Molecular Theory of Microemulsions

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In this paper, a molecular thermodynamic approach is developed to predict the structural and compositional characteristics of microemulsions. The theory can be applied not only to oil-in-water and water-in-oil droplet-type microemulsions but also to bicontinuous microemulsions. This treatment constitutes an extension of our earlier approaches to micelles, mixed micelles, and solubilization but also takes into account the self-association of alcohol in the oil phase and the excluded-volume interactions among the droplets. Illustrative results are presented for an anionic surfactant (SDS)–pentanol–cyclohexane–water–NaCl system. Microstructural features including the droplet radius, the thickness of the surfactant layer at the interface, the number of molecules of various species in a droplet, the size and composition dispersions of the droplets, and the distribution of the surfactant, oil, alcohol, and water molecules in the various microdomains are calculated. Further, the model allows the identification of the transition from a two-phase droplet-type microemulsion system to a three-phase microemulsion system involving a bicontinuous microemulsion. The persistence length of the bicontinuous microemulsion is also predicted by the model. Finally, the model permits the calculation of the interfacial tension between a microemulsion and the coexisting phase.

1. Introduction

Microemulsions are thermodynamically stable dispersions of oil and water stabilized by a surfactant and, in many cases, also a cosurfactant.[1–4] The microemulsions can be of the droplet type, either with spherical oil droplets dispersed in a continuous medium of water (oil-in-water microemulsions, O/W) or with spherical water droplets dispersed in a continuous medium of oil (water-in-oil microemulsions, W/O). The droplet-type microemulsions can be either a single-phase system or part of a two-phase system wherein the microemulsion phase coexists with an excess dispersed phase (an upper phase of excess oil in the case of O/W and a lower phase of excess water in the case of W/O microemulsions). There are also non-droplet-type microemulsions, referred to as middle-phase microemulsions. In this case, the microemulsion phase is part of a three-phase system with the microemulsion phase in the middle coexisting with an upper phase of excess oil and a lower phase of excess water. One possible structure of this middle-phase microemulsion, characterized by randomly distributed oil and water microdomains and bicontinuity in both oil and water domains, is known as the bicontinuous microemulsion. Numerous experimental studies have shown[1,2,4] that one can achieve a transition
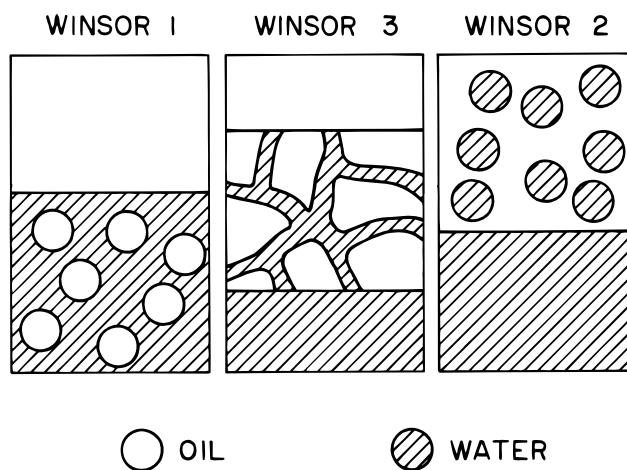
Figure 1. Schematic representation of the transition from a two-phase system with an oil-in-water droplet microemulsion to a three phase system with a bicontinuous microemulsion and to a two-phase system with a water-in-oil droplet microemulsion.

from a two-phase system involving an O/W droplet-type microemulsion to a two-phase system involving a W/O droplet-type microemulsion by passing through a three-phase system containing a bicontinuous microemulsion (Figure 1). Such phase transitions can be realized in many different ways, e.g., by increasing the concentration of added electrolytes when the surfactant employed is ionic, by increasing the temperature when the surfactant is nonionic, and by increasing the concentration of alcohol (typically butanol to hexanol) when the surfactant is ionic, nonionic, or zwitterionic.

Theoretical studies of microemulsions have focused on various features of the complex systems mentioned

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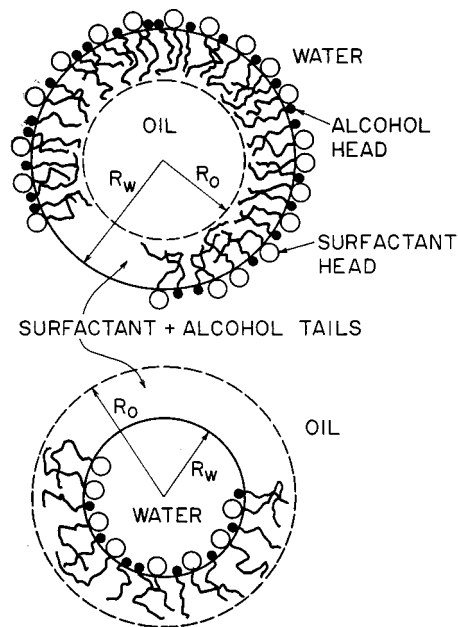
above.[3-10] However, currently there exists no model which can predict the detailed phase behavior and the microstructural characteristics of the microemulsion systems starting from the composition and molecular structures of the constituent molecules. Such models were formulated in our earlier work for micelles, vesicles, and mixed micelles in aqueous media and for the solubilization of oil inside such aggregates.[11-15] These models are extended here to microemulsions. On this basis, a predictive approach for the various characteristics of microemulsions, such as the droplet radius, the number of molecules of various species in a droplet, and the size and composition dispersions of the droplets, is developed. The model also allows the prediction of the interfacial tension between the microemulsion and the coexisting phase. Further, the model allows one to examine the transition from a two-phase system involving a droplet-type microemulsion to a three-phase system involving a bicontinuous microemulsion. The persistence length in bicontinuous microemulsions is also predicted.

In developing a molecular treatment for microemulsions, we take into account the chain packing, which depends on the curvature of the aggregates, the self-association of alcohol in the oil, the penetration of the interfacial layer region of the microemulsion by the oil molecules, their effects on chain packing and interfacial energies, and the hard-core interactions among the droplets. Since the present treatment of microemulsions is an extension of our approach to micellization and solubilization, many of the above aspects of the model that were presented in detail in earlier papers are only briefly summarized here. Two additional features included in this paper are self-association of alcohol in oil domains and hard-sphere repulsive interactions among droplets.

To illustrate the present theory, calculations were carried out for a system consisting of an anionic surfactant, oil, water, alcohol, and electrolyte. Obviously, this model can be readily applied to simpler microemulsions free of alcohol, wherein the phase transitions are caused by varying the electrolyte concentration or the temperature.

2. Geometric Characteristics of Microemulsions

Both O/W and W/O droplet structures have a core region surrounded by an interfacial film, depicted schematically in Figure 2. The interfacial film excludes the headgroups of the surfactant and the alcohol. This region is analogous to the micelle core and, as confirmed by many experiments, is free of water molecules and is thus hydrophobic in character. Each droplet contains g_k molecules of kind k

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Figure 2. Geometrical variables R_W and R_O characterizing the size of O/W and W/O droplets in microemulsions.

(with k = S for surfactant, A for alcohol, O for oil, and W for water), among which g_{kI} molecules are present in the interfacial layer and the remaining ones are present in the core containing mainly the dispersed phase. For the reason mentioned above, there are no water molecules in the interfacial layer (i.e., $g_{WI} = 0$). The radii R_O and R_W provide the boundaries of the interfacial layer. The volume of the aggregate V_g can be related to the radii R_O and R_W via

$$V_g = \frac{4\pi R_O{}^3}{3} \tag{2.1}$$

for the water-in-oil droplets and

$$V_g = \frac{4\pi R_W{}^3}{3} + g_{SI}v_{SP} + g_{AI}v_{AP} \tag{2.2}$$

for the oil-in-water droplets, where v_{SP} and v_{AP} are the volumes of the polar headgroups of the surfactant and alcohol molecules, respectively. The volume V_I of the interfacial layer per surfactant molecule is given by

$$V_I = \frac{4\pi}{3g_{SI}}|R_O{}^3 - R_W{}^3| = \frac{g_{SI}v_{ST} + g_{AI}v_{AT} + g_{OI}v_O}{g_{SI}} \tag{2.3}$$

where v_{ST}, v_{AT}, and v_O are the volumes of surfactant tail, alcohol tail, and oil, respectively. The surface area of the droplet in contact with water, per surfactant molecule, is given by

$$a = \frac{4\pi R_W{}^2}{g_{SI}} \tag{2.4}$$

Combining eqs 2.3 and 2.4 yields

$$\frac{R_O}{R_W} = \left(\frac{3V_I}{a|R_O - R_W|} - \frac{3}{4}\right)^{1/2} - \frac{1}{2} \tag{2.5}$$

For the sake of simplicity, the thickness of the interfacial layer $|R_O - R_W|$ is taken to be the composition average of the surfactant tail length l_S and the alcohol tail length l_A:

$$|R_O - R_W| = \frac{l_S + (g_{AI}/g_{SI})l_A}{1 + (g_{AI}/g_{SI})} \quad (2.6)$$

The determination of this thickness from free energy minimum considerations require a more detailed treatment of the interfacial film than justified by the available experimental information.

Consequently, a particular O/W or W/O droplet can be completely characterized by three geometrical variables. A set of convenient variables is (i) the surface area of the droplet in contact with water per surfactant molecule, a, (ii) the ratio of alcohol-to-surfactant molecules in the interfacial layer, g_{AI}/g_{SI}, and (iii) the ratio of oil-to-surfactant molecules in the interfacial layer, g_{OI}/g_{SI}. For a flat interfacial layer, denoting the layer thickness by $|R_O - R_W|_F$ and the area per surfactant molecule of the flat interface by a_F, one can write the following on the basis of molecular packing considerations:

$$a_F|R_O - R_W|_F = V_I \quad (2.7)$$

Therefore, for a flat interface, only two geometrical variables are needed for its complete specification, instead of the three needed for a spherical droplet.

3. Size Distribution of Droplet-Type Microemulsions

For a W/O microemulsion, the size and composition distribution of the aggregates can be written as for micelles, mixed micelles, and solubilization. However, whereas the earlier expressions were formulated for dilute solutions where interaggregate interactions are negligible, the size and composition distribution for microemulsions will take into account the hard-sphere repulsions among the droplets. For a single-phase microemulsion, the mole fraction X_{gO} of water-in-oil droplets is given by the following expression (see Appendix A for the derivation):

$$X_{gO}\gamma_{gO} = \Omega^{g_{SI}}f_{WO}{}^{g_W}$$

$$\Omega = (X_{SW}\gamma_{SW})(X_{AW}\gamma_{AW})^{g_{AI}/g_{SI}}(X_{OO}\gamma_{OO})^{g_{OI}/g_{SI}} \exp\left(-\frac{\Delta\mu_{gI}^\circ}{kT}\right)$$

$$\Delta\mu_{gI}^\circ = \frac{1}{g_{SI}}\mu_{gI}^\circ - \mu_{SW}^\circ - \frac{g_{AI}}{g_{SI}}\mu_{AW}^\circ - \frac{g_{OI}}{g_{SI}}\mu_{OO}^\circ \quad (3.1)$$

In the preceding equations, the subscript g refers to a droplet containing a total of g molecules ($g = g_S + g_A + g_O + g_W$), X_{gO} is the mole fraction of aggregates of size g in the continuous oil (O) phase, X_{SW} and X_{AW} are the mole fractions of singly dispersed surfactant and alcohol molecules, respectively, in the dispersed water phase, μ_{SW}° and μ_{AW}° are their standard chemical potentials, and γ_{SW} and γ_{AW} are their activity coefficients. X_{OO} denotes the mole fraction of oil in the continuous oil phase, μ_{OO}° is its standard chemical potential, and γ_{OO} is its activity coefficient.

It is important to emphasize that the alcohols used as cosurfactants have high solubility in the oil phase because they are present there as both single molecules and aggregates. Therefore, in calculating X_{OO}, one must consider the self-association of alcohol in the oil phase. The activity coefficients arise because of the hard-sphere interactions among the droplets. Therefore, in the dispersed phase, which is free of droplets, the activity coefficients are equal to unity, whereas, in the continuous phase, which contains the droplets, the activity coefficients differ from unity.

The fractional saturation of water in the oil phase is denoted f_{WO}. For a single-phase microemulsion, f_{WO} is less than unity. As the amount of water in the phase increases, f_{WO} progressively increases and reaches the constant value of unity when an excess aqueous phase coexisting with the microemulsion phase appears, creating a two-phase system.

The standard free energy difference $\Delta\mu_{gI}^\circ$ in eq 3.1 is due to the transfer of one surfactant molecule and (g_{AI}/g_{SI}) alcohol molecules from water and (g_{OI}/g_{SI}) oil molecules from pure oil to the interfacial layer of the microemulsion droplet. Expressions for $\Delta\mu_{gI}^\circ$ are provided in section 7 of the paper.

When eq 3.1 is used to calculate the size and composition distributions of droplets in a single-phase O/W microemulsion, X_{gO} and γ_{gO} should be replaced by X_{gW} and γ_{gW} and the factor $f_{WO}^{g_O}$ should be replaced by $f_{OW}^{g_O}$, where f_{OW} denotes the fractional saturation of oil in the water phase. As before, f_{OW} is less than unity for a single-phase microemulsion and reaches the constant value of unity when a two-phase system comes into existence with an excess oil phase coexisting with the microemulsion phase.

To predict the characteristics of a microemulsion on the basis of the size distribution relation (3.1), only two control variables, X_{SW} and X_{AW}, must be specified. This is equivalent to fixing the total amounts of surfactant and alcohol in the microemulsion. Detailed calculations of the size and composition distributions involved in eq 3.1 are not required. Instead, as shown in the following section and Appendix C, the size and composition dispersions can be obtained from calculations involving only the maximum term of the size distribution. By calculating how the size and composition corresponding to the most populous aggregates (i.e., the maximum in X_g) vary when the surfactant concentration is slightly perturbed, one can obtain the variance in the size and composition of aggregates with respect to their average values.

In eq 3.1, the activity coefficients appear as a result of the hard-sphere repulsions among the droplets. Since the calculations focus on the most populous aggregates, the hard-sphere repulsions will be expressed in terms of a single droplet size corresponding to the most populous aggregates. One can derive expressions for the activity coefficients γ_{kO} of a component k in the continuous phase O starting from an equation for the osmotic pressure of a hard-sphere fluid,[3,4] such as that based on the Carnahan–Starling equation of state (see Appendix B for the derivation):

$$\ln \gamma_{kO} = -\frac{v_k}{V_{gO}}\Phi_{gO}\frac{1 + \Phi_{gO} + \Phi_{gO}{}^2 - \Phi_{gO}{}^3}{(1 - \Phi_{gO})^3} \quad (3.2)$$

where V_{gO} is the volume of a droplet and Φ_{gO} is the volume fraction of the droplets in the microemulsion. Combining eq 3.2 with the Gibbs–Duhem equation, we obtain the following expression for the activity coefficient γ_{gO} of the droplet (Appendix B):

$$\ln \gamma_{gO} = \ln\left(\frac{\Phi_{gO}/V_{gO}}{X_{gO}\sum_{k\neq g}\Phi_{kO}/v_k}\right) + \frac{7\Phi_{gO} - 3\Phi_{gO}{}^2 - \Phi_{gO}{}^3}{(1 - \Phi_{gO})^2} \quad (3.3)$$

where Φ_{kO} is the volume fraction of component k in the continuous phase O.

Equation 3.1 is an implicit relation because the activity coefficients γ_{gO} and γ_{gW} depend on the volume fractions

of the droplets and hence on the mole fractions X_{gO} and X_{gW}, respectively. The volume fractions of the droplets can be related to the mole fractions of various components and their respective volumes through the relations

$$\Phi_{gW} = \frac{X_{gW} V_{gW}}{X_{gW} V_{gW} + X_{SW} v_S + X_{WW} v_W + X_{AW} v_A}$$

$$\Phi_{gO} = \frac{X_{gO} V_{gO}}{X_{gO} V_{gO} + \sum j X_{jAO} v_A + X_{OO} v_O} \quad (3.4)$$

In the first expression, X_{WW} can be replaced by $(1 - X_{gW} - X_{AW} - X_{SW})$ because the sum of all mole fractions should be unity. In the second expression, the total mole fraction $\sum j X_{jAO}$ of alcohol in the oil phase accounts for the alcohol present as both monomers and aggregates in the oil phase and is calculated on the basis of the continuous-association model[16] as described in Appendix D.

For given values of the control variables X_{SW} and X_{AW}, the maximum in X_{gO} (or X_{gW}) was found, using the IMSL subroutine ZXMWD, by solving the implicit eq 3.1 in combination with eq 3.4. As mentioned in section 2, the area per surfactant molecule a, the alcohol-to-surfactant ratio g_{AI}/g_{SI}, and the oil-to-surfactant ratio g_{OI}/g_{SI} in the interfacial layer were selected as the three independent variables with respect to which the maximization was carried out. The total volume fraction Φ_S of surfactant present in the microemulsion is given by

$$\Phi_S = \Phi_{gO} \frac{g_{SI} v_S}{V_{gO}} \text{ (for W/O)} \qquad \Phi_S = \Phi_{gW} \frac{g_{SI} v_S}{V_{gW}} \text{ (for O/W)}$$
$$(3.5)$$

because the amount of singly dispersed surfactant molecules is relatively small and can be neglected. The total volume fraction of alcohol in the microemulsion, Φ_A, can be obtained from a species balance, since the concentrations of alcohol in the water domain, the oil domain, and the interfacial layer are known.

4. Size and Composition Dispersions of Droplets

The size and composition dispersions of droplets can be estimated by using the maximum-term method, without performing detailed distribution calculations. This is accomplished by adapting the approach used for micellar systems,[17,18] as described in Appendix C. The aggregate corresponding to the maximum of X_{gO} or X_{gW} is considered to provide the number-average size and composition of the equilibrium droplets. For each component k (=S, A, O, or W) present in the microemulsion, the mean-square deviation $\sigma_n^2(k)$ from the number-average number of molecules $g_n(k)$ can be shown to be

$$\frac{\sigma_n(k)}{g_n(k)} = \left(\frac{\Delta \ln g_n(k)}{\Delta \ln(g_n(k) X_{gM})} \right)^{1/2} \quad (4.1)$$

where X_{gM} (=X_{gO} or X_{gW}) is the mole fraction of the droplet corresponding to the maximum in the distribution, $g_n(k)$ are the numbers of molecules of kind k in that droplet, and Δ denotes the difference between two values. Con-

sequently, by calculating the maximum X_{gM} and the corresponding numbers of molecules $g_n(k)$ for two slightly different conditions (for example, through marginal variations in X_{SW}), one can estimate $\sigma_n(k)$ for each of the four components k and thus provide information about the size and composition dispersions of the droplet.

The root-mean-square deviation in the droplet radius σ_R is obtained from purely geometric considerations using the calculated values of $\sigma_n(k)$. Equating the volume of the droplet to the volumes contributed by all the component molecules yields

$$\frac{4\pi R^3}{3} = \sum g_n(k) \ v_k$$

$$\frac{4\pi (R + \sigma_R)^3}{3} - \frac{4\pi R^3}{3} = \sum \sigma_n(k) \ v_k \quad (4.2)$$

By rearranging eq 4.2, we obtain the following expression for the dispersion in the droplet radius:

$$\frac{\sigma_R}{R} = \left(1 + \frac{\sum \sigma_n(k) \ v_k}{\sum g_n(k) \ v_k} \right)^{1/3} - 1 \quad (4.3)$$

5. Calculation of Interfacial Tension

The interfacial tension γ_F refers to that at the flat interface (denoted by subscript F) that separates the microemulsion from the coexisting excess dispersed phase. The flat interface can be treated as a planar infinite aggregate. The chemical potentials of the molecules in this interfacial layer should be equal to the chemical potentials of the molecules in the bulk phases and hence

$$\left(\frac{1}{g_{SI}} \right)_F \frac{(u_{gI}^\circ)_F}{kT} - \frac{\gamma_F a_F}{kT} = \frac{\mu_{SW}}{kT} + \left(\frac{g_{AI}}{g_{SI}} \right)_F \frac{\mu_{AW}}{kT} + \left(\frac{g_{OI}}{g_{SI}} \right)_F \frac{\mu_{OO}}{kT} \quad (5.1)$$

In the preceding equation, the first term on the left-hand side is the reference state chemical potential per surfactant molecule of an infinite-size aggregate and the second term involving γ_F accounts for the interfacial tension to which this infinite aggregate is subjected. The terms on the right-hand side represent the chemical potentials of the surfactant, alcohol, and oil in the bulk phase in equilibrium with the molecules at the interface. Using eq 3.1, the above equation can be rewritten as

$$\frac{\gamma_F a_F}{kT} = \frac{(\Delta \mu_{gI}^\circ)_F}{kT} - \left[\ln \gamma_{SW} X_{SW} + \left(\frac{g_{AI}}{g_{SI}} \right)_F \ln g_{AW} X_{AW} + \right.$$
$$\left. \left(\frac{g_{OI}}{g_{SI}} \right)_F \ln \gamma_{OO} X_{OO} \right] = -\ln \Omega_F \quad (5.2)$$

where $(\Delta \mu_{gI}^\circ)_F$ is the standard free energy difference associated with the transfer of one surfactant molecule and $(g_{AI}/g_{SI})_F$ alcohol molecules from their infinitely dilute states in water and $(g_{OI}/g_{SI})_F$ oil molecules from a pure oil phase to the flat interfacial layer. For given chemical potentials of various components in the system, the composition of the flat interfacial film (namely, a_F, $(g_{AI}/g_{SI})_F$, and $(g_{OI}/g_{SI})_F$) is obviously different from the composition of the interfacial film of droplets in the microemulsion phase (namely, a, g_{AI}/g_{SI}, and g_{OI}/g_{SI}).

6. Bicontinuous Microemulsions

No well-defined structural characterization of a bicontinuous microemulsion is currently available. However, it has been suggested that oil and water domains are

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randomly distributed within the bicontinuous microemulsion separated by locally planar interfaces.[3-8] A characteristic domain size or persistence length ξ_K has been defined[7] such that, for length scales smaller than ξ_K, the interface is essentially flat. Using this concept, one can establish conditions for the formation of a three-phase system containing a bicontinuous microemulsion phase coexisting with excess oil and water phases. One can also calculate, on the basis of the present molecular theory, the persistence length and the interfacial tensions between microemulsion and excess phases.

Considering a planar configuration, the size distribution of microemulsion domains in a bicontinuous microemulsion coexisting with two excess phases can be written, in a form similar to eq 3.1, as

$$X_g = \frac{1}{K}\Omega_F{}^{g_{SI}}$$

$$\Omega_F = X_{SW}X_{AW}{}^{(g_{AI}/g_{SI})_F}X_{OO}{}^{(g_{OI}/g_{SI})_F}\exp\left(-\frac{\Delta\mu_{gI}^\circ}{kT}\right)_F$$

$$(\Delta\mu_{gI}^\circ)_F = \left(\frac{1}{g_{SI}}\right)_F(\mu_{gI}^\circ)_F - \mu_{SW}^\circ - \left(\frac{g_{AI}}{g_{SI}}\right)_F\mu_{AW}^\circ - \left(\frac{g_{OI}}{g_{SI}}\right)_F\mu_{OO}^\circ \tag{6.1}$$

In these equations, the standard free energy terms are approximated as for a flat interface since the domains are considered locally flat and the activity coefficients have been taken as unity since there are no droplets in the water and oil domains. The factor K accounts for the fact that some molecules must remain at the corners and edges of the surfaces separating the oil and the water domains and not on the flat regions. Thus, K is a measure of the free energy cost of having molecules in such locations compared to those in the flat regions. While, for droplet microemulsions, an optimal value for g_{SI} could be obtained by maximizing X_g in eq 3.1, there is no maximum for X_g in eq 6.1, since Ω_F is independent of g_{SI}. The equilibrium characteristics of the microemulsion are obtained by maximizing Ω_F for given values of the control variables X_{SW} and X_{AW}.

One may note the analogy between the above equation and the equation $X_g = (1/K)Y^g$, where $Y = X_1 \exp(-\Delta\mu_{cyl}^\circ/kT)$, governing the formation of rodlike micelles.[11,18] The equilibrium structural characteristics of rodlike micelles are obtained from the maximum of Y or, equivalently, minimum of $\Delta\mu_{cyl}^\circ$, which is the standard state free energy difference between a molecule in the cylindrical part of the micelle and a singly dispersed molecule. K is the factor that accounts for the free energy cost of having molecules at the two globular ends of the cylinder rather than in the cylindrical part of the micelle and is thus analogous to the K of eq 6.1. Since Y is independent of g, the size distribution X_g does not have a maximum and rodlike micelles of all aggregation numbers are present in appreciable concentrations. Y is the analogue of Ω_F in eq 6.1.

The maximum of Ω_F is determined with respect to the two independent variables, the area per surfactant molecule of the interface, a_F, and the alcohol-to-surfactant ratio in the interfacial layer, $(g_{AI}/g_{SI})_F$. In contrast to that in the droplet-type microemulsion, the oil-to-surfactant ratio in the interfacial layer, $(g_{OI}/g_{SI})_F$, is not an independent variable but is determined by the packing constraint (eq 2.7) for flat layers.

The maximum value of Ω_F will be close to but smaller than unity, since otherwise the domain size distribution would diverge. Since the domain size g_{SI} can assume all possible values, the average domain size of the bicontinuous microemulsion is given by

$$(g_{SI})_{avg} = \frac{\sum g_{SI}X_g}{\sum X_g} = \frac{1}{1-\Omega_F} \tag{6.2}$$

where the last equality is obtained by performing the analytic summation of the two factors in the above expression on the basis of eq 6.1. The equilibrium area per surfactant molecule being a_F, the total surface area of the average domain is $a_F(g_{SI})_{avg}$, which can be used to obtain the following expression for the persistence length ξ_K:

$$6\xi_K{}^2 = (g_{SI})_{avg}a_F = \frac{a_F}{1-\Omega_F} \tag{6.3}$$

The numerical constant 6 in the preceding equation implies the cubic domain assumed by de Gennes and Taupin,[7] and the surface area $a_F(g_{SI})_{avg}$ is that of a cube of characteristic size ξ_K. For other domain geometries, such as the polyhedra considered by Talmon and Prager,[6] this numerical coefficient will be different. The relative proportions of the oil and water domains are related to the persistence length ξ_K and the volume fraction Φ_S of the surfactant present through the species balance relation

$$\xi_K = \frac{6\Phi(1-\Phi)v_S}{\Phi_S a_F} \tag{6.4}$$

In this equation, Φ stands for the volume fraction of the oil domain and includes the hydrophobic tails of the surfactant and alcohol in the interfacial layer, while $(1 - \Phi)$ stands for the volume fraction of the water domain and includes the headgroups of the surfactant and alcohol in the interfacial layer.

For given values of the control variables X_{SW} and X_{AW}, the maximum of Ω_F (eq 6.1) and the equilibrium characteristics of the flat layer can be calculated by employing the IMSL optimization subroutine ZXMWD. The concentration X_{SW} does not affect the equilibrium characteristics a_F, $(g_{AI}/g_{SI})_F$, and $(g_{OI}/g_{SI})_F$ of the interfacial layer but does influence the magnitude of Ω_F and the total amount of surfactant in the bicontinuous microemulsion. The persistence length can be calculated from eq 6.3 using the optimized value of Ω_F. For a specified total volume fraction Φ_S of surfactant in the microemulsion, the proportions of the oil and the water domains in the microemulsion can then be determined from eq 6.4. Finally, the volume fraction of the total alcohol Φ_A in the microemulsion can be calculated from a species balance, since the concentrations of alcohol in the water and the oil domains and in the interfacial layer are known.

To determine whether a droplet-type microemulsion coexists in equilibrium with an excess dispersed phase or a bicontinuous microemulsion coexists with both excess phases, one has to carry out the maximizations of X_g (eq 3.1) and Ω_F (eq 6.1) for given values of X_{AW} and X_{SW}. For low values of X_{AW} as well as for sufficiently large values of X_{AW}, a maximum in X_g occurs, indicating the formation of a two-phase droplet-type microemulsion system. However, for intermediate values of X_{AW}, no maximum of X_g exists and the radius of the equilibrium droplet diverges to infinity. In this region, a three-phase system involving a bicontinuous microemulsion is favored.

The interfacial tension at the flat interface is calculated using eq 5.2, but with the activity coefficients equated to unity. Hence

$$\frac{\gamma_F a_F}{kT} = \frac{(\Delta\mu_{gI}^\circ)_F}{kT} - \left[\ln X_{SW} + \left(\frac{g_{AI}}{g_{SI}}\right)_F \ln X_{AW} + \left(\frac{g_{OI}}{g_{SI}}\right)_F \ln X_{OO}\right] = -\ln \Omega_F \quad (6.5)$$

Since for physical reasons Ω_F is close to unity, the logarithmic term in the above equation can be expanded in series, and after taking into account eq 6.3, one obtains

$$\gamma_F = \frac{kT}{a_F}(-\ln \Omega_F) = \frac{kT}{a_F}(1 - \Omega_F) = \frac{kT}{6\xi_K^2} \quad (6.6)$$

This expression was suggested previously by de Gennes and Taupin[7] on the basis of scaling arguments. Experimentally, one can measure three different interfacial tensions in the three-phase system, namely, at the microemulsion−excess water phase boundary (γ_{MW}), at the microemulsion−excess oil phase boundary (γ_{MO}), and between the excess oil and excess water phases (γ_{OW}). On the basis of intuitive arguments, it has been suggested[8] that

$$\gamma_F = \gamma_{OW} \qquad \gamma_{MW} = \Phi\gamma_{OW} \qquad \gamma_{MO} = (1 - \Phi)\gamma_{OW} \quad (6.7)$$

7. Free Energy of Formation of the Interfacial Layer

The equations developed in previous sections can be used to calculate the structural features of microemulsions, provided explicit expressions for the standard free energies of transfer of surfactant and alcohol molecules from their infinitely dilute states in water and of oil molecules from the pure oil phase to the interfacial layer of the microemulsion droplets are available. Such expressions are given below for spherical layers of O/W droplets and W/O droplets and also for flat layers. The difference in the standard state free energy consists of a number of contributions:

$$\Delta\mu_{gI}^\circ = (\Delta\mu_{gI}^\circ)_{tr} + (\Delta\mu_{gI}^\circ)_{def} + (\Delta\mu_{gI}^\circ)_{int} + (\Delta\mu_{gI}^\circ)_{steric} + (\Delta\mu_{gI}^\circ)_{dipole} + (\Delta\mu_{gI}^\circ)_{ionic} + (\Delta\mu_{gI}^\circ)_{mix} \quad (7.1)$$

which account respectively for the transfer of surfactant and alcohol tails from water to the interfacial film, the deformation of the tails to satisfy packing constraints, the free energy of formation of the oil−water interface, the steric, dipolar, and ionic interactions among the headgroups, and the free energy of mixing of surfactant, alcohol, and oil in the film region. These contributions were previously examined in our treatments for micelles, mixed micelles, and solubilization in micelles.[11,18] Consequently, only the modifications required for the treatment of microemulsions are emphasized below.

7.1. Transfer Free Energy of Surfactant and Alcohol Tails. For the interfacial layer that contains g_{SI} surfactant and g_{AI} alcohol molecules, the transfer free energy per surfactant molecule is obtained by adding the contributions of the surfactant and alcohol molecules:

$$\frac{(\Delta\mu_{gI}^\circ)_{tr}}{kT} = \frac{(\Delta\mu_{gI}^\circ)_{tr,S}}{kT} + \left(\frac{g_{AI}}{g_{SI}}\right)\frac{(\Delta\mu_{gI}^\circ)_{tr,A}}{kT} \quad (7.2)$$

The expressions for the transfer free energy of methyl and methylene groups obtained previously[11] are used to calculate the transfer free energies of the surfactant and alcohol tails. The expression for a methylene group of an aliphatic tail at temperature T (in kelvins) has the form

$$(\Delta\mu_{gI}^\circ)_{tr}/kT = 5.85 \ln T + 896/T - 36.15 - 0.0056T \quad (7.3)$$

while that for a methyl group in the aliphatic chain has the form

$$(\Delta\mu_{gI}^\circ)_{tr}/kT = 3.38 \ln T + 4064/T - 44.13 + 0.02595T \quad (7.4)$$

For the short-chain alcohols considered here, the methylene group adjacent to the hydroxyl group is considered to make no contribution to the transfer free energy because it is located close to the hydrophilic domain of the aggregate.

High concentrations of electrolyte affect the transfer free energy, and the extra contribution due to the presence of NaCl at 25 °C is given by[19]

$$(\Delta\mu_{gI}^\circ)_{tr}^{ex}/kT = (-0.322 - 0.064n_C)C_{add} \quad (7.5)$$

where C_{add} is the molarity of NaCl in the aqueous domain of the microemulsion and n_C is the number of methyl and methylene groups of the surfactant or alcohol tails. Since no direct information on this extra contribution at other temperatures is available, the temperature dependence of the methyl and methylene group contributions in the presence of added electrolyte in the above equation will be taken as equal to that in salt-free systems.

7.2. Deformation Free Energy of Surfactant and Alcohol Tails. As in the treatment of mixed micelles,[12,18] this free energy contribution is calculated by adding the contributions from both surfactant and alcohol tails. Since the thickness of the interfacial layer $|R_O - R_W|$ is larger than the extended length l_A of the alcohol tail, a part of the interfacial film is not accessible to the alcohol tails. Such a packing problem for molecules of differing tail lengths was treated in an earlier paper,[12] giving

$$\frac{(\Delta\mu_{gI}^\circ)_{def}}{kT} = \frac{10\pi^2}{80}\left(P\frac{|R_W - R_O|^2}{N_S L^2} + \frac{g_{AI}}{g_{SI}}\frac{l_A^2}{N_A L^2}\right) \quad (7.6)$$

where N_S ($=l_S/L$) and N_A ($=l_A/L$) are the number of segments of the surfactant and alcohol tails, L ($=4.6$ Å) is the effective segment length (defined such that L^2 is the cross-sectional area of the tail), and P is the packing factor defined as

$$P = \frac{V_I}{a|R_W - R_O|} \quad (7.7)$$

For flat interfaces, $P = 1$, because of the packing constraint provided by eq 2.7.

7.3. Interfacial Free Energy of the Layer-Water Contact. This free energy contribution is calculated using the expression

$$\frac{(\Delta\mu_{gI}^\circ)_{int}}{kT} = \frac{\sigma_{agg}}{kT}\left(a - a_{oS} - \frac{g_{AI}}{g_{SI}}a_{oA}\right) \quad (7.8)$$

where σ_{agg} is the macroscopic interfacial tension between the hydrophobic domain and water, a is the surface area per surfactant molecule of the interfacial layer, and a_{oS} and a_{oA} are the areas per molecule shielded from contact

(19) Tanford, C. *The Hydrophobic Effect*; Wiley: New York, 1973; 2nd ed., 1980.

with water by the headgroups of surfactant and alcohol molecules, respectively. For surfactants, a_{oS} is equated to the smaller between a_{pS} and L^2, as described in refs 11 and 18, where a_{pS} is the cross-sectional area of the polar headgroup. For alcohols, the cross-sectional area of the hydroxyl headgroup a_{pA} is about 8 Å^2, which is smaller than L^2; hence, $a_{pA} = a_{oA} = 8$ Å^2.

The interfacial tension σ_{agg} depends on the composition of the hydrophobic domain of the layer and thus on the surfactant tail−water, alcohol tail−water, and oil−water interfacial tensions. Since the surfactant and alcohol tails considered here are aliphatic chains, their interfacial tensions against water are practically the same and are taken to be σ_{SW}, for which expressions are provided in refs 11 and 18. If the oil in the interfacial layer is a saturated hydrocarbon, the oil−water interfacial tension σ_{OW} is practically the same as the tail−water interfacial tension. However, if the oil is an aromatic hydrocarbon, its interfacial tension against water is appreciably different from that between the tails and water. Depending upon the oil−water interfacial tension, a preferential location of the oil molecules in contact with water will occur, and this affects the overall interfacial tension σ_{agg}. For a volume fraction η_O of the oil in the interfacial layer, the interfacial tension σ_{agg} can be estimated using the approach of Prigogine,[20,21] as in our earlier paper dealing with solubilization.[11] In that approach, the interfacial tension of a solution was obtained by first calculating the composition of the surface monolayer, thus accounting for the preferential location of any one component at this surface monolayer. It is not possible to identify a bulk region and surface monolayer region in the present case, since the interfacial layer itself consists only of a monolayer. Nevertheless, the formal application of the Prigogine approach provides a way to at least approximately take into account the specificity of the oil. Thus, the interfacial layer is considered to be a solution with a uniform oil volume fraction of η_O. Corresponding to this composition, the volume fraction of the oil in the surface monolayer η_O^S is determined using the equation

$$\ln\left[\frac{(\eta_O^S/\eta_O)^{v_{ST}/v_O}}{(1 - \eta_O^S)/(1 - \eta_O)}\right] = \frac{\sigma_{SW} - \sigma_{OW}}{kT}v_S^{2/3} +$$
$$\chi_{OS}\left[\frac{3}{4}((1 - \eta_O) - \eta_O)\right] - \chi_{OS}\left[\frac{1}{2}((1 - \eta_O^S) - \eta_O^S)\right] \quad (7.9)$$

where the parameter χ_{OS} denotes the interaction parameter for the oil and the surfactant and alcohol tails. After eq 7.9 is solved for η_O^S, the interfacial tension σ_{agg} is calculated using the equation

$$\frac{\sigma_{agg} - \sigma_{SW}}{kT}v_S^{2/3} = \ln\left(\frac{1 - \eta_O^S}{1 - \eta_O}\right) + \left(1 - \frac{v_{ST}}{v_O}\right)(\eta_O^S - \eta_O) +$$
$$\chi_{OS}\left[\frac{1}{2}(\eta_O^S)^2 - \frac{3}{4}(\eta_O)^2\right] \quad (7.10)$$

The parameter for the interaction between the oil and the tails χ_{OS} is expressed in terms of the solubility parameters δ_S^H, δ_A^H, and δ_O^H of the surfactant tail, the alcohol tail and the oil, respectively, using the expression

$$\chi_{OS} = \frac{v_O(\delta_O^H - \delta_{mix}^H)^2}{kT} \qquad \delta_{mix}^H = \eta_S\delta_S^H + \eta_A\delta_A^H + \eta_O\delta_O^H \quad (7.11)$$

where η_S, η_A, and η_O are the volume fractions of the surfactant tail, alcohol tail, and oil, respectively, in the interfacial layer. The volume fractions are readily calculated from the respective molecular volumes and the composition of the interfacial layer. The solubility parameters[22,23] are estimated to be 16.76 MPa$^{1/2}$ for the surfactant tail, 9.1 MPa$^{1/2}$ for the pentanol tail, and 16.8 MPa$^{1/2}$ for cyclohexane (selected as the oil for illustrative purposes).

7.4. Headgroup Steric Interactions. This contribution is expressed as that for mixed surfactants. Because, in the present case, the free energy is expressed per surfactant molecule (not surfactant + alcohol molecule), one can write

$$\frac{(\Delta\mu_g^\circ)_{steric}}{kT} = -\left(1 + \frac{g_{AI}}{g_{SI}}\right)\ln\left(1 - \frac{a_{pS}}{a} - \frac{g_{AI}}{g_{SI}}\frac{a_{pA}}{a}\right) \quad (7.13)$$

where, as mentioned before, a_{pS} is the cross-sectional area of the polar headgroup of the surfactant and a_{pA} is the cross-sectional area of the hydroxyl headgroup.

7.5. Headgroup Dipole Interactions. For zwitterionic surfactants, the dipole−dipole interactions are evaluated using the expression

$$\frac{(\Delta\mu_g^\circ)_{dipole}}{kT} = \frac{2\pi e^2 d}{\epsilon a_\delta kT}\frac{1}{H} \quad (7.14)$$

where d is the dipole length, δ is the distance from the oil−water contact surface at which the dipole is located, a_δ is the surface area per surfactant molecule evaluated at the distance δ, and H is a curvature correction given by one of the following expressions

$$H = 1 + (d + \delta)/R_W, \quad a_\delta = a(1 + \delta/R_W)^2$$
$$\text{for O/W droplets}$$

$$H = 1 - (d + \delta)/R_W, \quad a_\delta = a(1 - \delta/R_W)^2$$
$$\text{for W/O droplets}$$

$$H = 1, \quad a_\delta = a \qquad \text{for a flat film} \quad (7.15)$$

The dielectric constant ϵ is a function of temperature[24] and is evaluated using the relation

$$\epsilon = 87.74 \exp[-0.0046(T - 273)] \quad (7.16)$$

7.6. Headgroup Ionic Interactions. Ionic interactions arise at the interfacial layer if the surfactant has a charged headgroup and are calculated using the expression

$$\left(\frac{\Delta\mu_g^\circ}{kT}\right)_{ionic} = 2\left\{\ln\left[\frac{S}{2} + \left(1 + \left(\frac{S}{2}\right)^2\right)^{1/2}\right] - \frac{2}{S}\left[\left(1 + \left(\frac{S}{2}\right)^2\right)^{1/2} - 1\right] - \frac{2C_g}{\kappa S}\ln\left[\frac{1}{2} + \frac{1}{2}\left(1 + \left(\frac{S}{2}\right)^2\right)^{1/2}\right]\right\} \quad (7.17)$$

where

(20) Defay, R.; Prigogine, I.; Bellemans, A.; Everett, D. H. *Surface Tension and Adsorption*; Wiley: New York, 1966.
(21) Siow, K. S.; Patterson, D. *J. Phys. Chem.* **1973**, *77*, 356.

(22) Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L. *Regular and Related Solutions*; Van Nostrand Reinhold: New York, 1970.
(23) Barton, A. F. M. *Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC Press: Boca Raton, FL, 1983.
(24) *CRC Handbook of Chemistry and Physics*, 60th ed.; CRC Press: Boca Raton, FL, 1980.

$$S = \frac{4\pi e^2}{\epsilon \kappa a_\delta kT} \qquad \kappa = \left(\frac{8\pi n_0 e^2}{\epsilon kT}\right)^{1/2}$$

$$n_0 = \frac{C_{1ion} + C_{add}}{10^3} N_{Av} \quad (7.18)$$

The area per molecule a_δ which appears in the preceding equation is evaluated at a distance δ from the surface in contact with water and is curvature dependent. Expressions for a_δ are given by eq 7.15. The distance δ is estimated as the distance from the surface in contact with water to the surface where the center of the counterion is located. κ is the reciprocal Debye length, n_0 is the number of counterions in solution per cubic centimeter, C_{1ion} is the molar concentration of the singly dispersed ionic surfactant molecules in water, C_{add} is the molar concentration of the salt added to the surfactant solution, and N_{Av} is Avogadro's number. The last term in the right-hand side of eq 7.17 provides a curvature correction to the ionic interaction energy. For normal droplets, $C_g = 2/(R_W + \delta)$; for reverse droplets, $C_g = -2/(R_W - \delta)$; and for flat layers, $C_g = 0$.

7.7. Free Energy of Mixing Inside the Layer Region. This free energy contribution is estimated using the Flory–Huggins expression[25]
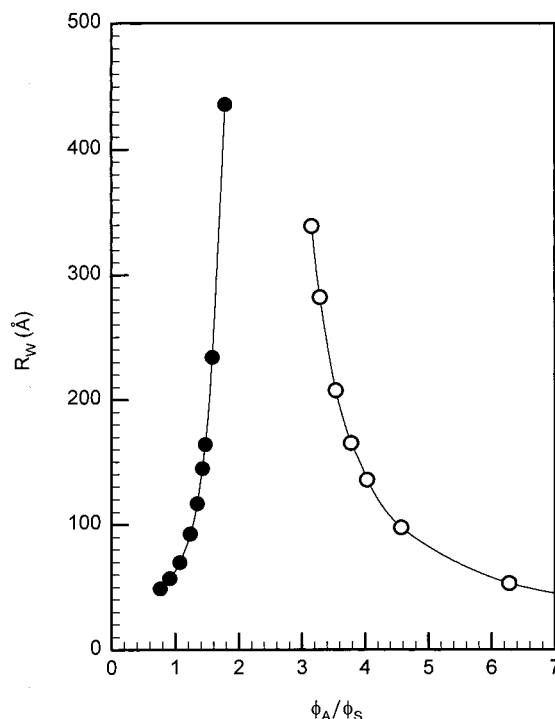
$$\frac{(\Delta\mu_{g1}^\circ)_{mix}}{kT} = \left[\ln \eta_S + \frac{g_{AI}}{g_{SI}} \ln \eta_A + \frac{g_{OI}}{g_{SI}} \ln \eta_O\right] +$$
$$\left[v_S \frac{(\delta_S^H - \delta_{mix}^H)^2}{kT} + \frac{g_{AI}}{g_{SI}} v_A \frac{(\delta_A^H - \delta_{mix}^H)^2}{kT} + \right.$$
$$\left. \frac{g_{OI}}{g_{SI}} v_O \frac{(\delta_O^H - \delta_{mix}^H)^2}{kT}\right] \quad (7.19)$$

8. Predictions for Droplet-Type Microemulsions

Calculations were carried out for a system consisting of the anionic surfactant sodium dodecyl sulfate, 1-pentanol (cosurfactant), cyclohexane, and water containing 0.3 M NaCl. As mentioned at the very beginning, the choice of this system was dictated by the possibility of identifying various types of phase behaviors for the same chemical components by merely changing the amount of added alcohol. In all calculations, we assumed the coexistence of an excess dispersed phase. This means that the droplet microemulsion phase is part of a two-phase system and that the amount of dispersed phase present in the droplet is the maximum achievable.

The total surfactant volume fraction Φ_S in the microemulsion is kept constant at 0.01 and the concentration X_{SW} of the singly dispersed surfactant is negligibly small compared to the total amount of surfactant in the microemulsion. The alcohol-to-surfactant ratio in the microemulsion and, correspondingly, the alcohol-to-surfactant ratio in the interfacial layer of the droplet increase with increasing X_{AW}. The radius R_W of the water–oil interface (see Figure 2 for the definition of R_W) predicted by the model is plotted as a function of the alcohol-to-surfactant volume ratio in the microemulsion in Figure 3. The calculations show that, for X_{AW} less than 0.00172 and, correspondingly, for Φ_A/Φ_S less than 2.0 and g_{AI}/g_{SI} less than 1.012, an O/W droplet-type microemulsion coexists with an excess oil phase. When X_{AW} is larger than 0.00184 (and, correspondingly, when Φ_A/Φ_S is larger than 3.15 and g_{AI}/g_{SI} is larger than 1.13), a W/O droplet-type microemulsion coexists with an excess water phase. For

(25) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.

Figure 3. Predicted radii of microemulsion droplets as a function of the volume ratios of alcohol to surfactant in microemulsions. The predictions are for a system consisting of the surfactant SDS, 1-pentanol, 0.3 M NaCl, water, and cyclohexane. The total volume fraction of the surfactant in the microemulsions is 0.01. Filled circles denote O/W droplets, and open circles correspond to W/O droplets.

intermediate values of X_{AW} (corresponding to Φ_A/Φ_S in the range 2.0–3.15), no maximum in the aggregate size distribution occurs because the equilibrium aggregate radius diverges. For these conditions, a three-phase system involving a bicontinuous microemulsion comes into existence. The radius of the droplet increases significantly as the two-phase system (corresponding to either O/W or W/O droplet microemulsions) nears the transition to a three-phase system.

The number of surfactant molecules in the interfacial layer of a droplet is plotted in Figure 4 for the systems described in Figure 3. Detailed information regarding the composition of the microemulsions is provided by Figure 5. The volume fractions of oil, water, and alcohol plotted in the figures represent the total amounts in the microemulsion, and the volume fraction of surfactant Φ_S is 0.01 in all cases. As the alcohol-to-surfactant ratio increases, the volume fraction of oil increases while that of water decreases, as has been generally observed in numerous experiments.[1,3] The total volume fractions of the surfactant (Φ_S) and alcohol (Φ_A) determine the volume fraction of oil solubilized or water solubilized in the microemulsion. Figure 6 displays the predicted interfacial layer thickness and the area per surfactant molecule at the oil–water interface of the droplets as functions of the alcohol-to-surfactant ratio in the microemulsion. The calculations indicate that the area per surfactant molecule of the droplet is not a constant but increases with an increasing amount of alcohol. The extent of penetration of the oil into the interfacial layer is illustrated in Figure 7. The oil-to-surfactant ratio in the interfacial layer exhibits a monotonic increase as the alcohol-to-surfactant ratio in the microemulsion increases.
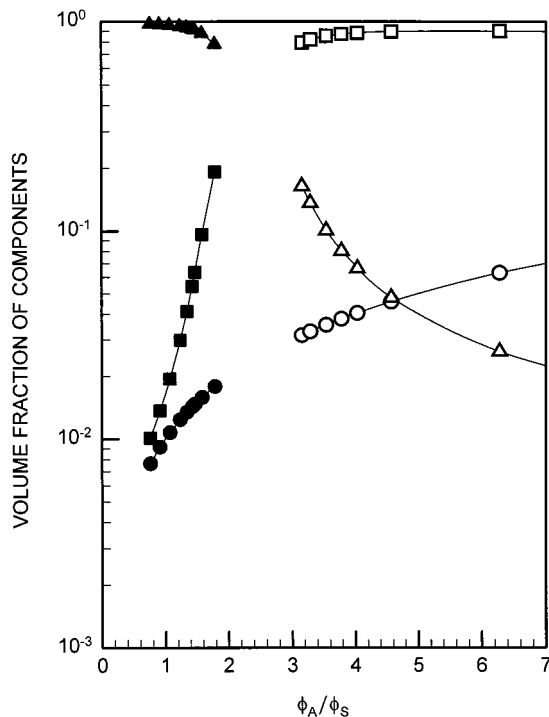
The volume fraction of droplets in the microemulsion phase predicted by the model is plotted in Figure 8, which
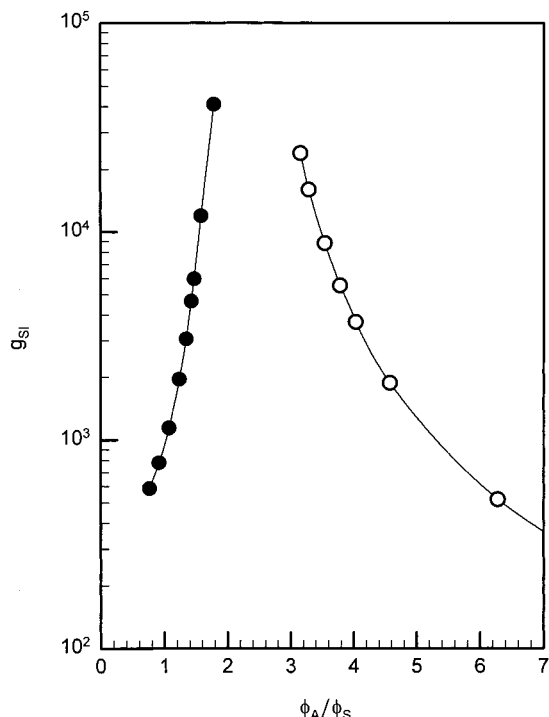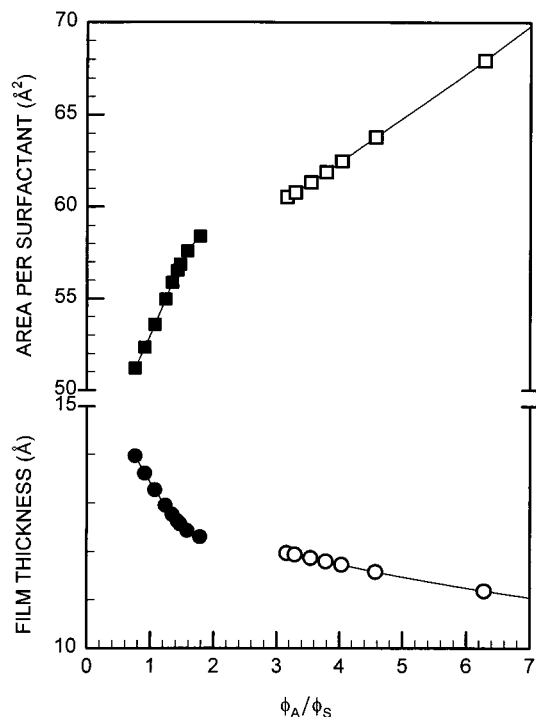
Figure 4. Numbers of surfactant molecules in the interfacial layers of droplets as a function of the volume ratios of alcohol to surfactant in microemulsions. All the system characteristics are identical to those described for Figure 3. Filled circles denote O/W droplets, and open circles correspond to W/O droplets.

Figure 6. Thicknesses of the interfacial layers of droplets (circles) and areas per surfactant molecule of the droplets at an oil–water interface (squares) as functions of the volume ratios of alcohol to surfactant in microemulsions for systems containing O/W (filled symbols) and W/O (open symbols) droplets. All the system characteristics are identical to those described for Figure 3.
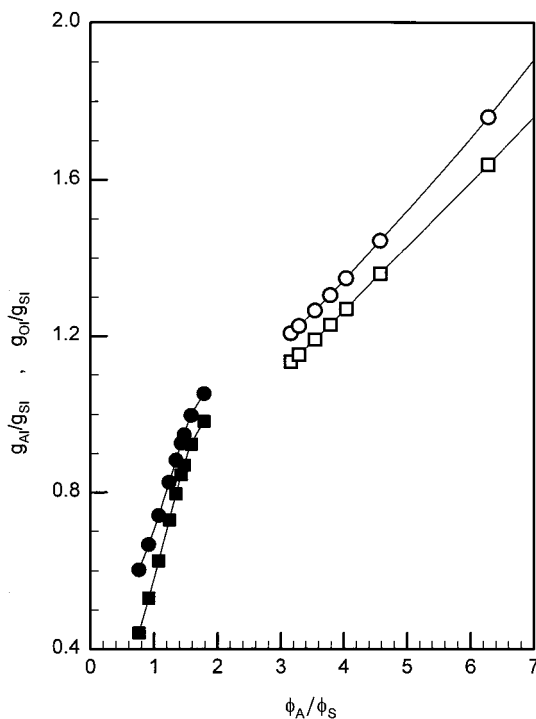

Figure 5. Volume fractions of oil (squares), water (triangles), and alcohol (circles) in microemulsions containing O/W and W/O droplets as a function of the volume ratios of alcohol to surfactant in the microemulsions. Filled symbols refer to O/W droplet microemulsions, and open symbols, to W/O droplet microemulsions. All the system characteristics are identical to those described for Figure 3. In all cases, the volume fraction of the surfactant in the microemulsions is 0.01.
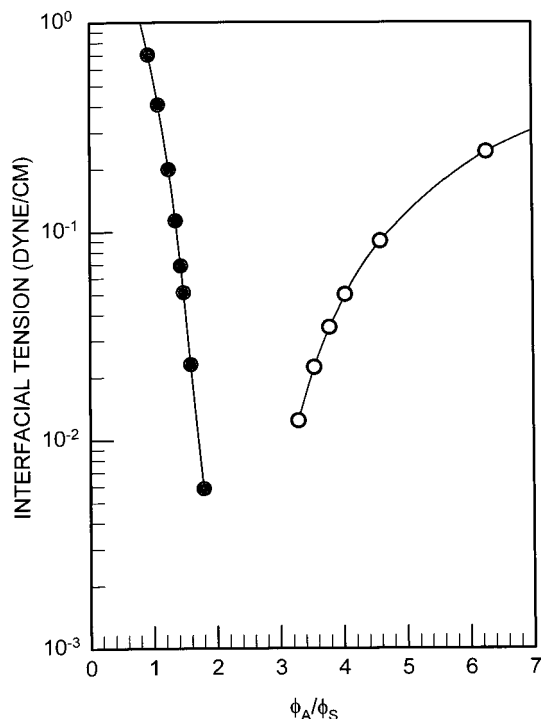

Figure 7. Alcohol-to-surfactant mole ratios and oil-to-surfactant mole ratios in the interfacial layers of O/W (filled symbols) and W/O (open symbols) droplets as functions of the volume ratios of alcohol to surfactant in microemulsions. All the system characteristics are identical to those described for Figure 3.

shows that the volume fraction increases as one moves from the two-phase toward the three-phase system. The interfacial tension at the flat surface between the micro-

emulsion phase and the coexisting excess phase calculated with eq 5.2 is plotted in Figure 9, which reveals that the interfacial tension decreases as one moves from the two-phase to the three-phase system.
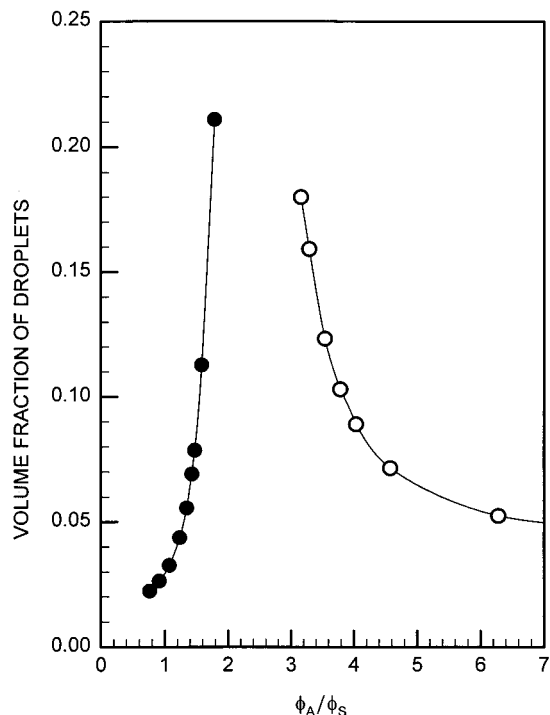
Figure 8. Volume fractions of droplets as a function of the volume ratios of alcohol to surfactant in microemulsions. All the system characteristics are identical to those described for Figure 3. Filled symbols are for O/W microemulsions, and open symbols refer to W/O microemulsions.

Figure 9. Oil−water interfacial tensions at the flat surfaces between microemulsion phases and excess dispersed phases as a function of the volume ratios of alcohol to surfactant in microemulsions. All the system characteristics are identical to those described for Figure 3. Filled symbols are for O/W microemulsions, and open symbols refer to W/O microemulsions.

Estimates of the size and composition dispersions of droplets in O/W and W/O droplet-type microemulsions, obtained using the maximum-term method described in Appendix C, are summarized in Table 1. The calculations for the O/W droplet-type microemulsions were carried out

Table 1. Predicted Size and Composition Dispersions of Microemulsion Droplets

| variable	O/W microemulsion	W/O microemulsion
$\langle R_W \rangle$, Å	233.9	282
$\langle g_{SI} \rangle$	11 940	16 460
$\langle g_{AI}/g_{SI} \rangle$	0.9228	1.152
$\langle g_{OI}/g_{SI} \rangle$	0.9965	1.226
Φ_S	0.01	0.01
Φ_A	0.0158	0.0329
Φ_O	0.0963	0.8206
Φ_W	0.8779	0.1365
$\sigma_n(S)/g_n(S)$	0.219	0.266
$\sigma_n(A)/g_n(A)$	0.241	0.278
$\sigma_n(O)/g_n(O)$	0.274	0.260
$\sigma_n(W)/g_n(W)$		0.326
$\sigma_R/\langle R_W \rangle$	0.0822	0.096
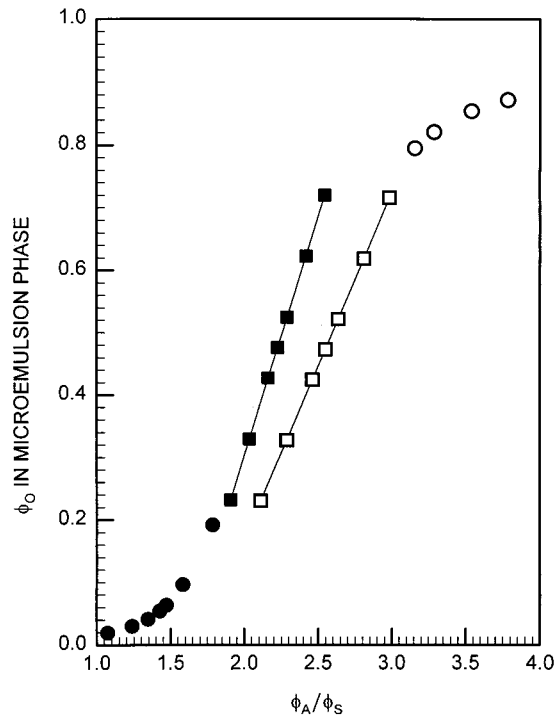
Figure 10. Volume fraction of oil in a bicontinuous microemulsion as a function of the volume ratio of alcohol to surfactant in the microemulsion. The values of X_{AW} and g_{AI}/g_{SI} are respectively 0.001 72 and 1.036 (filled squares) and 0.001 84 and 1.074 (open squares). In all cases, the volume fraction of surfactant is 0.01 and the volume fraction of water is found by subtraction from unity. The system consists of SDS, 1-pentanol, cyclohexane, water, and 0.3 M NaCl. Also shown are the corresponding results for O/W droplet microemulsions (filled circles) and for W/O droplet microemulsions (open circles).

for $X_{AW} = 0.001 62$, while the calculations for the W/O droplet-type microemulsion were for $X_{AW} = 0.00185$. In all cases, the volume fraction of the surfactant in the microemulsion Φ_S was kept constant at 0.01. The average radii of the droplets, the average numbers of surfactant, alcohol, and oil molecules in the interfacial layers of the droplets, the overall compositions of the microemulsions, and their dispersions are listed in Table 1. The values of σ_n/g_n for all components are generally small, implying relatively narrow composition dispersions of the droplets. Consequently, the standard deviations σ_R of the droplet radii are also small.
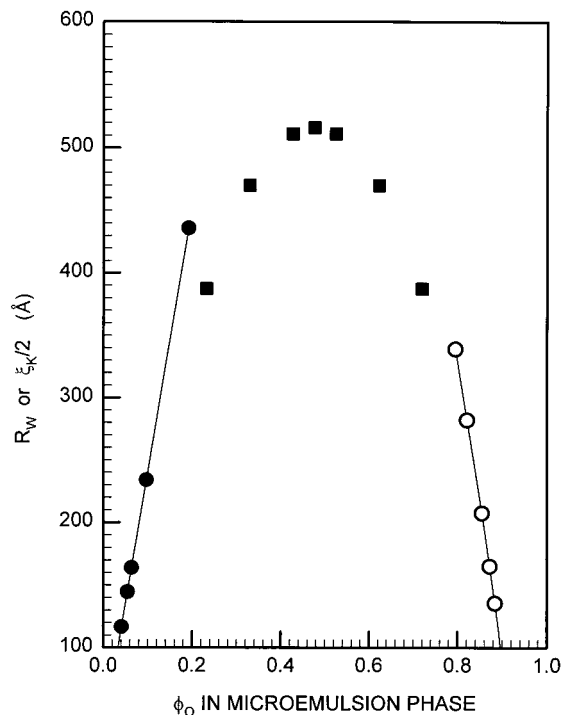
9. Predictions for Bicontinuous Microemulsions

As mentioned previously, for alcohol concentrations X_{AW} in the water domain in the range 0.001 72−0.00 184 (corresponding to a Φ_A/Φ_S in the microemulsion between
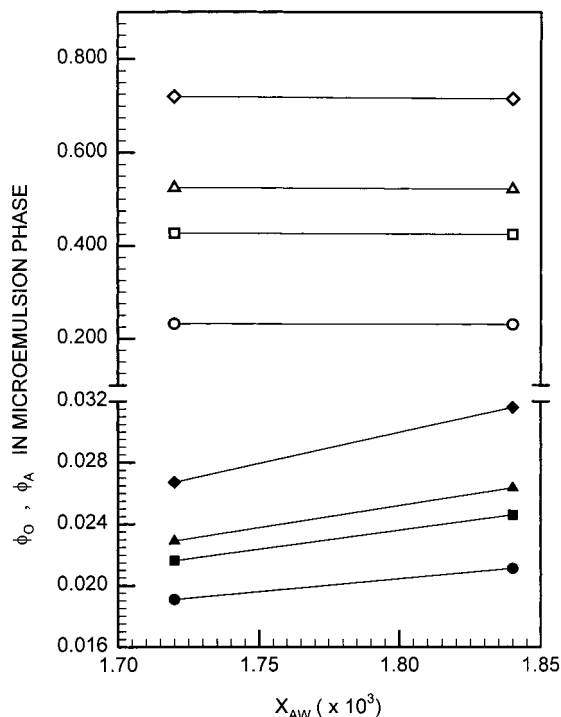
Figure 11. Dependence of the volume fractions of oil (open symbols) and alcohol (filled symbols) in a bicontinuous microemulsion as a function of the mole fraction of alcohol in the water phase. The different symbols refer to different volume fractions of oil and water domains in the microemulsion: $\Phi = 0.25$ (circles), 0.45 (squares), 0.55 (triangles), and 0.75 (diamonds). The system consists of SDS, 1-pentanol, cyclohexane, water, and 0.3M NaCl.
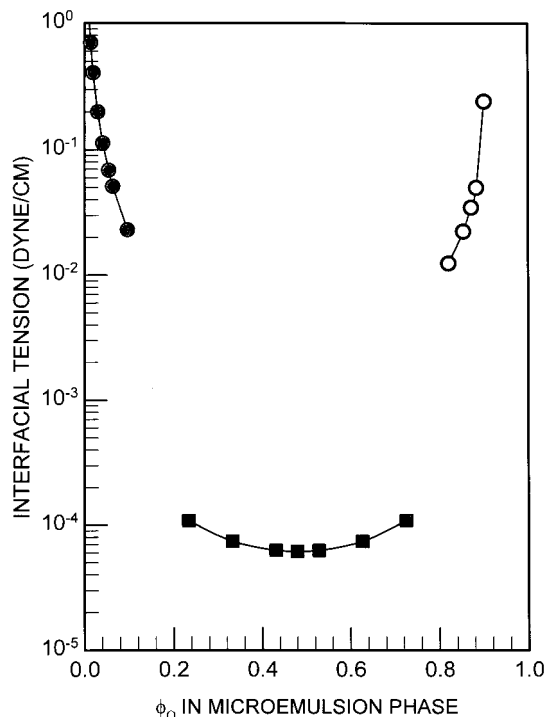

Figure 12. Dependence of the droplet radii in two-phase systems containing O/W (filled circles) or W/O microemulsions (open circles) and of persistence length/2 of a bicontinuous microemulsion (filled squares) on the volume fraction of oil in the microemulsion. In all cases, the volume fraction of the surfactant is 0.01. The system consists of SDS, 1-pentanol, cyclohexane, water, and 0.3 M NaCl.

2.0 and 3.25), three-phase systems involving a bicontinuous microemulsion are preferred thermodynamically. The overall composition limits within which a bicontinuous microemulsion can be generated are presented in Figure 10. The two lines correspond to $X_{AW} = 0.001\ 72$ and 0.001 84. For overall phase compositions between these two lines and for $\Phi_S = 0.01$, a three-phase system is favored thermodynamically. As X_{AW} increases from 0.00172 to 0.00184, the area per surfactant molecule a_F increases from 59.06 to 59.88 Å², while the alcohol-to-surfactant ratio in the interfacial layer $(g_{AI}/g_{SI})_F$ increases from 1.036 to 1.074. All the bicontinuous microemulsions marked by points on a line are characterized by the same values of X_{AW}, a_F, and $(g_{AI}/g_{SI})_F$.

One can observe from Figure 10 that, for a given Φ_A/Φ_S, there is a unique value of Φ_O for an O/W or W/O droplet microemulsion, but a range of Φ_O values lying between the two lines is possible for a bicontinuous microemulsion. The volume fraction of oil Φ_O in the bicontinuous microemulsion, for a given value of Φ_A/Φ_S, is determined by the concentration X_{AW} of the alcohol in the coexisting water phase. The volume fractions of oil Φ_O (unfilled symbols) and alcohol Φ_A (filled symbols) in the bicontinuous microemulsion are plotted in Figure 11 as a function of X_{AW}, with the volume fraction of surfactant Φ_S kept constant at 0.01. Because the sum of all volume fractions should be unity, the volume fraction of water Φ_W can be determined. Each symbol in Figure 11 corresponds to a given volume fraction of oil in the bicontinuous microemulsion: $\Phi = 0.25$ (circle), 0.45 (square), 0.55 (triangle), and 0.75 (diamond). For a given value of Φ_O, as X_{AW} increases, Φ_A increases, implying a corresponding decrease in Φ_W (because all volume fractions sum to unity). This predicted increase in the oil-to-water ratio in a bicon-

tinuous microemulsion system with increasing alcohol content constitutes a well-known experimental result.

The persistence length of the bicontinuous microemulsion predicted by the model is plotted in Figure 12 as a function of the volume fraction of oil in the microemulsion for $X_{AW} = 0.001\ 72$. The calculated persistence lengths for $X_{AW} = 0.001\ 84$ practically coincide with the former, because the areas per surfactant molecule in the interfacial layer a_F are close to one another for the two values of X_{AW}. The persistence length has a maximum when the oil and water domains have equal volume fractions. The radii of the O/W droplets increase with an increasing amount of alcohol in the low alcohol content range, while the radii of the W/O droplets decrease with an increasing amount of alcohol in the high alcohol content range. The interfacial tension calculated using eq 6.6 is plotted in Figure 13 as a function of the volume fraction of oil in the bicontinuous microemulsion. The calculated interfacial tensions for the two values of $X_{AW} = 0.001\ 72$ and 0.001 84 practically coincide (as expected, since the persistence lengths also practically coincide). The interfacial tension has a minimum when the oil and water domains have equal volume fractions.

10. Conclusions

In this paper, a predictive molecular thermodynamic approach is developed to calculate the structural and compositional characteristics of microemulsions. The theory applies not only to oil-in-water and water-in-oil droplet-type microemulsions but also to bicontinuous microemulsions. The treatment is an extension of our earlier theories for micelles, mixed micelles, and solubilization but also takes into account the self-association of alcohol in oil and the volume-excluded interactions among

$$G = N_{OO}\mu_{OO} + N_{SO}\mu_{SO} + \sum N_{jAO}\mu_{jAO} + N_{WO}\mu_{WO} + \sum N_{gO}\mu_{gO} \quad (A.1)$$

where μ refers to the chemical potentials of given kinds of species. The last subscript on N and μ stands for the nature of the continuous phase, with O denoting the oil. The subscripts O, W, S, A, and jA refer to molecules of oil, water, surfactant, alcohol, and alcohol aggregates containing j alcohol molecules, respectively. The summations over j extend from 1 to ∞ in all the equations in this paper. A summation over g in the last term of eq A.1 accounts for the size and the composition distribution of droplets.

(c) Equilibrium Condition. The chemical potentials of the singly dispersed alcohol molecules and alcohol aggregates are related via the expression

$$\mu_{jAO} = j\mu_{1AO} \quad (A.2)$$

which, combined with eq A.1, yields

$$G = N_{OO}\mu_{OO} + N_{SO}\mu_{SO} + N_{AO}\mu_{1AO} + N_{WO}\mu_{WO} + \sum N_{gO}\mu_{gO} \quad (A.3)$$

where

$$N_{AO} = \sum jN_{jAO} \quad (A.4)$$

For a given composition of the system

$$N_{kO} + \sum g_k N_{gO} = \text{constant} \qquad k = O, S, A, W \quad (A.5)$$

The condition $\delta G = 0$, subjected to the mass constraints of eq A.5, leads to

$$\mu_{gO} = g_O\mu_{OO} + g_S\mu_{SO} + g_A\mu_{1AO} + g_W\mu_{WO} \quad (A.6)$$

The chemical potentials of the components in the oil phase other than the droplets are expressed in the form

$$\mu_{kO} = \mu_{kO}^\circ + kT\ln(\gamma_{kO}X_{kO}) \qquad k = S, 1A, W, O \quad (A.7)$$

The standard chemical potential μ_{OO}° corresponds to the pure oil phase, the standard chemical potential μ_{1AO}° refers to the standard state of the monomeric alcohol in pure alcohol, and the standard chemical potentials μ_{SO}° and μ_{WO}° of the surfactant and water, respectively, correspond to their infinitely dilute solution states in the oil phase. For the droplets, the chemical potential is written as

$$\mu_{gO} = \mu_{gO}^\circ + kT\ln(\gamma_{gO}X_{gO}) \quad (A.8)$$

where μ_{gO}° is the standard chemical potential of the aggregate defined as that of an isolated aggregate in the continuous oil phase and γ_{gO} is the activity coefficient arising from the hard-sphere interactions.

The standard chemical potential μ_{gO}° of the aggregate can be split into a part due to the interfacial layer (denoted with the subscript I) and another part due to the dispersed water phase of the droplet (denoted with the subscript W). Thus, one can write

$$\mu_{gO}^\circ = \mu_{gI}^\circ + g_{OW}\mu_{OW} + g_{SW}\mu_{SW} + g_{AW}\mu_{AW} + g_{WW}\mu_{WW} \quad (A.9)$$

where μ_{gI}° is the standard chemical potential of the interfacial layer of the droplet, while μ_{kW} are the chemical potentials of the components k present in the dispersed

Figure 13. Interfacial tension at the oil−water interface in a bicontinuous microemulsion system (filled squares) as a function of the volume fraction of oil in the microemulsion. In all cases, the volume fraction of surfactant is 0.01. The system consists of SDS, 1-pentanol, cyclohexane, water, and 0.3 M NaCl. Also shown are the interfacial tensions at the flat surface between the O/W droplet microemulsion phase and the excess oil phase (filled circles) and between the W/O droplet microemulsion phase and excess water phase (open circles) in two-phase systems.

the droplets. Illustrative numerical results are provided for an anionic surfactant (SDS)−pentanol−cyclohexane−water−NaCl system. Microstructural features including the droplet radius, the thickness of the interfacial layer, the numbers of molecules of various species in a droplet, the size and composition dispersions of the droplet, and the distributions of the surfactant, oil, alcohol, and water molecules in the various microdomains have been calculated. Further, the model allows the identification of the transition from a two-phase to a three-phase system. The characteristic persistence length of the bicontinuous microemulsion is also predicted. Finally, the model permits the calculation of the interfacial tension between the microemulsion and the coexisting phase.

Appendix A: Equilibrium Size Distribution of Droplets

A.1. A Water-in-Oil Droplet Microemulsion. (a) Description of the Phase. The microemulsion system is composed of N_{gO} droplets of various sizes g (each consisting of surfactant, alcohol, oil and water molecules) and outside the droplets, N_{OO} oil molecules, N_{SO} surfactant molecules, N_{AO} alcohol molecules, and N_{WO} water molecules. The subscript g for a droplet denotes the total number of molecules of different kinds present in it (i.e., $g = g_S + g_A + g_O + g_W$). The N_{AO} alcohol molecules outside the droplets are present both as singly dispersed molecules and as aggregates. The number of alcohol aggregates containing j alcohol molecules is denoted by N_{jAO}.

(b) Free Energy of the Phase. The total Gibbs energy G of the microemulsion can be written as

water phase. The number of molecules g_{OW}, g_{SW}, g_{AW}, and g_{WW}, which refer to the oil, surfactant, alcohol, and water molecules in the dispersed water phase, are related to g_{OI}, g_{SI}, g_{AI}, and g_{WI}, the number of molecules in the interfacial layer of the droplet, via

$$g_{kI} = g_k - g_{kW} \qquad k = S, A, O, W \qquad (A.10)$$

(d) Relation between Chemical Potentials. The chemical potentials μ_{kO} of all the components k in the oil phase are equal to the chemical potentials μ_{kW} of the same components in the dispersed water phase. For oil, surfactant, and alcohol, one can write

$$\mu_{OO} = \mu_{OO}^\circ + kT\ln(\gamma_{OO}X_{OO}) = \mu_{OW} = \\ \mu_{OW}^\circ + kT\ln(\gamma_{OW}X_{OW}) \quad (A.11)$$

$$\mu_{SO} = \mu_{SO}^\circ + kT\ln(\gamma_{SO}X_{SO}) = \mu_{SW} = \\ \mu_{SW}^\circ + kT\ln(\gamma_{SW}X_{SW}) \quad (A.12)$$

$$\mu_{1AO} = \mu_{1AO}^\circ + kT\ln(\gamma_{1AO}X_{1AO}) = \mu_{AW} = \\ \mu_{AW}^\circ + kT\ln(\gamma_{AW}X_{AW}) \quad (A.13)$$

where X_{SW}, X_{AW}, and X_{OW} are the concentrations of the singly dispersed surfactant, alcohol, and water, respectively, in the dispersed water phase. μ_{SW}°, μ_{AW}°, and μ_{OW}° are their standard chemical potentials for infinitely dilute solutions in water, while γ_{SW}, γ_{AW}, and γ_{OW} are the activity coefficients in the dispersed water phase. For the fourth component, water, the concentration of singly dispersed water X_{WO} will be smaller than the value at saturation X_{WO}^{sat} if the microemulsion is a single-phase system and becomes equal to X_{WO}^{sat} when an excess water phase is present. Therefore

$$\mu_{WO} = \mu_{WO}^\circ + kT\ln(\gamma_{WO}\,X_{WO}^{sat}\,f_{WO}) = \mu_{WW} = \\ \mu_{WW}^\circ + kT\ln(\gamma_{WW}X_{WW}) \quad (A.14)$$

where

$$f_{WO} = X_{WO}/X_{WO}^{sat} \qquad (A.15)$$

(e) Size and Composition Distribution. One can now introduce into the equilibrium relation (A.6) the relations between the various chemical potentials, eqs A.7–A.15, to obtain the size and the composition distribution function of the droplets. For a single-phase microemulsion

$$X_{gO}\gamma_{gO} = \Omega^{g_{SI}} f_{WO}^{\,g_W} \qquad (A.16)$$

In eq A.16

$$\Omega = X_{SW}\gamma_{SW}(X_{AW}\gamma_{AW})^{g_{AI}/g_{SI}}(X_{OO}\gamma_{OO})^{g_{OI}/g_{SI}} \\ \exp(-\Delta\mu_{gI}^\circ/kT) \quad (A.17)$$

and

$$\Delta\mu_{gI}^\circ = \frac{1}{g_{SI}}\mu_{gI}^\circ - \mu_{SW}^\circ - \frac{g_{AI}}{g_{SI}}\mu_{AW}^\circ - \frac{g_{OI}}{g_{SI}}\mu_{OO}^\circ \quad (A.18)$$

The standard free energy difference $\Delta\mu_{gI}^\circ$ is due to the transfer of one surfactant molecule and g_{AI}/g_{SI} alcohol molecules from water and g_{OI}/g_{SI} oil molecules from pure oil to the interfacial layer of the droplet. Equations A.16–A.18 imply that the number of water molecules in the interfacial layer (g_{WI}) is zero.

A.2. An Oil-in-Water Droplet Microemulsion. Similarly, for the oil-in-water droplet-type microemulsion, the size and composition distribution of droplets is given by

$$X_{gW}\gamma_{gW} = \Omega^{g_{SI}} f_{OW}^{\,g_O} \qquad (A.19)$$

where

$$\Omega = X_{SW}\gamma_{SW}(X_{AW}\gamma_{AW})^{g_{AI}/g_{SI}}(X_{OO}\gamma_{OO})^{g_{OI}/g_{SI}} \\ \exp(-\Delta\mu_{gI}^\circ/kT) \quad (A.20)$$

and

$$\Delta\mu_{gI}^\circ = \frac{1}{g_{SI}}\mu_{gI}^\circ - \mu_{SW}^\circ - \frac{g_{AI}}{g_{SI}}\mu_{AW}^\circ - \frac{g_{OI}}{g_{SI}}\mu_{OO}^\circ \quad (A.21)$$

As in the previous case, f_{OW} is less than unity for a single-phase microemulsion but becomes equal to unity when an excess oil phase coexists. The activity coefficients γ_{SW} and γ_{SA} of the singly dispersed surfactant and alcohol molecules and the activity coefficient γ_{gW} of the aggregates differ from unity, since the water phase contains the droplets which contribute to solution nonideality through the hard-sphere interactions. For the same reason, the activity coefficient γ_{OO} of the oil in the dispersed oil phase is unity since no droplets are present in the oil phase.

Appendix B: Calculation of Activity Coefficients for Multicomponent Mixtures Containing Hard Spheres

Let us consider a solution composed of hard-sphere droplets of a single size g present in a multicomponent solvent. The expression for the osmotic pressure due to the hard spheres allows us to calculate the chemical potentials of the components in the mixed solvent. Subsequently, the Gibbs–Duhem equation is used to calculate the chemical potentials of the hard-sphere droplets.[26] The mole fraction X_i of the components and their volume fraction Φ_i are related via the expressions

$$X_i = \frac{\Phi_i/v_i}{\sum \Phi_i/v_i} \qquad \Phi_i = \frac{X_i v_i}{\sum X_i v_i} \qquad (B.1)$$

where v_i are the volumes of the various components including the hard-sphere aggregates. For all components other than $i = g$ (which refers to the hard spheres), considering their partial molar volumes equal to the molar volumes of the pure components, one can write

$$\left(\frac{\partial\mu_i}{\partial p}\right)_{T,N_j} = v_i \qquad \mu_i(\Phi_g = 0) - \mu_i(\Phi_g) = \Pi v_i \quad (B.2)$$

where μ_i is the chemical potential of component i in the solution, while Π is the osmotic pressure due to the hard-sphere droplets of volume fraction Φ_g. The Carnahan–Starling equation of state leads to

$$\Pi = kT\frac{\Phi_g}{V_g}\frac{1 + \Phi_g + \Phi_g^{\,2} - \Phi_g^{\,3}}{(1 - \Phi_g)^3} \qquad (B.3)$$

where V_g is the volume of a single hard-sphere droplet. Therefore, the chemical potential of component i is given by

(26) Reed, T. M.; Gubbins, K. E. *Applied Statistical Mechanics*; Butterworth-Heinemann: Boston, MA, 1973. Overbeek, J. Th. G. *Faraday Discuss. Chem. Soc.* **1978**, *65*, 7.

$$\mu_i = \mu_i^\circ + kT \ln X_i - kT \frac{v_i}{V_g} \frac{1 + \Phi_g + \Phi_g^{\,2} - \Phi_g^{\,3}}{(1 - \Phi_g)^3} \quad \text{(B.4)}$$

The first term on the right-hand side μ_i° is the standard chemical potential of component i, the second term is the ideal mixture contribution, and the third term is the nonideality caused by the hard-sphere interactions. The chemical potential of the hard-sphere droplet (component g) is obtained using the Gibbs–Duhem equation

$$\sum X_i \, d\mu_i = 0 \qquad d\mu_g = -\frac{\displaystyle\sum_{i \neq g} X_i \, d\mu_i}{1 - \displaystyle\sum_{i \neq g} X_i} \quad \text{(B.5)}$$

and has the form

$$\mu_g = \mu_g^\circ + kT \ln X_g +$$
$$kT \left[\ln\!\left(\frac{\Phi_g / V_g}{X_g \displaystyle\sum_{i \neq g} \Phi / v_i} \right) + \Phi_g \frac{7 - 3\Phi_g - \Phi_g^{\,2}}{(1 - \Phi_g)^2} \right] \quad \text{(B.6)}$$

In obtaining the expression for the activity coefficient part of the chemical potential, we have considered droplets of a single size represented by the most populous size (corresponding to the maximum in the size distribution). A more formal equation allowing for droplets of various sizes can be written according to the Mansoori–Carnahan–Starling equation of state for mixtures of hard spheres.[26] The results based on such an expression are not expected to be essentially different from those obtained on the basis of a single droplet size.

Appendix C: Approximate Method for Obtaining Size and Composition Polydispersity of Droplets Using the Maximum-Term Method

The size and composition distribution of droplets will be first rewritten in a general form applicable to both oil-in-water and water-in-oil microemulsions (by deleting the second subscripts):

$$X_g = X_S^{\,g_S} X_A^{\,g_A} X_O^{\,g_O} X_W^{\,g_W} \, Z(g_S, g_A, g_O, g_W) \quad \text{(C.1)}$$

where Z represents all the other factors that appear in the expression for the size distribution. The number- and weight-average numbers of the various constituents in the droplet are denoted by $g_n(k)$ and $g_w(k)$, respectively and are defined as

$$g_n(k) = \frac{\sum g_k X_g}{\sum X_g} \qquad g_w(k) = \frac{\sum g_k^{\,2} X_g}{\sum g_k X_g} \quad \text{(C.2)}$$

where k stands for the four components present in a droplet (S, A, O, and W). In the above equation, as elsewhere in this paper, we employ the single-sum notation to represent the summation over all sizes and compositions of the droplets. One can write the following relations involving the derivatives by combining eqs C.1 and C.2:

$$\frac{\partial \ln \sum X_g}{\partial \ln X_k} = \frac{\sum g_k X_g}{\sum X_g} = g_n(k)$$

$$\frac{\partial \ln \sum g_k X_g}{\partial \ln X_k} = \frac{\sum g_k^{\,2} X_g}{\sum g_k X_g} = g_w(k) \quad \text{(C.3)}$$

Further, from the definition of the number average (eq C.2), one can write the following derivative, which combined with eq C.3, leads to

$$\frac{\partial \ln g_n(k)}{\partial \ln \sum g_k X_g} = \frac{\partial \ln \sum g_k X_g}{\partial \ln \sum g_k X_g} - \frac{\partial \ln \sum X_g}{\partial \ln \sum g_k X_g} = 1 - \frac{g_n(k)}{g_w(k)} \quad \text{(C.4)}$$

The root-mean-square deviation of g_k from its number-average value $g_n(k)$ is given by

$$\sigma_n^{\,2}(k) = \frac{\sum [g_k - g_n(k)]^2 X_g}{\sum X_g} = g_n(k)\, g_w(k) - [g_n(k)]^2 \quad \text{(C.5)}$$

which, combined with eqs C.4 and C.5, leads to

$$\frac{\sigma_n(k)}{g_n(k)} = \left[\left(1 - \frac{\partial \ln g_n(k)}{\partial \ln \sum g_k X_g} \right)^{-1} - 1 \right]^{1/2} \approx \left[\frac{\partial \ln g_n(k)}{\partial \ln \sum g_k X_g} \right]^{1/2} \quad \text{(C.6)}$$

Replacing the derivatives in eq C.6 by difference terms and restricting ourselves to the maximum term, we obtain eq 4.1 of section 4.

Appendix D: Model for Alcohol Self-Association in Oil

The partitioning of alcohol into the oil, water, and interfacial layer domains of a microemulsion controls whether a two-phase or a three-phase microemulsion system is formed, as well as the microscopic characteristics of the microemulsion phases. For the typical alcohols used, the amount of alcohol present in the oil domain can be large and comparable to the amount present in the interfacial layer. This is in contrast to the behavior of the surfactant, most of which remains at the interfacial layer and only a negligibly small amount of which are partitioned into the oil and the water domains. Therefore, the accurate accounting of the partitioning of alcohol into the oil domain is a necessary part of any quantitative theory of microemulsions. Such a theory must account for the facts that the alcohol is present in the oil phase as both monomers and aggregates and that the self-association of alcohol in the oil is responsible for its appreciable presence in the oil domain.

The thermodynamic treatments of the self-association of alcohols in hydrocarbon solvents[16] involve various levels of complexity and detail, depending on which of the following physical features are accounted for: (a) The alcohol molecules exist as self-associated aggregates. (b) The association can be represented by linear polymers, cyclic polymers, or aggregates of one or more distinct sizes. (c) The alcohol molecules can associate with the oil molecules to form oil–alcohol complexes. (d) The size differences between the various aggregates are appreciable and contribute to the solution properties. (e) In addition to the chemical association phenomenon, physical interactions between the various aggregates and the oil molecules constituting the solvent medium are also important. To keep the molecular theory of microemulsions at the simplest level possible, we treat the alcohol–oil systems by placing the emphasis on the most important source of nonideality, namely, the self-association of alcohol.[16]

D.1. Formulation of the Self-Association Model. Consider a mixture of N_{OO} oil molecules and N_{AO} alcohol molecules constituting a binary system from the stoichio-

metric point of view. The alcohol molecules are present as N_{jAO} aggregates of size j ($j = 1$, for the monomer), making the mixture a multicomponent system from the viewpoint of the true chemical species present. The true mole fractions of the aggregates of size j and of the oil are

$$X_{jAO} = \frac{N_{jAO}}{N_{OO} + \sum N_{jAO}} \qquad X_{OO} = \frac{N_{OO}}{N_{OO} + \sum N_{jAO}} \quad \text{(D.1)}$$

while the stoichiometric mole fractions of alcohol and oil are

$$X_A = \frac{N_{AO}}{N_{AO} + N_{OO}} = \frac{\sum j N_{jAO}}{N_{OO} + \sum j N_{jAO}} \qquad X_O = 1 - X_A \quad \text{(D.2)}$$

The self-association of alcohol in oil is represented by the association equilibria

$$A_1 + A_j \rightleftarrows A_{j+1} \qquad j = 1, 2, 3, \dots \quad \text{(D.3)}$$
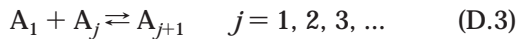
where the association equilibrium constants are considered to be the same for all association steps. If we denote the stepwise association equilibrium constant by K_X, the mole fraction of alcohol aggregates of size j is

$$X_{jAO} = K_X^{j-1} X_{1AO}{}^j \quad \text{(D.4)}$$

Because $K_X X_{1AO}$ must be less than unity to ensure that all mole fractions remain finite

$$\sum X_{jAO} = \frac{X_{1AO}}{1 - K_X X_{1AO}} \qquad \sum j X_{jAO} = \frac{X_{1AO}}{(1 - K_X X_{1AO})^2} \quad \text{(D.5)}$$

$$X_{OO} = 1 - \sum_j X_{jAO} = \frac{1 - K_X X_{1AO} - X_{1AO}}{1 - K_X X_{1AO}} \quad \text{(D.6)}$$

The average aggregation number of alcohol aggregates is therefore given by

$$j_{avg} = \frac{\sum j X_{jAO}}{\sum X_{jAO}} = \frac{1}{1 - K_X X_{1AO}} \quad \text{(D.7)}$$

and the ratio of the total number of alcohol molecules to those in monomeric form is

$$\frac{N_{AO}}{N_{1AO}} = \frac{\sum j X_{jAO}}{X_{1AO}} = \frac{1}{(1 - K_X X_{1AO})^2} \quad \text{(D.8)}$$

Finally, the stoichiometric mole fraction X_A can be used to calculate the true mole fraction X_{1AO} of the monomeric species using the expression

$$X_{1AO} = \frac{1 + 2K_X X_A - (1 + 4K_X X_A - 4K_X X_A{}^2)^{1/2}}{2K_X X_A(1 + K_X)} \quad \text{(D.9)}$$

The alcohol-partitioning calculations allow us to calculate X_{OO}, provided the self-association equilibrium constant K_X is known.

D.2. Determination of K_X from Thermodynamic Data for Alcohol–Hydrocarbon Mixtures. Using the available excess Gibbs energy and excess enthalpy data for alcohol–hydrocarbon mixtures,[16] the value of K_X can be estimated as described below. The Gibbs energy of the

solution is given by

$$G = N_{OO}\mu_{OO} + \sum N_{jAO}\mu_{jAO} = N_{OO}\mu_{OO} + N_{AO}\mu_{1AO} \quad \text{(D.10)}$$

where $\mu_{jAO} = j\mu_{1AO}$. The standard chemical potential of oil μ_{OO}° is taken to correspond to the pure oil, while the standard chemical potential of the monomeric alcohol μ_{1AO}° is taken to be that of the monomers in pure alcohol. One can find μ_{1AO}° by equating the chemical potential μ_{1AO}^* of the pure alcohol to the chemical potential of the monomers defined in terms of their standard state and their concentration X_{1AO}^* in pure alcohol:

$$\mu_{1AO}^* = \mu_{1AO}^\circ + kT \ln X_{1AO}^* \quad \text{(D.11)}$$

The monomeric mole fraction X_{1AO}^* in the pure alcohol is obtained from eq D.9 by setting the stoichiometric alcohol mole fraction X_A equal to unity:

$$X_{1AO}^* = \frac{1}{1 + K_X} \quad \text{(D.12)}$$

The excess Gibbs energy is thus provided by the expression

$$G^E = G - [N_{OO}\,\mu_{OO}^\circ + N_{AO}\,\mu_{1AO}^* + kT(N_{OO}\ln X_O + N_{AO}\ln X_A)] \quad \text{(D.13)}$$

and the molar excess Gibbs energy by

$$\frac{G^E}{N_{OO} + N_{AO}} = kT\left[X_A \ln\left(\frac{X_{1AO}}{X_{1AO}^*}\right) + X_O \ln\left(\frac{X_{OO}}{X_O}\right)\right] \quad \text{(D.14)}$$

The excess enthalpy can be related to the number of alcohol–alcohol hydrogen bonds formed in the alcohol–hydrocarbon solution compared to those formed in pure alcohol. Considering the enthalpy of formation of a hydrogen bond h_A to be independent of the degree of aggregation, the excess enthalpy is given by

$$H^E = h_A[\sum(j - 1)N_{jAO} - \sum(j - 1)N_{jAO}^*] \quad \text{(D.15)}$$

where N_{jAO}^* denotes the number of aggregates with a degree of association j in pure alcohol. Because $\sum j N_{jAO}^* = N_{AO}$ and $\sum j N_{jAO} = N_{AO}$, eq D.7 can be written as

$$\frac{N_{AO}}{\sum N_{jAO}} = \frac{\sum j N_{jAO}}{\sum N_{jAO}} = \frac{\sum j X_{jAO}}{\sum X_{jAO}} = \frac{1}{1 - K_X X_{1AO}} \quad \text{(D.16)}$$

Therefore

$$\sum N_{jAO} = N_{AO}(1 - K_X X_{1AO})$$

$$\sum N_{jAO}^* = N_{AO}(1 - K_X X_{1AO}^*) \quad \text{(D.17)}$$

and, consequently, the molar excess enthalpy is given by the relation

$$\frac{H^E}{N_{OO} + N_{AO}} = h_A X_A K_X(X_{1AO} - X_{1AO}^*) \quad \text{(D.18)}$$

The thermodynamic models available in the literature[16] employed a constant value of -6000 cal/mol for the hydrogen-bonding energies h_A of various alcohols. Therefore

$$\frac{\mathrm{d}\ln K_X}{\mathrm{d}(1/T)} = -\frac{h_A}{R} \tag{D.19}$$

where R is the gas constant.

By fitting the available excess Gibbs energy data to eq D.14, the excess enthalpy data to eq D.18, the average aggregation number of the alcohol to eq D.7, and the ratio between the total and the monomeric alcohol to eq D.8 and incorporating the temperature dependence provided by eq D.19, we have developed the following expression for an alcohol with n_{cA} carbon atoms:

$$K_X = 92 n_{cA}^{-0.47} \exp\left[3000\left(\frac{1}{T} - \frac{1}{323}\right)\right] \tag{D.20}$$

The preceding equation is valid for aliphatic alcohols ranging from propanol to decanol. For example, at 25 °C, the association equilibrium constants are 104.6, 94.2, 86.4, and 80.4, respectively, for butanol, pentanol, hexanol, and heptanol.

D.3. Use of the Alcohol Self-Association Model. In performing the computations for microemulsions, one first estimates K_X using eq D.20 for a given chain length of alcohol and a given temperature. By equating the chemical potential of the alcohol in the oil phase to the chemical potential of the alcohol in the water phase, one obtains

$$\frac{X_{AW}}{X_{AW}^{\mathcal{S}}} = \frac{X_{1AO}}{X_{1AO}^{*}} = (1 + K_X) X_{1AO} \tag{D.21}$$

where $X_{AW}^{\mathcal{S}}$ is the saturation concentration of alcohol in water when the water phase coexists with a pure alcohol phase. At 25 °C, the solubility of aliphatic alcohols in water is given[19] by the expression

$$\ln X_{AW}^{\mathcal{S}} = 1.40 - 1.38 n_{cA} \tag{D.22}$$

To estimate $X_{AW}^{\mathcal{S}}$ at any other temperature, the temperature dependence of alcohol solubility is assumed comparable to that of aliphatic hydrocarbons and the relations provided for the methyl and methylene groups by eqs 7.3 and 7.4, respectively, are used to obtain this temperature dependence. For a given value of X_{AW}, the mole fraction X_{1AO} of the monomeric alcohol in the oil phase is calculated by combining eqs D.21 and D.22. Finally, the true mole fraction of oil X_{OO} is calculated using eq D.6.