Study of Dynamics of Microemulsion Droplets by Neutron Spin-Echo Spectroscopy

J. S. Huang and S. T. Milner
Exxon Research and Engineering, Annandale, New Jersey 08801

and

B. Farago and D. Richter
Institut Laue-Langevin, Grenoble, France

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We have employed neutron spin-echo techniques to study the dynamics of the shape fluctuation of microemulsion droplets. It is found that the scattering spectrum of a droplet system with a labeled layer of surfactants exhibits a sharp peak in the relaxation frequency spectrum. We have determined that the fluctuations are driven mainly by the bending modes on the surface, and the height of the peak allows us to measure the surface elastic bending coefficient directly.

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Microemulsions,[1] being homogeneous mixtures of oil, water, and surfactants, generally contain large internal interfacial areas that separate the hydrocarbon domains from the aqueous domains. For a microemulsion containing 10% surfactant, the typical value[2] for the interfacial surface area is of the order of 100 m^2/cm^3. It is thus expected that the properties and structure of microemulsions will be dependent on the nature of this surfactant layer.

When microemulsions were first formulated, it was thought that the surface tension of the interfaces (of the microscopic droplets) must be extremely low[3,4] so that the free energy of formation of the dispersed droplets would not be unduly penalized by a large surface-energy contribution. Alternatively, it could also be argued[5] that the formation of microemulsion droplets is mainly due to the natural bending tendency of the surfactant layer, the minimization of the bending elastic energy resulting in the observed structure. Recent experiments[6,7] using a double-contrast variation method in static small-angle neutron scattering have discovered the existence of a droplet phase in the sodium di-2-ethylhexyl sulfosuccinate (AOT) system (at equal water-oil ratio) and a random bicontinuous structure[8-10] for other systems. The only way to understand the roles of interfacial tension and the bending energy in the microemulsion formation is to study the dynamics of the surfactant layer.

In the case of a three-component microemulsion containing a surfactant AOT, water, and decane, it is well established that a droplet structure exists in the single-phase region.[6,11] It is also known for this system that the mean radius of the water droplets depends linearly on the surfactant-to-water ratio.[11-13]

The basic idea of the experiment is as follows: Thermal fluctuations of the surfactant film distort the droplet from its average (presumably spherical) form, and the amplitude of these fluctuations is expected to be small as indicated by the moderate effective polydispersity determined through small-angle neutron-scattering measurements.[11] To measure the relaxation frequency of these small fluctuations, it is important to reduce the scattering volume to the actually fluctuating part. Therefore, we arranged contrast matching of the neutron-scattering-length density of the droplet internal phase to that of the continuous phase. Under these conditions the scattering originates solely from the fluctuating shell of surfactant layer. Furthermore, to ensure that the observed scattering is not obscured by interparticle interaction effects which could modify the relaxation times, we also investigated non-contrast-matched spheres where the scattering originates from the volume of the droplets. Possible interaction effects would affect both droplets in the same way and could be eliminated. From the dispersion relation of the relaxation frequency, we can ascertain whether surface tension or elastic bending energy drives the dynamics.

The time- and momentum-dependent scattering intensity $I(Q,t)$ from a fluctuating droplet of radius r_0 can be written as

$$I(Q,t) = e^{-DQ^2 t} V_s^2 (\Delta\rho)^2 \left[f_0(Qr_0) + \sum_{l>1} \frac{2l+1}{4\pi r_0^2} f_l(Qr_0) \langle a_l(0) a_l(t) \rangle \right]. \qquad (1)$$

The scattering wave vector Q is expressed in terms of the neutron wavelength λ and the scattering angle θ as $Q = 4\pi\lambda \sin(\theta/2)$.

Equation (1) can be derived by expansion of the shape fluctuation into spherical harmonics[14] with coefficients $a_l(t)$. Thereby f_0 is the static form factor of the droplet: $f_0 = [\sin(Qr_0)/Qr_0]^2$ for the shell and $f_0 = [3j_1(Qr_0)/Qr_0]^2$ for the sphere; the inelastic form factors are

$$f_l = [(l+2)j_l(Qr_0) - Qr_0 j_{l+1}(Qr_0)]^2$$

for the shell and $f_l = [3j_l(Qr_0)]^2$ for the sphere; V_s is the scattering volume, $\Delta\rho$ the scattering length contrast, and j_l the spherical Bessel function of order l. For the shell it is assumed that $Q\Delta \ll 1$ (Δ is the surface-layer thickness).

The time-dependent amplitudes of the fluctuations $\langle a_l(0)a_l(t)\rangle \sim \exp(-t/\tau_l)$ are expected to be overdamped.[15] Finally $D = kT/6\pi\eta r_0$ is the translational diffusion coefficient, where η is the viscosity of the solvent.

The form factor of the lowest-order fluctuation ($l = 2$) at small Qr_0 is effectively given by j_2^2. Its first maximum occurs in the vicinity of the first zero of the form factor of the shell j_0^2, while in the case of the sphere the elastic form factor still overwhelmingly dominates the spectrum in this Qr_0 range. Therefore, we expect a much better visibility of the lowest-order fluctuation for the shell labeling.

The dynamic experiment was carried out on the neutron spin-echo spectrometer (IN11) at Institut Laue-Langevin in Grenoble, France. The energy change of the scattered neutron was measured directly through the Larmor precessions of the neutron spin in an external guide field. The intermediate scattering function $S(Q,t) = I(Q,t)/I(Q,0)$ is directly given by the final polarization of the scattered neutron.[16]

Five shell-like microemulsion samples were used for this study. The water-to-AOT molar ratios ranged from 8 to 40, giving mean droplet radii (distance from the center to the outer edge of the surfactant tails) from 70 to 24 Å. The dispersed volume was held constant at 5%. The continuous phase was a perdeuterated decane which matches the neutron-scattering-length density of the internal D_2O phase almost exactly so that the surfactant coated droplet appears to be only an empty shell to the scattering beam. In addition, for an intermediate size of $r_0 = 49$ Å, a droplet with a protonated core representing a scattering sphere was investigated.

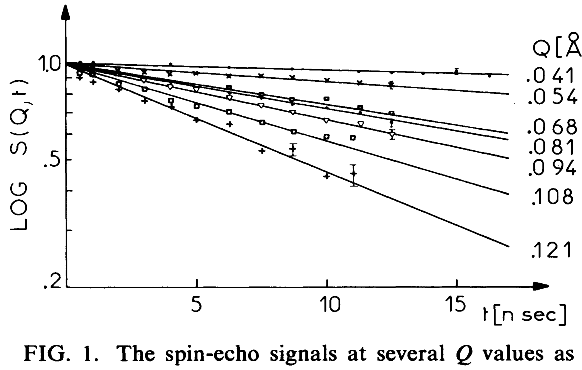

FIG. 1. The spin-echo signals at several Q values as functions of the delay time. The curves are the first-cumulant fits to the data.

Figure 1 presents a set of relaxation curves determined from a droplet with $r_0 = 38$ Å. The line represents a first-cumulant fit to the data. In Figs. 2(a) and 2(b) we plot the effective diffusion constant Γ/Q^2 (where Γ is the first cumulant of the echo signal) as a function of Q obtained for samples in which the mean droplet radius of the microemulsion are 70 and 50 Å, respectively. In addition, Fig. 2(b) presents the effective diffusion coefficients found from the $r_0 = 50$-Å protonated core.

In fact, a pronounced peak is observed for each of the samples, and the position of the peak does occur at $Qr_0 = 3.2 \pm 0.1$ for all the shells measured (Table I). On the other hand, for the sphere we have a maximum at higher Q which corresponds to the minimum of the form factor of the nonfluctuating part of the sphere. A comparison of the two sets of data clearly shows that the observed structure cannot be related to any interdroplet interaction since those effects should influence the shell and the sphere in the same way.

It is also found that as $Q \rightarrow 0$, Γ/Q^2 approaches the value for the center-of-mass diffusion coefficient estimated for each of the droplet sizes. Both the low-Q limit and the occurrence of a peak in our spectra are qualita-

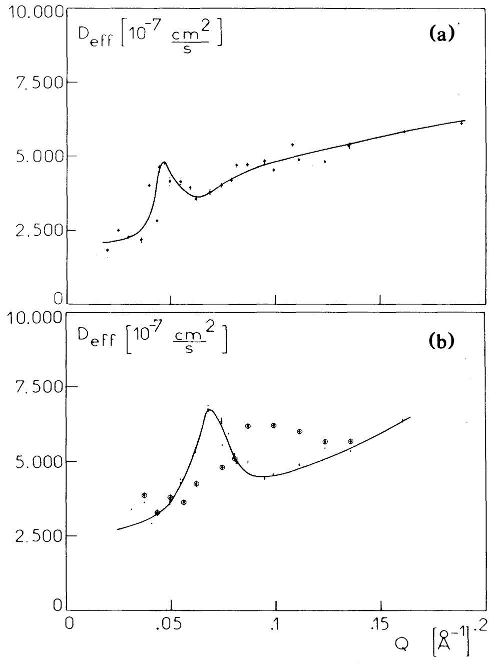

FIG. 2. (a) The effective diffusion constant Γ/Q^2 vs Q for the microemulsion with a mean droplet radius of 70 Å. The solid curve is drawn to guide the eye. (b) The effective diffusion constant Γ/Q^2 vs Q for the microemulsion with a mean droplet radius of 50 Å. The solid curve is drawn through the crosses to guide the eye. The crosses represent data obtained for scattering from shells, and the filled circles are data obtained for scattering from spheres of the same size.

TABLE I. The molar ratio of D_2O to AOT in this study is listed in column 1. The mean radius is listed in column 2, the peak position in column 3, and the peak height in column 4.

D_2O/AOT	Radius r_0 (Å)	$Q_m r_0$	$S=\Gamma/DQ_m^2$
40.8	70	3.15	2.4
32.6	59.2	3.2	2.3
4.5	48.7	3.30	2.3
16.3	38.3	3.16	2.2
8.2	27.5	3.16	2.2

tively understood on the basis of the scattering function of Eq. (1), which holds independently of any specific model of the dynamics.

We can distinguish between modes driven by elastic bending forces and those dominated by surface tension. From dimensional analysis we obtain in the case of bending elasticity a relaxation rate scaling as $\tau^{-1} \sim K_c/\eta r_0^3$, where K_c is the curvature elastic modulus. For the case of modes driven by surface tension σ, $\tau^{-1} \sim \sigma/\eta r_0$ should hold.[15] Since the line broadening due to translation diffusion at the peak position ($Qr_0 \simeq 3.1$) DQ_m^2 scales as r_0^{-3}, we obtain for the ratio of peak height to diffusion constant $s \equiv \Gamma/DQ_m^2$, a value which is independent of r_0 for bending forces and goes as r_0^2 for surface tension. According to Table I, the measurements performed on samples with radii from 70 to 30 Å give $S \simeq$const, consistent with a mode driven by bending elasticity.

To calculate the peak height beyond simple scaling arguments, the work of Schneider, Jenkins, and Webb[17] has been extended and modified by Milner and Safran.[18] The expression of Schneider, Jenkins, and Webb for mode relaxation rates is extended to nonzero spontaneous curvature. Reference 18 also accounts for the effect on the dynamics of nearly constant interfacial area per surfactant molecule under varying conditions. (A constant interfacial area per surfactant head is assumed with some experimental justification.[19])

In equilibrium, microemulsion droplets exchange surfactant, and only the total volume of surfactant (and thus total droplet area) is conserved. Safran[20] has calculated mean square shape fluctuations in equilibrium, which give rise to a mean excess surface area. (The excess area is the difference between the actual droplet area and that of a sphere with equivalent volume.) On the time scale of the shape fluctuations of a droplet, which at concentrations of a few percent is shorter than the mean collision time of droplets, surfactant is not exchanged between droplets. Thus, the mean excess surface area of Ref. 20 is taken as a constraint of the shape dynamics of a droplet.

For the damping frequency of the lth mode, the result from Ref. 18 is

$$\omega_l = \tau_l^{-1} = \frac{K_c}{\eta r^3} \frac{(l+3)(l-2)+4w}{Z(l)}, \tag{2}$$

and (invoking equipartition) the amplitude of the lth mode is

$$\langle |a_{lm}|^2 \rangle = \frac{kT}{K_c} \{(l+2)(l-1)[l(l+1)-6+4w]\}^{-1}, \tag{3}$$

where $w=r_0/r_s$ (r_s is the spontaneous radius of curvature), and

$$Z(l)=(2l+1)(2l^2+2l-1)/l(l+1)(l+2)(l-1)$$

is given in Ref. 18. At finite r_s, a small temperature-dependent entropy-of-mixing term can be neglected in the above expressions.

Since the experimental spectra show a smooth decay even in the peak region, the droplet shape relaxation rates have to be of the same order as the relaxation rate due to translational diffusion. Therefore, to a good approximation, the experimentally measured decay times are identical to the initial slope of $S(Q,t)$, the mean decay rate of the modes weighted by their amplitudes and form factors. Thus the effective decay rate is

$$\bar{\Gamma}(Q) = DQ^2 + \left(\sum_{l>1} \omega_l f_l(Qr)(2l+1)\langle |a_{lm}|^2 \rangle \right) \left\{ 4\pi[j_0(Qr)]^2 + \sum_{l>1} f_l(Qr)(2l+1)\langle |a_{lm}|^2 \rangle \right\}^{-1}. \tag{4}$$

For the range of accessible Qr_0, the denominator (the static structure factor) is dominated by the first two terms (the undistorted spherical shell and the $l=2$ mode). In the numerator the $l=2$ mode accounts for about half of the sum, on the assumption that the summation cuts off at $l \sim r_0/l_0 \sim 5$, where l_0 is the surfactant size.

We take into account polydispersity in the expression for $\Gamma(Q)$ by averaging numerator and denominator over the different radii in the sample. Near $Qr_0=\pi$, the main effect is to replace the vanishing $j_0^2(\pi)$ with $\langle \delta r_0^2 \rangle / r_0^2$; this variance is an equilibrium property which may be either measured or predicted.[11,13,20] According to Safran, the dispersion corresponding to the mean $l=0$ fluctuation of the ensemble is given by

$$\langle \delta r_0^2 \rangle / r_0^2 = kT/8K_c(3-2r_0/r_s).$$

With this a simple semiquantitative result for $\Gamma(Qr_0=\pi)$ follows:

$$\bar{\Gamma}(Qr=\pi) \simeq D\left(\frac{\pi}{r}\right)^2 + \frac{(0.53)K_c}{\eta r^3} \left(\frac{\pi/2}{\frac{3}{2}-w} + \frac{0.15}{w} \right)^{-1}. \tag{5}$$

For $w = r_0/r_s$ intermediate between zero and $\frac{3}{2}$ (which are the limits of stability of droplet phase microemulsions), the r_0 dependence of the denominator is weak, giving $\Gamma \sim r_0^{-3}$.

Using Eq. (5), we can estimate the value for the bending elastic constant K_c. For $r_0/r_s = 0.5$, we have

$$K_c/kT = (\pi/0.9)[\Gamma/DQ_m^2 - 1]. \tag{6}$$

For $\Gamma/DQ^2 \approx 2.5$ and $Qr_0 = \pi$, we have $K_c \approx 5kT$, an eminently reasonable value.[21]

In summary, we have successfully used quasielastic neutron scattering to probe the dynamics of the shape fluctuations of microemulsion droplets. It is found that these thermal fluctuations can be described by the overdamped bending elastic modes of the surfactant layer while the surface tension seems to play a very minor role, if any. The bending elastic constant for this layer is estimated to be about $5kT$.

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

[2] This is estimated by the surfactant packing area per molecule for an AOT-water-decane system. It is known that the surfactant resides almost exclusively on the interface and the packing density is about 65 Å^2 per molecule.

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[15] The Reynolds number is $R_e = \rho v L/\mu \simeq 0.001$ for the microemulsion system, and so the motion is completely dominated by viscous forces. (μ is the kinematic viscosity of the solution.) Also see J. S. Huang and W. W. Webb, Phys. Rev. Lett. **23**, 160 (1969).

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