

Study of Interfacial Curvature in a Three-Component Microemulsion with Equal Volumes of Water and Oil

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We have used a double-contrast-variation method in small-angle neutron scattering to study the structure of a single-phase microemulsion containing equal amounts of oil (decane) and water stabilized with an aerosol OT surfactant. It is determined that the water-internal-droplet structure persists in this concentrated regime. We believe that this is the first observation of a nonvanishing mean curvature of the interfacial surfactant film in microemulsions with an oil-water ratio of unity.

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Microemulsions¹ are thermodynamically stable multicomponent liquids consisting of two mutually immiscible phases such as oil and water and a solubilizing agent called a surfactant (soap). In order to solubilize appreciable amounts of one of the major components in the other, a cosurfactant (generally a short- to medium-chain alcohol) is required. Depending on the system, it is common to find the surfactant-to-cosurfactant molar ratio to exceed 10:1. In the simplest case, where one of the two bulk phases constitutes a minor component, say a few volume percent, and where only a few percent of surfactant is required to form a clear stable liquid, the structure is generally shown¹ to consist of a droplet phase of the minor component coated with the surfactant molecules, dispersed in a continuum of the major component.

On the other hand, the structure of a microemulsion containing equal amounts of oil and water solubilized by surfactant is generally thought to be bicontinuous.²⁻⁶ Auvray *et al.* demonstrated recently⁷ that in a microemulsion containing sodium dodecylsulfate, 1-butanol, brine, and toluene, the mean curvature for the interfacial film is zero when the brine-to-toluene ratio is 1. However, in a simpler three-component microemulsion when the cosurfactant (alcohol) is absent the surfactant molecular packing geometry plays a dominant role in the determination of the interfacial curvature. It is likely that the droplet structure may persist in the middle phase region where the volumes of oil and water are equal. For instance, in the system containing aerosol OT (sodium di-2-ethyl-hexyl sulfosuccinate), D₂O, and decane, the spectra of small-angle neutron scattering can be analyzed in terms of D₂O droplets in oil.^{8,9} In this work we shall demonstrate conclusively that for aerosol OT (AOT) microemulsions containing equal oil and water, the surfactant film has a thickness of 5 Å, consistent with a mean radius of curvature of 76 Å, enclosing the water as the interior phase of a dropletlike structure.

This is done by employment of a contrast-variation scheme first employed by Auvray *et al.*⁷ In the present experiment, we have varied the neutron scattering-length density of both the internal and external phases.

One can learn something of the properties of the surfactant film by performing a small-angle neutron scattering (SANS) contrast-variation experiment. To understand qualitatively such an experiment, consider a system of monodisperse, spherical, surfactant-coated water-in-oil or oil-in-water droplets. By varying the scattering-length density of either the oil or water component, one can search for the scattering-length density of that component for which the $Q=0$ scattering vanishes, i.e., $I(0)=0$. At that contrast, the average scattering-length density of the internal phase of a sphere and the surfactant film must be equal to the scattering-length density of the external phase, i.e.,

$$R^3\rho_I + [(R+d)^3 - R^3]\rho_f = (R+d)^3\rho_E, \quad (1)$$

where ρ_I , ρ_E , and ρ_f are the scattering-length densities of the internal phase, the external phase, and the surfactant film, respectively. R is the radius of the internal phase and d is the thickness of the interfacial film. This results in the following relation to first order in d/R :

$$(\rho_I - \rho_E)/(\rho_E - \rho_f) \approx 3d/R. \quad (2)$$

Suppose water is the internal phase and the contrast of the water is the only varied quantity. Then, the scattering-length density of the water ρ_w^m at which the $Q=0$ scattering intensity is minimized, i.e., when $I(0)=0$, must satisfy the relation,

$$(\rho_w^m - \rho_o)/(\rho_o - \rho_f) \approx 3d/R. \quad (3)$$

$\rho_o - \rho_f$ can be chosen to be a fixed positive quantity, so $\rho_w^m > \rho_o$. If a contrast variation is performed with the oil component on the same system, then $\rho_o^m < \rho_w$. In an

analogous fashion, it can easily be demonstrated that the inequalities above are reversed if oil is the internal phase. Thus the sign of the left-hand side of Eq. (3) yields the important information on the average direction of the interfacial curvature.

If one relaxes the conditions that the particles be monodisperse and spherical and allows for interactions in the system, then the optimal contrast, ρ_w^m or ρ_o^m , does not in general correspond to $I(0)=0$, but only results in $I(0)$ being minimized. In addition, Eq. (3) only acts as a crude approximation. An exact formulation of the problem has been worked out by Auvray *et al.*⁷ They show that the quantity $3d/R$ in Eqs. (2) and (3) must be replaced with $X_{wf}(0)/X_{ww}(0)$, where $X_{wf}(0)$ is a measure of the cross correlation between the water and film volume-fraction fluctuations and $X_{ww}(0)$ measures the water-water correlation function. These correlation functions were defined in terms of the fluctuations of the volume fractions $\phi_a(r)$ of the a th component:

$$X_{\alpha\beta}(Q) = \int d^3r e^{iQ \cdot r} (\delta\phi_\alpha(0)\delta\phi_\beta(r)). \quad (4)$$

The scattering intensity $I(Q)$ is just

$$I(Q) = \sum_{\alpha,\beta} \rho_\alpha \rho_\beta X_{\alpha\beta}(Q), \quad (5)$$

where ρ_a is the scattering-length density of the a th component. In an incompressible three-component system with $a=w$ (water), o (oil), and f (film), one has the additional constraint

$$\delta\phi_f(r) = -\delta\phi_o(r) - \delta\phi_w(r). \quad (6)$$

One can rewrite Eq. (6) as the following:

$$I(Q) = (\rho_w - \rho_o)^2 X_{ww}(Q) + (\rho_f - \rho_o)^2 X_{ff}(Q) + 2(\rho_w - \rho_o)(\rho_f - \rho_o) X_{wf}(Q). \quad (7)$$

When either ρ_o or ρ_w is varied, the minimum intensity can be obtained by a quadratic fit to obtain ρ_o^m or ρ_w^m . A nonzero value for the left-hand side of Eq. (3) will yield the direction (sign) of the curvature and the ratio d/R .

Two series of contrast-variation measurements were performed on an AOT-water-decane microemulsion with $\phi_o = \phi_w$ and surfactant volume fraction $\phi_s = 0.23$. The first series was a water-contrast-variation experiment, where the oil component was a 50-50 mixture of $C_{10}H_{22}$ and $C_{10}D_{22}$. The deuteration of the water component was varied from 37.5% to 100%. In the second series, an oil-contrast-variation was performed, where the water component was a 50-50 mixture of H_2O and D_2O . The deuteration of the oil was varied from 0% to 62.5%.

The SANS experiments were performed at the H-9 small-angle spectrometer at the high flux beam reactor at the Brookhaven National Laboratory. The wavelength was $\lambda = 6.33 \text{ \AA}$ giving a usable Q range of $0.008 \leq 0.172 \text{ \AA}^{-1}$. Here $Q = (4\pi/\lambda)\sin\theta/2$ is the scattering wave vector determined by the scattering angle θ and the wavelength λ .

Figure 1 shows representative SANS spectra for the water-contrast-variation series. The zero-angle intensity is most readily obtained by replotting of the low- Q data as a function of Q^2 and by extrapolation to zero. In Fig. 2 the relative zero-angle intensities of both the water- and oil-contrast series are plotted as functions of the scattering-length density of the varied component. For the case of the water-contrast-variation series [curve a in Fig. 2(a)], one sees that $\rho_w^m > \rho_o$, and for the oil-contrast-variation series [curve b in Fig. 2(b)] $\rho_o^m < \rho_w$. These results indicate that the interfacial film curves toward the water component.

Furthermore, we can estimate the thickness of the surfactant film by using Eq. (3) and the data shown in Fig. 2. A parabolic fit to the data (shown by the solid curve) yields $\rho_w^m = 3.42 \times 10^{-6} \text{ \AA}^{-2}$ for Fig. 2(a) and $\rho_o^m = 2.28 \times 10^{-6} \text{ \AA}^{-2}$ for Fig. 2(b). The core radius R_c was estimated⁸ to be 76.2 \AA . (This value is consistent with the core size of the water droplets in a dilute system with the same AOT-to-water ratio.) Equation (3) then gives $d = 4.6 \text{ \AA}$ for the parameter given by Fig. 2(a) and $d = 5.2 \text{ \AA}$ for Fig. 2(b). In a previous work¹⁰ we have shown that for a dilute AOT micellar solution, the length of a fully stretched hydrocarbon tail of the surfactant in a spherical aggregate is found to be 8 \AA . Thus the aver-

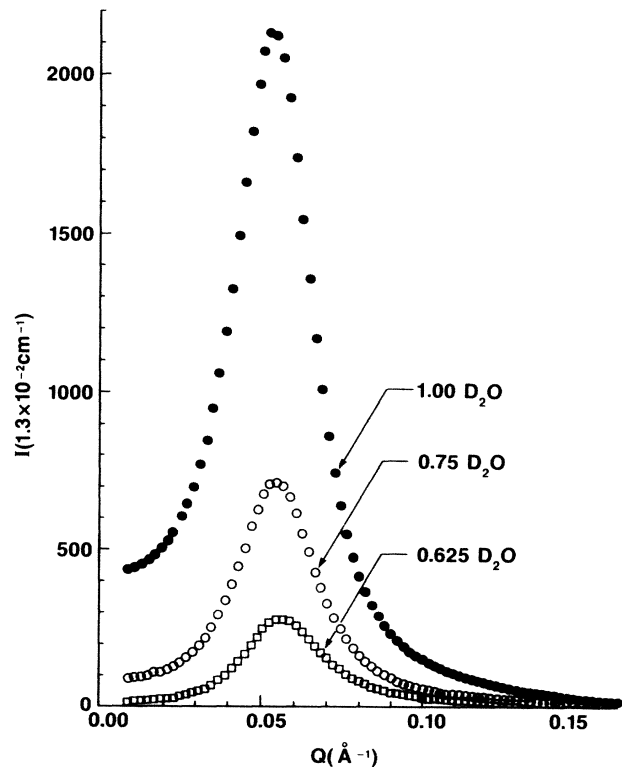


FIG. 1. $I(Q)$ vs Q is plotted for three representative samples containing 23.7% surfactant and equal amounts of oil and water. The water phase contains different D_2O/H_2O ratios: closed circles, $D_2O/H_2O = 1.00$; open circles, $D_2O/H_2O = 0.75$; squares, $D_2O/H_2O = 0.625$.

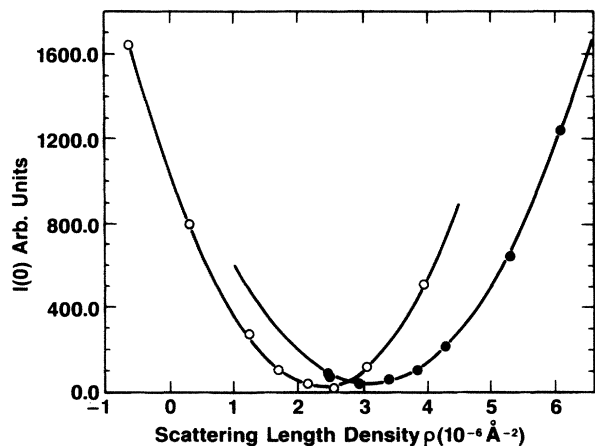


FIG. 2. Extrapolated $I(0)$ vs the scattering-length density of the variable phase. Closed circles represent systems with constant $\rho_o = 2.65 \times 10^{-6} \text{ \AA}^{-2}$ and a variable ρ_w . Open circles represent systems with constant $\rho_w = 2.72 \times 10^{-6} \text{ \AA}^{-2}$ and a variable ρ_o .

age length of 5 Å for the film thickness defined by the portion of the surfactant which is sandwiched between the external deuterated oil phase and the internal deuterated water phase seems to be quite reasonable. The densely packed water droplets in the present case (the dispersed phase volume fraction $\phi = 0.60$) may also cause the interfacial film thickness to be less than that of the fully stretched surfactant molecule as a result of the crowding of the neighboring droplets.

We believe that in this model three-component microemulsion for which alcohol or another form of cosurfactant is absent, the packing of a cone-shape surfactant dictates a finite curvature of the interfacial film. The droplet phase persists into the region of the phase diagram where the volumes of water and the oil are equal. When cosurfactants are present, these small surface-active molecules usually absorb on the interface with a

20:1 ratio over the surfactant molecules; thus the interface will not have any intrinsic bending tendencies and a bicontinuous structure is found to be present. Recently Safran *et al.*¹¹ have proposed a theory combining the earlier droplet model¹² and the lattice model^{3,6} to show that middle-phase microemulsions can possess a droplet structure in addition to the bicontinuous phases when the curvature term is considered explicitly in the free energy of the system.

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¹For a general survey, see for instance *Surfactants in Solution*, edited by K. Mittal and B. Lindman (Plenum, New York, 1984).

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