

Theory of Microemulsions: Comparison with Experimental Behavior[†]

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A thermodynamic model for microemulsions (previously described) is used to predict some further aspects of the phase behavior. The stability of the microemulsion under variation of molecular parameters (such as the bending constant and spontaneous curvature of the surfactant monolayer) is discussed. An appropriate cut through the multidimensional parameter space yields the characteristic "fish" phase diagram, as found experimentally. Our model exhibits a phase behavior close to the experimental one, not only in terms of the variation with surfactant concentration but also in terms of the sensitivity of the phase diagram to the nature of the surfactant, particularly its spontaneous curvature.

1. Introduction

In this paper, we study the phase behavior of microemulsions using a simple thermodynamic model. The model has been described in detail previously;¹ here we focus on some aspects of phase stability that appear particularly relevant to recent experimental investigations.²⁻⁸ Specifically, in section 3 we consider the case when oil and water volume fractions are equal and study the evolution of phase equilibria under variation of surfactant volume fraction (Φ_s), temperature (τ), and the elastic bending modulus (K_0) and spontaneous curvature (C_0) of the surfactant film. This film is modeled as an incompressible fluid monolayer, which covers the (extensive) two-dimensional interface between coherent domains of oil and water.¹

In experimental terms, the elasticity parameters K_0 and C_0 are expected to depend strongly on the particular surfactant selected, on the type and concentration of cosurfactant, on salt concentration, and also on temperature. While the relationships involved are rather complex, one expects qualitative comparison with experiment to be possible without knowing them in detail. For example, if the salt and/or cosurfactant concentration is chosen so as to obtain a maximally symmetric pseudoternary phase diagram, we expect this to correspond to a case when the monolayer has little or no spontaneous curvature ($C_0 \approx 0$).¹ By making small changes in salt and cosurfactant concentration, one can trace out some path in the (K_0, C_0) plane. To a first approximation, it seems reasonable to assume the salt concentration affects mainly C_0 rather than K_0 , whereas the cosurfactant concentration probably influences both parameters at once.⁹ In this way, a corre-

spondence can be made between the parameters of the model and experimental variables. Moreover, in some cases it is possible to study experimentally the elasticity parameters;¹⁰⁻¹² these measurements, when available, appear consistent with the various trends predicted by our model, as outlined in ref 1 and further elucidated in section 3.

Experimentally, two properties are of special interest. A microemulsion system is specially useful when the phase diagram presents a continuous path from pure oil to pure water. That means that adapting the amount of surfactant or surfactant-cosurfactant mixture allows one to prepare microemulsions of any water to oil ratio. The efficiency of the microemulsion can be characterized by the minimum amount of surfactant (Φ_s^m) needed to get a stable (one-phase) microemulsion phase for a mixture of equal amount of water and oil. It is of practical importance to make this value Φ_s^m as small as possible, since the cost of any commercial microemulsion is directly related to the amount of surfactant needed to make it. Generally for a given system, the amount of surfactant Φ_s^m is optimized when the phase diagram is symmetrical in oil and water; the microemulsion is then called balanced.

In the case of ternary systems with nonionic surfactant, an elegant way of representing such a behavior has been proposed by Kahlweit and colleagues.²⁻⁶ For these systems

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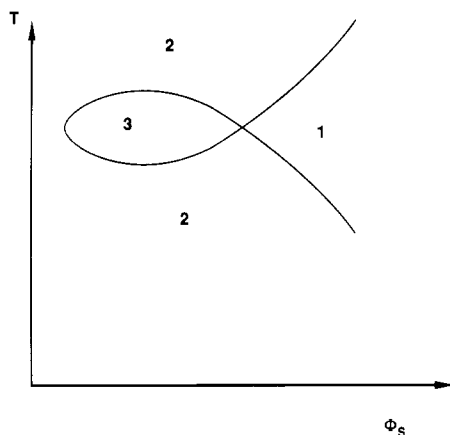


Figure 1. Schematic representation of a "fish". It corresponds to a cut of a ternary phase diagram for $\Phi_o/\Phi_w = 1$. The one-phase region is indicated as 1; 2 and 3 correspond respectively to two- and three-phase equilibria.

the temperature is the experimental parameter which controls the balance of the phase diagram. A cut of the phase diagram is made at a given oil/water ratio (usually 1) as a function of the temperature. The phase diagram has a characteristic shape (named "fish" by the authors). Figure 1 shows a schematic representation of a fish. The body corresponds to the three-phase equilibrium, and the tail is the one (microemulsion) phase. The characteristic shape indicates that Φ_s^m is minimum for the symmetric microemulsion.

2. Model for Microemulsions

The model presented here has evolved from earlier work of Talmon and Prager,¹³ Jouffroy, Levinson and de Gennes,¹⁴ and Widom.¹⁵ It has been described in detail elsewhere;¹ here we recall only the essential features.

The microemulsion is characterized by a single structural length scale, ξ . For convenience, we describe the structure in terms of a cubic lattice of side ξ ; the elemental cells of the lattice correspond to domains filled at random with either water (probability Φ) or oil (probability $1 - \Phi$). The surfactant resides in an incompressible monolayer at the oil-water interface; taking the thickness of this monolayer to be a , we find (using the random mixing approximation)

$$\xi/a = (6\Phi(1 - \Phi))/\Phi_s \quad (1)$$

This uniquely determines the cell size ξ in terms of the volume fractions of surfactant (Φ_s), water ($\Phi_w = \Phi - \Phi_s/2$), and oil ($\Phi_o = 1 - \Phi_w - \Phi_s$). The entropy density, according to this construction, is simply

$$S = -(1/\xi^3)k_B[\Phi \ln \Phi + (1 - \Phi) \ln (1 - \Phi)] \quad (2)$$

We now need to estimate the bending energy of the microemulsion. As constructed above, the curvature of the surfactant film at the oil-water interface is localized along the edges of the elementary cubes. A more realistic estimate of the bending energy density may be found by "rounding out" these edges into spherical sections, of radius $\xi/2$. Doing this, we obtain the following form:¹

$$F_{\text{bend}} = (8\pi/\xi^3) K(\xi) \Phi(1 - \Phi)[1 - 2C_0\xi(1 - 2\Phi)] \quad (3)$$

This expression corresponds to a harmonic expansion about the preferred curvature $C_0/2$; an unimportant term

(linear in Φ_s) has been adsorbed into the surfactant chemical potential. We define C_0 as positive for curvature toward water; note that $C_0 = 1/\rho_0$, where ρ_0 is the spontaneous radius of curvature as used in ref 1.

In eq 3, we have allowed for the fact that the effective bending constant, $K(\xi)$, evaluated at the coarse-grained length scale ξ , may differ from the microscopic value, K_0 . This difference reflects the fact that the interfacial film is subject to thermal fluctuations, corresponding to the excitation of undulation modes. These introduce a characteristic persistence length given by⁹

$$\xi_K = \alpha e^{(4\pi K_0)/(\alpha k_B T)} \quad (4)$$

where α is a numerical constant of order unity. At length scales ξ comparable to or larger than the persistence length, the effective rigidity of the surfactant film is much reduced, since the thermal undulations cause it to wander randomly at this scale. An estimate of the effect is given by perturbation theories,¹⁷ which predict

$$K(\xi) = K_0[1 - \tau \ln (\xi/a)] \quad (5)$$

with $\tau = (\alpha k_B T)/(4\pi K_0)$. In our calculations, we take $\alpha = 1$ as the numerical constant in eq 4 and 5.¹ In fact, the predictions are quite sensitive to α , but this dependence cannot be separated from the variation with other numerical parameters of the model (such as the geometrical factor 8π in eq 3, whose exact values are equally uncertain).

Equations 1-3 and 5 complete the specification of the microemulsion "branch" of the free energy surface, as a function of the parameters Φ , Φ_s , K_0 , C_0 , and T :

$$F_\mu = F_{\text{bend}}(K_0, C_0, \Phi, \Phi_s) - TS(\Phi, \Phi_s) \quad (6)$$

A detailed description of the resulting phase equilibria, as found by using a common tangent plane construction, is given in ref 1. Note that, since salt and cosurfactant enter only through the parameters K_0 and C_0 , our results admit a natural pseudoternary representation in terms of the oil, water, and surfactant volume fractions.

Obviously, the estimates given above for S and F_{bend} are not very accurate for extreme oil/water asymmetry ($\Phi \approx 0$ or $\Phi \approx 1$). In these limiting cases, the system is more accurately described as a dilute solution of surfactant in either water or oil, whose free energy may not be simply related to the elasticity parameters, K_0 and C_0 , of a nearly flat monolayer. This is significant, because we are interested in two-phase (or three-phase) equilibria between a microemulsion and a very dilute phase of surfactant in water or oil (or two such phases). Qualitatively, however, as discussed in ref 1, we expect eq 1-3 to give a reasonable description of the dilute phases, at least in the case when the solubilities of the surfactant in water and in oil are both small and not too different from one another.

To further characterize the phase equilibria, we may also consider the possibility of ordered mesophases. The simplest of these is the lamellar phase, whose free energy may be estimated¹ as

$$F_l = \chi \frac{k_B T}{4\pi K_0} \Phi_s^3 \left(\frac{1}{(1 - \Phi)^2} + \frac{1}{\Phi^2} \right) \frac{k_B T}{a^3} \quad (7)$$

This represents a heuristic generalization, to our three-component system, of Helfrich's result¹⁹ for the free

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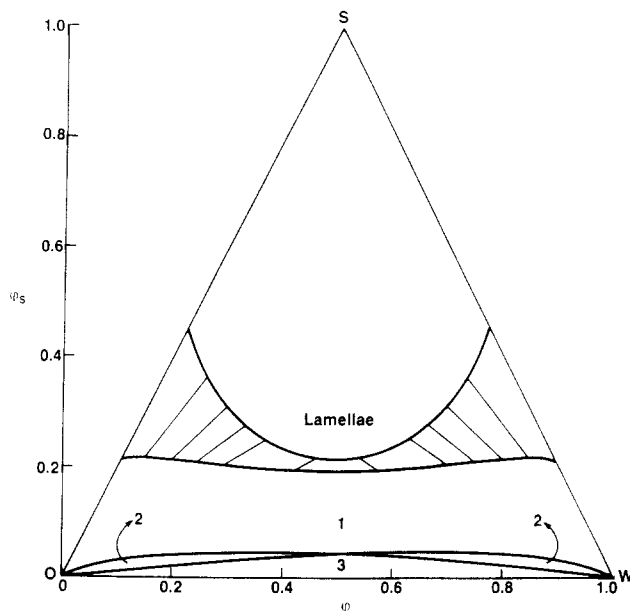


Figure 2. Typical phase diagram obtained from the free energy expressions 6 and 7. Region 1 corresponds to the microemulsion phase; 2 and 3 correspond respectively to two- and three-phase equilibria. Lamellae correspond to a lamellar phase. This phase diagram has been obtained for a value of $\kappa = 5$.

energy of undulating lamellar liquid crystals. The free energy is positive and represents the entropic repulsions between fluctuating sheets that cannot cross; the zero of free energy is that of a state of infinitely separated monolayers.²⁰ In eq 7, χ is a numerical parameter to which we assign the value 0.15, as in ref 1.

3. Predictions and Comparison with Experiment

From F_μ and F_1 the full pseudoternary phase diagram can be found for arbitrary K_0 , C_0 and T ; representative examples are given in the figures of ref 1. It is convenient to introduce two reduced variables. The reduced microscopic bending modulus is

$$\kappa = (4\pi K_0)/k_B T \quad (8)$$

The reduced spontaneous curvature is

$$x_0 = C_0 \xi_h \quad (9)$$

With these definitions, the phase equilibria computed from eq 1-7 depend only on κ , x_0 , and the volume fractions, two of which are independent; the parameter space is thus four dimensional.

Already, though, many features of the experimentally observed pseudoternary phase diagrams are qualitatively reproduced (see Figure 2). Specifically for $x_0 \leq 1$, and κ in the range of about 4-8, the model exhibits a stable middle-phase microemulsion, coexisting with extremely dilute phases of surfactant in water and in oil. The resulting three-phase triangle is flanked by two two-phase regions (upper- and lower-phase microemulsions coexisting with nearly pure water and nearly pure oil). The remainder of the phase diagram corresponds to single-phase microemulsions, except that at high surfactant volume fraction there is a first-order separation between these states and lamellae.

For $x_0 = 0$ the pseudoternary phase diagram is symmetric between water and oil (Figure 2); as x_0 is increased (decreased) from zero, the apex of the three-phase triangle,

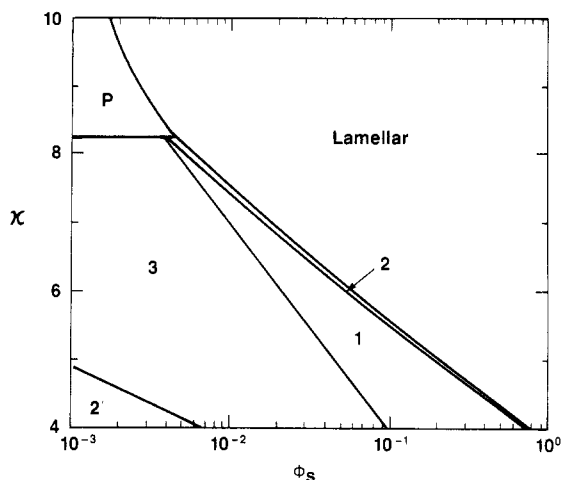


Figure 3. Cut of the phase diagram corresponding to a fixed value of the Φ_o/Φ_w ratio ($\Phi_o/\Phi_w = 1$). The spontaneous curvature C_0 is kept at 0.

at which the middle phase resides, moves toward the oil (water) corner. Finally, for x_0 of order unity, the three-phase triangle disappears, leaving a coexistence of the "emulsification failure" type,²¹ in which a globular microemulsion, containing droplets of size ρ_0 , coexists with an excess phase of the interior component.

For comparison with experiments, it is also interesting to consider cuts through parameter space in various directions other than those corresponding to pseudoternary phase diagrams. Clearly, no new phase behavior will be found other than that implicit already in the evolution of these diagrams, under variation in the elastic constants and temperature. Nonetheless, since we are dealing with a parameter space of several dimensions, features which were obscure before can emerge much more clearly when a well-chosen cut is taken. With this in mind, we now present two alternative representations, illustrating respectively the phase behavior as a function of κ and x_0 .

The first (Figure 3) is a plot for the fixed ratio $\Phi_w/\Phi_o = 1$, at zero spontaneous curvature ($C_0 = 0$). The remaining variables are Φ_s and the reduced microscopic bending constant κ (eq 8). This cut should be seen as the evolution of the phase behavior along a vertical line through Figure 2 at $\Phi = 1/2$ as a function of κ . Region 1 corresponds to the case where the microemulsion phase is stable. The lamellar phase is stable for large value of Φ_s . Regions 2 and 2' are respectively two-phase equilibria between the lamellar and the microemulsion and between water and oil phases. Region 3 corresponds to the region of the three-phase equilibrium and P to a complicated region of polyphasic equilibria. This representation illustrates several interesting features of the model. First of all, the boundaries between the microemulsion phase and other phases (lamellar or water and oil) are nearly linear in this semilog representation. This is closely related to the fact that $\ln \Phi_s^m$ is inversely proportional to $\ln \xi_h$ (i.e., $\propto \kappa$).

Figure 3 illustrates also the competition between the lamellar and the microemulsion phases. Indeed, for small κ (very flexible surfactant films) the lamellar phase is stable only for very high concentration of surfactant, and the microemulsion phase is stable for a large range of concentration, though Φ_s^m is large. When κ increased, Φ_s^m decreased as $\exp(-\kappa)$. However, in the meantime, the lamellar phase is more stable and the first-order phase transition between the microemulsion and the lamellar

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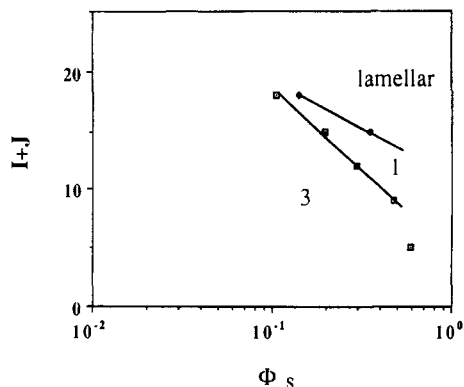


Figure 4. Experimental data from ref 5 for a series of nonionic surfactants (C_iE_j). This experimental phase diagram has to be compared with Figure 3. The sum $i + j$ is assumed to be directly related to the elastic constant κ . The open points correspond to the limit of stability of the microemulsion phase toward the three-phase equilibrium and the filled points to the phase separation with the lamellar phase.

phase occurs at smaller Φ_s . Since the slope of the boundary between the microemulsion and the region of three-phase equilibrium is larger than the slope of that between the microemulsion and lamellae, these two lines meet (for $\kappa \approx 8.3$, $\Phi_s^m \approx 4 \times 10^{-3}$). Above this value there is no longer a stable microemulsion phase, and the P region corresponds to complex polyphasic equilibria between water, oil, lamellar phase, and microemulsion phases with a water/oil ratio different from 1. This region corresponds in the ternary representation (at constant κ) to a loss of the continuous path between oil and water. Consequently, the price to pay for having a micromulsion phase made with a very small amount of surfactant is to have a narrow region of stability. This illustrates the competition between small values of κ , which favor microemulsion phases of small characteristic sizes (and which need a lot of surfactant), and large values of κ , which favor large structures (microemulsion with less surfactant, but also the lamellar phase).

Following these remarks, the "recipe" for making a microemulsion that is stable over a wide range of surfactant concentration is to make κ small, in order to push the lamellar phase to higher Φ_s . However, Φ_s^m will then be quite large, and the microemulsion will use a lot of surfactant. On the other hand, if one wants a very small value of Φ_s^m , κ should be made as large as possible while keeping a connecting single-phase pathway between the water and oil sides of the apex of the three-phase triangle, so that the pathway will be very narrow. Consequently, there exists a range of values of κ ($\sim k_B T$) which favors microemulsion phases (for $C_0 = 0$). This behavior is well illustrated by the series of phase diagrams of the nonionic surfactants given in Figure 3 of ref 5. Indeed, for small surfactant length, Φ_s^m is large but there is no lamellar phase even for high concentration of surfactant. On the contrary, for large surfactant length (corresponding to a higher elastic constant κ), Φ_s^m is much smaller and the lamellar phase comes much closer to the three-phase triangle. This is shown in Figure 4, where we took the data from ref 5 and plotted Φ_s^m , and the boundary with the lamellar phase, as a function of the surfactant length.²² We have plotted the value of Φ_s^m for different surfactant characterized by the sum $i + j$ (related to the total length of the surfactant). The length of the surfactant is assumed

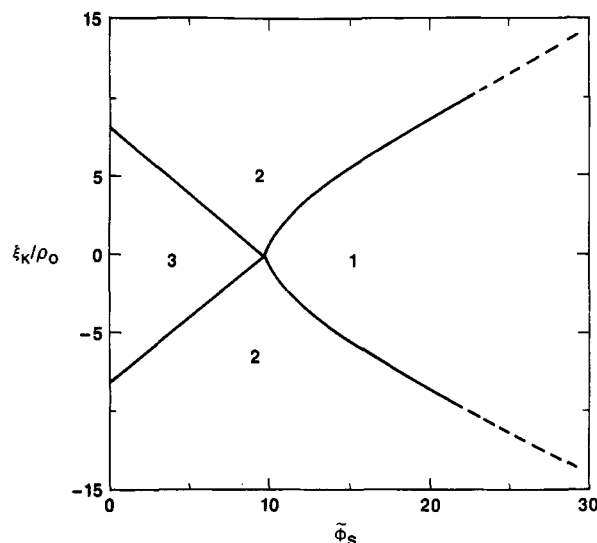


Figure 5. Cut of the phase diagram for a fixed value of the Φ_o/Φ_w ratio ($\Phi_o/\Phi_w = 1$). The value of κ is kept constant ($\kappa = 6.6$), and C_0 ($1/\rho_0$) varies.

to be directly related to the elastic constant κ . The similarity between Figure 4 (experimental data) and Figure 3 (theory) is striking and suggests that our model describes correctly the competition between the lamellar and microemulsion phases.

The second plot (Figure 5) is one in which the reduced spontaneous curvature C_0 (eq 10) is varied, along with surfactant volume fraction, again at a fixed ratio $\Phi_w/\Phi_o = 1$. The parameter κ is held fixed. In this case we find a large fish, as seen experimentally.²⁻⁵ The head of this fish is squashed against the left-hand edge of the figure. This fact is a result of the approximation, made in the model, that the dilute phases of surfactant in water and surfactant in oil can be represented by points on edges of the triangle of the ternary representation. This could easily be corrected by taking a more realistic description of the dilute phases.¹ The comparison with experiment, in the representation of Figure 5, is qualitatively easy to make, assuming that, in nonionic systems, the spontaneous curvature is a smoothly varying function of temperature. A possible explanation could be that the water contents in the hydrophilic region of the film decreased with temperature (the polar heads are less solvated at high temperature than at low temperature).

4. Conclusions

In this paper we have focused on comparing more closely with experiment the results of a previously proposed model for microemulsions. The simplest comparisons are with true ternary systems of oil, water, and nonionic surfactants; these are extensively studied in the literature.²⁻⁸ We have shown that in terms of two phenomenological parameters κ and C_0 we can qualitatively explain the dependence of the phase behavior not only on the surfactant concentration but also on its microscopic properties, i.e., shape and length. Indeed, a balance and optimized microemulsion can be obtained from our model for $C_0 \approx 0$ and κ in an intermediate range, around a few $k_B T$. Recently the model has been extended to calculate the structure factor; this compares well with X-ray and neutron small-angle scattering experiments and with freeze fracture pictures.²³ For a more quantitative comparison with experiments, a model

(22) The nonionic surfactants considered are C_iE_j , where i is the carbon number of the aliphatic chain and j the number of oxyethylene groups. We used $i + j$ to characterize the surfactant length.

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relating κ and C_0 to surfactant, water, and oil interactions on a molecular basis is needed.

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Properties and Structures of Three- and Four-Component Microemulsions[†]

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We report phase behavior, small-angle X-ray scattering (SAXS), fluorescence spectroscopy, conductimetry, and differential scanning calorimetry of didodecyldimethylammonium bromide (DDAB)/cyclohexane/water and DDAB/decane/water microemulsions with and without NaBr. We demonstrate that the hydrocarbon tails of the surfactant are fluid in microemulsions at room temperature. The observed phase behavior exhibits a complex dependence upon salt concentration, yet microemulsion structure as probed by SAXS and conductimetry is not altered by the addition of salt. Pyrene fluorescence is used to probe the internal interfacial layers, and evidence for the compression of the surfactant tails with decreasing curvature is obtained.

1. Introduction

Surfactants have the remarkable ability to self-assemble in solution.¹ When that solution contains both oil and water there are diverse possibilities for the microstructure of the resulting microemulsions. The usual case is that the minor component—either oil or water—clusters into quasispherical droplets to disperse in the major component. Oil and water are separated by a surfactant-rich film. As the curvature of that film tends to zero, the droplets may merge and fuse into an equilibrium bicontinuous structure.² The evidence for this progression of structure has been extracted from the results of experiments on microemulsions formed with five components: oil, water, surfactant, cosurfactant, and electrolyte.^{3,4} Interpretation of experiments on such systems is made difficult by the partitioning of cosurfactant and surfactant between the oil and water domains. In addition, the influence of critical points (i.e., critical opalescence) in the phase diagram can obscure some structural details.

To remove some of the complexity attendant to the study of five-component systems, it is useful to detail the behavior of microemulsions found with the minimum number of components: oil, water, and surfactant. Once the behavior of the prototypical systems is understood then the roles of, for example, an electrolyte mitigating electrostatic interactions, a cosurfactant altering the rigidity of the surfactant film, or approach to a critical point can

be explored in a controlled fashion. Kahlweit and Strey⁵ and Shinoda and Friberg⁶ have focused on the phase behavior of simple nonionics with the question of structure in those mixtures just now being explored.⁷ Evans and Ninham⁸⁻¹² and others¹³ have examined the structural details in microemulsions formed with the cationic surfactant didodecyldimethylammonium bromide (DDAB), water, and hydrocarbons. The structure and phase behavior of AOT-oil-water mixtures has also been explored.^{14,15}

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