Structure of Dense Sodium Di-2-Ethylsulfosuccinate/D_2O/Decane Microemulsions

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(Received 4 June 1984)

Small-angle neutron scattering is used to investigate the structure of single-phase AOT (sodium di-2-ethylsulfosuccinate)/D_2O/decane microemulsions containing equal volumes of water and oil and a variable concentration of surfactant. Each scattered-neutron spectrum exhibits a pronounced interaction peak. As the volume fraction of AOT is increased from 0.18 to 0.42, the peak position shifts to larger values of Q, and the peak height diminishes. The spectra are consistent with an ordered droplet phase, as opposed to a bicontinuous structure.

PACS numbers: 61.12.Dw, 61.25.-f

Certain proportions of oil and water, sufactant, and usually, alcohol (cosurfactant) can be dissolved to form a transparent, isotropic fluid referred to as a microemulsion. For dilute water-in-oil systems, it is widely accepted that microemulsions are dispersions of submicroscopic surfactant-coated water droplets in a continuous oil phase.[1-3] However, for microemulsions containing comparable proportions of the various components, the microstructure is still unclear.[2,3]

At present, the literature shows that extensive experimental studies are primarily being performed on two model microemulsion systems. The first is the SDS-alcohol-brine-oil system, where SDS (sodium dodecyl sulfate) is a single-chain amphiphile with a hydrocarbon tail length of 16.7 Å and a tail-to-head volume ratio of about 4. Recent experimental data on SDS microemulsions containing comparable volumes of water and oil indicate the presence of a bicontinuous structure, characterized by randomly intertwined continuous water and oil domains.[4] The second system, AOT-water-oil, where AOT stands for sodium di-2-ethylsulfosuccinate, contains a branched double-chain surfactant with a tail length of about 9 Å and a tail-to-head volume ratio of about 7. According to a recent statistical thermodynamic theory developed by Safran,[5] the structure of a microemulsion is primarily determined by the elastic bending energy of the surfactant film separating the oil and water domains. The bulkiness of the AOT surfactant tail relative to the head group causes adjacent surfactant molecules to pack so that the film develops a highly preferred radius of curvature. The tendency for the surfactant layer to bend spontaneously is much greater in the AOT system than in the SDS system, suggesting that it may be possible that droplets continue to exist even at high concentrations in AOT-water-oil microemulsions. In this Letter, we report small-angle neutron-scattering (SANS) experiments performed on single-phase AOT-D_2O-n-decane microemulsions containing equal volumes of water and oil. The data seem to indicate that the droplet structure is indeed maintained.

The three-component microemulsions consisted of AOT dissolved in equal volumes of heavy water and normal decane. The AOT surfactant, supplied by Fluka, was twice recrystallized from methanol,[1] and the n-decane was a 99+% gold label product from Aldrich Chemical Company. The heavy water contained 99.96 at.% D_2O and 0.04 at.% H_2O. The volume fraction ϕ_s of surfactant was varied from 0.18 to 0.42, corresponding to a volume fraction ϕ of water + surfactant of 0.59 to 0.71. The volume fraction of surfactant was computed from the specific volume of dry AOT (0.8789 cm^3/g). Each sample was enclosed in a 1-mm path length cylindrical reentrant cell with 1-mm-thick quartz windows, and maintained at 25 °C.

The experiment was conducted at the National Center for Small Angle Scattering Research at the Oak Ridge National Laboratory. The incident neutron wavelength of $\lambda = 4.75$ Å ($\Delta\lambda/\lambda \cong 0.04$) was derived from the Oak Ridge research reactor. An 18×17-cm^2 two-dimensional position-sensitive proportional counter with a pixel size of 0.3×0.3 cm^2 was used for neutron detection. SANS spectra were obtained for a range of wave-vector transfers of $1.2\times10^{-2} \leq Q \leq 1.2\times10^{-1}$ Å^{-1}; $Q = (4\pi/\lambda) \times \sin\theta/2$, where θ is the scattering angle. The average instrumental broadening $\langle \delta Q^2 \rangle^{1/2}$ was determined to be 3×10^{-3} Å^{-1}. A pure *n*-decane sample was used both to calibrate spatial nonuniformity of the detector sensitivity and to determine incoherent scattering. After correcting the two-dimensional data sets for sensitivity, transmission, solvent scattering, and background, an on-line computer performed a radial average of the data arrays, giving values of the relative scattering intensity versus Q. Finally, the intensity spectra were converted to an absolute scale in units of differential cross section per unit volume $d\Sigma/d\Omega$ (cm^{-1}).

Three representative SANS spectra are shown as a function of surfactant concentration in Fig. 1. The respective microemulsion compositions are indicated in the single-phase region of the accompanying ternary phase diagram. Each spectrum is characterized by a pronounced maximum in the scattered intensity. As the surfactant volume fraction ϕ_s increases, the peak position $Q_{\max}$ exhibits an approximately linear shift to larger values of Q, while the peak height rapidly diminishes. Because the widths of the peaks are much broader than the experimental Q resolution determined from instrumental broadening, one can conclude that the scattering maxima represent interaction peaks characteristic of a liquid microemulsion structure, rather than pure Bragg scattering. Furthermore, the position of the peak is not appreciably affected by the finite Q resolution.

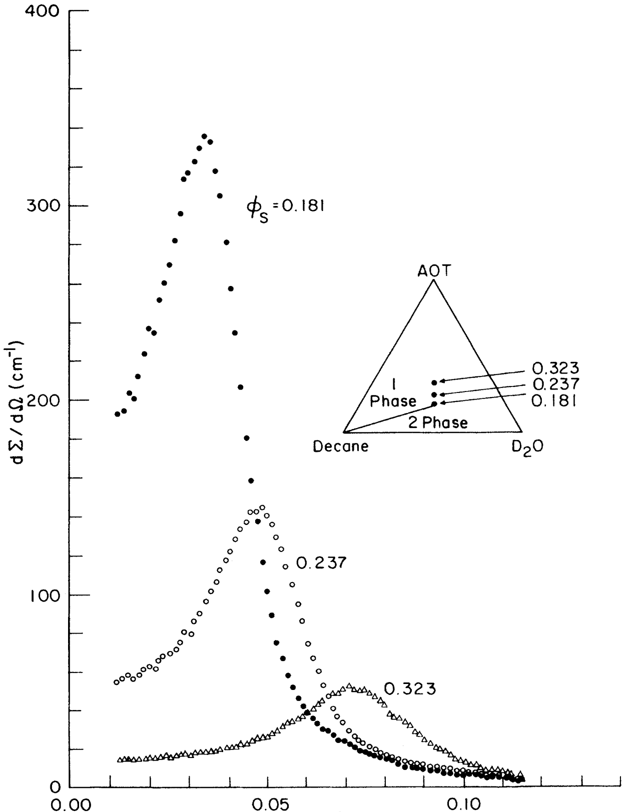

FIG. 1. Representative SANS spectra from concentrated AOT–D$_2$O–*n*-decane microemulsions with equal volumes of water and oil. ϕ_s is the volume fraction of surfactant. The microemulsion compositions are indicated in the single-phase region of the ternary phase diagram (25 °C).

The shift in peak position can be explained by assuming that the microemulsion is a dispersion of surfactant-coated water droplets having a very well-defined nearest-neighbor structure, e.g., resembling a face- or body-centered cubic (fcc or bcc) lattice. The surfactant layer is invisible to neutrons since its scattering length density is closely matched to that of the solvent oil. By the assumption of a local crystallike structure that does not persist to infinite range, the liquid nature of the phase is preserved, and diffraction past the first-order peak should be relatively insignificant.

For spherical particles, the area per droplet is just

$$A_d = 4\pi R^2, \tag{1}$$

where R is the radius of the droplet water core. If we assume that each surfactant molecule tends to arrange itself in such a way that it subtends a constant surface area and occupies a constant volume, then the number of surfactant molecules coating each droplet is given by

$$N_d = (\phi_s/v_s)/n_p. \tag{2}$$

v_s is the volume occupied by a surfactant molecule and n_p is the number density of droplets, given by

$$n_p = \phi_c/\tfrac{4}{3}\pi R^3. \tag{3}$$

Here, ϕ_c is the volume fraction occupied by the droplet cores. One can now define an area per surfactant molecule, a_H, by using $a_H = A_d/N_d$. The net result is

$$R = (3v_s/a_H)(\phi_c/\phi_s). \tag{4}$$

A second equation can be written by use of the Bragg scattering condition. For either an fcc or a bcc lattice, the first-order diffraction condition is given in terms of the mean distance between a particle and its nearest neighbors $\bar{d}$ as

$$Q_{\max} = \pi\sqrt{6}/\bar{d}. \tag{5}$$

A final equation is obtained by using the packing condition of spheres in a cubic unit cell:

$$R = \alpha\phi_c^{1/3}\bar{d}. \tag{6}$$

Here, the constant α is 0.5527 for an fcc lattice and 0.5685 for a bcc lattice. By combining Eqs. (4)-(6), one can eliminate R and $\bar{d}$ to obtain

$$Q_{\max} = (1.418/\Delta)(\phi_s/\phi_c^{2/3}), \tag{7}$$

where $\Delta = v_s/a_H$ is approximately the length of an AOT molecule. We have taken the fcc lattice to be the most probable local structure in a system of attracting spherical droplets.[1]

One should assume that the volume fraction of droplet cores includes the volume fraction of water ϕ_w, plus that of the surfactant head groups ϕ_H, i.e., $\phi_c = \phi_w + \phi_H$. This relation, along with the condition for equal water and oil volumes, $\phi_w = (1-\phi_s)/2$, allows one to eliminate ϕ_c from Eq. (7) to obtain

$$Q_{\max} = \frac{2.25}{\Delta}\frac{\phi_s}{(1-\phi_s)^{2/3}}\left(1+\frac{\phi_H}{\phi_w}\right)^{-2/3}. \tag{8}$$

Consider the factor $(1+\phi_H/\phi_w)^{-2/3}$. This can be rewritten as $[1+2(v_H/v_s)\phi_S/(1-\phi_s)]^{-2/3}$, where v_H is the volume of a single surfactant head. For AOT, the ratio v_H/v_s is approximately 0.12. By use of the largest surfactant concentration encountered in our measurements, i.e., $\phi_s = 0.42$, the entire factor turns out to be 0.9. Lower surfactant concentrations give values even closer to unity. We therefore proceed by neglecting this factor in Eq. (8) with the understanding that the expression for $Q_{\max}$ is being affected by less than 10%. The equation we will use is

$$Q_{\max} = (2.25/\Delta)[\phi_s/(1-\phi_s)^{2/3}]. \tag{9}$$

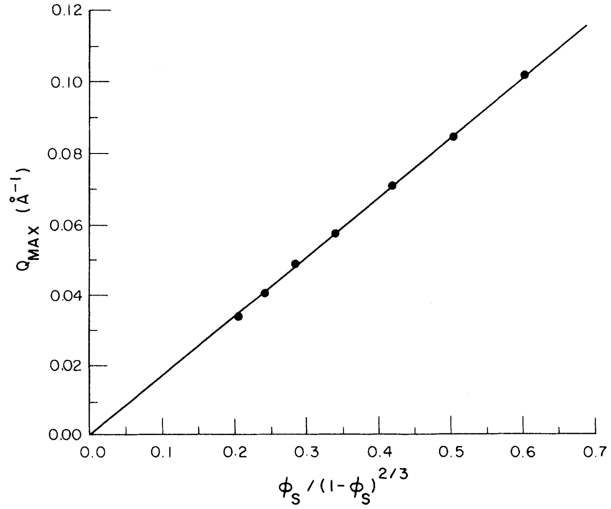

FIG. 2. SANS peak position $Q_{\max}$ vs $\phi_s/(1-\phi_s)^{2/3}$, where ϕ_s is the volume fraction of surfactant.

The experimental values of $Q_{\max}$ are plotted against $\phi_s/(1-\phi_s)^{2/3}$ in Fig. 2. It is shown that the data points follow a straight line passing through the origin, as predicted by Eq. (9). It turns out that this is possible only when the denominator of the abscissa, $(1-\phi_s)^{2/3}$, is present. This factor is a consequence of assuming that spherical droplets exist. From the slope of the line, one extracts a surfactant length Δ of 13.3 Å, a value very close to what one expects for AOT.

The parameters of the ordered droplet phase can be easily extracted from the previous equations. Table I summarizes the numerical results. As the surfactant concentration increases, the sphere size diminishes. At the same time, the packing density of the spheres increases.

In order to characterize the liquidlike structure more quantitatively, we attempted to extract the average interparticle structure factor $\bar{S}(Q)$ from the cross-section data $d\Sigma(Q)/d\Omega$ by using the relation[1]

$$d\Sigma(Q)/d\Omega = n_p P(Q)\bar{S}(Q), \tag{10}$$

where $P(Q)$ is the average form factor for a sphere, as given by

$$P(Q) = \left\langle\left[\Delta\rho\left(\frac{4\pi}{3}R^3\right)\frac{3j_1(QR)}{QR}\right]^2\right\rangle. \tag{11}$$

$\Delta\rho$ is the scattering-length density difference between decane and D_2O (6.832×10^{-6} Å^{-2}). The angular brackets represent an average over droplet polydispersity, assuming a Schultz distribution.[6] The mean size of the droplet core is taken as R from Table I, and the half-width of the size distribution is taken to be 20% of the mean, i.e., a polydispersity consistent with previous results from

TABLE I. Parameters of ordered droplet phase as determined from the SANS peak position $Q_{\max}$ at various values of the surfactant volume fraction ϕ_s. R is the radius of the droplet core and n_p is the droplet number density. $\bar{d}$ denotes the mean distance between a central particle and its nearest neighbors.

ϕ_s	$Q_{\max}$ (Å^{-1})	$\bar{d}$ (Å)	R (Å)	n_p (10^{17} cm^{-3})
0.181	0.034	226	92.9	1.22
0.209	0.041	188	76.2	2.14
0.237	0.049	157	63.0	3.65
0.275	0.058	133	52.3	6.05
0.323	0.071	108	41.8	11.10
0.371	0.085	91	34.0	19.04
0.420	0.102	75	27.6	32.90

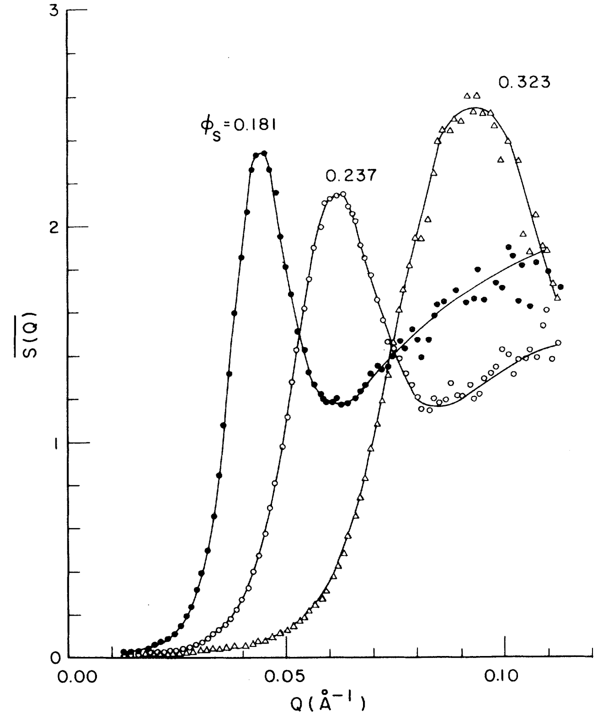

FIG. 3. Average structure factors $\bar{S}(Q)$ extracted from the SANS spectra of Fig. 1.

dilute droplet phases.[1] The value of n_p is obtained from Eq. (3) and is listed in Table I.

Some extracted structure factors are depicted in Fig. 3. $\bar{S}(Q)$ exhibits a liquidlike oscillatory behavior, with the first diffraction peak gradually shifted to a larger Q value and broadened as ϕ_s increases. The zero-angle structure factor $\bar{S}(Q)$ nearly vanishes, indicating the incompressibility of the high-density droplet structure. The fact that the height of the first peak is nearly constant at about 2.4 is evidence that the particle form factor $P(Q)$ was calculated correctly from the R values given in Table I. It is also seen that the determination of $\bar{S}(Q)$ past the first diffraction peak is difficult because of the poorer SANS counting statistics at large values of Q and because of polydispersity. The height of the first peak and subsequent minimum depend sensitively on the choice of droplet polydispersity.

In summary, we have demonstrated that the major features of the SANS spectra from high-concentration microemulsions can be understood in terms of an ordered arrangement of densely packed droplets. It is nevertheless interesting to compare the features of the SANS data with the model of a bicontinuous structure.[7] If ξ is the correlation length in such a phase, then it can be demonstrated that $\xi^{-1}=(2/3\Delta)\phi_s$.[8] By assuming that $Q_{\max}=2\pi(\sqrt{3}\xi)^{-1}$, one obtains the result $Q_{\max}=(2.96/\Delta)\phi_s$. A plot of $Q_{\max}$ vs ϕ_s does indeed give a straight line with approximately the correct slope; however, the line fails to pass through the origin by a wide margin.[8] This is because the factor $(1-\phi_s)^{2/3}$ is absent from the denominator of the abscissa.

This research is supported by the National Science Foundation, the Petroleum Fund of the American Chemical Society, and the Exxon Research and Engineering Company.

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