Effect of Elastic Bending Energy on the Emulsification Failure in a Microemulsion

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Small-angle neutron scattering experiments have been carried out to study the phase stability of a very dilute water-in-oil microemulsion. At the fixed water to surfactant molar ratio of ω = 30, we observed a decrease in the microemulsion droplet radius and an increase in the polydispersity when the dispersed-phase volume fraction, ϕ, was dilute to less than 1%. Upon further dilution to below 0.1%, the droplets disappeared. This suggested that in the concentration range, 0.1% < ϕ < 1%, a single-phase microemulsion was unstable, and a phase separation, known as the emulsification failure, occurred. To understand the interesting phase behavior, we have formulated an analytic solution for the droplet size distribution function for a two-phase microemulsion based on the theory of Borkovec et al. (J. Colloid Interface Sci. 131, 366 (1989)). We found that the distribution function obtained a simple Gaussian form, and the width of the distribution function was inversely proportional to the renormalized elastic bending energy of the microemulsion droplets. Other features predicted by the theory were also in good agreement with the small-angle neutron scattering measurements.

I. INTRODUCTION

A microemulsion is a thermodynamically stable three-component mixture of oil, water, and surfactant. An example of such a mixture contains decane (oil), water, and sodium di-2-ethylhexylsulfosuccinate (AOT surfactant). For certain compositions of these three components, a homogeneous and optically clear single-phase solution can be obtained at room temperature. Many previous scattering experiments (2, 3) have established that at moderately low dispersed-phase (Water + AOT surfactant) volume fraction, ϕ > 0.02, the microemulsion consists of surfactant-coated spherical water droplets dispersed in the oil-continuous medium. The size of the droplets is rather uniform and it is determined by the water to surfactant molar ratio (4, 5). At higher concentrations, there are indications that the microemulsion consists of densely packed droplets which exhibit interesting glassy behaviors (6–8).

In contrast to the extensively studied microemulsions in the above mentioned droplet concentrations, much less is known concerning the structure of such a single-phase microemulsion when it is continuously diluted such that the surfactant concentration is too low to coat all the droplets. In this case the microemulsion will have a phase separation as signified by a precipitation of a water phase from the bulk oil phase. The coexistence of a microemulsion phase with an excess water phase is known as type-II microemulsion. The transition of a single-phase water-in-oil microemulsion to type-II microemulsion is called emulsification failure. A careful study of the microemulsion in this region will not only give us insights about the key factors which control the emulsification process, but also provide a quantitative measurement of thermodynamic parameters, such as the elastic bending energy (9), κ, the spontaneous radius, R₀, and the critical micellar concentration (CMC), X_c.

Recently, Borkovec et al. (10) have proposed a theoretical model to study the phase behavior of the microemulsion in the emulsification failure region. However, there are no prior experimental studies to compare with the theoretical predictions.

In this paper we present an experimental study of this emulsification failure phenomenon using the small-angle neutron scattering (SANS) technique. The system under study was an AOT microemulsion with the fixed water-to-surfactant molar ratio of ω = 30. We found that at high dispersed-phase volume fractions, ϕ > 1%, both the droplet size and the polydispersity remained constant; at the intermediate volume fraction, 0.1% < ϕ < 1%, the microemulsion droplet size decreased and the polydispersity of these droplets increased as the sample was diluted; and at very low volume fractions, ϕ < 0.1%, the microemulsion droplets apparently disappeared. The above experimental observation is interesting, particularly for the intermediate concentration range. For fixed water-to-surfactant molar ratio and fixed surfactant monomer concentration (X_c), the surfactant dilution decreases the surface-to-volume ratio of the dispersed-phase due to the finite CMC. Therefore, the microemulsion droplet size is expected to increase in the single-phase region. The fact that we observed a reversed behavior in the intermediate concentration range suggests that some of the water molecules were removed from the microemulsion phase and this causes the phase separation. To explain the experimental results quantitatively we have derived an analytic form for the size distribution function in the two-phase region based on a model proposed by Borkovec et al. (10). Our calculations showed good agreements between the theory (10) and the experiment, indicating that the theory has captured the essential physics of this three-component microemulsion. More specifically, we found that the elastic bending energy κ was ~k_b T, the spontaneous radius R₀ was ~60 Å, and the critical micellar mole fraction X_c was ~2 x 10^-4 for our system.

We believe that this is the first time R₀ has been measured experimentally for this system. It is interesting to observe that the elastic bending energy measured in our static scattering measurement is smaller than that obtained from the dynamic scattering (neutron spin-echo) measurement (10). The difference between the static and dynamic measurements may be explained by the saddle-splay energy, κ, which normalizes both the elastic bending energy, κ, and the spontaneous radius, R₀, as suggested recently by Safran (11). We will show later that in the static measurement one actually measures a renormalized elastic bending energy and a renormalized spontaneous radius. For simplicity we still denote them as κ and R₀, respectively.

In the next section, we will present the theory of Borkovec et al. (10) and our own calculations, which we used to interpret our experimental results. The theory of the neutron scattering from polydispersed spherical shells is also briefly reviewed for the purpose of analyzing the scattering data. Section III contains experimental details, including the sample preparation and the neutron scattering measurements. Our own experimental results also appear in that section. Finally the work is summarized in Section IV.

II. THEORY

II.1 Thermodynamics of Water-in-Oil Microemulsion

Formation of droplets in a dilute water-in-oil microemulsion can be viewed as an aggregation of water and surfactant monomers. To describe this process, Borkovec et al. (10) have developed a statistical model which combines features of thermodynamics of mixed micelle formation and the established characteristics of the free energy of microemulsion. The predicted phase diagram is shown in Fig. 1. As shown in the figure, for a fixed water to surfactant molar ratio, ω, the solution has three different thermodynamic regions depending on the surfactant concentration, X_c. The boundaries between these regions are char-
dius $\rho = \sqrt{N}$, the elastic bending energy $\kappa$, and the spontaneous radius $\rho_0$, the size distribution function can be written as

$$f(\rho) = \rho e^{-\kappa}$$  \hspace{1cm} \text{III.1.1}$$

where

$$g(\rho) = \xi_0^2 + \lambda n_0 + 8\eta(1 - \rho/\rho_0)^2 - \beta \Delta_{\mu_0}$$  \hspace{1cm} \text{III.1.2}$$

Here $\lambda (\sim 1.3)$ is the volume ratio of surfactant to water molecules ($12\sigma$), $\beta$ is the reciprocal of $k_BT$, and $\beta \Delta_{\mu_0}$ is a constant which determines the total number of droplets present in the system. The exponent $n$ is used to characterize contributions from the entropy of mixing and the thermal fluctuations of the droplets. Obviously, the size distribution depends on both of these effects, since the former favors more but smaller droplets and the latter tends to have a bigger effective radius. Because the dominant contribution to $f(\rho)$ is from the exponential part, the particular value of $\kappa$ does not affect the final result strongly. On the other hand, in order for the distribution function, $f(\rho)$, to be zero at the origin, $\lambda_0$ must be a positive finite number. The calculation below can be easily generalized to any value of $\kappa$, but for the simplicity we will take $\beta = 1$, in accordance with Ref. (1). (3) The distribution function, $f(\rho)$, also depends on two other parameters:

$$\xi = \beta \Delta_{\mu_0} - \log x_0$$  \hspace{1cm} \text{III.1.3}$$

and

$$\eta = \beta \Delta_{\mu_0} - \log x_0$$  \hspace{1cm} \text{III.1.4}$$

where $\Delta_{\mu_0}$ is the standard chemical potential difference between surfactant (water) molecules, and $x_0$ is the mole fraction of surfactant (water) monomers. Physically, the parameter $\xi$ is the chemical potential difference between a surfactant in the saturated oil/water interfaces and a surfactant dissolved in the oil, and it measures the concentration of free water monomers. Alternatively, $\xi$ and $\eta$ can be viewed as Lagrangian multipliers which fix the overall mole fractions of surfactant and water molecules, respectively.

Using the distribution function, $f(\rho)$, the $n$th moment of the dimensionless radius, $\rho$, can be defined as

$$\langle \rho^n \rangle = \frac{\int_0^{\infty} dp \rho^n f(\rho)}{\int_0^{\infty} dp f(\rho)}$$  \hspace{1cm} \text{III.1.5}$$

where the lower integration limit, $\rho_0$, denoting the smallest aggregation size, should be taken to be greater than one. Since $\rho = \sqrt{N}$, where $N$ is the surfactant aggregation number, the actual size $R$ is related to the dimensionless radius $\rho$ by

$$R = \rho \left(\frac{\Sigma_0}{4\pi} \right)^{1/3}$$  \hspace{1cm} \text{III.1.6}$$

where $\Sigma_0 = (60 \sigma^3)$ is the surface area per head group of the surfactant ($S$).

Finally, by denoting the overall surfactant (water) mole fraction as $X_0$, the mass conservation law for both surfactant and water molecules can be simply expressed in terms of the second and the third moment of $R$,

$$X_0 = e^{-\xi \Delta_{\mu_0}} (\rho_0)^2 x_0$$  \hspace{1cm} \text{III.1.7}$$

$$x_0 = e^{-\eta \Delta_{\mu_0}} + \lambda (\rho_0)^2 x_0$$  \hspace{1cm} \text{III.1.8}$$

where $x_0$ is the droplet mole fraction which is defined as

$$x_0 = \frac{1}{\rho_0^2} \int_0^\infty dp f(\rho).$$  \hspace{1cm} \text{III.1.9}$$

Here the lower integration limit, $\rho_0$, corresponding to the smallest aggregates, should be $\sqrt{2}$. As it stands, the first terms on the right hand side of Eq. (III.1.7) and (III.1.8) are originated from monomers, whereas the second terms are contributions from the droplets.

Equations [III.1]-[III.1.9] complete the description of the three-component micromulsion in terms of its physical parameters, and they can also be used to determine the phase boundaries for a given system. To calculate the distribution function, $f(\rho)$, we need first to evaluate the two Lagrangian multipliers $\xi$ and $\eta$ using Eqs. (III.1.7) and (III.1.8) for given $X_1$ and $X_2$. Once $\xi$ and $\eta$ are determined the distribution function itself is uniquely defined. It is interesting to note that the distribution function $f(\rho)$ has very different asymptotic behaviors in the single-phase and in the two-phase regions because of different thermodynamic constraints. In the single-phase region, since both $\xi$ and $\eta$ are nonzero, the large droplets are inhibited by the energy cost ($\sim n^2\rho^2$) of water cores of the droplets, therefore $f(\rho)$ decays as $\sim e^{-\eta \rho^2}$ for $\rho \rightarrow \infty$. On the other hand, in the two-phase region, since $\xi$ is nonzero but $\eta$ is zero, the existence of large droplets is only inhibited by the energy cost ($\sim \xi^2$) of the surfactants on the interfaces, therefore $f(\rho)$ decays as $\sim e^{-\xi \rho^2}$ for $\rho \rightarrow \infty$.

In the rest of the paper we will focus on the two-phase region and seek an analytic solution in this region using the theory outlined above. In the two-phase region, water molecules inside the droplets can exchange freely with the water reservoir, hence we have $\eta = 0$. By relaxing this thermodynamic constraint the solution of Eqs. (III.1.7) and (III.1.8) is greatly simplified, because these two equations become decoupled and $\xi$ can be solved from Eq. (III.1.7) alone. Physically it means that the distribution function is unaffected by the amount of water present in the reservoir. We notice that in this thermodynamic region the distribution function, $f(\rho)$, is peaked at

$$R_{\rho_{\text{max}}} \approx \rho_0 \left(\frac{\Sigma_0}{8\pi \rho_0^2} \right)^{1/3} \hspace{1cm} \text{III.1.10}$$

and has a half width

$$\sigma \approx \frac{\rho_0}{\sqrt{2(\rho_0^2 + 8\pi \rho_0^2 \rho)\rho_{\text{max}}}}$$  \hspace{1cm} \text{III.1.11}$$

For $8\pi \rho_0 \gg \rho_0^2$, we have (14) $\rho_{\text{max}}/\sigma \approx V_0/\rho_0 \gg 1$. This allows us to further simplify Eqs. (III.1.5) and (III.1.9) by extending the lower integration limit from a finite value, $\rho_0$, to the minus infinity. Such an approximation
sacrifices little numerical accuracy since the integrand decays exponentially fast for \( \rho \approx \rho_0 \), (see III.3 for more discussions). Therefore we can write \( \langle \rho^a \rangle_x \) in an analytical form,

\[
\langle \rho^a \rangle_x = \frac{(n + 1)\sqrt{2\pi}y}{x_{\text{d}}\sqrt{1 + \frac{1}{y^2}}} \exp\left[\frac{\beta V_{\text{d}} - 8\pi \rho_y + \frac{1}{2}}{1 + \frac{1}{2}y^2}\right] - \frac{\rho_0}{2(8\pi \rho_y)^{1/2}}.
\]

This last equation can also be expressed in terms of \( \langle \rho \rangle \) by eliminating \( y \) using Eq. [III.1.16]. The final result is

\[
e = \frac{1}{16\pi V_{\text{d}}} \frac{\rho_0}{(n - 2k)(1 + O(\rho^2))}.
\]

The above equation should be compared with that for a single-phase microemulsion. Safran (15) and Borkovec et al. (1) have calculated the variance \( \epsilon \) when the total surfactant mole fraction is relatively high so that the surfactant monomer concentration can be neglected. Their result is

\[
e = \frac{1}{40\pi \rho_y (1 - \frac{\rho_0}{\rho_y})} \times (1 + O(\rho^2)).
\]

where \( \rho_0 \) is the Schulman's radius which is related to the mean droplet radius by \( \rho_0 \approx \rho_0 - 1 - 2\pi \epsilon(\rho^2) \) [1]. For a system with a stable surfactant layer \( 48\rho_y \geq 1 \), \( \langle \rho \rangle = \rho_0 \). It should be pointed out that for a single-phase microemulsion, the system consists of, intrinsically, of two length scales \( \rho_0 \) and \( \rho_y \), whereas for a two-phase microemulsion the system has only one length scale \( \rho_0 \). This makes the two-phase region particularly useful for measuring the spontaneous radius, \( \rho_0 \), for a given system. Physically the spontaneous radius \( \rho_0 \) characterizes the natural bending curvature of surfactant molecules, and to a large extent \( \rho_0 \) only depends on the surfactant molecular shape and the solvent condition. The Schulman's radius, \( \rho_0 \), on the other hand, characterizes the ultimate size of the droplets at high volume fraction \( \epsilon \) and depends solely on the water to surfactant molar ratio \( \omega \). It should also be pointed out that in the limit of very small polydispersity \( \epsilon \to 0 \), i.e., when \( \epsilon \) is very large, the mean droplet radius \( \langle \rho \rangle \) approaches two different limiting values in the different phases. In the single-phase region \( \langle \rho \rangle = \rho_0 \) and in the two-phase region \( \langle \rho \rangle = \rho_y \). Therefore in the limit of small polydispersity we can replace \( \rho_0 \) by \( \langle \rho \rangle \) in Eq. [III.1.21] and write \( \epsilon \) as

\[
\epsilon = \frac{\langle \rho^2 \rangle}{\langle \rho \rangle^2} = 1 - \frac{1 - y}{1 + y^2}.
\]

where

\[
e = \frac{1}{40\pi \rho_y (1 - \frac{\rho_0}{\rho_y})} \times (1 + O(\rho^2)).
\]

Because the polydispersity is a continuous function of the droplet size, Eqs. [III.1.20] and [III.1.22] should be equal at the phase boundary, and hence we find the emulsification failure condition \( \langle \rho \rangle = \rho_0 \). This phase stability limit for the small polydispersity is consistent with that obtained by Safran and Turkevich (16) using a different approach.

II.2 SANS from a Distribution of Polydispersed Spherical Shells

To test the above theoretical calculations we have used the small-angle neutron scattering technique to determine the mean radius of droplets, \( \langle R \rangle = \langle \rho \rangle \sqrt{2\pi/4\pi} \), and the polydispersity, \( \epsilon \), at different droplet concentrations. The microemulsion droplets in real space can be obtained by deconvoluting the measured neutron scattering intensity \( I(Q) \) based on certain reliable scattering models.

First, let us consider the neutron scattering intensity, \( I(Q) \), from a set of identical particles; this is given by

\[
I(Q) = N_0 \rho P(Q)S(Q)\rho_0.
\]

where \( N_0 \) is the number density of the scattering particles, \( P(Q) \) is the particle form factor, and \( S(Q) \) is the structure factor. Unlike an aqueous solution, the interaction between the droplets in a water-in-oil microemulsion is mainly due to a hard-core repulsion. For the hard-sphere interaction we found, using the Percus–Yevick approximation (17), that the first maximum in \( S(Q) \) is about 1.01 for the highest concentration \( \epsilon = 2\% \) used in the experiment. This suggests that the interaction between the droplets is negligible and the scattering intensity is dominated by the form factor \( P(Q) \). For a spherical shell with the inner radius \( R_i \) and the outer radius \( R_o \),

the form factor \( P(Q) \) can be calculated using a linear superposition of scattering amplitudes \( F(R_i) \) and \( F(R_o) \) of solid spheres with radius \( R_i \) and \( R_o \), respectively. This gives

\[
P(Q) = [F(R_o) - F(R_i)]^2,
\]

where

\[
F(R) = \frac{4\pi R^2}{3}(\frac{1}{2} - \frac{1}{R})
\]

and

\[
sin(Q) = \frac{Q R_o \cos(Q) \rho_o}{(Q R)^2}.
\]

where \( Q \) is the scattering vector. In Eqs. [II.2.3] and [II.2.4] and \( \rho_0 \) and \( \rho_1 \) are the neutron scattering length densities of the sphere and the solvent, respectively.

Next, we consider the scattering from a distribution of particles with different sizes. We assume the size of the scattering particle can be characterized by a distribution function \( f(R) \). In this case we can differentiate Eq. [II.2.1] and write \( dN_0 = N_0 f(R) dR \), and \( dQ R \) represents the fraction of droplets with the radii in the interval \( R \) and \( R + dR \). Integrating over the scatterings from particles of all sizes we obtain the total scattering intensity:

\[
I(Q) = N_0 \int_0^\infty f(Q) I(Q) f(R) dR.
\]

For simplicity, hereafter, we use the Schultz distribution function \( f(R) \) to model the size distribution of AOT microemulsion droplets (3). Such an approximation has been used previously, and has been shown to be consistent with various analysis procedures, such as inverse Laplace transformation and histogram method, for neutron scattering and light scattering data (2, 3). Simple form of Schultz distribution function also allows an analytic calculation of the scattering intensity for various shapes of scattering entities. For spherical scattering objects the Schultz distribution function is given by

\[
I(Q) = N_0 \int_0^\infty f(Q) I(Q) f(R) dR.
\]
\[ f(R) = \left( \frac{z + 1}{\langle R \rangle} \right)^{z+1} \left( \frac{R}{\langle R \rangle} \right)^{-z} \times \exp \left[ - \left( \frac{z + 1}{\langle R \rangle} \right) \frac{R}{\langle R \rangle} \right], \]  

where \( \langle R \rangle \) is the mean droplet size and \( z \) is related to the polydispersity by \( e = 1/(z + 1) \).

The final expression for the total scattering intensity, \( I(Q) \), is given in the Appendix (18).

III. Experimental

III.1 Sample Preparation

The surfactant, sodium di-2-ethylhexylsulfosuccinate, was purchased from Fluka Chemical Company. The surfactant was treated with the activated charcoal and then twice recrystallized from methanol. It was stored in the vacuum before usage. Our previous measurements indicated that with such a purification process the experimental results were reproducible within each batch, and variations could occur among different batches.

We have used deuterated water, D\(_2\)O (19), as the internal phase of the microemulsion and used deuterated decane (19), C\(_{10}\)D\(_2\), as the solvent. The scattering length densities of D\(_2\)O (\( \rho_{D_2O} = 6.33 \times 10^{-6} \text{Å}^2 \)) and C\(_{10}\)D\(_2\) (\( \rho_{C_{10}D_2} = 6.36 \times 10^{-6} \text{Å}^2 \)) are closely matched and they are very different from the scattering density of the surfactant tail, which consists mainly of hydrocarbons, (\( \rho_{\text{tail}} = -0.49 \times 10^{-6} \text{Å}^2 \)). Therefore the scattering entities in the sample are spherical shells with only the surfactant "tails" being visible to the neutrons. As mentioned in our earlier publication (5), such a scattering sample is superior to a sample consisting of solid-spheres with normal water, H\(_2\)O, as the internal phase of the microemulsion. This is because the spherical-shell sample has a very low hydrogen incoherent scattering and the coherent scattering intensity as a function of the scattering wave-number exhibits a sharp minimum, which enabled us to set a tight fit for both the mean radius and the polydispersity of the droplets.

All the scattering samples, with the dispensed-phase (D\(_2\)O + AOT) volume fraction of \( \phi = 2.1, 0.5, 0.2, 0.1, \) and 0.05%, have the fixed water to surfactant molar ratio of \( \alpha = 30 \). This was achieved by successively diluting a master solution of \( \alpha = 2 \). To convert the volume fraction \( \phi \) to the surfactant mole fraction \( X \), we use the equation (20)

\[ X = \frac{A \phi}{B \phi + C(1 - \phi)}, \]  

where \( A = 194.9 \text{ cm}^3/\text{mol}, B = 6042.4 \text{ cm}^2/\text{mol}, \) and \( C = 936.6 \text{ cm}^3/\text{mol} \).

III.2 Small-Angle Neutron Scattering Measurements

The small-angle neutron scattering experiment was performed on a high resolution spectrometer of the High Flux Beam Reactor at Brookhaven National Laboratory. The incident neutron wavelength, \( \lambda \), was 5.3 ± 0.3 Å. We successively used a set of collimation pinholes of diameters 10, 8, and 6 mm, with the 6-mm pinhole being closest to the sample. The distance between the sample and the detector was 1800 mm, which gives a usable \( Q \)-range of 0.01 Å\(^{-1} \) < \( Q \) < 0.2 Å\(^{-1} \). Here the magnitude of the scattering wave-vector \( Q \) is related to the scattering angle \( \theta \) by \( Q = (4\pi/\lambda) \sin(\theta/2) \). The neutron scattering intensity was measured by a two-dimensional detector, and a circular integration over the scattering intensity at the fixed scattering angle was performed to give better statistics. We subtracted out the background scatterings due to quartz windows and the solvent. The incoherent scattering from hydrogens in AOT molecules was also subtracted out. Further precaution was taken to eliminate inhomogeneities in the detector’s sensitivities at different pixels by normalizing all the scattering intensities with that from a 1-mm water sample. Therefore our scattering data are given in the absolute units of water scattering intensity.

III.3 Experimental Results and Data Analysis

Three sets of the SANS data measured at \( \phi = 2.0, 0.5, \) and 0.1\% are shown in Fig. 2. Two distinct features must be emphasized: first, all the data contain a minimum, which is a characteristic of the scattering from the spherical shells. The location of this minimum moves to larger \( Q \) as the solution is diluted. This indicates that the size of the droplets is decreased at lower surfactant concentration. Secondly, the scattering intensity peak at \( q \to 0 \) becomes broader and the second scattering peak becomes less pronounced at lower surfactant concentrations. This suggests an increase in the polydispersity as the sample is diluted. Using a non-linear least-squares fitting routine (21), we obtained good fits to the spherical shell-model (Eqs. [II.2.2]–[II.2.3]), and they are shown by the solid lines in the figure. The thickness of the shell determined by the sample with \( \phi = 2 \% \) is \( \sim 8 \) Å, which is close to our earlier measurement (5). This thickness was kept fixed for the fittings to the rest of concentrations.

For the sample with the lowest surfactant concentration, i.e. \( \phi = 0.05 \%), the scattering intensity decreases dramatically and the data (not shown) is essentially flat on the scale of Fig. 2. This suggests that there is no aggregation at this concentration and the scattering is from the surfactant monomers only. From this observation we conclude that the CMC value is in the range 0.05% < \( \phi < 0.1 \% \) (or 1.04 \( \times 10^{-4} < X < 2.07 \times 10^{-4} \)).

The mean droplet radius, \( <R> \), and the polydispersity, \( \delta_{\text{R}} \), extracted from the above fitting can be used to check the theoretical prediction of Eq. (II.1.20). In Fig. 3 we plot \( \delta_{\text{R}} \) vs. \( <R> \), where we expect a linear curve with a slope of \( 16\pi\delta_{\text{R}}/R_\infty \) and an intercept of zero. Our experimental data can be fit reasonably well to a straight line with the slope of 0.53 Å\(^{-1} \). The two dash lines in the figure indicate the errors, ±0.04 Å\(^{-1} \), of the slope. From the measured slope, if either value of the elastic constant, \( \epsilon \), or the spontaneous radius, \( R_\infty \), is known, the other value can be deduced.

In Fig. 4 we plot, for various surfactant concentration \( X \), the mean droplet radius, \( <R> \), and the polydispersity, \( \delta_{\text{R}} \), simultaneously. We find that the microemulsion droplet size decreases...
FIG. 4. The mean radius \( \langle R \rangle \) (circles) and the polydispersity \( X_2/X_1 \) (triangles) vs. the reduced surfactant concentration \( X_1/X_2 \). The vertical dash line indicates the calculated emulsion failure boundary. As shown in the figure, in the two-phase region the microemulsion droplet size decreases and the polydispersity increases as the CMC is approached, i.e., when \( X_1/X_2 < 1 \). In the single-phase region both the droplet size and the polydispersity remain constant. The solid curves are the theoretical fits which show good agreements with the measurements.

FIG. 5. The mole fraction of droplets \( x_d \) vs. the reduced surfactant concentration \( X_1/X_2 \). The mole fraction of droplets \( x_d \) decreases as the reduced surfactant concentration \( X_1/X_2 \) decreases. The droplets disappear at \( X_1/X_2 = 1 \). The solid curve is a theoretical calculation based on Eqs. [III.1.15]. Large deviation at the highest surfactant concentration, \( X_1/X_2 \approx 12 \), or \( \phi > 1 \%), is expected because the system is already in the single-phase region. The vertical dash line indicates the calculated emulsion failure boundary.

The SANS experiment gives measurements for \( \langle R \rangle \) and \( \epsilon \) as a function of \( X_1 \), which we can self-consistently determine all these parameters. As shown by the solid curves in Fig. 4, our experimental data can be well fitted to the theory using the following set of parameters: \( \beta_0 = 0.6 \pm 0.1 \), \( \beta_\Delta \mu_0 = -8.5 \pm 0.1 \), and \( \beta_\Delta \mu_0 = -17 \pm 3 \). Since we already knew the ratio \( 16\pi R_0/\gamma = 0.53 \) from Fig. 3, we obtain the spontaneous radius for our system to be \( R_0 = 57 \pm 14 \). By the definition of CMC (1), \( X_1 \exp (-\beta_\Delta \mu_0) = 1 \), we obtain \( X_1 = 2.0 \times 10^{-4} \) for our system. Using \( \omega = 30 \) and the parameters obtained above, we are able to determine the phase boundary, \( X_{c,1}^* \), between the single-phase and the two-phase region by Eqs. [III.1.5] and [III.1.7]. This gives \( X_{c,1}^* \approx 2.4 \times 10^{-3} \), which is shown by a vertical dash line in Fig. 4. This calculation is consistent with the observation that above \( X_1 \approx 2 \times 10^{-3} \), \( \phi = 1 \%), the mean droplet radius and the polydispersity remain constant as expected for a single-phase microemulsion.

We also examine the mole fraction \( x_d \) of the droplets as a function of \( X_1 \). Here \( x_d \) is proportional to the total number, \( N_\gamma \), of scattering droplets in the scattering volume, i.e., \( x_d = CN_\gamma \). Using the calculated \( x_d \) at different surfactant concentrations and \( N_\gamma \) obtained from the measured scattering intensity, we find the proportional constant \( C \approx 8 \times 10^{-14} \). In Fig. 5 we plot both the measured and the calculated \( x_d \) as a function of \( X_1/X_2 \). We find that the mole fraction of droplets \( x_d \) decreases dramatically as the surfactant concentration decreases, and vanishes as the CMC is approached (\( X_1/X_2 \approx 1 \)). As it can be seen in Fig. 5, our measurement is consistent with the theory except at the highest surfactant concentration (\( \phi = 2 \%), where the deviation is expected because the microemulsion is already in the single-phase region in which our calculation is not applicable.

Finally, we compare the Schultz distribution function with the statistical model at volume fractions \( \phi = 0.1 \) and \( \phi = 1 \). These concentrations represent the two extremes in the two-phase region as shown in Fig. 4. For \( \phi = 0.1 \% \), the system is close to the CMC, the microemulsion droplets attain the minimum size (\( \langle R \rangle \approx 30 \) A) and the maximum polydispersity (\( \psi_\epsilon \approx 26 \% \)). For \( \phi = 1 \% \), the system is close to the single-phase region; the microemulsion droplets attain the maximum size (\( \langle R \rangle \approx 50 \) A) and the minimum polydispersity (\( \psi_\epsilon \approx 19 \% \)). In Fig. 6 we plot the Schultz (dash-dot curves) and the statistical (solid curves) distribution functions together for the two concentrations. We find that even though these two distribution functions have the same mean and variance, the peak positions are slightly different (the difference is \( 4 \) A at \( \phi = 0.1 \% \) and \( 1 \) A at \( \phi = 1 \% \)). The Schultz distribution being consistently lower than the statistical one. This is because the Schultz distribution function has a slower roll-off at large radius. Overall, however, the Schultz distribution function mimics the statistical model reasonably well. From Fig. 6 we also find that dilution shifts the peak position of the distribution functions toward smaller values of \( R \), while the width of the distribution functions is almost constant. Therefore the apparent increase of the polydispersity at the lower concentration is mainly due to the decrease of the microemulsion droplet size. Note that even at the lowest surfactant concentration, the statistical distribution still decays very fast toward the small droplet radius, which justifies the approximation we made earlier for obtaining Eq. [III.1.5] by extending the lower integration limit to minus infinity.

In passing, we want to mention that a simpler derivation for the mean droplet radius, \( \langle R \rangle \), as a function of the dispersed-phase volume fraction, \( \phi \), was given by Safran recently (25). Assuming zero solubility of water in oil, Safran found (24)

\[
\langle R \rangle = \frac{1}{8 \pi \rho} \left[ \frac{\log \frac{\sigma}{\phi - \phi_0}}{\beta_0 \Delta \mu_0} \right],
\]

[III.3.1]

where \( \sigma = 4 \pi \langle R \rangle^3 \) is the mean volume of the droplets and \( \phi_0 \) is the volume fraction at the CMC. Using \( \nu_0 = 30.3 \) A and Eq. [III.1.1], we obtain \( \phi_0 = 0.065 \%. By fitting the measured \( \langle R \rangle \) with Eq. [III.1.5] (see Fig. 7), we find \( \beta_0 \approx 1 \) and \( R_0 \approx 2.9 \). Considering the simplicity of Safran’s theory, the obtained numerical values for \( \beta_0 \) and \( R_0 \) are still reasonably close to the experimental ones.
FIG. 7. The mean droplet radius $R$ vs. the dispersed-phase volume fraction \( \phi \). Here \( \phi_0 \) is the volume fraction at the CMC. Circles are experimental data, and the solid curve is the fit to Eq. (III.3.1).

sonable. However, we expect the calculation to be less reliable for systems with higher CMC values.

### III.4.4 Conclusions

We have performed small-angle neutron scattering experiments for a very dilute water-in-oil AOT microemulsion. At the fixed water-to-surfactant molar ratio of \( \omega = 30 \), we observed a decrease in the microemulsion droplet radius and an increase in the polydispersity when the dispersed-phase volume fraction was diluted to less than 1%. This interesting phase behavior was investigated in terms of emulsification failure process. In doing so, we have derived an analytic solution for a three-component microemulsion in the two-phase region based on the theory of Borkovec et al. (1). This solution allows us to make a connection between the thermodynamic phase behaviors and various physical parameters. Among them the elastic bending energy, \( \kappa \), the spontaneous radius, \( R_s \), and the critical micellar concentration, \( C_m \), are of great theoretical and practical interests. Our calculations show that in the two-phase region the microemulsion droplet size is governed by a single length scale, namely the spontaneous radius \( R_s \). While in the single-phase region there are two relevant length scales, namely the spontaneous radius \( R_s \) and the Schulman radius \( R_s \). This unique feature of the two-phase microemulsion allows us to make a quantitative measurement of the spontaneous radius \( R_s \), which we found to be \( R_s = 57 \pm 14 \text{ Å} \) for AOT microemulsion. Our calculations also show that near the critical micellar concentration (CMC) all the physical parameters, such as the mean droplet radius, the polydispersity, and the number density of the microemulsion droplets, are extremely sensitive to the surfactant concentration. This entails a reliable measurement of the CMC value for the microemulsion. Experimentally we found \( R_s = 2.0 \times 10^{-11} \text{ cm} \). The CMC value determined by the SANS measurement compares favorably to that of AOT in a variety of hydrocarbon solvents (30). Finally, we find that the effective elastic bending energy for this AOT microemulsion is \( \kappa = 0.6 \text{ mN/m} \). A plausible mechanism is proposed which explains the large difference in the elastic bending energy, \( \kappa \), measured statically and dynamically.

### APPENDIX

The neutron scattering intensity distribution \( I(Q) \) from a dilute dispersionsample is given by

$$I(Q) = N_Q \int_0^\infty F(Q,R) f(R) dR, \quad [A.1]$$

where \( N_Q \) is the number density of the scattering particles, \( P(Q) \) is the particle form factor, and \( f(R) \) is the particle size distribution function. For a concentric spherical shell with an inner radius \( R_i \) and an outer radius \( R_e \), \( P(Q) \) can be written as

$$P(Q) = \frac{F(Q,R_e) - F(Q,R_i)}{R_e^2 - R_i^2}, \quad [A.2]$$
where

$$F(Q R) = \frac{4\pi R}{3} \left( \hat{\rho}_1 - \hat{\rho}_2 \right) \times \sin(Q R) - Q R \cos(Q R) \right) \right)^3. \quad [A.3]$$

Here $\hat{\rho}_1$ and $\hat{\rho}_2$ are the neutron scattering length densities of the sphere and the solvent, respectively. For a spherical-shell sample the matching condition for the scattering length densities is given by $\hat{\rho}_1 = \hat{\rho}_2 + \rho_s$. Using the Schultz distribution function,

$$I(R) = \frac{(z + 1)^{\gamma + 1}}{(R)^{\gamma + 1}} \left( \frac{R}{R} \right)^{\gamma} \times \exp \left[-(z + 1) \frac{R}{(R)} \right]. \quad [A.4]$$

the scattering intensity distribution $I(Q)$ in Eq. [A.1] has the following form (18):

$$I(Q) = \frac{\rho_0 - \rho_s}{3} \int I(Q R) \, dQ + \int I(Q R) - 2 \int I(Q R_0, p) \right) \right)^3. \quad [A.5]$$

Here $(=4\pi R^2/3)$ is the volume of the droplet, $p = (R_1/R_0)$ is a thickness parameter, and $t_1$ and $t_2$ are functions which are defined as

$$I_2(z) = \frac{9}{2(z + 1)^{\gamma} \right) \times \left( \frac{z + 1}{1 + 4(z + 2)^{2\gamma/3}} \right) \times \cos(z + 2) + \gamma \right) \times \left( \frac{1 + \cos(z + 3)w}{1 + 4(z + 2)^{2\gamma/3}} \right) \right). \quad [A.6]$$

and

$$I_2(z) = \frac{9}{2(z + 1)^{\gamma} \right) \times \left( \frac{z + 1}{1 + 4(z + 2)^{2\gamma/3}} \right) \times \cos(z + 2) + \gamma \right) \times \left( \frac{1 + \cos(z + 3)w}{1 + 4(z + 2)^{2\gamma/3}} \right) \right). \quad [A.6]$$

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9. As we shall see later in the text, this effective elastic bending energy is the splat elastic bending energy $\epsilon$ renormalized by the saddle-splay elastic energy $\epsilon$.
12. By definition $A = \frac{e}{2\pi R}$. Here we have used commonly accepted values for the specific volume of water, $\nu_w = 30.3 \AA^3$, and the surface area per AOT surfactant, $\nu_a = 60 \AA^2$.
13. The exponent is given by $x = 2(1 - \epsilon - 2\alpha)$, where $\epsilon$ comes from the entropy of mixing and $\alpha$ is from renormalization of the elastic bending energy, $\epsilon$, due to the solvation. Depending on different models, $\alpha$ can have very different values. Since the strongest $\epsilon$-dependence is in the exponential part of the distribution function, we simply set $x = 1$.
14. It can be shown numerically that for the parameters used in the experiment $I(Q)$ is a monotonic function of $\chi$, and $(I(Q)_{\text{obs}} - \chi) \sim -\chi$. Therefore, the condition $\chi \gg \chi$ always holds.