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Theoretical Model and Phase Behavior for Binary Surfactant Mixtures

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A new model for micellization behavior of binary surfactant mixtures in solution is presented. A packing parameter, P^*, has been introduced to describe the nonrandom mixing in mixed micelles. The significant feature of this model is that it considers asymmetric behavior of micellization in binary surfactant mixtures and predicts the changes in the structures of mixed micelles with concentration that are dependent on the overall ratio of the surfactant components and their chemical characteristics. On the basis of the results obtained, a schematic model for the structural changes of mixed micelles has been proposed here. This model can be considered as a generic model for binary surfactant mixtures, with regular solution theory being a special case for a packing parameter approaching infinity.

I. Introduction

Mixed surfactants are of considerable interest because of their wide commercial use. The properties of surfactant mixtures have received some attention in the past;[1-3] however, their behavior cannot yet be predicted from available theory. As in the case of individual surfactants, the formation of mixed micelles in aqueous solution leads to marked changes in the physicochemical properties of the system, but the micellization behavior of mixed surfactant systems is indeed much more complex than that of single surfactants. In this work, a model which can predict the behavior of mixed surfactants is developed by taking the major interactions between the components into consideration.

The thermodynamic models of mixed micelle formation can be divided into two broad categories. At one level, which may be considered the more fundamental, the process is treated as a reversible chemical reaction and the mass action approach is used.[4-6] The reactants are the surfactants, the bound counterions, and, when appropriate, solubilizates. The standard free energy associated with this reaction is in reference to a standard state in which the reactants are dispersed at infinite dilution. This type of model is appropriate because micelle formation is reversible. Micelles have a finite lifetime, as do the individual components that make up a micelle.[7-9] The aggregation number is a dynamic variable and, at any instant, various individual micelles will be composed of differing numbers of surfactant molecules. Furthermore, in the case of mixed micelles, the number of surfactant molecules of a given structure may also vary from micelle to micelle. In principle, this kind of treatment can be extended to multicomponent systems, but the calculations required for the model then become complex. Many parameters and assumptions have to be made to get the data for the changes in standard free energy associated in the micellization process.[9,10]

The second approach is to consider the micelle as a separate bulk phase having an infinite lifetime.[1,11-13] The chemical potentials of the components in the micellar phase, sometimes called a pseudophase to emphasize the fact that it is not quite a true thermodynamically different phase, can then be equated to those of the molecules that are dispersed in the aqueous phase. Various models for chemical potential can be used to account for the nonideal behavior in both the micellar and solution phases.

The phase separation model defines the proportions of various components that exist within the micellar phase, and it also provides equations for the cmc of mixtures; but it does not address factors that relate to the size of the micelles or their aggregation number. This type of model is usually simple to use. Calculation using a monodisperse mass action model suggests that for micelles of 50 molecules or more, the pseudophase separation model should provide a good approximation. One of the most popular models for this type of treatment is the regular solution theory introduced first by Rubingh.[13] The basic assumption in regular solution theory is that the excess entropy and mixing volume are zero and hence the excess enthalpy of mixing is equal to the excess free energy, which can be expressed using the results applied to "regular solution" mixtures.

Even though the regular solution treatment is simple, it is to be noted that the basic assumption in this treatment, i.e. mixing entropy is zero, is not thermodynamically valid for describing *nonideal* mixed micelles. Therefore, this model should be viewed only as a useful empirical model. Furthermore, regular solution treatment is successful mainly with respect to the correlation of mixed critical micelle concentrations with one interaction parameter β.[13]

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It is not suitable for describing many other micellization properties in surfactant mixtures.[13-18]

The aim of this modeling work was to develop a model for describing properties such as monomer concentrations and micellar composition in binary surfactant systems. As a first step, this model will be limited to ionic–nonionic surfactant systems, where the nonionic surfactant has a lower cmc than the ionic surfactant.

II. Development of the Model

2.1. Pseudophase Separation Approach for Treating Nonideal Mixed Micellization. A general model can be developed for nonideal mixed micellization processes by considering the chemical potentials of the individual surfactant components. For mixed surfactant component *i* in solution:

$$\mu_i = \mu_i^{\circ} + RT \ln C_i^{\mathrm{m}} \tag{1}$$

where μ_i° is the standard chemical potential and C_i^{m} is the monomer concentration of component *i*.

For a micelle of pure *i*th component:

$$\mu_i^{\mathrm{oM}} = \mu_i^{\circ} + RT \ln C_i \tag{2}$$

where C_i is the cmc of pure component *i*.

For a mixed micelle:

$$\mu_i^{\mathrm{M}} = \mu_i^{\mathrm{oM}} + RT \ln \gamma_i X_i \tag{3}$$

where X_i is the mole fraction of surfactant *i* in mixed micelles and γ_i is the activity coefficient of *i* in mixed micelles. From phase equilibrium:

$$\mu_i^{\mathrm{M}} = \mu_i \tag{4}$$

Equations 1–3 can be combined to give the general result:[20]

$$C_i^{\mathrm{m}} = \gamma_i X_i C_i \tag{5}$$

By simply rearranging this basic equation and mass balance, monomer concentrations and mixed micellar composition in binary surfactant systems can be easily calculated using the following equations:

$$\frac{1}{C^*} = \sum_{i=1}^{n} \frac{\alpha_i}{\gamma_i C_i} \tag{6}$$

$$X_1 = \left[\frac{-(C - \Delta) + [(C - \Delta)^2 + 4\alpha C\Delta]^{1/2}}{2\Delta}\right] \quad (7$$

$$C_1^{\mathrm{m}} = \left[\frac{-(C - \Delta) + [(C - \Delta)^2 + 4\alpha C\Delta]^{1/2}}{2\cdot(\gamma_2 C_2/\gamma_1 C_1 - 1)}\right] \tag{8}$$

$$C_2^{\mathrm{m}} = \left(1 - \frac{C_1^{\mathrm{m}}}{\gamma_1 C_1}\right)\gamma_2 C_2 \tag{9}$$

$$(\Delta = \gamma_2 C_2 - \gamma_1 C_1)$$

where X_1 is the mole fraction of surfactant 1 in mixed micelles, γ_i $(i = 1, 2)$ is the activity coefficient of *i* in mixed micelles, C^* is the cmc for the mixed surfactant systems, *C* is the total concentration of the surfactant in the mixture, and α is the overall mixing ratio of surfactant 1 in binary mixture.

The mathematical calculations using all the above equations are relatively simple. The key element for this type of calculation is the actual definition of the activity coefficients γ_i in the system. This will be discussed next.

2.2. Excess Properties for Mixtures. The behavior of mixtures can be conveniently characterized by introducing the thermodynamic function of mixing, Δ*m*. Denoting a generic molar mixture property by the symbol *m*, Δ*m* can be defined as the difference between the value of any function in a mixture *m* and the sum of its values of unmixed components at the same pressure and temperature:

$$\Delta m = m - \sum X_i m_i \quad (\text{constant } T \text{ and } P)$$

Expressions for Δ*m* are particularly simple for ideal mixing systems. The basic results are summarized in Table 1. It can be seen that both the volume change of mixing, Δv^{id}, and the enthalpy change of mixing, ΔH^{id}, are zero, reflecting the molecular assumptions inherent in the ideal mixing model. However, neither the entropy change of mixing, ΔS^{id}, nor the Gibbs energy change of mixing, ΔG^{id}, is zero: ΔS^{id} is always positive, and ΔG^{id} is always negative. The composition dependence of the scaled quantities $\Delta S^{\mathrm{id}}/R$ and $\Delta G^{\mathrm{id}}/RT$ for binary systems is shown in Figure 1.

In general, real mixtures are not ideal. Nevertheless, one can take the ideal mixture as a basis for the definition of a class of functions m^{E} called excess properties:

$$m^{\mathrm{E}} = m - m^{\mathrm{id}} \quad (\text{constant } T, P, \text{ and } X)$$

or equivalently

$$m^{\mathrm{E}} = \Delta m - \Delta m^{\mathrm{id}} \quad (\text{constant } T, P, \text{ and } X) \tag{12}$$

A common feature of all excess properties is that m^{E} approaches zero as any component approaches purity:

$$\lim_{x \to 1} m^{\mathrm{E}} = 0 \quad (\text{any } i)$$

The excess properties provide global measures of deviations from the ideal solution behavior, and they are interrelated. In fact, choosing *T*, *P*, and composition as independent variables, one can view the excess Gibbs energy G^{E} as a generating function for all the other excess properties, as well as for the activity coefficients. All these relations can be easily derived using classical thermodynamics.

The activity coefficient is related to G^{E} in a special way. The logarithm of activity coefficient is a partial molar property with respect to the scaled excess Gibbs energy, and the quantity $\ln \gamma_i$ therefore has those features common to all partial molar properties. It obeys an additive relationship:

$$G^{\mathrm{E}} = RT \sum X_i \ln \gamma_i$$

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Table 1. Change in Properties for Mixing of the Ideal Mixture Systems

$$\Delta V^{id} = 0$$
$$\Delta H^{id} = 0$$
$$\Delta S^{id} = -R\Sigma X_i \ln X_i$$
$$\Delta G^{id} = RT\Sigma X_i \ln X_i$$

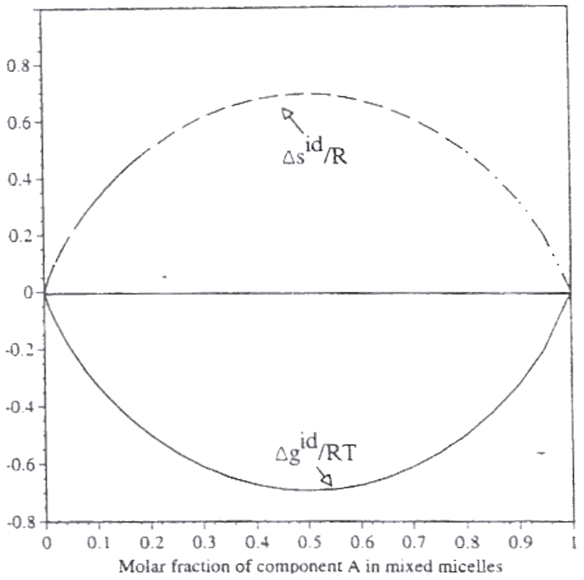

Figure 1. Entropy change of mixing and the Gibbs energy change of mixing for an ideal binary solution.

For binary systems, the activity coefficient can be readily found from an expression for G^E by the application of the following equations, which come from eq 14:

$$\ln \gamma_1 = \frac{1}{RT}\left[G^E + X_2 \frac{dG^E}{dX_1}\right] \tag{15}$$

$$\ln \gamma_2 = \frac{1}{RT}\left[G^E - X_1 \frac{dG^E}{dX_1}\right] \tag{16}$$

It becomes clear that if one can find a way to model the excess free energy G^E, all the other properties of mixed system can be easily predicted using the above equations. This is the advantage of using G^E to model nonideal mixture systems.

2.3. Evaluation of Excess Free Energy G^E in Binary Surfactant Mixtures. There exists no general theory yet that can adequately describe the composition dependence of the excess thermodynamic properties of liquid mixtures. As mentioned earlier in the Introduction, regular solution theory is one of the most popular models which has been used so far to examine the behavior of surfactant mixtures. It will be useful to analyze the problems existing in the application of this model, so that guidelines for developing a new model could be obtained. Holland[1,15] has measured the heat of mixing in surfactant mixtures using calorimetric methods. Comparison of his experimental results with the expected behavior of the excess heat of mixing from the regular solution approximation shows poor agreement. These results demonstrate that, in spite of the success of this model for predicting critical micellar concentrations (cmc's) in nonideal mixtures, it does not properly account for the heats of mixing in these systems. This implies that there must be a large TS^E contribution to the excess free energy of mixing. Synergism between different surfactant species is usually observed in the formation of mixed micelles. This apparently indicates that the interaction between different surfactant species is stronger than that between the same surfactant species. Due to this specific interaction, the mixing process in real systems is not completely random. On the other hand, the basic assumption of the regular solution theory is that the excess entropy of mixing is zero. This means that regular solution theory treats the mixed systems as ideal mixing from the viewpoint of randomness in mixing. Since the micellar phase is not a real separate phase, the aggregation number of micelles is limited. This fact will also make totally random mixing not valid for such cases. So when mixed surfactant systems are modeled, some constraints must be applied to account for the nonrandom mixing in the formation of mixed micelles.

Instead of using a very complex statistical thermodynamical model to treat this nonrandom mixing phenomenon, the concept of the relative solubility of each surfactant component in mixed micelles is considered. A packing constraint parameter can be introduced to describe such nonrandom mixing. For example, for the case of a mixture of an ionic surfactant A and a nonionic surfactant B, where the latter is more surface active than the former, it is reasonable to assume that the nonionic surfactant B will form micelles first when the total concentration exceeds the mixture cmc, and then species A can dissolve in B micelles to form mixed micelles. When a small quantity of A is dissolved in the B-rich mixed micelles, the formation of mixed micelles will be enhanced due to the synergism between the two surfactants. But a further increase in the A component in mixed micelles may then decrease the stability of mixed micelles, since excessive A in mixed micelles may cause packing problems and introduce strong electrostatic repulsion among head groups in the micelles. It is clear that there will be a packing limit for surfactant A in mixed micelles. When the A composition in the micelles is lower than this limit, the micellization process will be enhanced due to synergism between the two surfactants. On the other hand, when the A composition exceeds the packing limit in the micelles, the micellization process will become energetically unfavorable. Here, the packing limit of ionic A in mixed micelles is considered. Instead of surfactant B, if A can form micelles by itself, the solubility of nonionic B in A micelles can be treated as infinity. In other words, there is no packing limit for nonionic B species in A micelles. This hypothesis indicates that the micellization process is not a symmetrical process in terms of the micellar composition. In other words, the mixed micelle with 20% of *component A* and the mixed micelle with 20% of *component B* will have different excess free energies G^E. This kind of asymmetrical effect has been reported in the literature for surfactant mixtures.[3] In regular solution theory, however, the micellization process of mixed surfactant is always a symmetrical process. It is clear that the asymmetrical behavior in the mixed micellization process is an important aspect which should be taken into account in any attempt to model surfactant mixtures.

On the basis of the above analysis of mixed surfactant systems, several fundamental assumptions for modeling binary surfactant mixtures A and B are proposed:

(1) Interactions between two types of surfactant species can be represented using an interaction parameter, W. Here, the interaction will arise mainly from van der waal's attractive forces, and W for binary surfactant mixtures is always ≤ 0. When $W = 0$, there is no special interaction between two different surfactant species, and the surfactant mixture can be treated as an ideal system.

(2) The formation of mixed micelles is affected by the packing properties of the surfactants. For binary surfactant mixtures, a packing parameter P^* can be employed to indicate the packing constraint of surfactant A in surfactant B-rich micelles. This packing constraint is directly related to the nonrandom mixing in the system. On the other hand, the packing limit of surfactant B in surfactant A-rich micelles is taken as infinity, where the surfactant B is defined to be more surface active than the surfactant A.

(3) By adapting the equation in the lattice model for the enthalpy of mixing in liquid mixtures, the excess free energy G^E for the formation of mixed micelles can be represented by the following equation:

$$G^E = RTWX(1 - X)\left(1 - \frac{X}{f(\alpha)P^*}\right) \tag{17}$$

where α is the overall surfactant ratio of component A in the mixture, $f(\alpha)$ is a function of α, X is the molar fraction of surfactant A in mixed micelles, W is the interaction parameter, and P^* is the packing parameter. The function $f(\alpha)$ is used here to modify the possible change of the packing parameter as a function of the overall mixing ratio α. Similar to the relationship of packing density of two different particles as a function of mixing ratio,[19] $f(\alpha)$ can be described by the following equation:

$$f(\alpha) = \begin{cases} \alpha, & \alpha > 0.5 \\ 1 - \alpha, & a \le 0.5 \end{cases} \tag{18}$$

This equation indicates that the packing constraint will keep changing with any change in the overall surfactant mixing ratio. When the overall mixing ratio approaches 0 or 1, the packing ability in mixed micelles will be better than that when the ratio is about 0.5 (1:1 mixture). For the same total concentration of the binary mixture, the possibility for A and B surfactant to contact with each other will be maximum when the overall mixing ratio is 0.5, and the packing constraint will then become more significant.

III. Characteristics of the Proposed Model. To better understand the micellization behavior predicted by eq 17, the excess free energy G^E is plotted at different levels of relevant parameters as a function of the mole fraction of component A in mixed micelles. For the purpose of comparison, the excess free energy calculated from regular solution theory with the interaction parameter $\beta = -3$[1] is also plotted. The effect of the interaction parameter on the excess free energy G^E is presented in Figure 2. In this figure, the packing parameter P^* is fixed at 1.2, and the overall mixing ratio of surfactant A is taken as 0.5 (1:1 mixture). It can be seen that the excess free energy G^E predicted by eq 17 is *not* symmetric with respect to the molar fraction of components in mixed micelles. Regular solution theory predicts that excess free energy is symmetric and will reach a minimum when the mole fraction of surfactant A is 0.5. But this is not the case with the model proposed in the form of eq 17. According to the new model proposed here, the excess free energy G^E will reach a minimum when the mole fraction of component A in mixed micelles is about 0.25. In other words, the mole fraction corresponding to the minimum excess free energy is shifted to a lower value in this case. This suggests that by taking the packing effect into account the optimum mole fraction of component A in mixed micelles is lower than that predicted by the regular solution theory. In other words, the mixing of component A in mixed micelles is not as easily achieved as predicted by the regular solution theory. This may be one of the reasons that regular solution theory cannot properly predict the micellization behavior above the cmc. It can be seen from Figure 2 that the asymmetry of the excess free energy becomes more marked with a decrease in the interaction parameter W. This will have a very significant effect on the activity coefficients of the mixed micelle system, and this will be discussed in detail later.

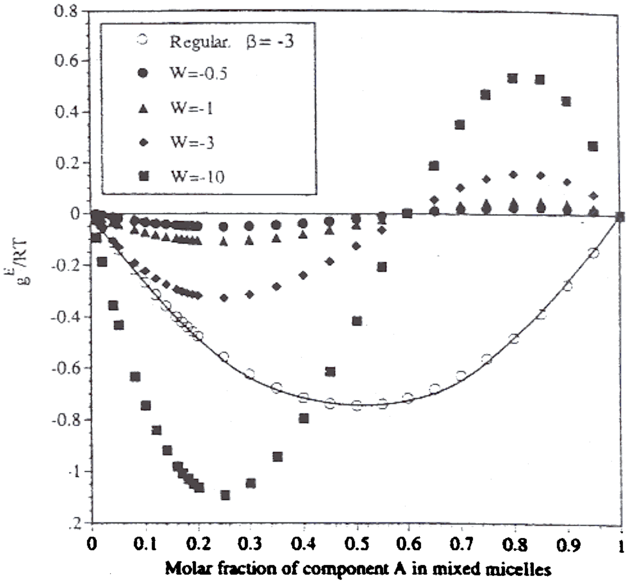

Figure 2. Effect of interaction parameter on the excess free energy.

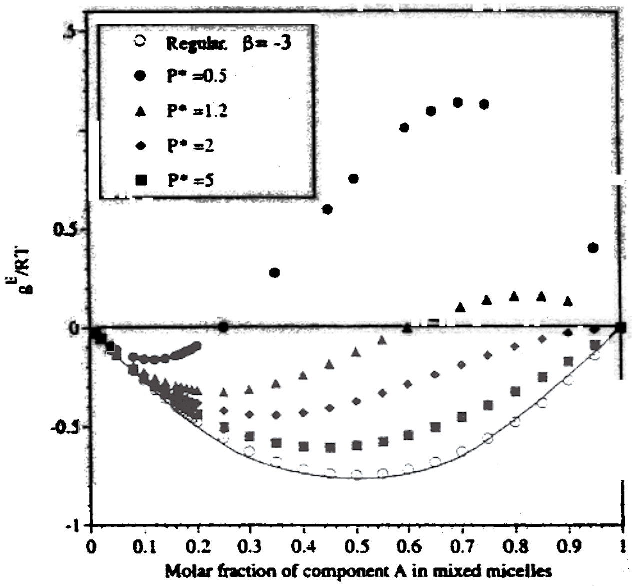

Figure 3. Effect of packing parameter on the excess free energy.

The effect of packing parameter on the excess free energy is illustrated in Figure 3. In this plot, the interaction parameter W is fixed at −3, and the overall mixing ratio α at 0.5. It can be seen that the excess free energy G^E calculated using equation 17 decreases with an increase in packing parameter and the G^E curve approaches the curve predicted by the regular solution theory ($\beta = -3$). It is clear that the asymmetry phenomenon in mixed micelles is controlled mainly by the packing parameter defined by eq 17. When the packing parameter approaches infinity, the model represented by eq 17 will be same as that in the regular solution theory. Hence the model proposed in the form of eq 17 can be regarded as a generic equation for binary surfactant mixtures, and the regular solution theory, as only a special case of eq 17. It is noted

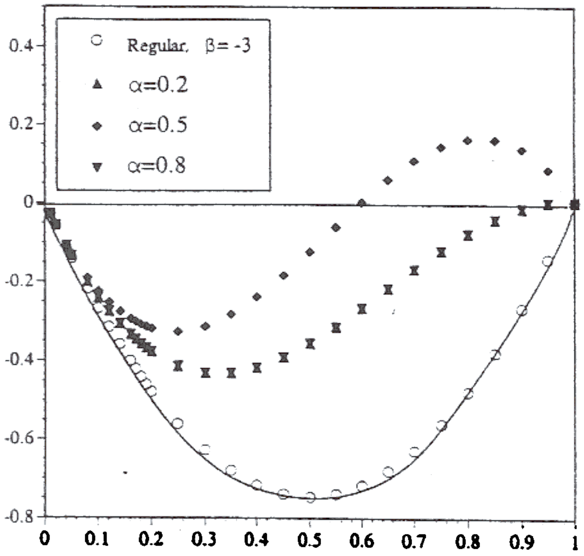

Figure 4. Effect of overall mixing ratio on the excess free energy.

that the minimum excess free energy shifts to the lower mole fraction region of component A in mixed micelles when the packing parameter for the mixture becomes smaller, and the negative value of the excess free energy becomes smaller also. This suggests that the formation of mixed micelles will be more difficult with a decrease in the packing parameter. This may be the case for the fluorocarbon–hydrocarbon surfactant mixtures. The effect of overall mixing ratio on the excess free energy G^E is shown in Figure 4. In this figure, the interaction parameter W is fixed at −3, and the packing parameter P^*, at 1.2. As mentioned above, the possibility for A and B surfactants to contact with each other will be maximum when the overall mixing ratio is 0.5, and the packing constraint will also become significant. This is what can be seen from Figure 4.

For binary surfactant mixtures of A and B, the activity coefficients of both the components in mixed micelles can be easily calculated using the following equations derived from eqs 15 and 16 and based on the excess free energy described by eq 17:

$$\ln \gamma_A = WX(1 - X)\left(1 - \frac{X}{f(\alpha)P^*}\right) + (1 - X)W\left(1 - 2X - \frac{2X}{f(\alpha)P^*} + \frac{3X^2}{f(\alpha)P^*}\right) \quad (19)$$

$$\ln \gamma_B = WX(1 - X)\left(1 - \frac{X}{f(\alpha)P^*}\right) - XW\left(1 - 2X - \frac{2X}{f(\alpha)P^*} + \frac{3X^2}{f(\alpha)P^*}\right) \quad (20)$$

The total surfactant concentration in the mixtures can be related to the mole fraction of component A, X, and the activity coefficients using the following equation:

$$C_{\text{total}} = \frac{(\gamma_B C_B - \gamma_A C_A)X(1 - X)}{X - \alpha} \quad (21)$$

where C_A and C_B are the cmc's of pure components A and B under the same conditions.

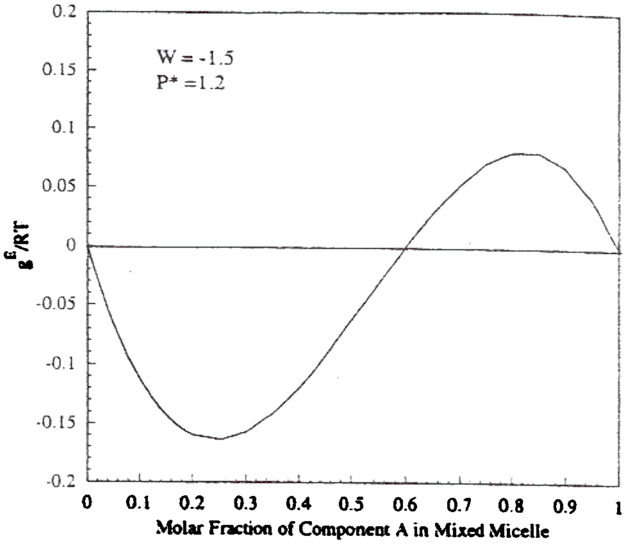

Figure 5. Excess free energy in the surfactant A and B mixture as a function of mole fraction of component A in mixed micelles.

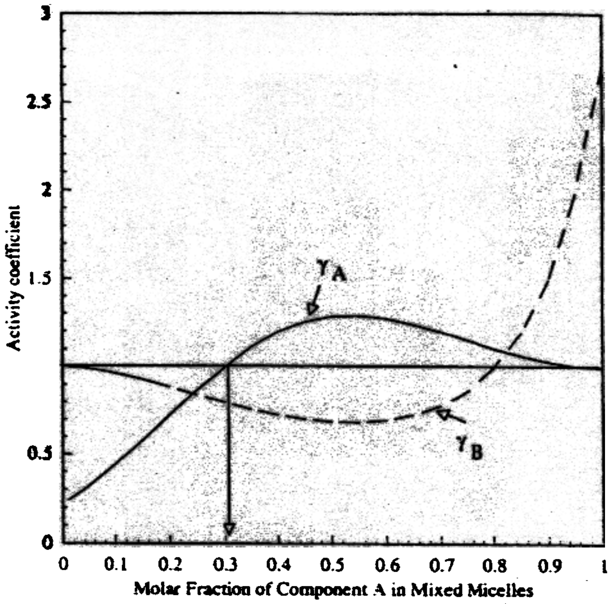

Figure 6. Activity coefficients of components A and B in mixed micelles.

The excess free energy G^E for a binary surfactant mixture of A and B with an overall mixing ratio of 0.5, calculated using an interaction parameter of −1.5 and a packing parameter of 1.2, is plotted in Figure 5. The activity coefficients of components A and B can then be calculated using eqs 19 and 20, and the results obtained are plotted in Figure 6. As mentioned before, surfactant B is more surface active than surfactant A in the system discussed here. When mixed micelles first form in the system, it is reasonable to assume that component B will be dominant in the initial micelles and then some surfactant A can dissolve in B-rich micelles. Due to the synergism between surfactants A and B, the excess free energy G^E for the system will decrease with the increase of component A in the mixed micelles, and G^E will reach a minimum point as the mole fraction of component A approaches 0.25. This minimum point is determined mainly by the packing parameter for the system. Above the A mole fraction of 0.25, the packing constraint in the mixed micelles becomes significant, and the excess free energy begins to increase, and this means that the stability of mixed micelles begins to decrease. Upon examining the change in activity coefficients in Figure 6, it can be seen that the activity coefficient of component A keeps increasing with an increase of component A in mixed

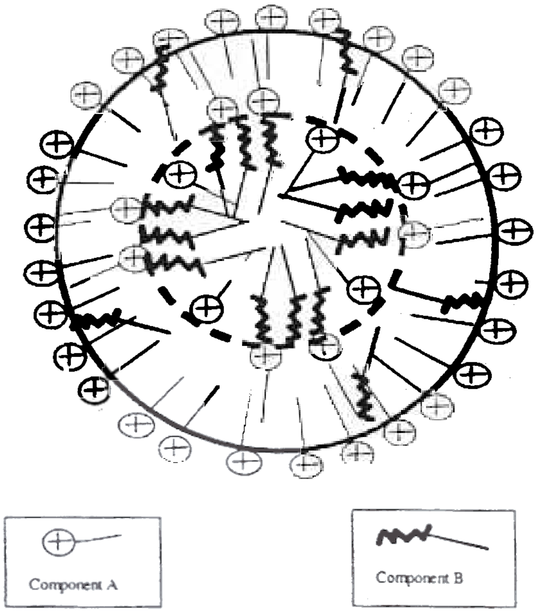

Figure 7. Schematic model for the micelle structural changes when the activity coefficient of component A in mixed micelles reaches 1.

micelles. When the mole fraction of component A is 0.31, the activity coefficient of A tends to 1. This must be the critical point for the formation of mixed micelles. The activity coefficient has the important limiting feature

$$\lim_{X_i \to 1} \gamma_i \qquad (22)$$

In other words, the activity coefficient γ_i approaches 1 when component *i* approaches purity. It can be seen that the activity coefficient of component A in the mixed micelles will have the same value as pure A when the mole fraction of A in mixed micelles is 0.31. Therefore, it is reasonable to conclude that component A in mixed micelles under this condition will begin to acquire some properties of pure component A. On the basis of the experimental results discussed in our previous paper,[14] it is proposed that the point at which $\gamma_A = 1$ is the point at which mixed micelles begin to change their structure. Possible structural change is schematically shown in Figure 7. With the increase in component A in mixed micelles, the excess free energy will go through the minimum point when the mole fraction of component A in mixed micelles is 0.25; a further increase in the mole fraction of component A in micelles will make the stability of the mixed micelles decrease. When the activity coefficient of component A reaches 1, the structure of the mixed micelles is proposed to split into an outer layer and an inner layer. Surfactant A will form a relatively loosely packed outer layer. This outer layer is similar to the vesicles and consists mainly of surfactant A. The inner layer is B-rich micelles, and the composition of inner layer micelles will revert to the point at which the excess free energy is minimum. Since surfactant B is more surface active and the outer layer is loosely packed, the solubility of component B in the outer layer micelles is unlimited, and the existence of the outer layer micelles will have no effect on the chemical potential of component B in the micellar phase. In other words, surfactant B can go through the outer layer freely and the chemical potential of surfactant B in the micellar phase will be dependent upon the properties of the inner layer only. The formation of the inner layer corresponds to the decrease of A in the inner layer and the increase of the activity coefficient of B in the micellar phase. Thus, the chemical potential of surfactant B in the micellar phase will increase, and this, in turn, will make the monomer concentration of B in the system increase. This phenomenon was evident in the experimental results discussed in our previous paper.[14] For surfactant A, once the outer layer forms, its behavior in it will be similar to that of pure A. The activity coefficient of surfactant A in the micellar phase will be dependent mainly on the outer layer and will stay constant at 1.

IV. Conclusions and Summary

In this work, a new model for binary surfactant mixtures of A and B and their micelles in solution has been proposed in the form of eq 17. Considering nonrandom mixing in the formation of mixed micelles, the concept of packing constraint is introduced, and this is represented by the packing parameter, P^*. The significant characteristic of this model is that it examines the asymmetric behavior of micellization in binary surfactant mixtures. This asymmetric behavior is controlled mainly by the value of the packing parameter. With an increase in the packing parameter, the formation of mixed micelles becomes more random.

This model also predicts that the structures of mixed micelles can change above the mixture cmc depending on the properties of the surfactant components and the overall mixing ratio; a schematic model for the mixed micelles has been presented. Once the activity coefficient of surfactant A approaches 1, the structure of the mixed micelles is proposed to consist of an outer layer and an inner layer. The outer layer is surfactant A-rich micelles and is loosely packed with a structure similar to that of vesicles, while the inner layer consists of surfactant B-rich micelles. This new model can be considered as a generic model of binary surfactant mixtures with the regular solution theory being a special case of it, when the packing parameter approaches infinity.

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