Molecular Thermodynamics of Partially-Ordered Fluids: Microemulsions

Mixtures of water, oil, and surfactant often form microemulsions where tiny drops of oil (or water) are dispersed in a matrix of water (or oil). A microemulsion is a partially-ordered fluid in which the surfactant molecules exist in an oriented layer at the boundary between the continuous phase and the discontinuous phase. This work proposes a molecular-thermodynamic model that is useful for calculating a variety of phase diagrams observed in microemulsion-forming systems.

The model is based on a revised form of Widom's abstract representation of a microemulsion; that representation provides a procedure for calculating essential contributions to the configurational entropy. In Widom's representation, all molecules are difunctional dumbbells such that all the hydrophilic ends are situated together in some lattice sites and all the lipophilic ends are situated together in other sites. A form of Guggenheim's quasichemical theory is used to evaluate the combinatorial contributions that correspond to Widom's picture. Chemical association of surfactant molecules and physical interactions are also taken into account. Minimization of the Gibbs energy yields a distribution function for representing micelle sizes.

Calculated ternary phase diagrams are in good agreement with experimental results. Different types of diagrams can be obtained upon changing physically significant model parameters. A study of how these parameters affect phase behavior provides insight on microemulsion stability.

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Introduction

Microemulsions are omnipresent in nature, including fluids essential for plant and animal life. Further, microemulsions are of much use in chemical technology (e.g., paints, coatings, detergents) and pharmaceuticals. Chemical processes are sometimes carried out in emulsions (e.g., emulsion polymerization, tertiary oil recovery) as discussed, for example, by Langevin (1984). Recently, Olien (1987) has called attention to the role of microemulsions in biotechnology, including the use of reverse micelles for enzymatic reactions (Shield et al., 1986). To move toward better understanding of the equilibrium properties of microemulsions, it is desirable to construct a quantitative molecular-thermodynamic model. This work provides a reasonable first-order version of such a model.

A microemulsion is a clear, transparent and stable fluid consisting essentially of oil-in-water (or water-in-oil) droplets with typical dimensions in the range 10–60 nm or of bicontinuous structures, as indicated in Figure 1. The general behavior of microemulsions has been discussed in a series of reviews (Winsor, 1968; Ekwall, 1975; Tiddy, 1980; Luisi and Straub, 1984).

Efforts to describe the structure of a microemulsion can be traced back at least 50 years. To explain the formation of clear isotropic solutions when benzene and water are mixed in the presence of potassium oleate, Schulman (Hoar and Schulman, 1943), a pioneer in this field, suggested that the aqueous droplet in oil is an aqueous sphere surrounded by a surfactant membrane. This drop with a membrane surface is called a micelle. Using simple geometry, we can evaluate the average radius of a micelle on the basis of Schulman's picture. More recently, Israelachivilli et al. (1976) and Mitchell and Ninham (1981) have discussed the conditions required for the formation of spherical, rodlike, bilayer, or other-shaped aggregates. Upon constructing a theory for chemical potentials, they could estimate the size dis-

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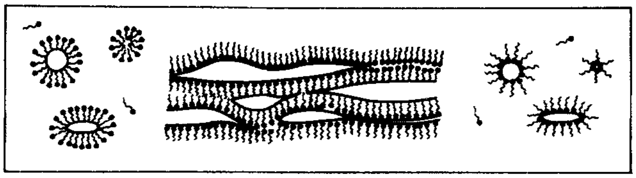

Figure 1. Typical structures in microemulsions.

tribution of micelles. Using similar ideas, Robbins (1977) showed that observed limits in a phase diagram are related to the structure of the surfactant molecules.

Various improvements in the theory of microemulsions have been developed along different directions. One of them is based on the idea of chemical equilibria (mass-action theory), which has long existed in the field of aqueous surfactant solutions. For example, Mazer et al. (1980) and Stecker and Benedek (1984) applied chemical-equilibrium theory to multicomponent micelles and microemulsions with the use of an empirical function to describe micelle size distribution. Ben-Shaul et al. (1986) considered cosurfactants; they assumed that the cosurfactant is a "spacer" that dilutes the charge density at the interface. Blankschtein et al. (1986) and Thurston et al. (1986) extended the mass-action theory by incorporating interactions between the micelles; their theory describes phase separation in binary surfactant solutions. Other theories, emphasizing the role of interfacial tension, have been put forward in papers by Ruckenstein et al. (1978), Ruckenstein and Krishnan (1980), and Nagarajan and Ruckenstein (1979). Considering a microemulsion to contain monodisperse spherical droplets, the radius of a droplet can be determined by minimizing the free energy. The most important terms in this theory reflect the effect of interfacial tension and entropy of mixing. Finally, Rosen et al. (1982) have presented a model based on the Flory-Huggins equation and Kilpatrick et al. (1985) have applied this model to a quaternary system containing brines.

Talmon and Prager (1978) modeled a microemulsion as a random geometry of interspersed domains generated by Voronoi polyhedrons with the surfactant adsorbed at the boundary. Larson et al. (1985) studied a two-dimensional microemulsion using Monte-Carlo simulation. De Gennes and Taupin (1982), and Widom (1984a), inspired by the model of Talmon and Prager, proposed a simplified version in which the domains are cubes packed in a regular array, and the entropy of the folded film is estimated as the entropy of random mixing of the components. Finally, Wheeler and Widom (1968) and Widom (1984b, 1986) have modeled a microemulsion as a mixture of difunctional groups and have mapped this picture onto an Ising model. These more sophisticated theories can describe phase separation in microemulsion systems. However, they are too abstract and cumbersome for practical use at this time.

The aim of the present work is to develop a molecular-thermodynamic description of the behavior of microemulsions in such a manner that on the one hand is realistic, yet on the other hand may serve as a basis for constructing engineering-oriented models.

Molecular-Thermodynamic Framework

The thermodynamics of liquid solutions has been dominated by the ideal-solution concept as exemplified by Raoult's law. Typical molecular-thermodynamic models for liquid mixtures offer first-order corrections to Raoult's law or else to Flory's expression for athermal solutions of chain molecules. Nearly all engineering-oriented models present variations on a theme where the liquid solution is considered to be an assembly of more-or-less randomly mixed molecules. For associated solutions (e.g., alcohols in hydrocarbons), some ordering is introduced by incorporating chemical equilibria into the model; however, for such solutions it is then assumed that the various molecular species (monomers, dimers, etc.) form a more-or-less random mixture.

To describe the equilibrium properties of a microemulsion, we cannot use conventional expressions for the entropy of mixing because a microemulsion is not even approximately a random mixture. In a microemulsion, not only are water and oil immiscible components but, more important, the surfactant molecules are not free to position themselves anywhere; they must be at the water-oil interface. In a microemulsion, we do not have a liquid that is homogeneous on a molecular scale, instead, we have a heterogeneous medium with microphases or domains. Therefore, conventional expressions yield an entropy of mixing that is too large. To describe the equilibrium properties of a microemulsion, we require a molecular-thermodynamic theory for a partially-ordered fluid.

We consider a ternary mixture of water, oil, and surfactant (W, O, S). We seek an expression for the Gibbs energy G as a function of temperature, pressure, and number of molecules N_W, N_O, and N_S (water, oil, surfactant). Initially, all components are in their standard states, designated by superscript o: pure liquid water, pure liquid oil, and surfactant monomer at infinite dilution in water, all at system temperature and pressure. The Gibbs energy of the microemulsion is given by

$$G = G^o + \Delta G_I + \Delta G_{II} + \Delta G_{III} \tag{1}$$

where G^o is the Gibbs energy of the system when each component is in its standard state; ΔG_I is the Gibbs energy change due to formation of oligomers (chemical association) of the surfactant; and ΔG_{II} and ΔG_{III} are, respectively, combinatorial and physical-interaction contributions due to mixing. Upon minimizing the Gibbs energy with respect to the concentration of the oligomers, we obtain the size distribution of the micelles. Upon differentiation with respect to nominal composition, we obtain chemical potentials and phase equilibria.

G^o: *Gibbs energy of the standard state*

The Gibbs energy of the standard state G^o is given by

$$G^o = N_W\mu_W^o + N_O\mu_O^o + N_S\mu_{S1(W)}^o \tag{2}$$

where μ_i^o is the chemical potential of component i in the standard state; subscript (W) indicates aqueous phase.

ΔG_I: *Gibbs energy change due to chemical association of the surfactant*

Monomer S_1 associates to form an oligomer S_j where j is an integer between j_m and ∞,

$$j(S_1) \rightarrow S_j \qquad j = j_m \rightarrow \infty$$

Here j_m is the smallest allowed aggregation number. The Gibbs energy change due to association is given by

$$\Delta G_I = \sum_{j=j_m}^{j=\infty} N_{Sj}[\mu^o_{Sj} - j\mu^o_{S1(W)}] \tag{3}$$

where N_{Sj} is the number of molecules of surfactant j-mer and μ^o_{Sj} is the corresponding standard-state chemical potential. For μ^o_{Sj}, the standard state is a hypothetical, infinite dilute solution of S_j such that the hydrophilic end of S_j is in water while its hydrophobic lipophilic end is in oil. For estimating μ^o_{Sj}, we use an expression based on the theory of Lennard-Jones, Devonshire, and Prigogine (Prigogine, 1957):

$$\mu^o_{Sj} = \epsilon^o_{Sj} - Ts^o_{Sj} = \epsilon^o_{Sj} - kT \ln v_{f,Sj} \tag{4}$$

where ϵ^o_{Sj} is the internal energy (more strictly, the enthalpy), S^o_{Sj} is the entropy, and $v_{f,Sj}$ is the free volume of oligomer S_j in its standard state, as defined above.

We assume that ϵ^o_{Sj} is a linear function of the aggregation number j,

$$\epsilon^o_{Sj} = j\epsilon^o_{S1} - D_o(j_m - 1) - D(j - j_m) \tag{5}$$

Here D_o is the association energy (per pair of monomers) for associated surfactant of the smallest micelles, which have the greatest curvature and which contain neither oil nor water at their centers. D is the average value of the association energy (per pair of monomers) for associated surfactant of those micelles that have oil or water at their centers or of bicontinuous segments; these larger micelles or segments have smaller curvature. The energy of monomer ϵ^o_{S1} depends on the oil-water ratio. We make the reasonable assumption

$$\epsilon^o_{S1} = \epsilon^o_{S1(W)} + \epsilon^o_{S1(O-W)}\Phi_O/(\Phi_O + \Phi_W) \tag{6}$$

Here $\epsilon^o_{S1(O-W)}$ is a characteristic constant determined by the binaries S-O and S-W. If the free volume of monomer is independent of its environment,

$$\epsilon^o_{S1(O-W)} = \mu^o_{S1(O)} - \mu^o_{S1(W)} \tag{7}$$

where subscript (O) indicates organic phase. Φ_O and Φ_W are the volume fractions of oil and water:

$$\Phi_O = N_O r_O / N_r, \quad \Phi_W = N_W r_W / N_r \tag{8}$$

$$N_r = N_W r_W + N_O r_O + N_S r_S \tag{9}$$

where r is a molecular size parameter. The free volume of associated surfactant is assumed to be additive:

$$v_{f,S_j} = j v_{f,S1} \tag{10}$$

Equation 10 is advantageous for calculating the size distribution, as shown in appendix A.

ΔG_{II}: Gibbs energy change due to mixing water, oil, and associated surfactant; combinatorial contribution

The combinatorial part of the Gibbs energy change is obtained from the athermal entropy of mixing water, oil, and surfactant. However, this entropy cannot be calculated from conventional expressions used in classical theories of solution because a microemulsion is not a random mixture in which molecules mix in an essentially disordered, statistical manner; instead, it is a partially ordered mixture. To take into account that nearly all of the surfactant oligomers are situated in an orderly fashion between the oil and water molecules, we derive here an expression for the entropy of mixing based on Widom's abstract lattice representation (Wheeler and Widom, 1968; Widom, 1984b, 1986). In that representation, all monomer molecules are considered to be difunctional species. Consistent with its amphiphilic nature, a surfactant is represented by a dumbbell where one end is a dot and the other a circle. Water and oil molecules are represented as dumbbells containing, respectively, two circles and two dots. Forming a lattice, all the difunctional species are arranged in such a way that all the dots are situated in some sites and all the circles are situated in other sites, as shown in Figure 2. To allow for the rare existence of monomers in this lattice, the bond between dot and circle can be unoccupied as a vacancy bond.

It is important to note that, in Figure 2, lattice sites are not molecule sites as in typical lattice theories of fluids. Instead, lattice sites here are points where the ends of selected dumbbells congregate. In the two-dimentional view shown in Figure 2, each lattice point can accommodate a maximum of four dumbbell ends.

In the next paragraphs we apply statistical and material-balance arguments that utilize the number of lattice sites as defined above. In these arguments we also use the number of bonds that link the nearest sites.

We designate with letter A those sites filled with dots, and with letter B those filled with circles. The numbers of such sites are given by N_A and N_B, respectively. Material balances give

$$N_A = (2N_W + N_S + N_V)/z_A \tag{11}$$

$$N_B = (2N_O + N_S + N_V)/z_B \tag{12}$$

where z_A and z_B are coordination numbers for site A and site B, respectively. N_V is the number of vacancy bonds; this is a very small number whose precise value has no effect on the final results of our calculations. However, we do not set N_V equal to

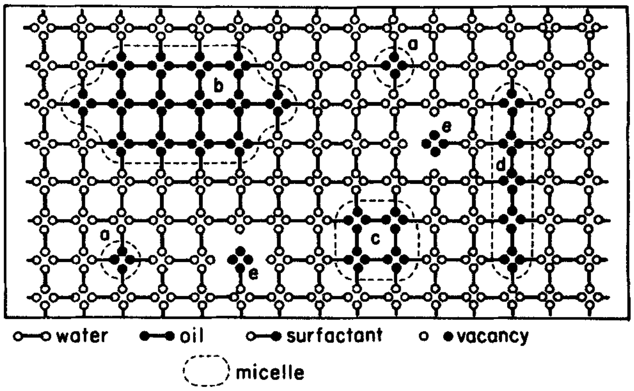

Figure 2. Lattice model for microemulsions.
a. Micelle with neither oil nor water in center
b,c,d. Micelle with oil in center
e. Surfactant monomer

zero because of a necessary boundary condition, as discussed in appendix B.

Coordination numbers z_A and z_B need not be identical. Their values need not be specified because, as shown below, the combinatorial entropy of interest here does not use N_A and N_B. Instead, the combinatorial entropy depends on the number of bonds.

To calculate the combinatorial entropy, we introduce the number of *A-A*, *A-B*, *B-A*, and *B-B* bonds designated by N_{AA}, $N_{AB(S)}$, $N_{AB(V)}$, $N_{BA(S)}$, $N_{BA(V)}$, and N_{BB}. Here subscripts (*S*) and (*V*) indicate surfactant and vacancy, respectively. They are given by material balances:

$$N_{AA} = N_W, \quad N_{BB} = N_O \tag{13}$$

$$N_{AB(S)} = N_{BA(S)} = N_S/2, \quad N_{AB(V)} = N_{BA(V)} = N_V/2 \tag{14}$$

The combinatorial contribution to the Gibbs energy change is the sum of two parts. The first follows from the configurational change of the system as a result of mixing. The second accounts for size distribution caused by chemical association.

$$\Delta G_{II} = \Delta G'_{II} + \Delta G''_{II} \tag{15}$$

First, we consider $\Delta G'_{II}$. Following the classical quasichemical procedure of Guggenheim (1952), the number of configurations in the lattice is given by

$$\begin{aligned}\Omega &= \frac{[N_{AA} + N_{AB(S)} + N_{AB(V)} + N_{BA(S)} + N_{BA(V)} + N_{BB}]!}{N_{AA}!N_{AB(S)}!N_{AB(V)}!N_{BA(S)}!N_{BA(V)}!N_{BB}!} \\ &= \frac{(N_W + N_O + N_S + N_V)!}{N_W!N_O![(N_S/2)!]^2[(N_V/2)!]^2}\end{aligned} \tag{16}$$

However, Eq. 16 does not meet the necessary boundary condition that when N_S goes to zero, Ω must approach unity, because oil and water are here considered totally immiscible. Therefore, we propose a more realistic formula for Ω. We distinquish between two kinds of bonds, those that are congregated at site *A* and those that are congregated at site *B*, and we treat them as independent of each other. This distinction suggests the following expression

$$\Omega = \frac{(N_W + N_S/2 + N_V/2)!(N_O + N_S/2 + N_V/2)!}{N_W!N_O![(N_S/2)!]^2[(N_V/2)!]^2} \tag{17}$$

The two factorials in the numerator reflect, respectively, the contributions of the bonds congregated at site *A* and those congregated at site *B*. Neglecting the minor volume change of mixing, the configurational Gibbs energy change for the mixing step is

$$\Delta G'_{II} = -kT \ln \frac{\Omega}{\Omega_W \Omega_O \Omega_S} \tag{18}$$

where $\Omega_W = \Omega_O = 1$. Because of symmetry, each surfactant molecule has two choices: "dot to circle" and "circle to dot"; therefore, $\Omega_S = 2^{N_S}$. Upon substituting Eq. 16 into Eq. 17, we have

$$\begin{aligned}\Delta G'_{II} &= N_W kT \ln \frac{N_W}{N_W + N_S/2 + N_V/2} \\ &+ N_O kT \ln \frac{N_O}{N_O + N_S/2 + N_V/2} \\ &+ N_S kT \ln \frac{N_S}{(N_W + N_S/2 + N_V/2)^{1/2}(N_O + N_S/2 + N_V/2)^{1/2}} \\ &+ N_V kT \ln \frac{N_V/2}{(N_W + N_S/2 + N_V/2)^{1/2}(N_O + N_S/2 + N_V/2)^{1/2}}\end{aligned} \tag{19}$$

We now consider $\Delta G''_{II}$. Equation 17 neglects the contribution to ΔG_{II} due to association of surfactant molecules. To correct for this neglect, we introduce a Flory-Huggins term to take into account the surfactant size distribution caused by chemical association,

$$\Delta G''_{II} = kT \sum_{j=1}^{j=\infty} N_{Sj} \ln \Phi_{Sj} - kTN_S \ln \Phi_S \tag{20}$$

where

$$\Phi_{Sj} = N_{Sj} r_{Sj}/N_r \tag{21}$$

and

$$r_{Sj} = jr_S \tag{22}$$

The combinatorial contribution ΔG_{II} is the sum of Eqs. 19 and 20, as indicated by Eq. 15.

ΔG_{III}: *Gibbs energy change due to mixing water, oil and associated surfactant; contribution from physical interactions*

We have six kinds of interactions; they are S-S, W-W, O-O, S-W, S-O, and W-O. However, interactions W-W and O-O are included in the standard states while interactions S-W and S-O are included in chemical association energies D_o and D. Therefore, only the remaining interactions S-S and W-O require attention here. For surfactant interactions, Huang (1985) has made extensive studies using a light-scattering technique. He found that the experimental results could be analyzed in terms of a Carnahan-Starling equation modified by a two-body attractive term. It is therefore reasonable in our model to choose a simple attractive van der Waals expression to account for these interactions:

$$\Delta G_{III} = -(N_S^2 a_{SS} + N_W N_O a_{WO})/V \tag{23}$$

Here a_{SS} is a function of temperature and of the oil-to-water ratio. We assume

$$a_{SS} = a_{SS(W)} + a_{SS(O-W)}\Phi_O/(\Phi_O + \Phi_W) \tag{24}$$

where $a_{SS(O-W)} = a_{SS(O)} - a_{SS(W)}$ and where subscripts (*W*) and (*O*) designate aqueous and organic phase, respectively. Because the surfactant molecules are always situated between the oil and water molecules, parameter a_{WO} depends on the properties of the surfactant in the microemulsions; therefore, it is a characteristic constant of the ternary system.

Substitution into Eq. 1 gives the Gibbs energy for a microemulsion.

Size Distribution of Micelles

To calculate the size distribution of the micelles, we first minimize the Gibbs energy with respect to N_{Sj}. As shown in appendix A, from Eq. 1, we can obtain an expression for the volume fraction of oligomer S_j:

$$\Phi_{Sj} = \frac{K_o^{jm-1}}{K^{jm}} j\Phi_{S1}^j K^j \tag{25}$$

where

$$K_o = \exp\left[(D_o/kT) - \ln v_{f,S1} + 1\right] \tag{26}$$

and

$$K = \exp\left[(D/kT) - \ln v_{f,S1} + 1\right] \tag{27}$$

Equations 26 and 27 define chemical equilibrium constants.

For convenience, we also define a generalized (relative) equilibrium constant

$$K_R = K/K_o \tag{28}$$

and we define a generalized volume fraction

$$\Phi_{Sj}^* = \Phi_{Sj}K \tag{29}$$

Substitution gives a generalized distribution,

$$\Phi_{Sj}^* = K_R^{1-jm} j \Phi_{S1}^{*j} \tag{30}$$

and

$$\Phi_S^* = \Phi_S K = \sum_{j=1}^{j=\infty} \Phi_{Sj}^* = \Phi_{S1}^* + K_R^{-jm}\Phi_{S1}^{*jm}\left[\frac{j_m}{1-\Phi_{S1}^*} + \frac{\Phi_{S1}^*}{(1-\Phi_{S1}^*)^2}\right] \tag{31}$$

Equations 25 and 31 give the size distribution of surfactant. When the oil-to-water ratio is very small or very large, and when the concentration of surfactant is sufficiently large, we can distinguish between an oil-in-water microemulsion and a water-in-oil microemulsion. (The latter corresponds to what is called reverse micelle.) For both cases, we can estimate the size distribution of the micelles as follows.

For a micelle with surfactant aggregation number j, the volume of the surfactant is proportional to j; the maximum volume for oil or water in the micelle is correspondingly proportional to $j^{3/2}$. Therefore, for an oil-in-water microemulsion,

$$\Phi_{Oj} \sim j^{1/2}\Phi_{Sj} \tag{32}$$

Substitution of Eqs. 29 and 30 yields

$$\Phi_{Oj} = \Phi_O \frac{j^{3/2}\Phi_{S1}^{*j}}{\sum_{j=j_m}^{j=\infty} j^{3/2}\Phi_{S1}^{*j}} \tag{33}$$

where Φ_{Oj} is the volume fraction of oil in those micelles whose surfactant aggregation number is j. The denominator of Eq. 33 is calculated numerically, e.g., by using the Gaussian-quadrature method.

Since the volume of the micelle is the sum of the volumes of surfactant and oil in it, the total size distribution of micelles is given by

$$\Phi_{Mj} = \Phi_{Sj} + \Phi_{Oj} \tag{34}$$

which is the sum of Eqs. 27 and 33. Φ_{Mj} is the volume fraction of micelles with aggregation number j of the surfactant.

We define the moment of distribution of order k by

$$M_{(k)} = \sum_{j=1}^{j=\infty} j^k \Phi_{Sj}^* \tag{35}$$

We can then obtain the following relations:

$$M_{(0)} = \Phi_S^* \tag{36}$$

$$M_{(1)} = \sum_{j=1}^{j=\infty} j\Phi_{Sj}^* = \langle j\rangle_{(S)} M_{(0)} \tag{37}$$

$$M_{(2)} = \sum_{j=1}^{j=\infty} j^2\Phi_{Sj}^* = \langle j^2\rangle_{(S)} M_{(0)} \tag{38}$$

$$\sigma_j^2 = \langle j^2\rangle_{(S)} - \langle j\rangle_{(S)}^2 = \frac{M_{(2)}}{M_{(0)}} - \left[\frac{M_{(1)}}{M_{(0)}}\right]^2 \tag{39}$$

where $\langle j\rangle_{(S)}$ is the average aggregation number of surfactant averaged with respect to the distribution of the surfactant and where σ_j^2 is the variance of the distribution. Similarly, we can define another average aggregation number of surfactant $\langle j\rangle_{(O)}$ by

$$\langle j\rangle_{(O)} = \sum_{j=j_m}^{j=\infty} j\Phi_{Oj}/\Phi_O \tag{40}$$

which is averaged with respect to the distribution of oil in the micelles.

The average aggregation number of surfactant (averaged with respect to the distribution of all micelles) can then be calculated from

$$\langle j\rangle_{(M)} = \langle j\rangle_{(S)}\frac{\Phi_S}{\Phi_O + \Phi_S} + \langle j\rangle_{(O)}\frac{\Phi_O}{\Phi_O + \Phi_S} \tag{41}$$

Figure 3 shows a series of typical distribution curves for Φ_{Sj} and Φ_{Mj} for different concentrations of surfactant. As the concentration of surfactant increases, the distribution becomes wider and shifts toward the high aggregation-number region. At a fixed value of surfactant concentration, the distribution of micelles favors the high aggregation-number region more strongly than that of surfactant.

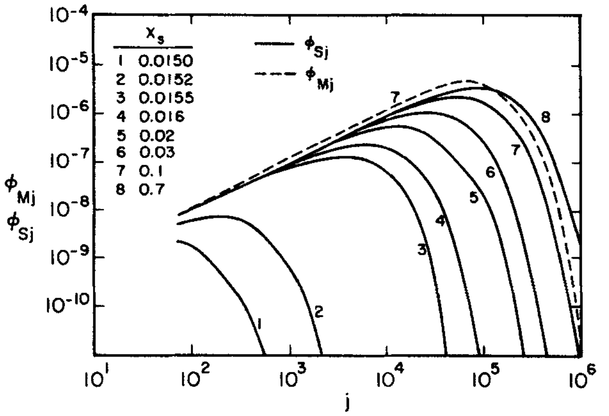

Figure 3. Size distribution of micelles.
$x_o/(x_o + x_w) = 0.2$; $r_S/r_W = 20.17$; $r_O/r_W = 10.08$; $K_R^{-1} = 0.7038$; $K = 0.1 * 10^2$

Chemical Potentials

Chemical potentials are obtained from Eq. 1 by classical thermodynamics. They are given in appendix B.

Parameters characteristic for the system are:

- $\epsilon_{(O-W)}/kT$. If we consider the critical micelle concentration (CMC) as a solution property similar to the saturated concentration, this parameter can be evaluated approximately by taking the logarithm of the ratio of the CMC of the surfactant in binary O-S to that in binary W-S.
- K_o and K. These parameters are best obtained from size-distribution data such as $\langle j \rangle$ and σ_j by Eqs. 30, 37, and 39.
- $a_{SS(W)}/v_S kT$, $a_{SS(O)}/v_S kT$, $a_{SS(O-W)} = a_{SS(O)} - a_{SS(W)}$, can be estimated by fitting binary phase-separation data.
- $a_{WO}v_S/v_W v_O kT$ must be estimated from ternary phase equilibrium data.
- r_O/r_W and r_S/r_W are estimated from pure-component molecular-size data.

Strictly speaking, K varies with the changing environment. However, as a good approximation for the systems considered here, under isothermal conditions it can be considered to be a constant because it depends only on the chemical association of the surfactant molecules and on the physical interactions of the surfactant with water and with oil; all of these do not change significantly over the entire composition range. It is evident that our approximate model is limited to relatively simple microemulsions. Extensive modifications are required for applicability to systems containing electrolytes and/or liquid-crystalline mesophases.

Phase Diagrams

Surfactant-containing systems exhibit a wide variety of phase behavior, as indicated in the compilation of phase diagrams by Ekwall (1975). The molecular-thermodynamic model developed here allows us to calculate phase behavior for several of these systems. We present some results for simple ternary systems containing water, oil, and surfactant.

A ternary homogeneous liquid phase separates into two liquid phases (phase-splitting) if the criterion for instability is satisfied. That criterion is

$$\frac{\partial^2 G}{\partial x_S^2}\frac{\partial^2 G}{\partial x_O^2} - \left(\frac{\partial^2 G}{\partial x_S \partial x_O}\right)^2 \le 0 \qquad (42)$$

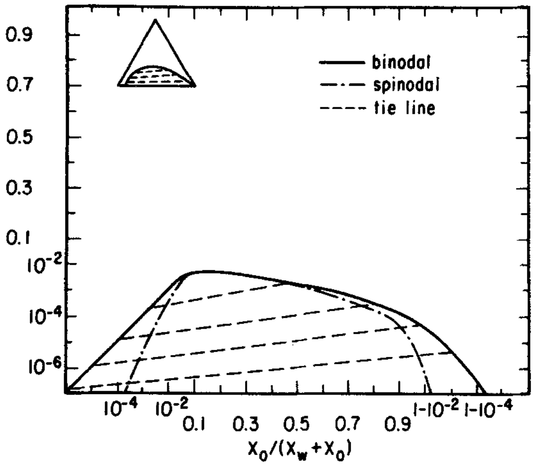

Figure 4. Calculated phase diagram with one two-phase region.
$r_S/r_W = 20.17$; $r_O/r_W = 10.08$; $j_m = 60$; $\epsilon_{(O-W)}/kT = 0.1$; $a_{SS(W)}/v_S kT = 1.0$; $a_{SS(O-W)}/v_S kT = 0.2$; $a_{WO}v_S/v_W v_O kT = -0.1$; $K_R^{-1} = 0.7038$; $K = 0.1 * 10$

Equation 42 gives the spinodal of the ternary mixture. However, to calculate the compositions of two (or more) phases at equilibrium, we require the binodal curve and the tie lines, as discussed elsewhere (Prausnitz et al. 1980). Figures 4–7 show four types of calculated phase diagrams; when mole fraction $x_i < 0.1$, the ordinates are on a logarithmic scale to show more clearly the phase behavior in the dilute region. For comparison, the corresponding triangular phase diagram is shown in the upper left of each figure. Binodals, spinodals, and tie lines are indicated.

Figure 4 shows only one two-phase region due to immiscibility of water and oil; an example is provided by the ternary hexaoxyethylene-glycol-monohexyl ether/octan-1-ol/water (Mulley and Metcalf, 1964).

Figure 5 has three two-phase regions arising from three partially immiscible binaries.

In Figure 6, two of the two-phase regions have merged, forming a folding-fan type region; two examples are provided by the

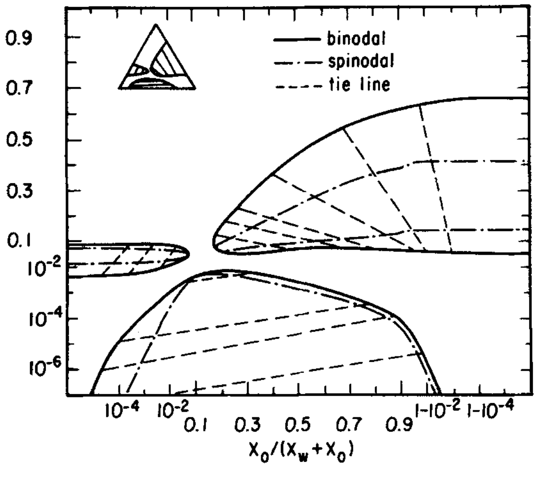

Figure 5. Calculated phase diagram with three two-phase regions.
$r_S/r_W = 20.17$; $r_O/r_W = 10.08$; $j_m = 60$; $\epsilon_{(O-W)}/kT = 0.1$; $a_{SS(W)}/v_S kT = 1.0$; $a_{SS(O-W)}/v_S kT = 0.2$; $a_{WO}v_S/v_W v_O kT = -0.1$; $K_R^{-1} = 0.7038$; $K = 0.4 * 10$

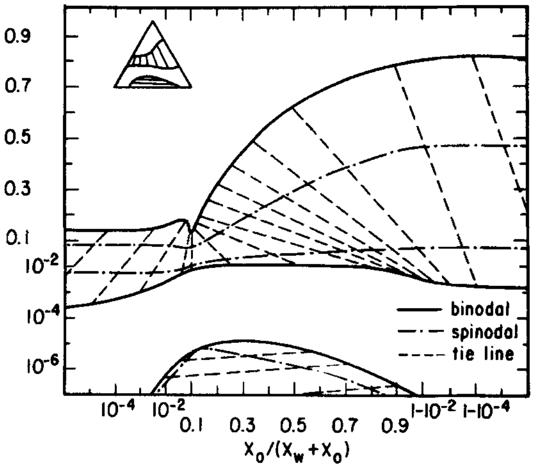

Figure 6. Calculated phase diagram with a folding-fan type two-phase region.

$r_S/r_W = 20.17$; $r_O/r_W = 10.08$; $j_m = 60$; $\epsilon_{(O-W)}/kT = 0.1$; $a_{SS(W)}/v_S kT = 1.5$; $a_{SS(O-W)}/v_S kT = 0.4$; $a_{WO} v_S/v_W v_O kT = -0.1 * 10^{-3}$; $K_R^{-1} = 0.7038$; $K = 0.1 * 10^2$

ternaries sodium cholate/decan-1-ol/water and sodium desoxycholate/decan-1-ol/water (Fontell, 1969).

In Figure 7, there is a three-phase region, indicated by a triangle; an example is provided by the ternary Aerosol OT/decan-1-ol/water (Ekwall et al., 1970).

Phase-diagram calculations require parameters that are shown on the figures. The position and magnitude of any two-phase region can be changed by adjusting these parameters. For example, as a_{WO} becomes increasingly negative, a higher binodal curve appears in Figure 4. As a_{SS} and K rise, there is an increase in the size of the two-phase regions from the binaries containing surfactant. Provided that K_R is in the vicinity of unity, it has virtually no effect on the phase diagram.

Stability of a Microemulsion

Many authors have concerned themselves with the well-known observation that when sufficient surfactant is added to an immiscible mixture of oil and water, a stable microemulsion is formed spontaneously.

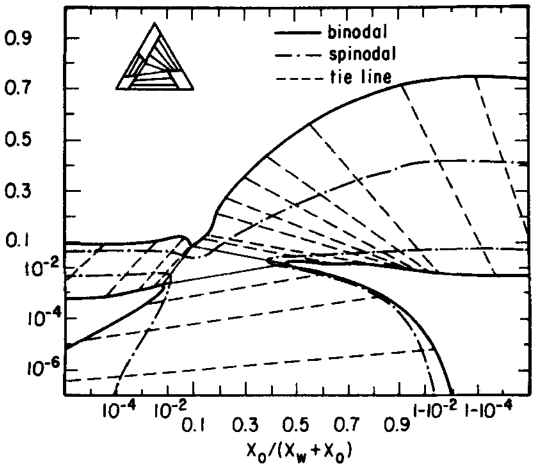

Figure 7. Calculated phase diagram with a three-phase region.

$r_S/r_W = 20.17$; $r_O/r_W = 10.08$; $j_m = 60$; $\epsilon_{(O-W)}/kT = 0.1$; $a_{SS(W)}/v_S kT = 1.0$; $a_{SS(O-W)}/v_S kT = 0.4$; $a_{WO} v_S/v_W v_O kT = -0.5$; $K_R^{-1} = 0.7038$; $K = 0.1 * 10^2$

Ruckenstein and coworkers (1978, 1980) have concluded that the thermodynamic stability of microemulsions is due first to a decrease in interfacial tension, and second, to a dilution effect that gives rise to a positive entropy of dispersion of the globules; these negative contributions to the Gibbs energy overcome that due to the small positive contribution from interfacial tension. Ruckenstein's view is no doubt correct. However, to construct a quantitative, predictive model, we have to consider in more detail the Gibbs energy of a microemulsion, as we have attempted to do here.

First, we consider the entropy of mixing. The common method for calculating the entropy of mixing is based on equations similar to that of Carnahan-Starling or that of Flory-Huggins. However, these equations are for random mixtures. As pointed out by Luisi (1984), microemulsions represent a form of self-organization of matter; they can be considered as a primitive step toward forming biosubstances. The entropy of mixing must reflect this semiorganization. In our model, we assure that nearly all surfactant molecules exist between the water and oil molecules. This partial ordering intuitively causes a decrease in the entropy of mixing.

For partially ordered systems, another shortcoming of the Flory-Huggins equation becomes clear when the surfactant concentration approaches zero; in that case, the number of possible configurations should return to a small value close to unity, corresponding to immiscible water and oil. However, if we use the Flory-Huggins random mixing approach, we overestimate the entropy.

Second, we consider the energy effect. Ruckenstein emphasizes that low interfacial tension gives a low Gibbs energy. However, in thermodynamically stable microemulsions there is no well-defined surface. We cannot determine the interfacial tension experimentally. In our model, the contribution of the so-called interfacial tension is represented by parameter a_{WO}, which provides a measure of the interaction between water and oil at the interface.

Figure 8 shows the variation of spinodals with a_{WO}. The more negative a_{WO}, the larger the binodal envelope, i.e., the more unstable the microemulsion. If the so-called interfacial tension

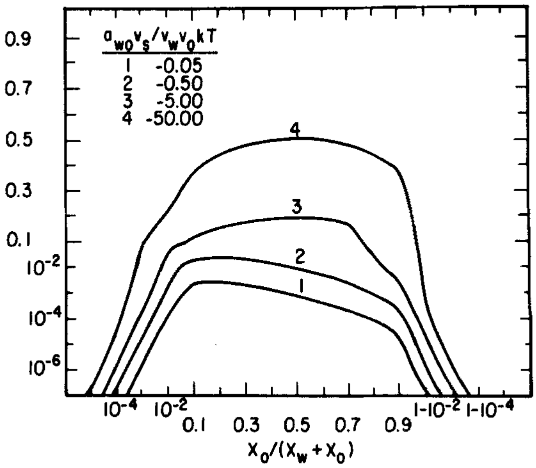

Figure 8. Influence of a_{WO} on spinodals.

$r_S/r_W = 20.17$; $r_O/r_W = 10.08$; $j_m = 60$; $\epsilon_{(O-W)}/kT = 0.1$; $a_{SS(W)}/v_S kT = 1.0$; $a_{SS(O-W)}/v_S kT = 0.2$; $K_R^{-1} = 0.7038$; $K = 0.1 * 10$

equals zero, a_{WO} also approaches zero. In that event, a stable microemulsion always occurs in the entire range of oil-to-water ratios. For real systems, however, in most cases there is a finite phase-separation region, indicating that there is no surface layer in the classical sense. Water and oil molecules more or less permeate or penetrate into the boundary and increase the instability of the system. While not considered quantitatively in this work, the role of a cosurfactant lies mainly in lowering the absolute value of a_{WO}, leading to increased stability.

Other properties, in addition to the interfacial tension (or a_{WO}) have much influence on stability. One of them is a_{SS}, which is usually positive and represents the interaction between the micelles whose boundaries are composed of surfactant. Figure 9 shows the variation of spinodals with respect to a_{SS}. As interaction becomes stronger, i.e., as a_{SS} increases, the immiscibility gap becomes wider, i.e., more unstable. The value of a_{SS} primarily changes the higher surfactant-concentration boundary; it has only a minor effect on the lower surfactant-concentration boundary, consistent with our expectation. In the lower boundary, the concentration of surfactant is usually very small; therefore, a change in a_{SS} may not exert an important influence as in the upper boundary where the surfactant concentration is large. When the surfactant is an electrolyte, the function of a salt is to change the electric double layer outside or inside the micelle, therefore changing interaction parameter a_{SS} and affecting stability.

Another important factor is association constant K. Figure 10 shows the variation of spinodals with respect to K. Similar to a_{SS}, the larger K, the wider the immiscibility gap. However, contrary to a_{SS}, K primarily influences the lower surfactant-concentration boundary. The higher concentration boundary is essentially unaffected because the association constant mainly determines the concentration of monomer. As K becomes very small, the concentration of monomer approaches the total concentration of surfactant. In that event, the upper gap in Figure 10 disappears.

Finally, the stability of a microemulsion is influenced by sizes of the molecules of oil and surfactant. Figures 11 and 12 show these effects, respectively. Generally speaking, the larger the size of the oil molecule, the wider the spinodals for the oil-sur-

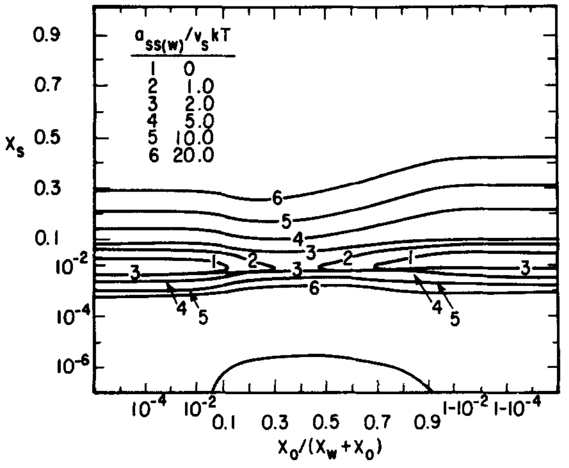

Figure 9. Influence of a_{SS} on spinodals.
$r_S/r_W = 20.17$; $r_O/r_W = 1.68$; $j_m = 60$; $\epsilon_{(O-W)}/kT = 0$; $a_{SS(O-W)}/v_S kT = 0$; $a_{WO} v_S / v_W v_O kT = -0.1 * 10^{-3}$; $K_R^{-1} = 0.7038$; $K = 0.1 * \cdot 10^2$

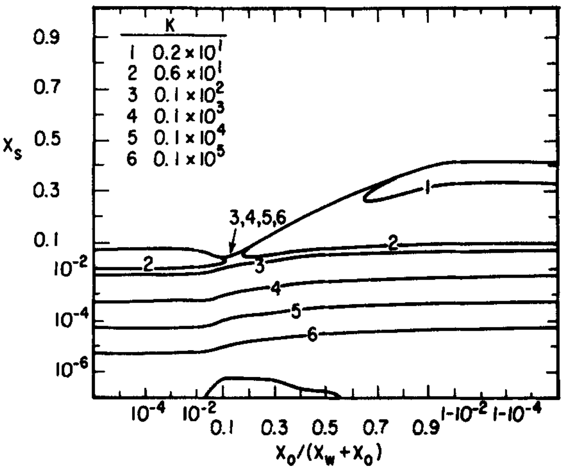

Figure 10. Influence of K on spinodals.
$r_S/r_W = 20.17$; $r_O/r_W = 10.08$; $j_m = 60$; $\epsilon_{(O-W)}/kT = 0.1$; $a_{SS(W)}/v_S kT = 1.0$; $a_{SS(O-W)}/v_S kT = 0.4$; $a_{WO} v_S / v_W v_O kT = -0.1 * 10^{-4}$; $K_R^{-1} = 0.7038$

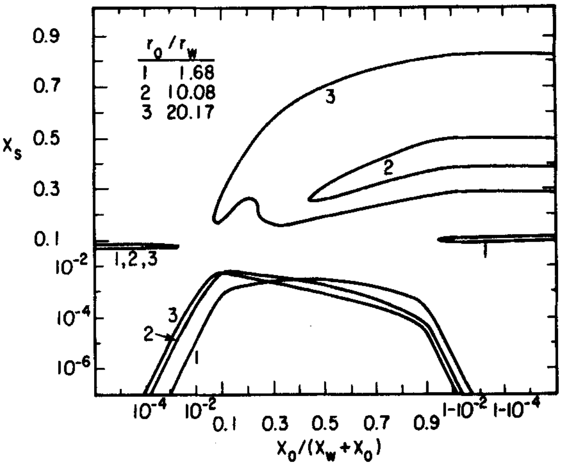

Figure 11. Influence of r_O/r_W on spinodals.
$r_S/r_W = 20.17$; $j_m = 60$; $\epsilon_{(O-W)}/kT = 0$; $a_{SS(W)}/v_S kT = 1.5$; $a_{SS(O-W)}/v_S kT = 0$; $a_{WO} v_S / v_W v_O kT = -0.1$; $K_R^{-1} = 0.7038$; $K = 0.18 * 10$

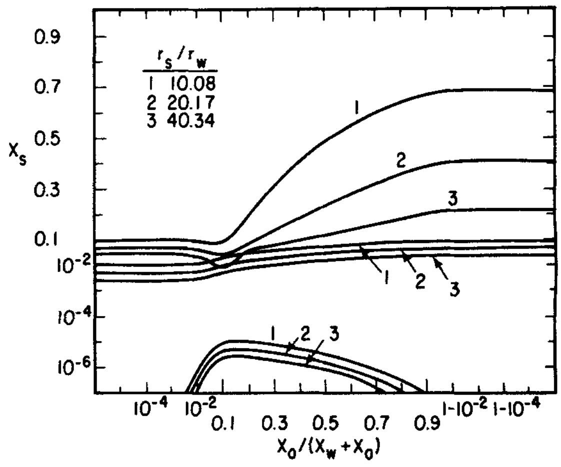

Figure 12. Influence of r_S/r_W on spinodals.

factant binary and the corresponding ternary two-phase region. By contrast, the larger the size of the surfactant molecule, the greater the stability.

The bottom of Figure 12 shows that as r_O/r_W rises, the spinodals become more unsymmetric.

Conclusions

In this work we have presented a molecular-thermodynamic model for microemulsions which reasonably describes the stability of these systems. Our equation for the Gibbs energy contains several parameters with clear physical meaning. These parameters make the equation flexible enough to reproduce a variety of different kinds of phase diagrams. While the present model is limited to relatively simple ternary systems containing water, oil, and surfactant, it comprises the essentials of a molecular-thermodynamic framework suitable for further development.

Acknowledgment

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Science Division of the U.S. Department of Energy. Additional support was supplied by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Notation

a = attractive parameter
D = association energy
G = Gibbs energy
j = aggregation number
j_m = smallest allowed aggregation number
k = Boltzmann constant
K = equilibrium constant
M = moment of distribution
N = number of molecules, sites, or bonds
r = size parameter
T = temperature
s = entropy
v = molecular volume
V = volume
x = mole fraction
z = coordination number
$\langle - \rangle$ = average

Greek letters

ϵ = potential energy
γ = activity coefficient
μ = chemical potential
Ω = number of configurations
Φ = volume fraction
σ^2 = variance

Subscripts

f = free volume
k = order of the moment of distribution
M = micelle
o = smallest micelle
O = oil
r = segment
S = surfactant
T = total number of molecules
T, mic = total number of micelles
W = water
V = vacancy

Superscripts

o = standard state
$*$ = generalized function

Appendix A: Derivation of the Size Distribution

For minimizing the Gibbs energy, we calculate the total differential from Eq. 1:

$$dG = \sum_{j=1}^{k=\infty} \frac{\partial G}{\partial N_{Sj}} dN_{Sj} = 0 \tag{A1}$$

$$\frac{\partial G}{\partial N_{Sj}} = \frac{\partial G^o}{\partial N_{Sj}} + \frac{\partial \Delta G_I}{\partial N_{Sj}} + \frac{\partial \Delta G_{II}}{\partial N_{Sj}} + \frac{\partial \Delta G_{III}}{\partial N_{Sj}} \tag{A2}$$

Substituting Eqs. 3, 15, and 23 into Eq. A2 yields

$$\frac{\partial G}{\partial N_{Sj}} = \mu^o_{Sj} + kT(\ln \Phi_{Sj} + 1 + jC) \tag{A3}$$

where

$$\begin{aligned} C = \ln & \frac{x_S}{(x_W + x_S/2 + N_V/2N_T)^{1/2}(x_O + x_S/2 + N_V/2N_T)^{1/2}} \\ & - \ln \Phi_S - 1 - r_S \frac{N_{T,mic} - N_S}{N_r} - \frac{2N_S a_{SS}}{VkT} \\ & + v_S \frac{N_S^2 a_{SS} + N_W N_O a_{WO}}{V^2 \mathrm{kT}} \end{aligned} \tag{A4}$$

$N_{T,mic} = \Sigma N_{Sj}$, is the total number of micelles and v_S is the molecular volume of the surfactant monomer.

We minimize the Gibbs energy subject to the constraint of mass conservation. We use Lagrange's method by introducing an undetermined multiplier α,

$$N_S = \sum_{j=1}^{j=\infty} jN_{Sj} \tag{A5}$$

$$\sum_{j=1}^{j=\infty} \alpha j dN_{Sj} = 0 \tag{A6}$$

We obtain

$$\ln \Phi_{Sj} = -\frac{\mu^o_{Sj}}{kT} - 1 - jC + j\frac{\alpha}{kT} \tag{A7}$$

$$\Phi_{Sj} = \Phi^j_{S1} \exp - \frac{\mu^o_{Sj} - j\mu^o_{S1}}{kT} \exp(j-1) \tag{A8}$$

From Eqs. 4, 5, and 10 we have

$$\begin{aligned} \mu^o_{Sj} - j\mu^o_{S1} = & -D_o(jm - 1) - D(j - jm) + kT \ln j \\ & - (j-1)kT \ln v_{f,S1} \end{aligned} \tag{A9}$$

Substitution into Eq. A8 yields Eq. 25.

Appendix B: Equations for Chemical Potentials

The relation between chemical potential and Gibbs energy is given by

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j=1}} \tag{B1}$$

For an associated system, the chemical potential of the associated component S equals the chemical potential of monomer S_1 (Prigogine and Defay, 1954):

$$\mu_S = \mu_{S1} \tag{B2}$$

For a microemulsion, the chemical potentials are derived from Eq. 1 as follows:

$$\begin{aligned}\frac{\mu_S}{kT} &= \frac{\mu_{S1}}{kT} = \frac{1}{kT}\frac{\partial G}{\partial N_{S1}} = \frac{\mu^o_{S1(W)}}{kT} \\ &+ \frac{\epsilon_{(O-W)}\Phi_O}{kT(1-\Phi_S)} + \ln\Phi_{S1} - \ln\Phi_S - \frac{N_{T,mic}r_S}{N_r} + \Phi_S \\ &+ \ln\frac{x_S}{(x_W + x_S/2 + N_V/2N_T)^{1/2}(x_O + x_S/2 + N_V/2N_T)^{1/2}} \\ &+ \ln\left(\frac{N_V}{2N_T}\right)^{1/2} + \frac{a_{SS(W)}}{v_S kT}(-2\Phi_S + \Phi_S^2) \\ &+ \frac{a_{SS(O-W)}}{v_S kT}(-2\Phi_S + \Phi_S^2)\frac{\Phi_O}{1-\Phi^s} + \frac{a_{WO}v_S}{v_W v_O kT}\Phi_W\Phi_O\end{aligned} \tag{B3}$$

$$\begin{aligned}\frac{\mu_W}{kT} &= \frac{1}{kT}\frac{\partial G}{\partial N_W} = \frac{\mu^o_W}{kT} \\ &- \frac{\epsilon_{(O-W)}}{kT}\frac{r_W\Phi_S\Phi_O}{r_S(1-\Phi_S)^2} - \frac{N_{T,mic}r_W}{N_r} + \Phi_S\frac{r_W}{r_S} \\ &+ \ln\frac{x_W}{x_W + x_S/2 + N_V/2N_T} + \frac{a_{SS(W)}}{v_S kT}\Phi_S^2\frac{r_W}{r_S} \\ &+ \frac{a_{SS(O-W)}}{v_S kT}\frac{r_W}{r_S}\frac{\Phi_S^2(2-\Phi_S)\Phi_O}{(1-\Phi_S)^2} + \frac{a_{WO}v_S}{v_W v_O kT}\frac{r_W}{r_S} \\ &\cdot(-\Phi_O + \Phi_W\Phi_O)\end{aligned} \tag{B4}$$

$$\begin{aligned}\frac{\mu_O}{kT} &= \frac{1}{kT}\frac{\partial G}{\partial N_O} = \frac{\mu^o_O}{kT} \\ &- \frac{\epsilon_{(O-W)}}{kT}\frac{r_O\Phi_S\Phi_W}{r_S(1-\Phi_S)^2} - \frac{N_{T,mic}r_O}{N_r} \\ &+ \Phi_S\frac{r_O}{r_S} + \ln\frac{x_O}{x_O + x_S/2 + N_V/2N_T} + \frac{a_{SS(W)}}{v_S kT}\Phi_S^2\frac{r_O}{r_S} \\ &+ \frac{a_{SS(O-W)}}{v_S kT}\frac{r_O}{r_S}\frac{\Phi_S^2}{(1-\Phi_S)^2}(-1 + \Phi_S + 2\Phi_O + \Phi_O\Phi_S) \\ &+ \frac{a_{WO}v_S}{v_W v_O kT}\frac{r_O}{r_S}(-\Phi_W + \Phi_W\Phi_O)\end{aligned} \tag{B5}$$

where v_W and v_O are volumes of water molecule and oil molecule, respectively. The term $\ln(N_V/2N_T)^{1/2}$ in Eq. B3 is necessary to conform with the standard state of surfactant, which should satisfy the boundary condition for a binary that, when mole fraction $x_S = 0$, activity coefficient (unsymmetric convention) of surfactant $\gamma_S = 1$. The value of N_V/N_T can be arbitrarily small, e.g., 10^{-9}; its exact value has virtually no influence on the final results of phase equilibrium calculations. In Eqs. B4 and B5, as $x_W = 1$ or $x_O = 1$, we have a very small residual term $\ln(1 + N_V/2N_T)$. For consistency, it can be considered as absorbed by the standard-state chemical potential corresponding to pure water or pure oil.

In these equations, Φ_{S1} for surfactant monomer is calculated from chemical-association equilibria, mainly Eq. 31.

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Manuscript received Sept. 29, 1987, revision received Dec. 31, 1987.