

## Attractive Interactions in Micelles and Microemulsions

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We have used small-angle neutron scattering to study surfactant interactions in an inverted micellar and a related microemulsion system. The structure-factor fits imply an attractive interaction between micelles with a short-ranged potential due to the overlapping of the surfactant hydrocarbon tails. The linear increase in this interaction with size accounts for the critical transition observed in the microemulsion. This analysis is confirmed by Monte Carlo simulations.

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The structure of a three-component water-in-oil microemulsion near the critical point has recently been determined by small-angle neutron scattering.<sup>1,2</sup> The microemulsion is composed of small water droplets (radius  $R \cong 50 \text{ \AA}$ ) coated with a layer of surfactant [aerosol OT (AOT)] dispersed in oil. This system is known to be thermodynamically stable<sup>3</sup> and exhibits critical phenomena<sup>4,5</sup> characteristic of a gas-liquid transition. However, the van der Waals-Hamaker interaction between the droplets is not sufficient to drive the critical phase transition at the observed droplet size and concentration ( $\cong 10 \text{ vol. \%}$ ).<sup>6,7</sup> Recently, Lemaire, Bothorel, and Roux<sup>7</sup> proposed that the attraction is due to the mutual interpenetration of the surfactant tails. This model is consistent with the light-scattering data by Roux and co-workers<sup>8</sup> for a four-component water-in-oil system.

In the present work we describe analysis of our small-angle neutron-scattering (SANS) data obtained in both the micellar and microemulsion systems containing AOT surfactant. We find that the analytical expression obtained by Sharma and Sharma<sup>9</sup> for the structure factor [ $S(Q)$ ] of the hard-sphere liquid with an attractive square-well potential can be suitably modified to deal properly with the short-ranged (compared with the diameter of the droplets) but strong (compared with the thermal energy  $k_B T$ ) interactions found in the micellar systems. The neutron studies provide detailed information since the fits to the structure factor are sensitive to both the range and the strength of the interaction. Light scattering measurements of  $S(0)$

measure only the second virial coefficient of the attraction,  $A = 8(\lambda^3 - 1)(e^{\epsilon'} - 1)$ , where  $\bar{\lambda} = \lambda - 1$  is the range of the attraction in units of the droplet diameter and  $\epsilon'$  is the strength of the interaction in units of  $k_B T$ .

The validity of the modified  $S(Q)$  was tested by Monte Carlo simulations. The fits to the structural data imply a square-well potential with a very short range of about  $3 \text{ \AA}$ . These values are used to fit our SANS data for inverted micellar (micelles in oil) solutions with volume fractions ranging from 0.88% to 34%. The same form of the interaction potential is used to describe the SANS measurements for the microemulsions satisfactorily; the physical range of the interaction ( $2R\bar{\lambda}$ ) is kept fixed, while the strength of the interaction is varied in accordance with the interpenetration model.<sup>8</sup> This interaction is sufficient to induce phase separation and the associated critical phenomena in the attractive hard-sphere system which models our microemulsions. The interaction is much stronger for the microemulsions than for the micelles because of the larger radius of the microemulsion droplets; the fits are consistent with the suggestion<sup>8</sup> that the interaction varies linearly with size.

In order to increase the contrast of the micelles for neutron scattering, we used a 98% deuterated octane as the solvent. The weight-to-volume ratio of surfactant to oil (in grams per  $100 \text{ cm}^3$ ) in the samples studied were 1.25, 3.79, 12.5, 24.08, 35.66, and 58.82. Typical results for a temperature  $T = 25^\circ \text{C}$  are shown in Fig. 1. The radius of gyration of the micelles at 1.25 wt. % is  $11.7 \text{ \AA}$ , corre-

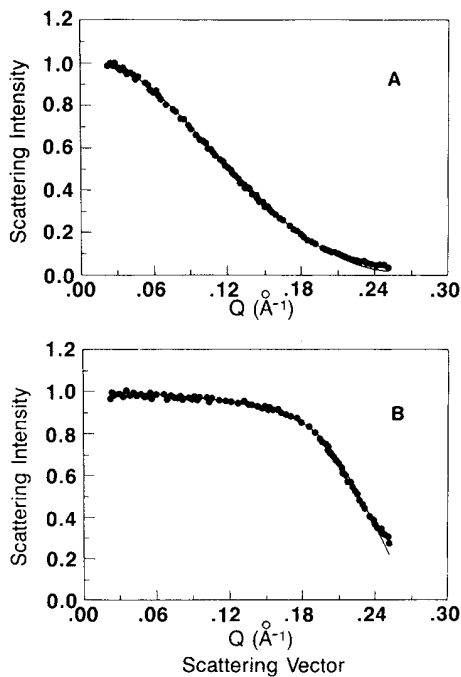


FIG. 1. Intensity spectra of the AOT micelles in deuterated octane at two concentrations: (a) 1.25 (wt./vol)%, and (b) 58.82%. The solid curves represent the mean-spherical-approximation fit with  $\epsilon=1.5$  and  $\lambda=1.08$ . Similar fits are obtained for other concentrations with the same fitting parameters.

sponding to a radius of  $15 \text{ \AA}$ , which agrees with the published values.<sup>10</sup> To analyze the data properly, we take into account the interparticle structure factor  $S(Q)$  as well as the single-particle scattering form factor,  $P(Q)$ :  $I(Q) = nP(Q)S(Q)$ , where  $I$  is the scattering intensity and  $n$  is the number density of the monodispersed particles. The form factor of uniform spheres can be expressed in terms of the first spherical Bessel function  $j_1$  and we use the expression for  $S(Q)$  derived by Sharma and Sharma<sup>9</sup> in the mean-spherical approximation with an attractive, effective square-well potential  $U(r)$ :  $U(r) = \infty$  for  $r < 2R$ ,  $U(r) = -\epsilon k_B T$  for  $2R \leq r \leq 2\lambda R$ ,  $U(r) = 0$  for  $r \geq 2\lambda R$ . Allowing  $\lambda$  and  $\epsilon$  to float, we find that the mean-spherical-approximation (MSA) calculations fit the measured spectra reasonably well at all concentrations for  $\lambda=1.08$  and  $\epsilon=1.5$  (Fig. 1, solid curves). For the microemulsion consisting of 7.5 vol% of AOT and  $D_2O$  in decane, we fit the scattering spectrum with  $\lambda$  fixed at 1.02 as determined from the micellar data and a value of  $\epsilon=46$  which corresponds (see below) to a microscopic interaction roughly four times the micellar value. This is consistent with the interpenetration model,<sup>8</sup> where the strength of in-

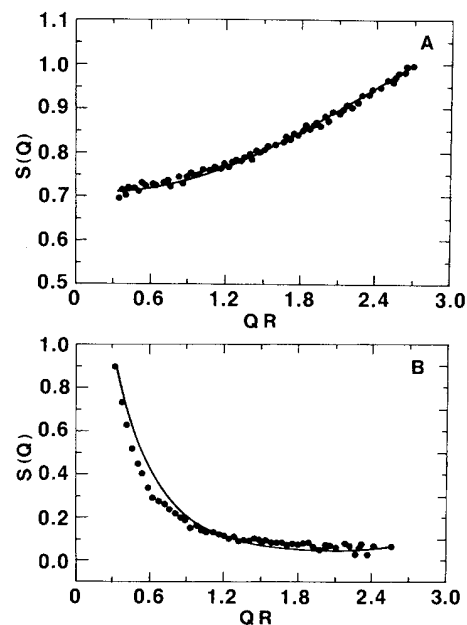


FIG. 2. Structure factor  $S(Q)$  determined from neutron-scattering spectrum, as a function of  $QR$ . The points are the experimental data and the line is a fit by the mean-spherical approximation described in the text. (a) Results for micelles (volume fraction  $\phi=6.6\%$ , well depth  $\epsilon=1.50$ , range  $\lambda=1.08$ , and radius  $R=15.5 \text{ \AA}$ ). (b) Results for microemulsions ( $\phi=7.5\%$ ,  $\epsilon=46$ ,  $\lambda=1.02$ , and  $R=60 \text{ \AA}$ ).

teraction scales linearly with the radius, for the best-fit radius of the microemulsion is  $R=60 \text{ \AA}$  including the surfactant layer while for the micelles,  $R=15 \text{ \AA}$ . Examples of the fits to  $S(Q)$  for both the micelles and microemulsions are shown in Fig. 2.

To test the validity of the mean-spherical approximation for  $S(Q)$ , we have performed Monte Carlo (MC) simulations on systems of spherical particles with attractive, square-well interactions. Standard<sup>11</sup> Metropolis algorithms were used for systems of both 500 and 108 particles in a cubic box with periodic boundary conditions. Typically, 2000 MC steps per particle were run to equilibrate the system and an additional 4000 MC steps per particle were run for the calculations of  $S(Q)$ . Simulations were performed for values of the volume fraction  $\phi$ , well breadth  $\lambda$ , and an effective well depth  $\epsilon$  appropriate to the experiments described above. However, because of the extremely short range of the interaction for the microemulsion case ( $\lambda \cong 0.02$ ), the value of the microscopic well depth  $\epsilon'$  is related to  $\epsilon$  in the Sharma formula by  $\epsilon' = \log(\epsilon + 1)$ . This substitution is consistent with a virial expansion of the free energy, whose second derivative is proportional

to  $S^{-1}(0)$ . For typical liquids, with weak but relatively long-ranged interactions,  $e^{\epsilon'} - 1 \cong \epsilon$ , while for the microemulsions the exponential form must be used.

With this modification, the mean-spherical approximation provides a satisfactory fit to the MC simulations as shown in Fig. 3. For the dilute micellar case,  $\phi = 7.0\%$ ,  $\epsilon' = 0.92$ , and  $\lambda = 1.1$ , the Sharma formula underestimates  $S(Q)$  at small wave vectors. On the other hand, for the dilute microemulsion ( $\bar{\lambda} = 0.02$ ,  $\epsilon' = 3.83$ ,  $\phi = 7\%$ ), conditions are much closer to criticality ( $A_c \cong 21$ ,  $\phi_c = 13\%$  in mean-field theory<sup>12</sup>). The mean-spherical model results in a value for  $A_c$  which is slightly larger than the true critical value and hence overestimates the small- $q$  fluctuations for  $A \sim A_c$ .

The physical importance of these results can be summarized as follows: Both the micelles and microemulsions are modeled by a system of spheres which interact with a short-range, but strong, potential. This is consistent with an attraction due to

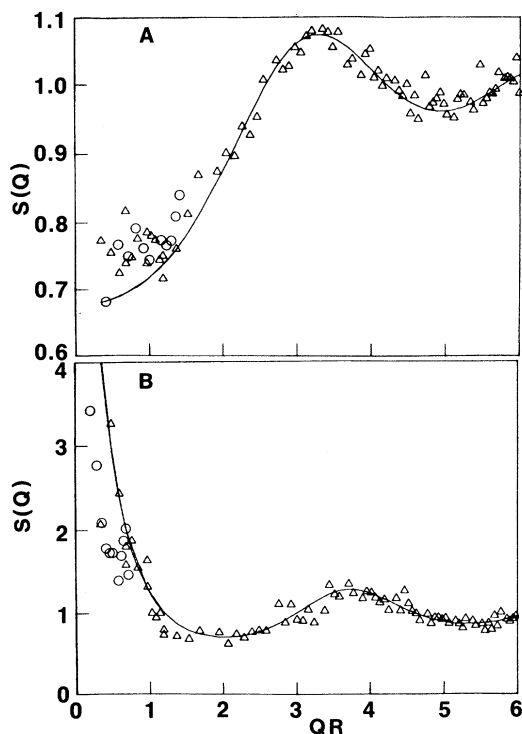


FIG. 3. Calculated structure factor  $S(Q)$  plotted as a function of  $QR$ . (a) Results for micelles (volume fraction  $\phi = 7\%$ , well depth  $\epsilon' = 0.92$ —corresponding to  $\epsilon = 1.5$ —and range  $\lambda = 1.1$ ); (b) Results for microemulsions ( $\phi = 7\%$ ,  $\epsilon' = 3.83$ —corresponding to  $\epsilon = 45$ —and  $\lambda = 1.02$ ). The solid line is the modified mean spherical approximation. The triangles are the Monte Carlo results for 108 particles and the circles are the results for 500 particles.

the penetration of the surfactant tails on two adjacent globules. In microemulsions with cosurfactants, this penetration length is limited by the alcohol,<sup>8</sup> while for the simpler AOT-water-decane systems, this length is limited by the double-chain structure of the surfactant.<sup>13</sup> The structural information obtained from  $S(Q)$  corroborates this interpretation. The range of the attraction relative to the sphere diameter,  $\bar{\lambda}$ , is 0.02 for microemulsions ( $R = 60 \text{ \AA}$ ) and 0.08 for micelles ( $R = 15 \text{ \AA}$ ); the microscopic penetration length is  $2.4 \text{ \AA}$  for both cases and is thus due to interactions only at the tips of the surfactant tails. In addition, the neutron-scattering fits are consistent with a linear increase of the microscopic well depth  $\epsilon'$  with radius, since for the microemulsions with  $R = 60 \text{ \AA}$ ,  $\epsilon' = 3.83$ , while for micelles with  $R = 15 \text{ \AA}$ ,  $\epsilon' = 0.92$ . The importance of the full expression for the virial ( $e^{\epsilon'} - 1$ ) can be seen from these values. The linear dependence of the well depth on the globule radius is due to the increase in interpenetration volumes. With the virial coefficient a known function of radius (and hence of water and surfactant volume fractions), the phase diagram as a function of concentration can be calculated.<sup>12</sup>

Finally, the identification of the interglobular attraction with the penetration of the surfactant tails over some short distance may explain the unusual increase of  $A$  with increasing temperature<sup>4</sup> and oil chain length<sup>8</sup> for these water-in-oil systems. The AOT-water-oil microemulsions show phase separation as the temperature is raised (lower critical solution temperature) in contrast to the conventional liquid-gas or binary fluid transitions. Since the interactions involve penetration to about  $3 \text{ \AA}$ , they are relatively insensitive to the detailed nature of the chains. In particular, surfactant-oil and surfactant-surfactant interactions should be almost identical. However, at finite temperatures the oil molecules are neither optimally oriented nor optimally packed to interact with the surfactant shell of the globules. On the other hand, surfactant molecules on adjacent globules are (in the absence of curvature effects) optimally oriented and packed, due to the globular geometry and hence provide a net attractive interaction. As the temperature is lowered, the attraction of the background oil fluid to the surfactant orients the oil molecules at the globule interface. The oil molecules thus take advantage of the surfactant attraction and decrease the net surfactant-surfactant interaction. At high temperatures, this reduces the bare surfactant-surfactant interaction by the factor proportional to  $1/T$  and thus causes lower critical solution behavior.

A similar argument applies to the observed trend of decreasing net attraction with decreasing oil chain length, where the larger radius of gyration of the longer chains prevents them from close packing on the surfactant interface. The surfactants from other globules are optimally packed and hence have a larger net attraction. As the oil chain length decreases, the difference between oil and surfactant packing decreases; the net attraction of two globules is thus reduced.

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<sup>1</sup>M. Kotlarchyk, S. H. Chen, and J. S. Huang, *Phys. Rev. A* **28**, 508 (1983).

<sup>2</sup>M. Kotlarchyk, S. H. Chen, J. S. Huang, and M. W. Kim, *Phys. Rev. A* **29**, 2054 (1984).

<sup>3</sup>John S. Huang and Mahn Won Kim, in Proceedings

of the Varenna Summer School, Varenna, Italy, 1983 (to be published).

<sup>4</sup>John S. Huang and Mahn Won Kim, *Phys. Rev. Lett.* **47**, 1462 (1981).

<sup>5</sup>John S. Huang and Mahn Won Kim, in *Scattering Techniques Applied to Supramolecular and Non-equilibrium Systems*, edited by S. H. Chen, B. Chu, and R. Nassal (Plenum, New York, 1981), p. 809.

<sup>6</sup>C. Huh, *J. Colloid Interface Sci.* **71**, 425 (1979).

<sup>7</sup>B. Lemaire, P. Bothorel, and D. Roux, *J. Chem. Phys.* **87**, 1023 (1983).

<sup>8</sup>S. Brunetti, D. Roux, A. M. Bellocq, G. Fourche, and P. Bothorel, *J. Chem. Phys.* **83**, 1028 (1983); D. Roux, A. M. Bellocq, and P. Bothorel, in Proceedings of the International Symposium on Surfactants in Solution, edited by K. L. Mittal and B. Lindman (Plenum, New York, to be published).

<sup>9</sup>P. V. Sharma and K. C. Sharma, *Physica (Utrecht)* **89A**, 213 (1977).

<sup>10</sup>Martin Zulfaff and Hans-Friedrich Eicke, *J. Chem. Phys.* **83**, 480 (1979).

<sup>11</sup>*Monte Carlo Methods in Statistical Physics*, edited by K. Binder (Springer, Berlin, 1979).

<sup>12</sup>S. A. Safran and L. A. Turkevich, *Phys. Rev. Lett.* **50**, 1930 (1983).

<sup>13</sup>See, for example, *Merck Index*, edited by P. G. Stecher (Merck and Co., Rahway, New Jersey, 1968).