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Asymmetric Excess Free Energies and Variable Interaction Parameters in Mixed Micellization

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The electrostatic contribution to the excess free energy of mixed micellization, considered to be the most important contribution for ionic/nonionic mixtures of hydrocarbon-based surfactants with similar tail lengths, was calculated for mixtures of sodium dodecyl sulfate and three different nonionic surfactants at two salt concentrations. A simplified analytical molecular thermodynamic approach was used where the electrostatic free energy contributions of both the pure ionic and mixed micelle were obtained by applying an approximate solution of the Poisson−Boltzmann equation. The results show that in general the excess free energies are not symmetrical with respect to the micellar composition. However, it is shown that even in this case the equations for the micellar properties given by the molecular thermodynamic approach at the optimal micellar composition remain identical to the ones produced by the phase separation approximation, including the expressions for the activity coefficients as a function of the excess free energy. Important differences in the activity coefficients, which determine the system behavior, are illustrated when either symmetric or asymmetric excess free energies are considered.

Introduction

Surfactant systems used in applications of surfactants are often mixed. Considerable theoretical and experimental work[1−18] has been done in the last several years to understand the properties of these complex systems.

A molecular thermodynamic theory of mixed surfactant solutions, which allows the prediction of certain thermodynamic properties, has been developed recently.[2−4,16−18] At the optimal micellar composition, an equation for the mixture critical micelle concentration (cmc) is obtained which is identical to the expression derived in the context of the pseudophase separation model using the regular solution theory with an empirical (constant) interaction parameter β:[4]

$$1/c_{\mathrm{Mmix}} = \alpha_s/\gamma_A c_{\mathrm{MA}} + (1 - \alpha_s)/\gamma_B c_{\mathrm{MB}} \qquad (1)$$

c_{Mmix}, c_{MA}, and c_{MB} are the critical micelle concentrations of the mixture and pure surfactants A and B, respectively, α_s is the overall surfactant composition, and γ_A and γ_B are the micellar activity coefficients of surfactants A and B, respectively.

The micellar activity coefficients can be calculated using the expressions

$$\gamma_A = \exp[\beta(1 - \alpha)^2/kT] \qquad (2)$$

$$\gamma_B = \exp[\beta\alpha^2/kT] \qquad (3)$$

where β is the interaction parameter for mixed micelles and α is the optimal micellar composition, namely, the composition at which the free energy for mixed micellization attains its minimum value, k is the Boltzmann constant, and T is the temperature. The values α and $\alpha_s = 1$ refer to pure surfactant A and α and $\alpha_s = 0$ refer to pure surfactant B.

Unlike the case of regular solution theories which involve an empirical parameter β by fitting experimental cmc values, the molecular thermodynamic approach provides a way of predicting β for a given surfactant mixture.[2−4,16−18] The rigorous theoretical treatment requires a very complex calculation of all contributions to the free energy of micellization including the micellar mixing nonidealities resulting from electrostatic and steric interactions between the surfactant hydrophilic heads and from the packing of the surfactant hydrophobic tails of unequal lengths in the micellar core. A simplified version of the theory assumes that, for binary mixtures of hydrocarbon-based surfactants, the main contribution to the interaction parameter comes from the electrostatic interaction between the surfactant's charged heads. The approximation is made that the electrostatic free energy contribution to the mixed micelle is proportional to the square of the average charge per monomer, and an approximate analytical solution to the Poisson−Boltzmann equation is applied to calculate the electrostatic free energy contributions of the pure ionic surfactant in order to obtain the proportionality constant. This simpli-

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fied "working model" has been used to calculate β values for a number of anionic/nonionic and cationic/nonionic systems with and without salt added. Values for a few anionic/cationic systems have also been obtained.[4]

For ionic/nonionic mixtures, the interaction parameters calculated in this way are dependent only on the molecular structure of the ionic surfactant and on the amount of salt added to the system. The nonionic surfactant is not considered at all in the calculation.

We have calculated excess free energies for mixed micellization considering the electrostatic contribution to be the most important one for hydrocarbon-based surfactants having tails of similar lengths. However, these contributions are obtained by using directly the approximate solution to the Poisson–Boltzmann equation for the calculation of the electrostatic free energies in both, the pure ionic surfactant and the mixed micelles. The excess free energies obtained by these calculations depend on the molecular structure of both surfactants and are found not to be, in general, symmetrical with respect to the micellar composition. To illustrate this dependence, a simple molecular model of the micelle will be used to treat mixtures of an ionic surfactant, sodium dodecyl sulfate (SDS), and three different nonionic surfactants at two salt concentrations. The three nonionic surfactants differ only by the length of their hydrocarbon tails, being equal,[12] greater,[16] and smaller[8] than 12 carbons, the length of the ionic hydrocarbon tail. Since the nonionic heads do not contribute to the electrostatic free energies, they are not considered in this approximation.

Excess free energies which are proportional to $\alpha(1-\alpha)$ are characterized by a constant interaction parameter β, as the ones used in regular solution theory.[25] However, when asymmetrical excess free energies are considered, β parameters become a function of the micellar composition and eqs 2 and 3 can no longer be used to calculate the activity coefficients. It will be shown that asymmetrical excess free energies (which yield $\beta(\alpha)$ parameters) in the molecular thermodynamic theory require the use of the same more general expression for the activity coefficients as in the pseudophase separation approach.[9] In other words, the relationships obtained using the molecular thermodynamic approach at the optimum micellar composition are identical to those obtained using the pseudophase separation approach, for both the symmetric and asymmetric excess free energy cases. The expression for the activity coefficients is the same in both approaches, having a dependence on $d\beta/d\alpha$ which becomes zero when β is a constant.

It will also be shown that the interaction parameter calculated for an ionic/nonionic surfactant mixture at a value of the ionic micellar molar fraction close to zero is equal to the negative of the electrostatic contribution to the free energy of micellization of the pure ionic micelle. This particular β value is the previously reported constant interaction parameter for all values of the micellar molar fraction.[4]

The activity coefficients calculated for symmetric excess free energies of mixed micellization may differ to a large extent from those obtained for asymmetric ones. To illustrate this point, a comparison was made between the activity coefficients calculated using the asymmetric excess free energy corresponding to a nonionic/ionic surfactant mixture and the activity coefficients obtained for the same system but using a symmetric excess free energy corresponding to a constant β equal to its average value. Although our simple molecular model and theoretical approach only allows for qualitative estimates of these quantities, a significant difference is found between them. This difference in the activity coefficients is likely to become more important when more rigorous calculations of the nonlinear contributions to the free energy of micellization are done, particularly for more complex surfactant structures.

Theory

In the molecular thermodynamic approach, a simplified analytical model for the free energy of mixed micellization per monomer gives the following equation:[2]

$$g_{\mathrm{mic}}(\alpha) \quad \alpha g_{\mathrm{mic}}^{A} + (1-\alpha) g_{\mathrm{mic}}^{B} + \alpha(1-\alpha) g_{\mathrm{mic}}^{AB} + kT[\alpha \ln \alpha + (1-\alpha)\ln(1-\alpha)] \tag{4}$$

where g_{mic}^{A} and g_{mic}^{B} are the free energy of micellization per monomer of pure surfactants A and B, respectively, g_{mic}^{AB} reflects contributions due to specific intramicellar interactions, and the last term corresponds to the free energy (entropy) of mixing the tails of the two surfactant species in the mixed micelle.

The excess free energy, given by the term $\alpha(1-\alpha)\, g_{\mathrm{mic}}^{AB}$ is zero for an ideal system. In the case of real systems there are two main contributions to the excess free energy: one associated with interactions between the hydrophobic moieties of the two surfactants A and B in the micellar core and another associated with the electrostatic interactions between the charged hydrophilic moieties of both surfactants. For binary mixtures of hydrocarbon-based surfactants, the first contribution is considered negligible, particularly when the tail lengths are not too different.[2–4] Therefore, in this approximation, to calculate the interaction parameter b given by g_{mic}^{AB}, we only need to calculate the excess free energy due to the electrostatic interactions. This is done here for a nonionic/ionic surfactant mixture.

The following expression will be used to calculate the electrostatic free energy per monomer of creating a charged surface for both the pure surfactant and the mixed micelle:[4,19,20]

$$g(\alpha) = 2kTz(\alpha)\{\ln[x(\alpha) + (1 + x(\alpha)^2)^{1/2}] - [(1 + x(\alpha)^2)^{1/2} - 1]/x(\alpha) - [2/x(\alpha)r(\alpha)\kappa(\alpha)]\ln[1/2 + 1/2(1 + x(\alpha)^2)^{1/2}]\} \tag{5}$$

where $z(\alpha)$ is the magnitude of the average charge per monomer and is given by the absolute value of

$$z(\alpha) \quad \alpha z_A + (1-\alpha) z_B \tag{6}$$

with z_A and z_B being the charges of the surfactants A and B, respectively; $x(\alpha)$ is given by

$$x(\alpha) = (1/2)[4\pi e\sigma(\alpha)/kT\epsilon\kappa(\alpha)] \tag{7}$$

where e is the electronic charge, ϵ is the solvent dielectric constant, and $\kappa(\alpha)^{-1}$ is the Debye screening length given by

$$\kappa(\alpha) = (8\pi C(\alpha) e^2/\epsilon kT)^{1/2} \tag{8}$$

where $C(\alpha)$ is the bulk ionic concentration, $\sigma(\alpha)$ is the surface charge density, and $r(\alpha)$ is the radius of the spherical charge distribution.

This equation is valid for charges distributed over a spherical surface of radius r and for fully dissociated 1:1 ionic surfactants and salts. This expression, derived from an analytical approximation to the nonlinear Poisson–

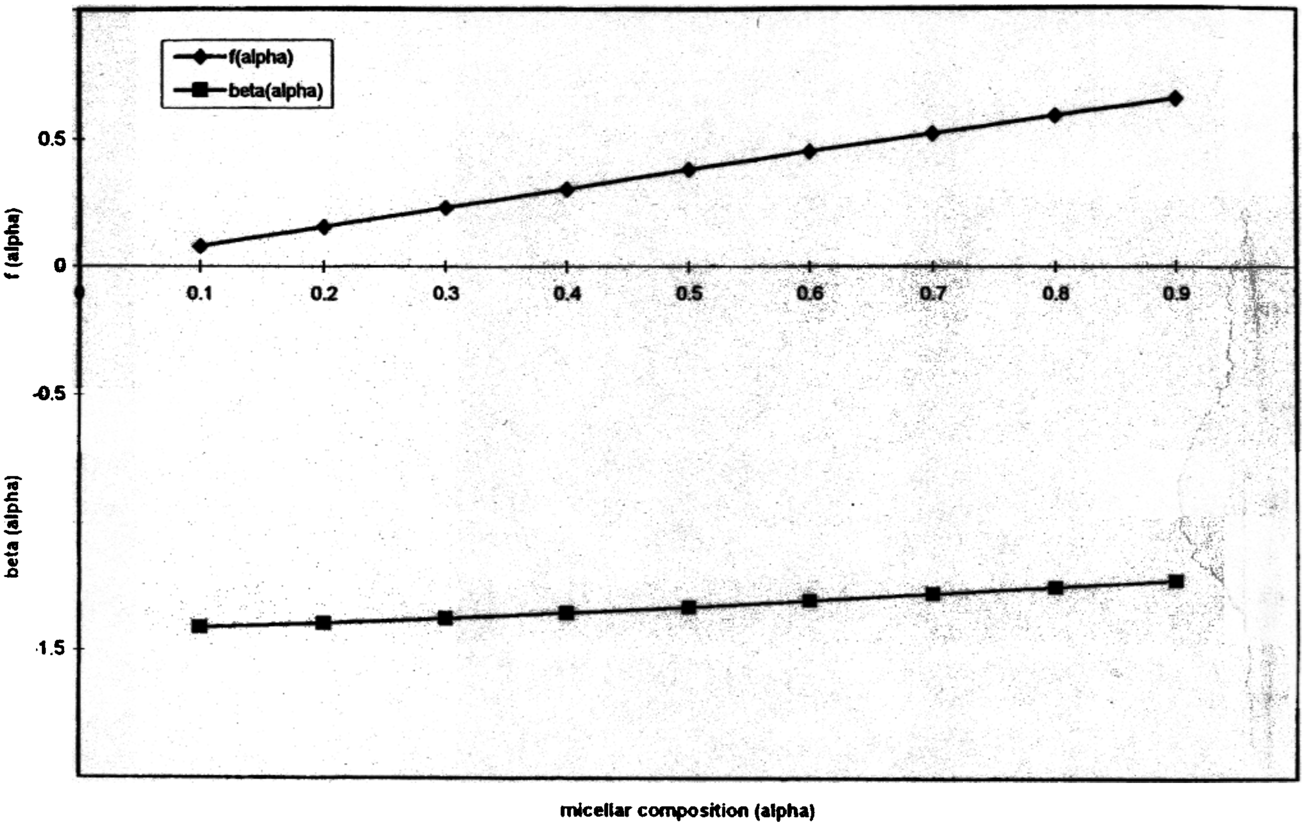

Figure 1. $f(\alpha)$ and $\beta(\alpha)$ in units of kT as a function of micellar composition for a mixture of sodium dodecyl sulfate and a C12 nonionic surfactant at a salt concentration of 0.5 M.

Boltzmann equation, is precise as long as the product $\kappa(\alpha)r(\alpha) > 1/2$.[19,20]

For the case of an ionic/nonionic surfactant mixture ($z_A = 1$, $z_B = 0$), the excess free energy per monomer $g^E(\alpha)$ due to the electrostatic interactions can be expressed as

$$g^E(\alpha) = \alpha(1 - \alpha)\beta \quad g(\alpha) - g^A \tag{9}$$

and therefore

$$\beta(\alpha) = \frac{g(\alpha) - \alpha g^A}{\alpha(1 - \alpha)} \tag{10}$$

Equation 5 will be used to calculate the electrostatic free energy of micellization per monomer for both the pure surfactant (g^A) and the mixed micelle ($g(\alpha)$).

There are two particular cases when the value of the interaction parameter is constant and given by the negative of the electrostatic contribution to the free energy of micellization of the pure ionic micelle. To show it, we will write the electrostatic free energy of micellization as $g(\alpha) = 2kT\alpha f(\alpha)$, where $f(\alpha)$ is given by the curly brackets in eq 5. Substituting this expression for $g(\alpha)$ in eq 10, we get

$$\beta(\alpha) = -(2kT)\left[\frac{f(1) - f(\alpha)}{1 - \alpha}\right] \tag{11}$$

When the assumption is made that the excess free energy is proportional to the square of the average charge per monomer,[4] $g(\alpha) = \alpha^2 2kTf(1)$ and then $f(\alpha) = \alpha f(1)$. Equation 11 yields $\beta(\alpha) = (-2kT)\, f(1) = -g^A$ in this case, which is the expression for the constant β value given previously.[4] However, there is no reason for this approximation to be always valid, and therefore β values are in general dependent on micellar composition, which only means that the excess free energies may not be proportional to the product $\alpha(1 - \alpha)$.

On the other hand, for any system, $f(\alpha)$ goes to zero for small values of α, and hence, we have from eq 11

$$\beta(0) = -2kTf(1) = -g^A$$

which is the constant β value given earlier. As mentioned before, this expression depends only on the properties of the ionic surfactant but not on those of the nonionic one.[4]

In the next section, eqs 5 and 11 will be used to calculate electrostatic excess free energies and $\beta(\alpha)$ values for mixtures of sodium dodecyl sulfate (SDS) and three different nonionic surfactants with different tail lengths, at two salt concentrations. When the excess free energy is proportional to the product of α and $(1 - \alpha)$, the β will be constant. Otherwise, these parameters will be a function of the micellar composition.

In these calculations we will assume the existence of spherical micelles only. To make sure that this is the case, bulky heads for the nonionic surfactants and a maximum salt concentration of 0.5 M of added salt will be considered. The bulky heads create a large steric repulsion which does not allow the formation of cylindrical micelles. Salt concentrations larger than 0.5 M screen the electrostatic interaction to such an extent that SDS cylindrical micelles begin to form.[22-24]

Results

To use eq 5 for the calculation of the electrostatic free energy, it is necessary to know several parameters as a

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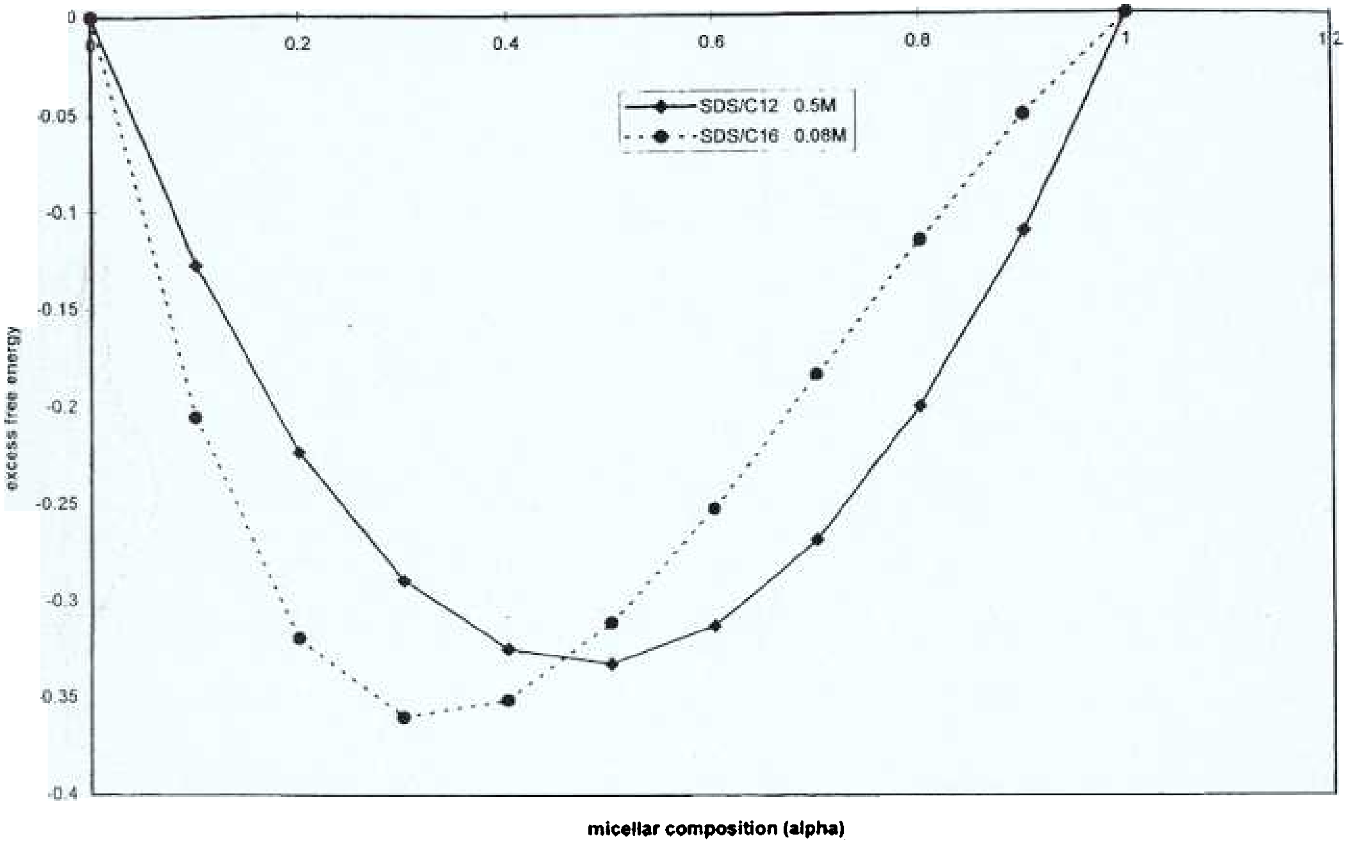

Figure 2. Excess free energy in units of kT as a function of micellar composition for two mixtures of sodium dodecyl sulfate: one with a C12 nonionic surfactant at a salt concentration of 0.5 M and the other one with a C16 nonionic surfactant at a salt concentration of 0.08 M.

function of the micellar composition. These are the average charge per monomer $z(\alpha)$, the bulk ionic concentration $C(\alpha)$, the surface charge density $\sigma(\alpha)$, and the radius of the spherical surface charge distribution $r(\alpha)$.

For an ionic/nonionic surfactant mixture, the average charge per monomer is equal to $z(\alpha) = \alpha$, for monovalent surfactant heads. The bulk ionic concentration will be given by the monomer concentration plus any salt added:

$$C(\alpha) = C_{\mathrm{surf}}(\alpha) + C_{\mathrm{salt}} \tag{12}$$

The surface charge is given by

$$\sigma(\alpha) = \frac{N(\alpha) z(\alpha) e}{A(\alpha)} \tag{13}$$

where $N(\alpha)$ is the total number of surfactant molecules in the micelle and $A(\alpha)$ is the area of the spherical surface charge distribution. The change in the total number of surfactant molecules in the micelle as a function of the micellar composition is approximated by a linear relationship, $N(\alpha) = \alpha N_A + (1 - \alpha) N_B$, where N_A and N_B are the aggregation numbers of the pure micelles. These aggregation numbers have been obtained by[4]

$$N_A = \frac{(4/3)\pi r_{cA}^{\;3}}{V_{cA}} \qquad N_B = \frac{(4/3)\pi r_{cB}^{\;3}}{V_{cB}} \tag{14}$$

where r_{cA} and r_{cB} are the radius of the micellar core of pure surfactants A and B and V_{cA} and V_{cB} are the volumes of the hydrocarbon chains that make up the micellar core for pure surfactants A and B, respectively. The values for these radii have been estimated by assuming that they are approximately equal to the fully extended (all trans) length of the linear hydrocarbon chain of the surfactants. However, an assumption is made that the CH_2 group adjacent to the hydrophilic moiety lies within the domain of hydration and therefore does not belong to the micellar core.[4]

The area of the spherical surface charge distribution $A(\alpha)$ is given by $4\pi r(\alpha)^2$, where $r(\alpha)$ is equal to the radius of the micellar core plus the distance of the surface of charge from the micellar core water interface. This distance is estimated from the known chemical structure of the ionic hydrophilic moiety and includes the length of one CH_2 group and will be approximated as a constant for all values of the micellar composition.

We selected to study a combination of an anionic surfactant, sodium dodecyl sulfate, and three different nonionic *n*-alkyl poly(ethylene oxide) surfactants with the same,[12] larger,[16] and shorter[8] number of carbon atoms in the tail than the ionic surfactant. To minimize additional free energy contributions to the excess free energy due to the mixing of tails of different lengths, the maximum difference studied is of 4 carbon atoms in the tail. In this work only the electrostatic contribution to the excess free energy is considered, and therefore the free energy contributions due to the difference in tail lengths between both surfactants or due to the heads of the nonionic surfactants are not taken into account.

The function $f(\alpha)$ for the above systems was calculated for two cases. The first one corresponds to a salt concentration of 0.5 M and the second one to a salt concentration

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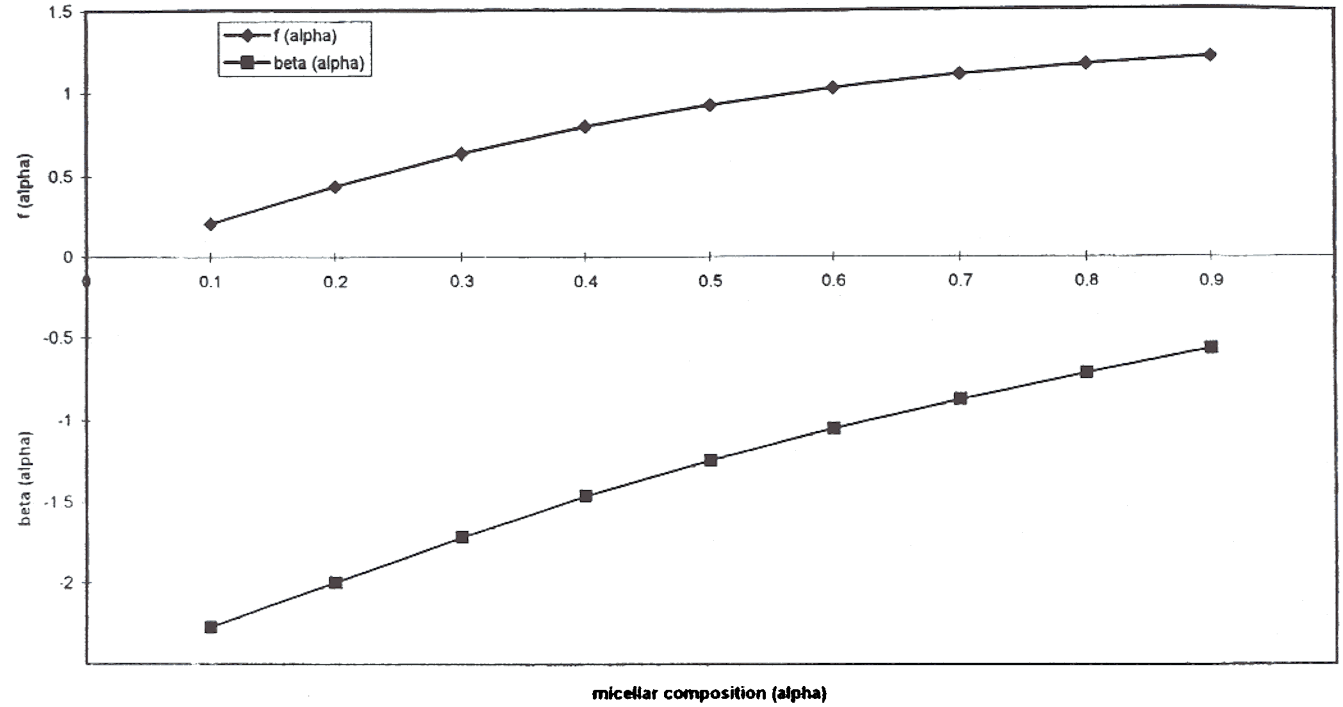

Figure 3. $f(\alpha)$ and $\beta(\alpha)$ in units of kT as a function of micellar composition for a mixture of sodium dodecyl sulfate and a C16 nonionic surfactant at a salt concentration of 0.08 M.

of 0.080 M. The highest salt concentration is 0.5 M to avoid the formation of cylindrical micelles. The lowest concentration is 0.08 M because then the condition that $\kappa(\alpha)r(\alpha)$ is equal to or greater than 1/2 is satisfied at all micellar molar fractions. This condition is required for eq 5 to yield reliable results. Figure 1 shows a plot of $f(\alpha)$ and $\beta(\alpha)$ versus α for the SDS/C12 ionic/nonionic surfactant mixture with 0.5 M NaCl. It can be seen that the $f(\alpha)$ graph is close to a straight line where $f(\alpha) = \alpha f(1)$. A plot of the excess free energy for this system as a function of micellar composition shows it to be symmetrical as illustrated in Figure 2. Therefore, the calculated β values should remain practically constant over the whole composition range, as they do in Figure 1. It should also be mentioned that the $\beta(0) = -1.41$ value agrees with the constant value predicted for this system.[4] Thus, a symmetrical excess free energy which can be written as $g(\alpha) = \alpha^2 f(1)$ will be characterized by a $f(\alpha)=\alpha f(1)$ straight line plot and will yield a constant β value.

Figure 3 shows a plot of $f(\alpha)$ and $\beta(\alpha)$ versus α for the SDS/C16 ionic/nonionic surfactant mixture with NaCl 0.080 M.. Since the cmc for the pure ionic surfactant is 10 times smaller than the salt concentration, there is no need to consider the contribution of the SDS monomers to the solution ionic strength. According to eq 11, the magnitude of $\beta(\alpha)$ will be given by the slope of the line drawn between $f(1)$ and $f(\alpha)$. It can be seen from Figure 3 that this slope is low at micellar molar fractions close to 1, and higher at α values close to zero. The β calculated for this system shows the expected change from higher to lower values in magnitude as the value of α is increased. The corresponding asymmetrical excess free energy for this system is given in Figure 2.

The β values obtained for the three different surfactant mixtures at the two salt concentrations are shown in Figures 4 and 5. All $\beta(0)$ values for the three nonionic mixtures at a given salt concentration are the same since, as mentioned previously, these particular values depend only on the ionic surfactant and the salt concentration. Furthermore, these values decrease at higher salt concentrations due to the screening of the electrostatic interactions between the charged heads.

In general, it can be seen that the interaction parameters are seldom constant, which means that the excess free energies involved will not be symmetrical.

Discussion

The main conclusion from the above results is that the excess free energies of mixed micellization are found, in general, not to be symmetrical with respect to micellar composition. This conclusion is in agreement with findings obtained by some authors.[9,21] It then becomes important to find out what are the consequences of having β values which are not constant.

In the molecular thermodynamic approach,[2] eqs 1−3 are derived when the mixture cmc is expressed as a function of the optimal micellar composition for the case of symmetric excess free energies (constant β values). Since the excess free energy should be written, in general, as

$$g^E(\alpha) = \beta(\alpha)\alpha(1 - \alpha)$$

this expression was used for the optimization of the micellar composition in this thermodynamic approach. The result of this derivation for the cmc was found to be eq 1 again. However, the expressions for the activity coefficients are now given by

$$\gamma_A = \exp(1/kT)[\beta(\alpha)(1 - \alpha)^2 + \alpha(1 - \alpha)^2\,d\beta(\alpha)/d\alpha] \tag{15}$$

$$\gamma_B = \exp(1/kT)[\beta(\alpha)\alpha^2 - \alpha^2(1 - \alpha)\,d\beta(\alpha)/d\alpha] \tag{16}$$

These expressions are identical to the activity coefficients produced by the phase separation approximation.[9] Thus, both the molecular thermodynamical approach at the optimum micellar composition and the phase separation approximation yield the same results for symmetrical and asymmetrical excess free energies. This conclusion is

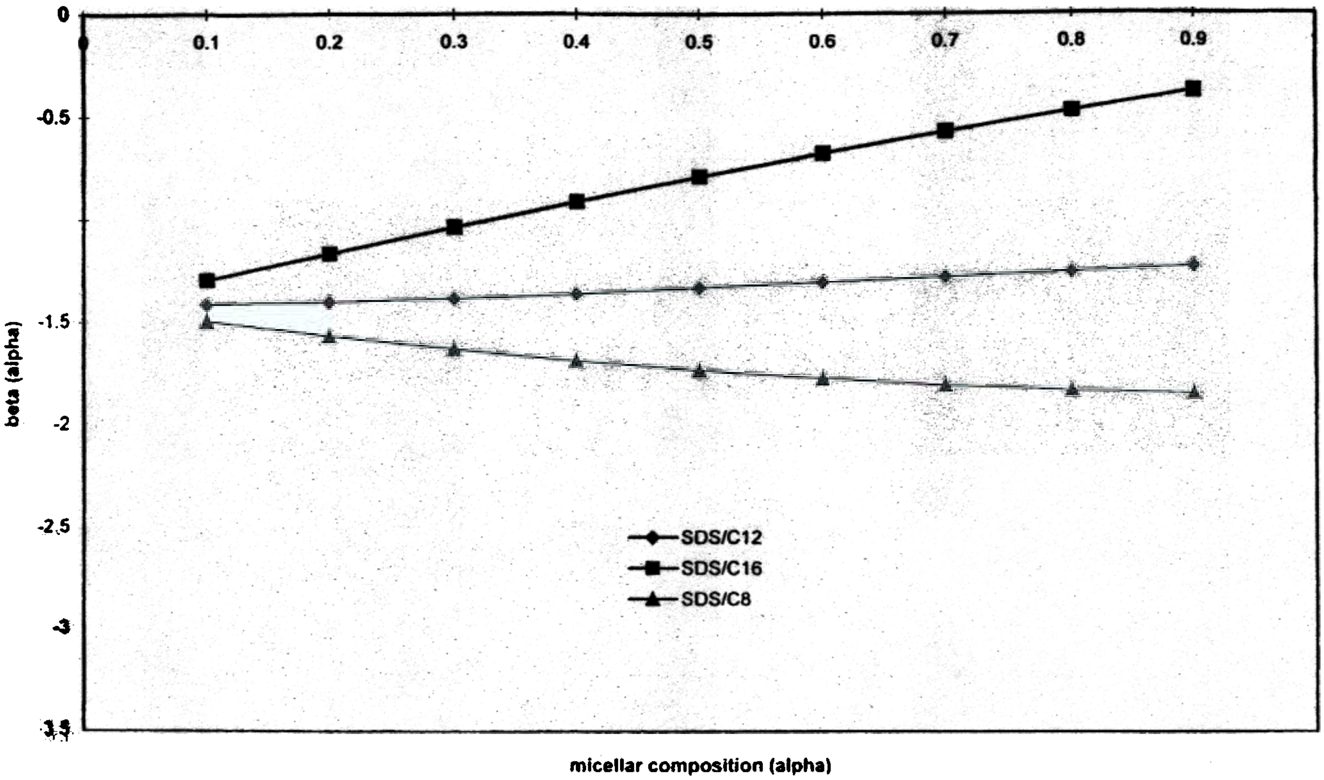

Figure 4. β values in units of kT as a function of micellar composition for three mixtures of sodium dodecyl sulfate and a C8, C12, and C16 nonionic surfactant at a salt concentration of 0.5 M.

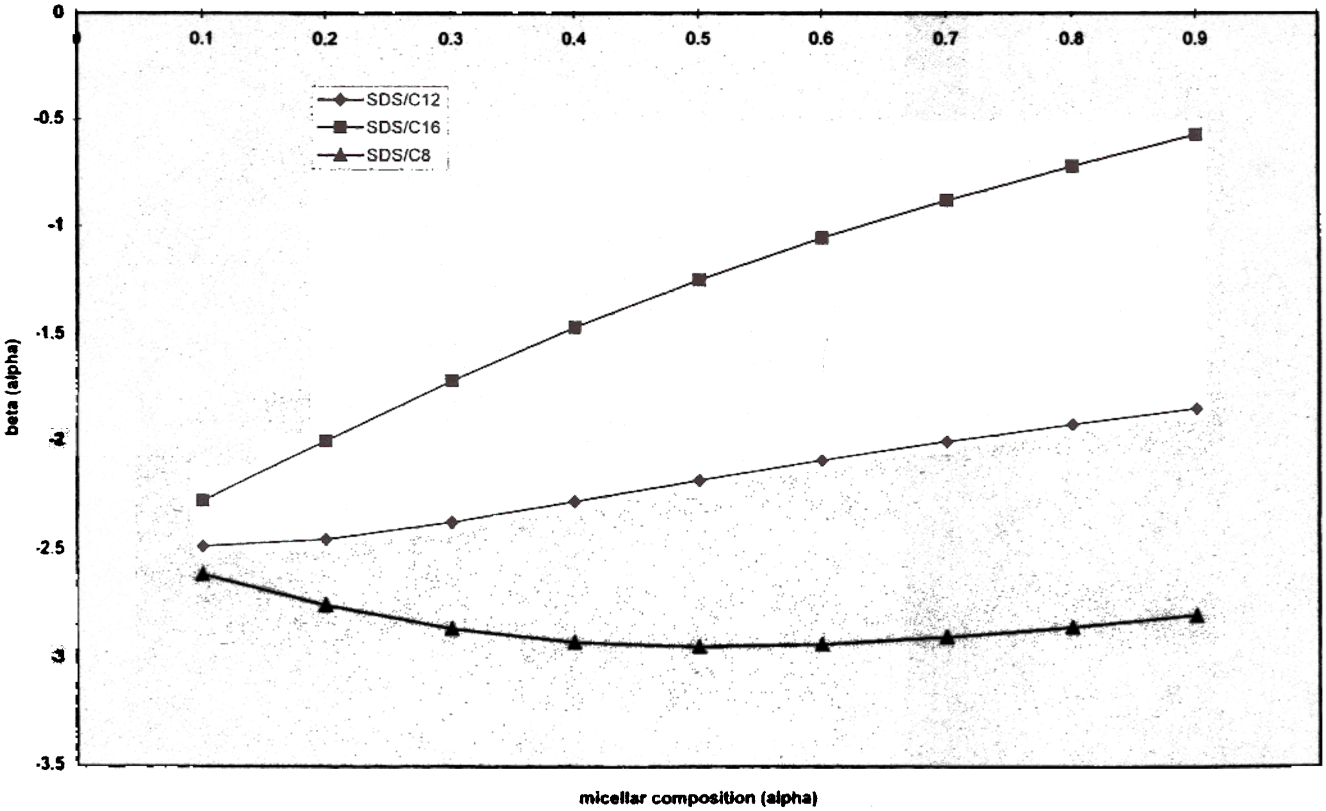

Figure 5. β values in units of kT as a function of micellar composition for three mixtures of sodium dodecyl sulfate and a C8, C12, and C16 nonionic surfactant at a salt concentration of 0.08 M.

in agreement with a recent paper on the subject.[18] Naturally, for the symmetric case the terms with the derivative do not contribute and eqs 2 and 3 are obtained.

To illustrate the differences between the activity coefficients produced when symmetric and asymmetric excess free energies are considered, a comparison was made for the SDS/nonionic C16 surfactant mixture with 0.08 M salt added. The activity coefficients calculated using the corresponding asymmetric excess free energy and the activity coefficients obtained for the same system but using

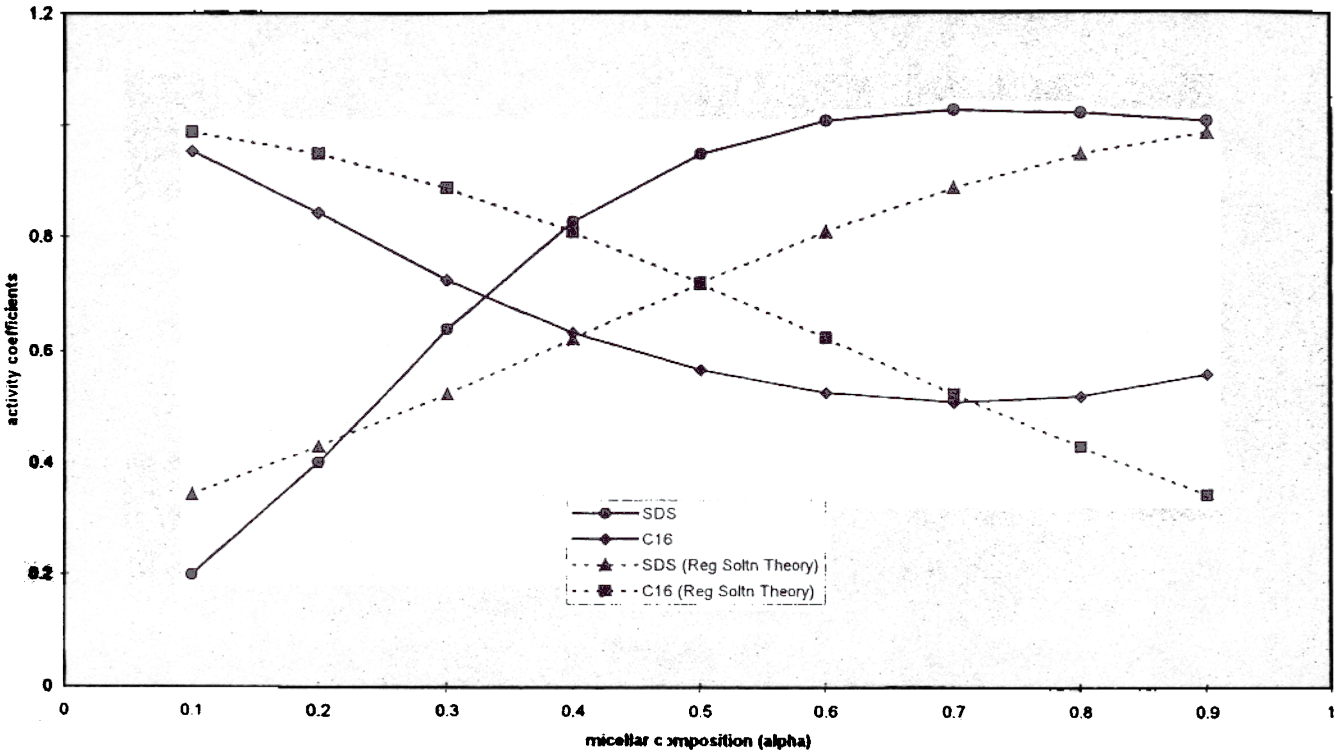

Figure 6. Comparison between activity coefficients calculated using the correct asymmetric excess free energy and those calculated using an average symmetric excess free energy for the mixture of sodium dodecyl sulfate and a C16 nonionic surfactant at a salt concentration of 0.08 M.

a symmetric excess free energy corresponding to a constant β equal to its average value are shown in Figure 6. Although our simple theoretical approach and molecular model allows only for qualitative estimates of these quantities, a significant difference is found. This difference in the activity coefficients, which are the parameters which control the system behavior, may become more important when more rigorous calculations are done using more complex molecular structures.

Activity coefficients for surfactant systems are generally obtained by using experimentally measured critical micelle concentration values and applying well-known equations developed using the regular solution theory which involve the use of eqs 2 and 3, where a symmetrical excess free energy and a constant β parameter is assumed.[25] However, composition-dependent β parameters obtained by this procedure have been reported for some surfactant systems.[10,26–30] It is important to note that these reported values are just an indication that the excess free energy is not symmetrical, but should not be used to calculate it. Instead, eqs 15 and 16 rather than eqs 2 and 3 should be used in the determination of the activity coefficients.

Conclusions

The electrostatic contribution to the excess free energy of mixed micellization, considered to be the most important one for ionic/nonionic mixtures of hydrocarbon-based surfactants with similar tail lengths, was calculated for mixtures of sodium dodecyl sulfate and different nonionic surfactants with tail lengths of 16, 12, and 8 carbon atoms at two different salt concentrations. A simplified analytical molecular thermodynamic approach was used where the free energy contributions of both the pure ionic and mixed micelle were obtained by applying an approximate solution of the Poisson–Boltzmann equation. The following conclusions are arrived at from the above: (a) Excess free energies for mixed micellization are generally asymmetrical, and therefore the interaction parameters are not constant with respect to micellar composition. (b) The molecular thermodynamic and the phase separation approaches yield the same equations for the mixed cmc and activity coefficients for both the symmetrical and asymmetrical cases. (c) The activity coefficients, and therefore the system behavior, may be quite different depending on whether symmetric or asymmetric excess free energies are considered.

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