0(T)}{\partial T}, \quad (4)$$

where the label i and j correspond to the phase before (i) and after (j) the transition. This leads to

$$\Delta Q \approx T\Delta S_{L_1 \rightarrow L_\alpha} = T\Delta S_{L_\alpha \rightarrow L_2} \approx 0.24 \ \text{J/cm}^3, \qquad (5)$$
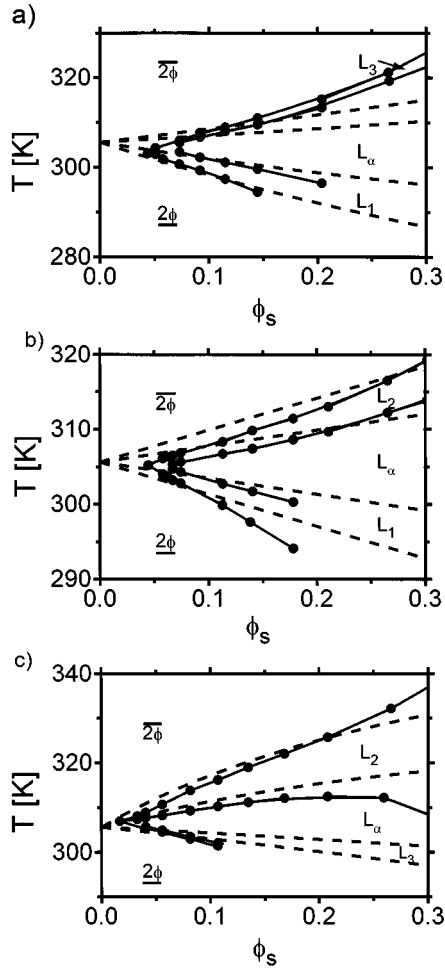
a)

b)

c)

FIG. 3. Calculated temperature-dependent phase diagrams (dashed line) as function of surfactant concentration and three choices for the oil to oil-plus-water volume fraction α_v (a) $\alpha_v = 0.26$; (b) $\alpha_v = 0.5$; (c) $\alpha_v = 0.85$. The circles show phase transition temperatures that are determined by visual inspection.

in close agreement with the experimentally determined values (Table I).

Assuming that the width of the two phase coexistence region of a lamellar and a microemulsion phase is small the intersection of $F_{L_1}^b$ with $F_{L_\alpha}^b$ and $F_{L_\alpha}^b$ with $F_{L_2}^b$, respectively, yield the phase transition temperatures. Inserting (2) in (3) and solving the equalities $F_{L_1}^b = F_{L_\alpha}^b$ and $F_{L_\alpha}^b = F_{L_1}^b$ for T leads to the following expressions for the temperature-dependent phase boundaries:

$$T_{L_1 \to L_\alpha} = \overline{T} - \frac{1}{2a|R_{\text{oil}}|}, \qquad (6a)$$

$$T_{L_\alpha \to L_1} = \overline{T} + \frac{1}{2a|R_{\text{w}}|}. \qquad (6b)$$

Analogously, one can calculate the emulsification boundaries. According to Safran, Turkevich, and Pincus [8] the excess phase is formed when the radius of the droplets R exceeds its optimal radius R^{opt}, i.e., when $|R| \geqslant |R^{\text{opt}}|$

$= (1 + \overline{\kappa}/2\kappa)/|c_0(T)|$. The optimum radius $R^{\text{opt}}(T)$ is specified by $\partial F_{L_1,L_2}/\partial R = 0$. Solving this inequality for T yields the emulsification boundaries

$$T^{\underline{2\phi}} = \overline{T} - \frac{1}{a|R_{\text{oil}}|}, \qquad (7a)$$

$$T^{\overline{2\phi}} = \overline{T} + \frac{1}{a|R_{\text{w}}|}. \qquad (7b)$$

As shown in Fig. 2 they do not coincide with the minima of the free energies of the droplet phases, but lie closer towards $\overline{T}$.

Equations (6) and (7) are our central result. They describe the temperature dependence of the boundaries between lamellar and droplet phases, and the emulsification boundary, respectively. In the remaining part of the paper we compare them to measured phase diagrams. Before, however, we want to stress a remarkable property of the equations: the positions of the phase boundaries do not depend on the bending moduli κ and $\overline{\kappa}$. Except, for R_{w} or R_{oil} only characteristics of the spontaneous curvature (2), namely, the parameters a and $\overline{T}$ enter the expressions. It is also intriguing that Eqs. (6) and (7) only differ by a factor $1/2$ in the second term. This is a consequence of $F_{L_i} - F_{L_\alpha} = \phi_s/l_s(2\kappa + \overline{\kappa})c(c - 2c_{\text{opt}})$, where $i = 1,2$, and $c = 1/R$ is the curvature of the droplets in the microemulsion phase: the change from lamellar structures to droplets occurs at $R = R^{\text{opt}}/2$, while $R = R^{\text{opt}}$ corresponds to the emulsification boundary.

Phase Diagrams: Figure 3 shows calculated (dashed lines) and experimentally determined (circles) phase diagrams for three oil to oil-plus-water volume ratios $\alpha_v = \text{oil}/\text{oil} + H_2O$ as a function of surfactant concentration and temperature. For $\alpha_v = 0.5$ [Fig. 3(b)] we observe the previously mentioned symmetry in the phase diagram, and for all ϕ_s we find the phase sequence under increasing temperature. Even though there is no fit parameter in our result for the phase boundaries, the values for the phase transition temperatures are close to experimentally determined ones. Also the broadening of the single phase channels upon increasing ϕ_s is accounted for. Only, the formation of a three phase region is not explained in this approach.

Figures 3(a) and 3(c) show calculated phase boundaries for $\alpha_v = 0.26$ [Fig. 3(a)] and $\alpha_v = 0.85$ [Fig. 3(c)], respectively. Again, large regions of the phase diagram are predicted correctly. There is quantitative agreement when $c_0(T)$ is directed towards the minor component, while it is slightly worse when $c_0(T)$ is directed towards the major component. Still, the correspondence between theoretical and experimental values in the latter case is remarkable because it is known that the underlying microstructure does not conform to a droplet structure but to an L_3 ("sponge") phase [10,19]. This suggests that it is not expensive for the free energy to form "necks" connecting droplets, and that the spontaneous curvature need to be considered in the free energy of an L_3 or other bicontinuous phases, too. In fact, the former statement can be substantiated by observing that the

free energies for droplet and cylindrical structures do not differ significantly in the parameter range where single phase bicontinuous structures are expected to occur.

In conclusion, we point out that by only considering bending contributions to the free energy of monodisperse spheres and flat lamellar structures we achieve a parameter free description of significant parts of the temperature dependent phase behavior of three component water-oil-surfactant mixtures. All free parameters in our model are known from previous experiments. The credibility of the model has been substantiated by microcalorimetric measurements which show that also the latent heat of the transitions is described by the model, and which point out that the transitions are strongly first order by showing that there is hysteresis. All theoretical predictions quantitatively match experimental findings. Remarkably, the results for the investigated phase boundaries do not even depend on the bending moduli, but only on geometrical parameters of the involved phases (droplet radii) and characteristics of the spontaneous curvature.

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