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## Mixed Surfactant Systems

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## Chapter 4

# Micellization of Binary Surfactant Mixtures Theory

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We develop a molecular theory of micelle formation in aqueous solutions of binary surfactant mixtures. The theory allows the prediction of the critical micelle concentration and the size and composition distribution of mixed micelles. Illustrative results are obtained for nonionic-nonionic, ionic-ionic, nonionic-ionic, anionic-cationic and hydrocarbon-fluorocarbon type of binary surfactant mixtures and compared against available experimental data. It is found that the theory predicts well the ideal and nonideal behavior exhibited by different mixtures. Of special interest are the predictions showing both the formation of miscible hydrocarbon-fluorocarbon mixed micelles and the coexistence of mutually immiscible hydrocarbon rich and fluorocarbon rich micelle populations. Finally, the theory allows one to identify the origin of mixture nonidealities in terms of various molecular interactions.

A molecular theory of mixed micelles was developed earlier by us [1], by extending the theory formulated by Nagarajan and Ruckenstein [2] for aggregation in single component surfactant systems. The theory predicted the size and the composition distribution of mixed micelles, thus allowing one to estimate the critical micelle concentration (cmc), the average micelle size and the average micelle composition, as a function of the composition of either the total surfactant mixture or the singly dispersed surfactants. The theory facilitated a molecular interpretation of the observed ideal and nonideal behavior of the mixed surfactant systems, in terms of the bulk and the surface interactions between surfactants constituting the micelles [1,3]. For hydrocarbon surfactant mixtures, the theory revealed that significant nonideality arises from the surface interactions.

The theory of mixed micelles was applied to surfactant-alcohol mixtures by Rao and Ruckenstein [4] who treated the short chain alcohols as nonionic surfactants. They showed that the decrease in cmc and the change in micellar aggregation number caused by the presence of alcohols, the extent of incorporation of alcohols inside the micelles and the alcohol partition equilibrium constant between the micellar and the aqueous phases are all predicted reasonably well for mixtures of some anionic, cationic, and nonionic surfactants with butanol, pentanol, hexanol and heptanol, respectively. Warr et al. [5] used fluorescence probe methods to measure the aggregation number of nonionic dodecyl maltoside (DM) and nonionic octaoxyethylene dodecyl ether ( $C_{12}E_8$ ) mixed micelles and found that the composition dependence of the aggregation number of the micelle was not linear but possessed a distinctive s-shape, qualitatively similar to that predicted by our molecular theory. From small angle neutron scattering study of nonionic dodecyl maltoside (DM) and anionic sodium dodecyl sulfate (SDS) mixed micelles, Bucci et al. [6] observed that the micelle aggregation number exhibits a maximum when the micelle composition is altered in qualitative agreement with our theoretical predictions for nonionic-ionic mixed micelles [1]. More recently, our theory of mixed micelles was applied to binary mixtures of hydrocarbon and fluorocarbon surfactants by Asakawa et al. [7]. They showed that the theory correctly predicted the coexistence of two distinct, fluorocarbon rich and hydrocarbon rich populations of micelles as well as the growth in micellar size accompanying the composition changes. However, the increased region of immiscibility between the two coexisting micellar populations that was experimentally observed at high electrolyte concentrations was not quantitatively well predicted.

The principal goal of this paper is to improve upon various features of our earlier theory [1] with respect to the quantitative estimation of the free energy of micelle formation. In particular, the free energy model is made strictly predictive by eliminating some of the empirical expressions employed in our earlier treatment and replacing them with results from our recent theory for single component surfactants [8]. Firstly, we replace the empirical expression for calculating the free energy of conformational constraints on surfactant tails inside the micelles, by an analytical expression recently derived by Nagarajan and Ruckenstein [8]. The analytical free energy expression which was derived for single surfactant systems in ref. [8] is extended in this paper to treat surfactant mixtures having different hydrophobic tail lengths. Secondly, we replace the Debye-Huckel expression (with an empirical correction factor of 0.46) used in our earlier theory to compute ionic interactions in surfactant aggregates, with an approximate analytical solution to the Poisson-Boltzmann equation developed by Evans and Ninham [9]. Thirdly, we apply the solubility parameter theory of Hildebrand [10] to estimate the free energy contribution due to the mixing of surfactant tails inside the mixed aggregates. Fourthly, while treating

spherocylindrical micelles, we allow the radii as well as the composition of the spherical ends of the micelles to be different from those of the cylindrical middle part as suggested by the work of Ben-Shaul et al. [11] on surfactant-alcohol mixtures.

The present work concentrates on binary surfactant mixtures but the approach developed here can readily be extended to solutions containing three or more surfactant components. The present theory does not take into account any interaggregate interactions and hence is strictly applicable only to dilute surfactant solutions. The interaggregate interactions, when present, have been shown to affect the aggregate size distribution by Ben-Shaul and Gelbart [12] in their study of single component surfactants. Blankshtein and coworkers [13-15], Goldstein [16] and Kjellander [17] have accounted for the interaggregate interactions in their treatments of phase separation in single component surfactant solutions. Indeed, both micelle formation and phase separation are simultaneously treated by Blankshtein and coworkers and by Goldstein. In their treatments, the form of interaggregate interaction energy assumed is such that the size distribution of aggregates is not affected by the interaggregate interactions. Recently, Puvvada and Blankshtein have extended the approach to binary mixtures of surfactants [18].

This paper is organized as follows. In the first section, we describe the general thermodynamic relations governing the molecular assembly of mixed surfactants. It is followed by a discussion of the geometrical characteristics of aggregates. Then we formulate the model for the free energy of aggregation. Finally, illustrative predictions for different types of surfactant mixtures are presented and wherever possible, compared with available experimental data. The details of the treatment relating to rodlike micelles are omitted from this text because of space restrictions, even though calculations exploring the formation of rods have been carried out for all the mixtures examined in this study. These details will be published elsewhere.

### Size and Composition Distribution of Micelles

We consider a surfactant solution that consists of water molecules, singly dispersed surfactant molecules of type A and B and mixed micelles of various sizes and compositions. We denote by  $g$  the aggregation number of the mixed micelle containing  $g_A$  molecules of type A and  $g_B$  molecules of type B. The aggregate of a given size and composition is viewed as a distinct chemical component and the surfactant solution is treated as a multicomponent solution. At equilibrium, the total Gibbs energy of the surfactant solution is a minimum and this leads [1] to the size and composition distribution equation:

$$X_g = X_{1A}^{g_A} X_{1B}^{g_B} \exp - \left( \frac{g \Delta \mu_g^0}{kT} \right); \quad \left( \frac{g \Delta \mu_g^0}{kT} \right) = \left( \frac{\mu_g^0 - g_A \mu_{1A}^0 - g_B \mu_{1B}^0}{kT} \right) \quad (1)$$

In the above equation,  $\mu_g^\circ$  is the standard chemical potential of a surfactant micelle containing  $g$  surfactant molecules while  $\mu_{1A}^\circ$  and  $\mu_{1B}^\circ$  are the standard chemical potentials of the singly dispersed A and B molecules, respectively. The standard chemical potentials are defined as those corresponding to infinitely dilute solution conditions.  $\Delta\mu_g^\circ$  is the difference in the standard chemical potentials between  $g_A/g$  molecules of surfactant A and  $g_B/g$  molecules of surfactant B present in an aggregate of size  $g$  and the same molecules present in their singly dispersed states in water.  $X_{1A}$  and  $X_{1B}$  are the mole fractions of the singly dispersed surfactants A and B while  $X_g$  is the mole fraction of the aggregates of size  $g$  in the solution. The mole fraction  $X_g$  is dependent not only on the size  $g$  but also on the composition of the micelle. We define the mole fraction of components A and B in the singly dispersed surfactant mixture, in the mixed micelle and in the total surfactant solution, respectively, by the relations:

$$\alpha_{1A} = \frac{X_{1A}}{X_{1A} + X_{1B}} = \frac{X_{1A}}{X_1}, \quad \alpha_{1B} = \frac{X_{1B}}{X_{1A} + X_{1B}} = \frac{X_{1B}}{X_1} \quad (2)$$

$$\alpha_{gA} = \frac{g_A}{g_A + g_B} = \frac{g_A}{g}, \quad \alpha_{gB} = \frac{g_B}{g_A + g_B} = \frac{g_B}{g} \quad (3)$$

$$\alpha_{1A} = \frac{X_{1A} + \sum g_A X_g}{X_1 + \sum g X_g}, \quad \alpha_{1B} = \frac{X_{1B} + \sum g_B X_g}{X_1 + \sum g X_g} \quad (4)$$

In equation (4), the summation is over two independent variables, namely, the aggregation number  $g = 2$  to  $\infty$ , and the micelle composition  $\alpha_{gA} = 0$  to 1. For simplicity of notations, in this paper, a single summation is used in the various equations to account for all independent variables.

The size and composition distribution equation (1) can be rewritten in a form identical to that for a single surfactant system by using equations (2) and (3).

$$X_g = X_1^g \exp - \left( \frac{g \Delta\tilde{\mu}_g^\circ}{kT} \right) \quad (5)$$

where

$$\frac{\Delta\tilde{\mu}_g^\circ}{kT} = \frac{\Delta\mu_g^\circ}{kT} - [\alpha_{gA} \ln \alpha_{1A} + \alpha_{gB} \ln \alpha_{1B}] \quad (6)$$

From the size and composition distribution one can compute the average sizes of the aggregates via the relations

$$g_n = \frac{\sum g X_g}{\sum X_g}, \quad g_w = \frac{\sum g^2 X_g}{\sum g X_g} \quad (7)$$

where  $g_n$  and  $g_w$  denote the number and the weight average aggregation numbers. Similarly, the average composition of the mixed micelle can be calculated from

$$\bar{\alpha}_{gA} = \frac{\sum \frac{g_A}{g} X_g}{\sum X_g}, \quad \bar{\alpha}_{gB} = \frac{\sum \frac{g_B}{g} X_g}{\sum X_g} \quad (8)$$

The critical micelle concentration  $X_{cmc}$  can be obtained by constructing a plot of one of the functions  $X_1$ ,  $\sum g X_g$  or  $\sum g^2 X_g$  (which are proportional to different experimentally measured properties of the surfactant solution) against the total concentration  $X$  of the surfactant in solution,  $X = X_1 + \sum g X_g$ . The cmc is estimated to be that value of the total surfactant concentration at which a sharp change in the plotted function (representing a physical property) occurs.

The critical micelle concentration, the average aggregation number and the average micelle composition can all be precisely estimated as specified above by computing the concentrations of aggregates of all possible sizes and compositions using the distribution equation (1). Such computations, though not complicated, are time consuming and are not always needed. A simpler approach yielding precise results is possible for systems displaying narrow size and composition dispersions. This is the case when micelles formed are spherical or globular with relatively small aggregation numbers (a condition met by most of the systems considered in this paper). In such systems, one can replace the entire size and composition distribution of aggregates with a single aggregate whose size and composition corresponds to the maximum in the distribution function,  $X_g$ . This approach is utilized in this paper for calculating the average composition and aggregation number for spherical or globular micelles. This is equivalent to approximating the size distribution or multiple equilibria model by the monomer-micelle equilibrium model. To estimate the cmc, we follow the suggestion of Hartley [19],  $X_1 = g X_g(\text{maximum}) = X_{cmc}$ , namely, the cmc is the concentration of the monomers when the amount of surfactant present as monomers is equal to that present as micelles. As mentioned earlier, the cmc can also be estimated by plotting one of the functions  $X_1$ ,  $\sum g X_g$  or  $\sum g^2 X_g$  against the total surfactant concentration. Another common method

for estimating the cmc assumes it to be the total surfactant concentration at which about five percent of the surfactant is present as micelles, the remaining surfactant being singly dispersed. The different procedures give estimates for cmc varying from one another by at most five percent. Similar variations occur in the experimental determination of the cmc depending on which measurement technique is employed since different physical measurements sense the formation of micelles at somewhat different surfactant concentrations. Thus, the cmc estimated by any one of the procedures mentioned should be comparable to the experimentally determined cmc.

To proceed further and calculate the aggregation behavior of surfactants, a model for the standard free energy difference associated with micelle formation is necessary. This, in turn, requires the specification of the shapes of the aggregates and of their geometrical characteristics.

#### Geometrical Properties of Micelles

The hydrophobic interiors of the surfactant aggregates are constituted of the surfactant tails. Molecular packing requirements suggest [20,21] that no point within the aggregate can be farther than  $\ell_{sA}$  or  $\ell_{sB}$  (whichever is larger) from the aggregate core-water interface, where  $\ell_{sA}$  and  $\ell_{sB}$  refer to the extended lengths of the surfactant tails of molecules A and B. Keeping this constraint in view, one can assume that the small micelles are spherical in shape. The shapes of somewhat larger micelles have been examined by Israelachvili et al. [21] on the basis of local and overall molecular packing considerations and they have suggested shapes generated via ellipses of revolution. We note that for aggregation numbers that are up to 3 times as large as that of the largest spherical micelles, the average area per molecule for the ellipses of revolution suggested by Israelachvili et al. [21] is practically the same as for prolate ellipsoids. Therefore, the average geometrical properties of the non-spherical globular aggregates will be computed here as for prolate ellipsoids without implying however, that prolate ellipsoidal micelles form. When micelles are very large, we consider them to be rodlike with spherical endcaps and a cylindrical middle part. The two regions of the micelle are allowed to have differing radii. Figure 1 illustrates the different micellar shapes.

**Spherical Micelles.** For spherical micelles containing  $g$  surfactant molecules, and having a radius  $R_s$  of the hydrophobic core, the total volume of the aggregate core,  $V_g$ , and the core surface area,  $A_g$ , are given by

$$V_g = \frac{4 \pi R_s^3}{3} = g v_s ; v_s = (\alpha_{gA} v_{sA} + \alpha_{gB} v_{sB}) \quad (9)$$

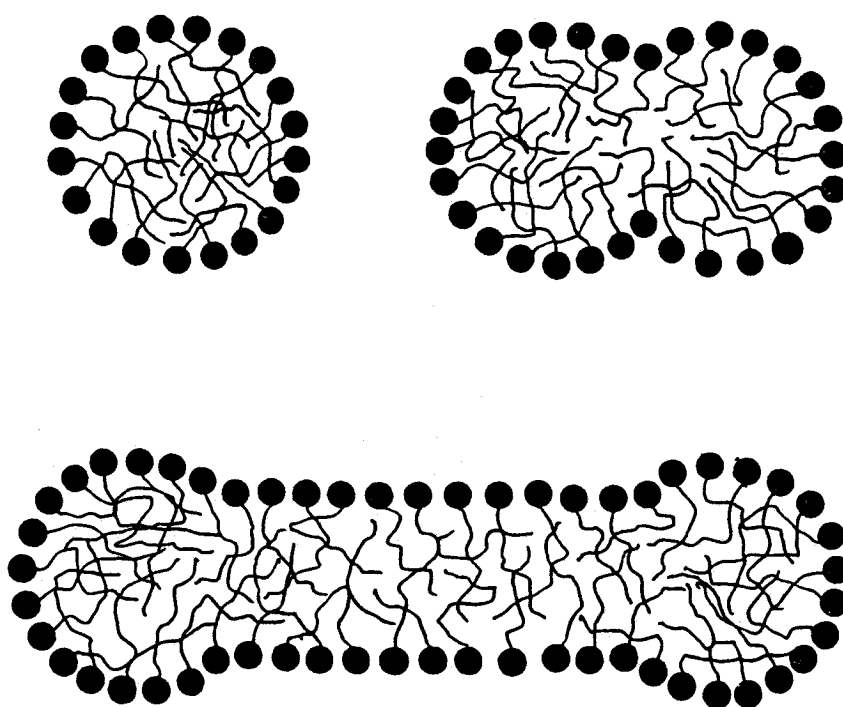


Figure 1. Schematic representation of spherical, globular and rodlike micelles. The geometrical characteristics of the globular micelles are calculated as those of prolate ellipsoids.



$$A_g = 4 \pi R_s^2 = g a \quad (10)$$

respectively. Here,  $v_{sA}$  and  $v_{sB}$  denote the volumes of the hydrophobic tails of A and B, while  $v_s$  is the micelle composition averaged volume of the hydrophobic tails. The variable,  $a$ , refers to the surface area of the hydrophobic core of the micelle per surfactant molecule. We define an area per molecule  $a_\delta$  at a distance  $\delta$  from the hydrophobic core of the micelle for latter use in the calculation of the ionic interaction energy at the micellar surface.

$$A_{g\delta} = 4 \pi (R_s + \delta)^2 = g a_\delta \quad (11)$$

We also define a geometrical ratio  $P$  that characterizes the average molecular packing in the aggregates for latter use in the calculation of surfactant tail deformation free energy.

$$P = \frac{V_g}{A_g R_s} = \frac{v_s}{a R_s} \quad (12)$$

**Globular Micelles.** The micelles whose sizes are somewhat larger than those allowed by the spherical shape are called globular and their average geometrical characteristics are computed as for prolate ellipsoids. Consequently, one dimension of the prolate ellipsoid should be the largest radius allowed for the spherical micelles. This dimension is the semi-minor axis of the globular micelle and is denoted by  $R_s$ , while the semi-major axis is denoted by  $b$ . The eccentricity  $E$  of the micelle is given by

$$E = [1 - (\frac{R_s}{b})^2]^{1/2} \quad (13)$$

The total volume of the hydrophobic core of the micelle is computed from

$$V_g = \frac{4 \pi R_s^2 b}{3} = g v_s \quad (14)$$

where  $v_s$  has already been defined as the composition averaged volume of the surfactant tails. The total surface area of the hydrophobic core is given by

$$A_g = 2 \pi R_s^2 \left[ 1 + \frac{\sin^{-1} E}{E(1-E^2)^{1/2}} \right] = g a \quad (15)$$

The eccentricity of the micelle at a distance  $\delta$  from the hydrophobic core is denoted by  $E_\delta$ .

$$E_\delta = \left[ 1 - \left( \frac{R_s + \delta}{b + \delta} \right)^2 \right]^{1/2} \quad (16)$$

and the area of the micelle at that surface is calculated from

$$A_{g\delta} = 2 \pi (R_s + \delta)^2 \left[ 1 + \frac{\sin^{-1} E_\delta}{E_\delta(1-E_\delta^2)^{1/2}} \right] = g a_\delta \quad (17)$$

Further, we define an equivalent radius  $R_{eq}$  of the globular micelle by considering the volume of the micelle to be the same as that of an equivalent sphere,

$$R_{eq} = \left( \frac{3 V_g}{4 \pi} \right)^{1/3} \quad (18)$$

The packing factor  $P$  for the globular micelle defined as in equation (12) is given by

$$P = \frac{V_g}{A_g R_s} = \frac{v_s}{a R_s} \quad (19)$$

### Free Energy of Formation of Mixed Micelles

We now formulate explicit expressions for the standard free energy difference between the surfactant molecules A and B present in a micelle and those present in the singly dispersed state in water. This free energy difference is composed of a number of contributions each of which has been described in our earlier work on single component surfactant systems [8]. Consequently, only the modifications warranted for the treatment of surfactant mixtures are discussed in detail here. For the derivation of the various equations one should consult reference [8].

**Transfer Free Energy of the Surfactant Tail.** When micelles form, the hydrophobic tail of the surfactant is transferred from its contact with water to the hydrophobic core of the micelle. The contribution to the free energy from this transfer process is estimated by considering the micelle core to be like a liquid hydrocarbon (For fluorocarbon micelles, we simply change the description to that of a liquid fluorocarbon). The fact that the micelle core differs somewhat from a liquid hydrocarbon gives rise to an additional free energy contribution that is evaluated separately. The transfer free energy of the surfactant tail from water to a liquid hydrocarbon state is estimated from independent experimental data regarding the solubility of hydrocarbons in water [22,23]. On this basis, we have estimated the transfer free energy for a methylene group in an aliphatic tail as a function of temperature to be

$$\frac{(\Delta\mu_{\text{R}}^{\circ})_{\text{tr}}}{kT} = 5.85 \ln T + \frac{896}{T} - 36.15 - 0.0056 T \quad (20)$$

For a methyl group in the aliphatic chain, the temperature dependent transfer free energy is

$$\frac{(\Delta\mu_{\text{R}}^{\circ})_{\text{tr}}}{kT} = 3.38 \ln T + \frac{4064}{T} - 44.13 + 0.02595 T \quad (21)$$

In the above two relations, the temperature  $T$  is expressed in  $^{\circ}\text{K}$ .

For surfactants containing two hydrocarbon chains, one can estimate the free energy contributions from the methyl and the methylene groups using the above equations. However, one expects considerable intramolecular interactions between the two chains in their singly dispersed state. Hence, the contribution to the transfer free energy of the two chains would be smaller than the estimate obtained by assuming there are two independent single chains. Tanford [20] estimated that the second chain of a dialkyl molecule contributes a transfer free energy that is sixty percent of an equivalent single chain molecule. In the absence of more detailed thermodynamic studies on such double chain molecules, we will assume Tanford's estimation to be adequate and use it in our free energy calculations.

For fluorocarbons, only limited thermodynamic transfer free energy data are available. Mukerjee and Handa [24] measured interfacial tension changes at the perfluorohexane-water interface caused by the adsorption of sodium perfluorobutyrate, sodium perfluorooctanoate and sodium perfluorodecanoate. From these interfacial tension changes, they estimated the free energy of transfer of the perfluoroalkyl chains from water to perfluorohexane. Using these data, we estimate the transfer free energy at  $25^{\circ}\text{C}$  to be

$$\frac{(\Delta\mu_g^{\circ})_{tr}}{kT} = -6.20 \text{ (for CF}_3\text{)}, -2.25 \text{ (for CF}_2\text{)} \quad (22)$$

Transfer free energies at other temperatures are presently unavailable.

For a mixed micelle having the composition  $(\alpha_{gA}, \alpha_{gB})$ , the transfer free energy per surfactant molecule is given by

$$\frac{(\Delta\mu_g^{\circ})_{tr}}{kT} = \alpha_{gA} \frac{(\Delta\mu_g^{\circ})_{tr,A}}{kT} + \alpha_{gB} \frac{(\Delta\mu_g^{\circ})_{tr,B}}{kT} \quad (23)$$

The transfer free energy estimates from equation (20) to (22) do not include any contributions arising from the mixing of hydrocarbon-hydrocarbon, fluorocarbon-fluorocarbon, or hydrocarbon-fluorocarbon chains inside the micellar core. Such a contribution is taken into account separately, below.

**Deformation Free Energy of the Surfactant Tail.** The surfactant tails inside the hydrophobic core of the aggregate are not in a state identical to that in liquid hydrocarbons (or fluorocarbons). This is because, one end of the surfactant tail in the aggregate is constrained to remain at the micelle-water interface, while the entire tail has to assume a conformation consistent with the maintenance of a uniform density equal to that of liquid hydrocarbon in the micelle core. Consequently, the formation of micelles is associated with a positive free energy contribution stemming from the deformation of the anchored surfactant tail. We have used a lattice picture for the micelle core to develop simple analytical expressions for the chain deformation free energy as explicit functions of the micelle aggregation number and micellar shape [8]. The use of a lattice requires the specification of the size of the molecular segment which can be placed on the lattice without any orientational constraints. As suggested by Dill and Flory [25], for aliphatic hydrocarbon chains, a suitable segment is that which contains about 3.6 methylene groups. Correspondingly, the linear dimension of a lattice site, denoted by  $L$ , is taken equal to about  $4.6\text{\AA}$ . This linear dimension also represents the typical spacing between alkane molecules in the liquid state, namely,  $L^2$  is equal to the cross-sectional area of a polymethylene chain. Consequently, a surfactant tail with an extended length of  $\ell$ , is considered as made up of  $N$  segments, where  $N = \ell/L$ . One end of the surfactant tail, namely that attached to the polar head group is constrained to be located at the micelle-water interface. The other end (the terminal methyl group) is free to occupy any position in the entire volume of the aggregate as long as an uniform segment density can be maintained within the micelle core. Obviously, the chains will be locally deformed in order to satisfy both the packing and the uniform density constraints. The conformational free energy per surfactant tail can be determined by calculating the integral of this local deformation energy over the entire volume of the micelle.

When the surfactants A and B have different hydrophobic tail lengths, segments of both molecules may not be present everywhere in the micellar core. Such a chain packing problem has been addressed by Szleifer et al. [26] and we will make use of some of their analysis. Let us assume that surfactant A has a longer tail than surfactant B,  $\ell_{sA} > \ell_{sB}$ . If the mixed micelles have the radius (semiminor axis in the case of globular micelles)  $R_s$ , that is less than both  $\ell_{sA}$  and  $\ell_{sB}$ , then even the tail of the short chain surfactant B can reach everywhere within the core of the micelle. On the other hand, if  $\ell_{sA} > R_s > \ell_{sB}$ , then clearly the inner region of the micellar core, of dimension  $(R_s - \ell_{sB})$  can only be reached by the A tails and not by the B tails, since the B tails cannot extend beyond their fully extended length,  $\ell_{sB}$ . In generalizing our earlier result [8] for the free energy contribution due to the deformation of the tails, we take into account the different extents to which the A and the B tails are stretched for the two situations described above. Consequently, we can write

$$\frac{(\Delta\mu_g^0)_{\text{def}}}{kT} = B_g \left[ \alpha_{gA} \frac{R_s^2}{N_A L^2} + \alpha_{gB} \frac{Q_g^2}{N_B L^2} \right], \quad B_g = \left( \frac{9 P \pi^2}{80} \right) \quad (24)$$

where

$$Q_g = R_s \text{ if } R_s < \ell_{sA}, \ell_{sB}; \quad Q_g = \ell_{sB} = N_B L \text{ if } \ell_{sA} > R_s > \ell_{sB} \quad (25)$$

$N_A$  and  $N_B$  refer to the number of segments in the tails of surfactants A and B, respectively.  $P$  is the packing factor defined before in equation (12) for spheres and equation (19) for globular aggregates.

For the condition,  $\ell_{sA} > R_s > \ell_{sB}$ , the innermost region of the micelle is not accessible to surfactant B. Therefore, the micelle must contain sufficient number of the A surfactants to completely fill up the inner region. This factor provides another condition for chain packing inside the micelles besides the more obvious criterion of  $R_s \leq \ell_{sA}$ . To establish this additional packing condition, we define by  $f$  the fraction of A tail that can reach the inner region of the micellar core. To a first order approximation,  $f = (\ell_{sA} - \ell_{sB}) / \ell_{sA}$ . Therefore, for spherical micelles one has to satisfy the condition

$$\frac{4\pi}{3} (R_s - \ell_{sB})^3 \leq g \alpha_{gA} v_{sA} f \quad (26)$$

This in conjunction with equation (9) for the volume of the hydrophobic core yields the packing condition

$$\left(\frac{R_s - \ell_{sB}}{R_s}\right)^3 \leq f \eta_A, \quad \eta_A = \frac{\alpha_{gA} v_{sA}}{\alpha_{gA} v_{sA} + \alpha_{gB} v_{sB}} = 1 - \eta_B \quad (27)$$

In this equation,  $\eta_A$  and  $\eta_B$  denote the volume fractions of A and B tails in the micelle core. Equation (27) defines the largest allowed value for  $R_s$  for a given micelle composition  $\alpha_{gA}$ , or, the smallest allowed value for the micelle composition  $\alpha_{gA}$  for a given micelle radius  $R_s$ . This equation was first derived by Szleifer et al. [26] in their study of chain packing in mixed surfactant aggregates. The parameter  $f$  is only defined to a first order approximation above, using its maximum possible value. Since there is no simple way to estimate  $f$ , we introduce a more restrictive packing criterion, that the radius be less than the composition averaged value of the tail lengths of the two surfactants,  $R_s \leq (\eta_A \ell_{sA} + \eta_B \ell_{sB})$ . If this criterion is satisfied, then equation (27) is automatically satisfied.

For surfactants with two chains in their hydrophobic part, the deformation free energy can be calculated following the same approach adopted for single chain surfactants. One can show that the deformation free energy calculated using equation (24) for a single chain should be multiplied by a factor of two in order to obtain the deformation free energy per double tailed surfactant molecule. Therefore, when a double tailed surfactant is present in the mixture (as surfactant A and/or B), the term accounting for its deformation free energy in equation (24) is simply multiplied by two to account for both tails. The molecular packing constraint given by equation (27) remains unaffected whether the surfactant is with a single or a double tail.

Fluorocarbon chains have different geometrical characteristics compared to hydrocarbon chains. Consequently, the definition of a lattice site for micelles involving fluorocarbon surfactants has to be different. Lattice models have no simple means of accomodating such differences in the geometrical properties of molecules that are to be located on the same lattice. This is a common problem in lattice theories of solutions when the same solute is mixed with solvent molecules of differing sizes. At the present time, the ambiguity in the definition of the lattice site for mixed systems cannot be easily resolved. Since most examples studied in this work pertain to hydrocarbon surfactants, we retain the lattice definition given earlier as a general one and apply it also to systems containing fluorocarbon surfactants. Specifically, we will estimate the number of lattice segments  $N$  for fluorocarbon chains via the length ratio,  $N = \ell_s/L$ . A more fundamental approach to this problem is not possible without considerable mathematical complexity and is not undertaken here.

**Aggregate Core-Water Interfacial Free Energy.** The formation of micelle generates an interface between the hydrophobic core region consisting of the surfactant tails and the surrounding water medium. The free energy associated with the formation of this interface has been taken in our previous calculations [1,2,8] as equal to the product of the area of the interface and the macroscopic interfacial tension characteristic of this interface. Such an expression is generalized for the case of binary mixtures.

$$\frac{(\Delta\mu^{\circ})_{g}^{int}}{kT} = \frac{\sigma_{agg}}{kT} [a - \alpha_{gA} a_{oA} - \alpha_{gB} a_{oB}] \quad (28)$$

Here,  $\sigma_{agg}$  is the macroscopic micelle core-water interfacial tension,  $a$  is the surface area of the hydrophobic core per surfactant molecule defined earlier, and  $a_{oA}$  and  $a_{oB}$  are the areas per molecule of the core surface shielded from contact with water by the polar head groups of surfactants A and B.

The interfacial tension  $\sigma_{sw}$  between the surfactant tail (s may refer to A or B) and the surrounding water (w) is calculated in terms of the surface tensions  $\sigma_s$  of the surfactant tail and  $\sigma_w$  of water via [27] the relation

$$\sigma_{sw} = \sigma_s + \sigma_w - 2.0 \psi (\sigma_s \sigma_w)^{1/2} \quad (29)$$

where  $\psi$  is a constant with a value of about 0.55 [27,28] for aliphatic hydrocarbon tailed surfactants. For such tails, it has also been shown [8] that

$$\sigma_s = 35.0 - 325 M^{-2/3} - 0.098 (T - 298) \quad (30)$$

where  $M$  is the molecular weight of the surfactant tail,  $T$  is in  $^{\circ}K$ , and  $\sigma_s$  is expressed in dyne/cm. The surface tension of water is correlated [8] by the expression

$$\sigma_w = 72.0 - 0.16 (T - 298) \quad (31)$$

where the surface tension is given in dynes/cm and the temperature in  $^{\circ}K$ .

Since the interfacial tension against water of various hydrocarbon tails of surfactants are close to one another as shown by the above equations, we approximate the aggregate core-water interfacial tension  $\sigma_{agg}$  by the micelle composition averaged value:

$$\sigma_{agg} = \eta_A \sigma_{Aw} + \eta_B \sigma_{Bw} \quad (32)$$

where  $\sigma_{Aw}$  and  $\sigma_{Bw}$  are calculated using equation (29). The composition averaging in equation (32) is carried out using the volume fractions of surfactant tails in the micellar core,  $\eta_A$  and  $\eta_B$ , defined in equation (27).

For fluorocarbon systems, water-perfluorohexane interfacial tension has been experimentally determined [24] at 25°C to be 56.45 dyne/cm. Temperature dependence of this interfacial tension is presently not available. Since this interfacial tension value is comparable to water-hydrocarbon interfacial tensions discussed above, even for the hydrocarbon-fluorocarbon mixed surfactants, we will use equation (32) for estimating the magnitude of  $\sigma_{agg}$ .

The areas  $a_{oA}$  and  $a_{oB}$  that appears in equation (28), depend on the extent to which the polar head group shields the cross-sectional area of the surfactant tail. As discussed in reference [8], if the polar head group of surfactant A has a cross-sectional area  $a_{pA}$  larger than  $L^2$ , (for double tailed surfactants,  $2L^2$ ) then for such a surfactant,  $a_{oA}$  is taken equal to  $L^2$  (for double tailed surfactants,  $2L^2$ ). If the polar head group area  $a_{pA}$  is less than  $L^2$  (for double tailed surfactants,  $2L^2$ ), then the head group shields only a part of the cross-sectional area of the tail from the contact with water and  $a_{oA}$  is taken equal to  $a_{pA}$ . Identical considerations apply to surfactant B in the determination of  $a_{oB}$ .

**Head Group Steric Interactions.** The formation of micelle brings the polar head groups of the surfactant molecules to the surface of the aggregate where they are crowded when compared to their isolated states as singly dispersed surfactant molecules. This generates steric repulsions among the head groups. The associated repulsive free energy has been estimated in our earlier work [1,2,8] using an excluded area concept borrowed from the van der Waals equation of state. This expression is generalized for binary surfactant mixtures as

$$\frac{(\Delta\mu_g^0)_{steric}}{kT} = -\ln \left[ 1 - \frac{(\alpha_{gA} a_{pA} + \alpha_{gB} a_{pB})}{a} \right] \quad (33)$$

The above expression is inadequate if the polar head groups cannot be considered as compact such as in the case of nonionic surfactants having polyoxyethylene chains as head groups. An alternate treatment for head group interactions in such systems was developed in our recent work [8]. However, the quantitative predictions from this approach are as yet unsatisfactory. Hence, given its simplicity, we retain equation (33) as the basis for calculating steric interactions even for polyoxyethylene surfactants.



**Head Group Dipole Interactions.** For zwitterionic surfactants, one has to consider the mutual interactions between the permanent dipoles of the polar head groups. In general, the dipole-dipole interactions are dependent on the orientation of the dipoles. Because of the chain packing in micelles, one expects to find the dipoles stacked such that the poles of the dipoles are located on parallel surfaces. The dipole-dipole interactions in such a case are repulsive and they can be estimated by visualizing the arrangement of the poles of the dipoles as constituting an electrical capacitor [21]. The distance between the planes of the capacitor is equated to the distance of charge separation on the zwitterionic head group. Consequently, the dipole-dipole interactions for dipoles having a charge separation  $d$  can be computed for spherical aggregates from [2]

$$\frac{(\Delta\mu_g^{\circ})_{\text{dipole}}}{kT} = \frac{2\pi e^2 R_s}{\epsilon a_{\text{dipole}} kT} \left[ \frac{d}{d + R_s} \right] \alpha_{g \text{ dipole}} \quad (34)$$

In the above relation,  $e$  denotes the electronic charge,  $\epsilon$  is the dielectric constant of the solvent,  $R_s$  is the radius of the spherical micelle and  $\alpha_{g \text{ dipole}}$  is the fraction of surfactant molecules in the micelle having a dipolar head group. The same equation is employed for globular aggregates. If both A and B are zwitterionic surfactants with the same headgroup then

$$\alpha_{g \text{ dipole}} = \alpha_{gA} + \alpha_{gB} = 1, \quad a_{\text{dipole}} = a. \quad (35)$$

If surfactant A is zwitterionic while surfactant B is nonionic or ionic, then

$$\alpha_{g \text{ dipole}} = \alpha_{gA}, \quad a_{\text{dipole}} = a/\alpha_{g \text{ dipole}}. \quad (36)$$

The dipole-dipole interactions may be relevant even when surfactants do not possess zwitterionic head groups. Such a situation occurs when the surfactant mixture consists of an anionic and a cationic surfactant. The two oppositely charged surfactants may be visualized as forming ion pairs. Depending upon the location of the charges on the two surfactant head groups, these ion pairs may be assigned with a dipole moment. The variable  $d$  in equation (34) which stands for the distance of charge separation in the zwitterionic head groups, now refers to the distance between the locations of the anionic and the cationic charges, perpendicular to the micelle core surface. Thus, for such systems

$$\alpha_{g \text{ dipole}} = \text{Smaller of } (\alpha_{gA}, \alpha_{gB})/2, \quad a_{\text{dipole}} = a/\alpha_{g \text{ dipole}}, \quad d = |\delta_A - \delta_B| \quad (37)$$

The factor 2 in the above equation accounts for the fact that a dipole is associated with two surfactant molecules, treated as a pair. The distance  $\delta$  refers to the location of the charge from the hydrophobic core surface as

explained below. In equation (34), the dielectric constant  $\epsilon$  is taken to be that of pure water. The dielectric constant as a function of temperature is correlated [8] by the relation

$$\epsilon = 87.74 \exp [ - 0.0046 ( T - 273 ) ] \quad (38)$$

where T is expressed in °K.

**Head Group Ionic Interactions.** Ionic interactions arise at the micellar surface if the surfactant has a charged head group. An approximate analytical expression to calculate this free energy contribution has been derived by Evans and Ninham [9] assuming that the surfactant molecules are completely dissociated.

$$\begin{aligned} \frac{(\Delta\mu_g^0)_{\text{ionic}}}{kT} = & 2 \left[ \ln \left( \frac{S}{2} + \left\{ 1 + \left( \frac{S}{2} \right)^2 \right\}^{1/2} \right) - \frac{2}{S} \left( \left\{ 1 + \left( \frac{S}{2} \right)^2 \right\}^{1/2} - 1 \right) \right. \\ & \left. - \frac{2C_g}{\kappa S} \ln \left( \frac{1}{2} + \frac{1}{2} \left\{ 1 + \left( \frac{S}{2} \right)^2 \right\}^{1/2} \right) \right] \alpha_{g \text{ ion}} \quad (39) \end{aligned}$$

where

$$S = \frac{4 \pi e^2}{\epsilon \kappa a_{\delta \text{ ion}} kT}, \quad \kappa = \left( \frac{8 \pi n_o e^2}{\epsilon kT} \right)^{1/2}, \quad n_o = \frac{(C_{1 \text{ ion}} + C_{\text{add}})}{10^3} N_{\text{Av}} \quad (40)$$

The area per molecule  $a_g$  which appears in the above equation is evaluated at a distance  $\delta$  from the hydrophobic core surface. This distance  $\delta$  is estimated [8] as the distance from the hydrophobic core surface to the surface where the center of the counterion is located.  $\kappa$  is the reciprocal Debye length,  $n_o$  is the number of counterions in solution per  $\text{cm}^3$ ,  $C_{1 \text{ ion}}$  is the molar concentration of the singly dispersed ionic surfactant molecules,  $C_{\text{add}}$  is the molar concentration of the salt added to the surfactant solution and  $N_{\text{Av}}$  is the Avogadro's number. The last term in the right hand side of equation (39) is the curvature correction term where  $C_g$  is given by

$$C_g = \frac{2}{R_s + \delta}; \quad \frac{2}{R_{\text{eq}} + \delta} \quad (41)$$

for spherical and globular micelles, respectively. If both A and B are ionic surfactants with the same kind of charged head groups, then

$$\alpha_{g \text{ ion}} = \alpha_{gA} + \alpha_{gB} = 1, \quad a_{\delta \text{ ion}} = a_{\delta}, \quad \delta = \alpha_{gA} \delta_A + \alpha_{gB} \delta_B. \quad (42)$$

If A is ionic while B is nonionic or zwitterionic, then

$$\alpha_{g\text{ ion}} = \alpha_{gA}, \quad a_{\delta\text{ ion}} = a_{\delta}/\alpha_{g\text{ ion}}, \quad \delta = \delta_A. \quad (43)$$

If A and B are both ionic but oppositely charged, i.e. one is anionic while the other is cationic, then

$$\alpha_{g\text{ ion}} = |\alpha_{gA} - \alpha_{gB}|, \quad a_{\delta\text{ ion}} = a_{\delta}/\alpha_{g\text{ ion}}, \quad \delta = \alpha_{gA} \delta_A + \alpha_{gB} \delta_B. \quad (44)$$

**Free Energy of Mixing of Surfactant Tails.** This is the only contribution not present in the free energy model for single component surfactant solutions. This contribution accounts for the entropy and the enthalpy of mixing of the surfactant tails of molecules A and B in the hydrophobic core of the micelle, with respect to the reference states of pure A or pure B micelle cores. We calculate this free energy contribution using the Flory-Huggins expression for the entropy of mixing and the solubility parameter based expression for the enthalpy of mixing. It is known that the free energy expression based on the solubility parameter theory of Hildebrand may not be adequate for precise phase equilibria calculations, but does provide reasonable estimates of solution nonidealities while describing liquid mixtures [29]. Moreover, the Hildebrand equation is characterized by simplicity of functional form. Hence, we employ the Hildebrand theory here for calculating the free energy of mixing inside the micelle core.

$$\frac{(\Delta\mu_g^{\circ})_{\text{mix}}}{kT} = [\alpha_{gA} \ln \eta_A + \alpha_{gB} \ln \eta_B] + [\alpha_{gA} v_{sA} (\delta_{\Lambda}^H - \delta_{\text{mix}}^H)^2 + \alpha_{gB} v_{sB} (\delta_B^H - \delta_{\text{mix}}^H)^2] / kT \quad (45)$$

In the above equation, the first term is the Flory-Huggins expression for the entropy of mixing of the surfactant tails inside the micelle core.  $\eta_A$  and  $\eta_B$  are the volume fractions of A and B tails, defined in equation (27). The second term represents the enthalpy of mixing written in the framework of the Hildebrand theory [10].  $\delta_{\Lambda}^H$  and  $\delta_B^H$  refer to the solubility parameters of the tails of surfactants A and B (not of the surfactant as a whole, but only of the tail) while  $\delta_{\text{mix}}^H$  is the volume fraction averaged solubility parameter of all the components within the micelle core,  $\delta_{\text{mix}}^H = \eta_A \delta_{\Lambda}^H + \eta_B \delta_B^H$ .

**Free Energy Model and Mixture Nonideality.** All the free energy contributions can be calculated as a function of the aggregation number and the composition of the mixed micelles using equations provided above. The free energy of formation of mixed micelles appearing in equation (1) is, thus

$$\begin{aligned}
(\Delta\mu_g^\circ) = & (\Delta\mu_g^\circ)_{tr} + (\Delta\mu_g^\circ)_{def} + (\Delta\mu_g^\circ)_{int} + (\Delta\mu_g^\circ)_{steric} \\
& + (\Delta\mu_g^\circ)_{dipole} + (\Delta\mu_g^\circ)_{ionic} + (\Delta\mu_g^\circ)_{mix} \quad (46)
\end{aligned}$$

In the framework of this free energy model, a molecular interpretation of the ideal and nonideal behavior exhibited by surfactant mixtures can be provided.

For ideal mixed micelles, the free energy of formation of mixed micelle is the composition averaged value of the free energies of formation of pure component micelles plus the ideal entropy of mixing of the two types of surfactants.

$$(\Delta\mu_g^\circ)_{A+B} = \alpha_{gA} (\Delta\mu_g^\circ)_A + \alpha_{gB} (\Delta\mu_g^\circ)_B + (\Delta\mu_g^\circ)_{mix}(\text{Ideal}) \quad (47)$$

Therefore, if the free energy of formation of mixed micelles, excluding the ideal entropy of mixing term is a nonlinear function of composition, then the surfactant mixture will exhibit nonideal behavior. Further, if the free energy of mixing contribution deviates from the ideal entropy of mixing, then also the mixed surfactant system will be nonideal. If the magnitude of the free energy of formation of the mixed micelles is larger than the ideal value, then we characterize the system as displaying a negative deviation from ideality. Obviously, positive deviation from ideality occurs when the free energy of formation of mixed micelles has a magnitude smaller than the ideal value.

Considering the various contributions to the free energy of micellization in equation (46), we note that they can be decomposed into bulk and surface contributions besides a free energy of mixing. (Note that although the free energy of mixing is a part of the bulk component, we view it as a separate term).

$$(\Delta\mu_g^\circ)_{A+B} = (\Delta\mu_g^\circ)_{A+B}(\text{Bulk}) + (\Delta\mu_g^\circ)_{A+B}(\text{Surface}) + (\Delta\mu_g^\circ)_{mix} \quad (48)$$

The transfer free energy of the surfactant tail and the tail deformation free energy provide the bulk contributions while the aggregate-water interfacial free energy and the steric, dipolar and ionic interaction energies between the head groups provide the surface contributions.

The transfer free energy of the surfactant tails is a composition averaged value of the two pure component micelles. The tail deformation free energy is also a composition averaged value if the two surfactants have equal tail lengths. For such conditions, the bulk component of the free energy of mixed micelles does not give rise to nonidealities of the surfactant mixture. However, if the surfactant tail lengths differ from one another, then the tail deformation free energy is a nonlinear function of the aggregate

composition. In such a case, the nonideality of the surfactant mixture can originate from the bulk component.

If we consider the surface component of the free energy of micellization, all the contributions depend upon the area  $a$  per molecule of the aggregate. When the surfactant tails are identical in size, the area  $a$  is composition independent. However, all the surface contributions have a nonlinear composition dependence because of the functional forms of the various free energy contributions. When the surfactant tails differ in their sizes, the area  $a$  is a nonlinear function of the aggregate composition. This additional nonlinearity simply adds on to the already existing nonlinear dependence of the surface free energy contributions on the micelle composition. Thus, in all situations, the surface component of the free energy of mixed micelles contributes to nonideal behavior.

Finally, the free energy of mixing contribution is estimated taking into account the size differences between the hydrophobic tails. Also an enthalpy of interaction is introduced. Thus this contribution deviates from the ideal entropy of mixing except when the two surfactants have identical tails. Therefore, the free energy of mixing contribution can also give rise to nonideal behavior of the surfactant mixture.

In summary, the nonideal behavior of mixed micelle originates from the nonlinear composition dependence of the various free energy contributions as well as due to the deviation of the free energy of mixing from the ideal entropy of mixing. Depending upon the relative importance of the various free energy contributions, the nonidealities may be pronounced or only slight, as will be seen below. Further, both positive and negative deviations from ideal behavior will be observed for different surfactant mixtures. These general observations are examined through calculations for different kinds of binary surfactant mixtures below.

#### **Predictions of Molecular Theory**

For spherical or globular micelles, the size and composition dispersion was found to be narrow based on our earlier theory [1]. Consequently, one can consider the average aggregation number and the average micelle composition to be those values of  $g$  and  $\alpha_{eA}$ , respectively, for which the micelle concentration  $X_e$  has a maximum. The computations in this paper are carried out as follows. For a given value of  $\alpha_{1A}$ , we search for the values of the mixed micelle composition  $\alpha_{eA}$  and the radius  $R_e$  (for spherical micelles) or the semimajor axis  $b$  (for the ellipsoidal micelles) for which  $X_e$  has a maximum, as a function of the concentration of singly dispersed surfactants,  $X_1$ . As noted earlier, the semiminor axis of the ellipsoidal micelles is the largest radius allowed for the spherical micelles for any given micelle composition. The critical micelle concentration reported in this paper is that value of  $X_1$  for which the total amount of the surfactant in the

micellized form is equal to that in the singly dispersed form, namely  $X_{cmc} = X_1 = g X_g(\text{maximum})$  [19]. The average aggregation numbers and the average micelle compositions reported in this paper (unless otherwise specified) correspond to the condition that the total concentration of the surfactant present is equal to the cmc. The search for the parameter values that maximize the aggregate concentration  $X_g$  was carried out using a standard IMSL (International Mathematical and Statistical Library) subroutine ZXMWD. This subroutine is designed to carry out the search for the global extremum of a function of  $q$  independent variables subject to any specified constraints on the variables.

**Molecular Parameters.** The surfactants considered in this study are represented in Figure 2 (along with symbols used to refer to them in the text) and the various molecular constants used in the calculations are summarized in Table I. For hydrocarbon surfactants, the molecular volume of the surfactant tail containing  $n_c$  carbon atoms is calculated from the group contributions of  $(n_c - 1)$  methylene groups and the terminal methyl group [8].

$$v(\text{CH}_3) = 54.6 + 0.124 (T - 298) \text{ \AA}^3;$$

$$v(\text{CH}_2) = 26.9 + 0.0146 (T - 298) \text{ \AA}^3 \quad (49)$$

where  $T$  is in  $^{\circ}\text{K}$ . The extended length of the surfactant tail  $\ell_s$  is taken to be temperature independent and is calculated using a group contribution of  $1.265 \text{ \AA}$  for the methylene group and  $2.765 \text{ \AA}$  for the methyl group.

For fluorocarbon surfactants, extensive volumetric data are not available in order to estimate the temperature dependent group molecular volumes for the  $\text{CF}_3$  and  $\text{CF}_2$  groups. Using data available [30-32] at  $25^{\circ}\text{C}$ , we estimate that  $V(\text{CF}_3) = 1.67 V(\text{CH}_3)$  and  $V(\text{CF}_2) = 1.44 V(\text{CH}_2)$ . The ratios between the volumes of the fluorocarbon and the hydrocarbon groups are taken to be the same at all temperatures in the absence of extensive experimental data. The extended length of the fluorocarbon chain is estimated using the same group contributions as for hydrocarbon tails, namely,  $2.765 \text{ \AA}$  for the  $\text{CF}_3$  group and  $1.265 \text{ \AA}$  for the  $\text{CF}_2$  group [7].

The solubility parameters for the hydrocarbon and fluorocarbon tails of surfactants can be estimated using a group contribution approach on the basis of the tabulated data available [10,29]. The solubility parameter estimated for the fluorocarbon tail of the surfactant SPFO on this basis is  $12.3 \text{ MPa}^{1/2}$ . This approach utilizes only the pure component properties for the determination of solubility parameters. Since, the solubility parameters estimated on this basis have been found inadequate for quantitative description of hydrocarbon-fluorocarbon mixture properties, an alternate

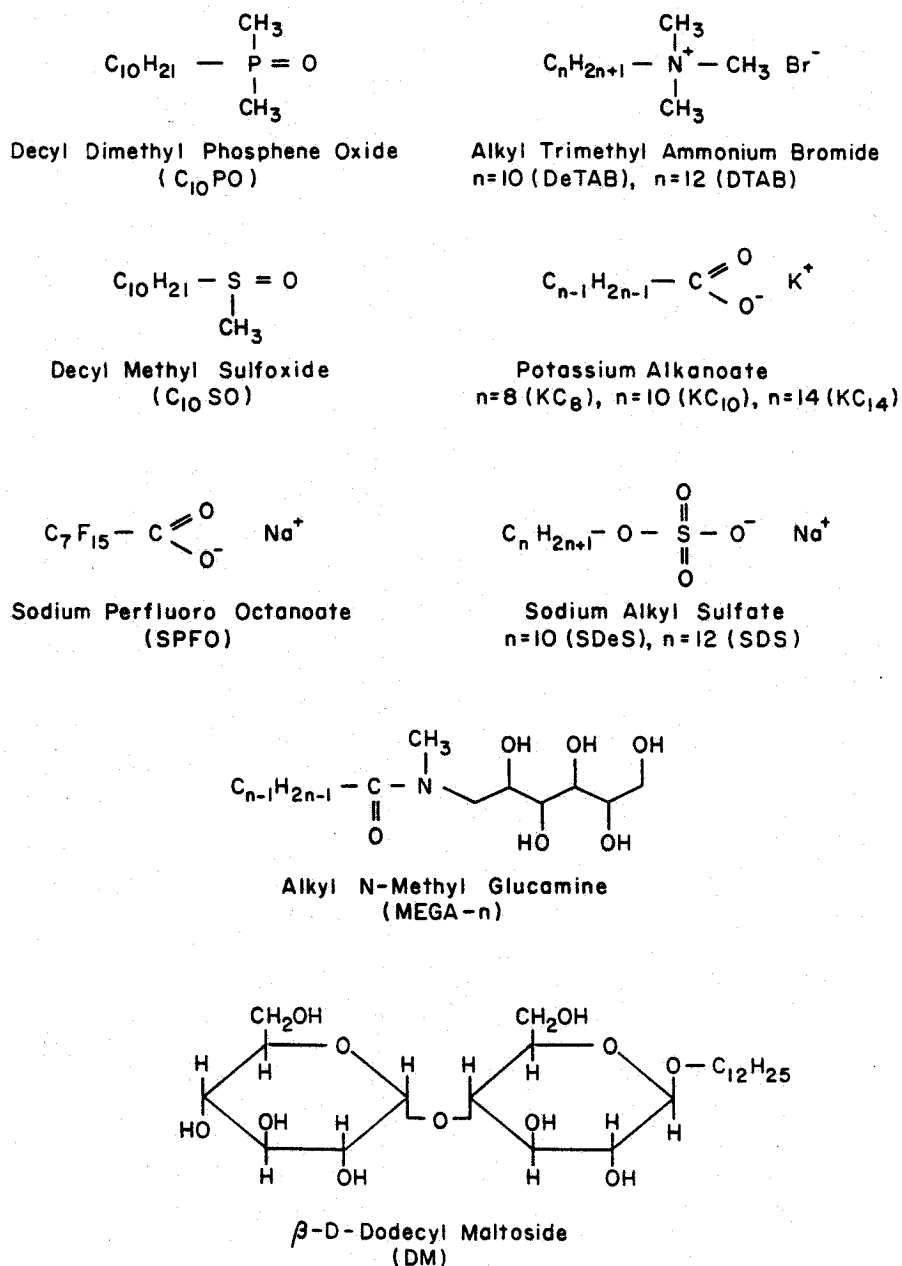


Figure 2. Chemical structure of the surfactant molecules considered in this study and the symbols used to refer to them in the text.

Table I. Molecular Constants for Surfactants

| Surfactant | $v_s$          | $\ell_s$     | $a_o$          | $a_p$          | $\delta$     | $d$          | $\delta^{H1}$      |
|------------|----------------|--------------|----------------|----------------|--------------|--------------|--------------------|
|            | $\text{\AA}^3$ | $\text{\AA}$ | $\text{\AA}^2$ | $\text{\AA}^2$ | $\text{\AA}$ | $\text{\AA}$ | $\text{MPa}^{1/2}$ |

**Nonionic Hydrocarbon Surfactants**

|            |     |      |    |    |   |   |       |
|------------|-----|------|----|----|---|---|-------|
| $C_{10}SO$ | 296 | 14.1 | 21 | 39 | - | - | 16.63 |
| $C_{10}PO$ | 296 | 14.1 | 21 | 48 | - | - | 16.63 |
| DM         | 350 | 16.7 | 21 | 43 | - | - | 16.76 |
| MEGA-8     | 217 | 10.4 | 21 | 34 | - | - | 16.31 |
| MEGA-9     | 244 | 11.6 | 21 | 34 | - | - | 16.44 |

**Anionic Hydrocarbon Surfactants**

|           |     |      |    |    |      |   |       |
|-----------|-----|------|----|----|------|---|-------|
| SDeS      | 296 | 14.1 | 17 | 17 | 5.45 | - | 16.63 |
| SDS       | 350 | 16.7 | 17 | 17 | 5.45 | - | 16.76 |
| $KC_8$    | 217 | 10.4 | 11 | 11 | 6.00 | - | 16.31 |
| $KC_{10}$ | 271 | 12.9 | 11 | 11 | 6.00 | - | 16.54 |
| $KC_{14}$ | 378 | 17.9 | 11 | 11 | 6.00 | - | 16.81 |

**Cationic Hydrocarbon Surfactants**

|       |     |      |    |    |      |   |       |
|-------|-----|------|----|----|------|---|-------|
| DeTAB | 296 | 14.1 | 21 | 54 | 3.45 | - | 16.63 |
| DTAB  | 350 | 16.7 | 21 | 54 | 3.45 | - | 16.76 |

**Anionic Fluorocarbon Surfactants**

|      |     |      |    |    |      |   |              |
|------|-----|------|----|----|------|---|--------------|
| SPFO | 325 | 10.4 | 11 | 11 | 5.55 | - | 12.30<br>9.5 |
|------|-----|------|----|----|------|---|--------------|

approach is to back calculate the solubility parameter values by fitting the mixture properties. Mukerjee and Handa [24] have estimated group contributions to the solubility parameters by fitting critical solution temperature data on hydrocarbon-fluorocarbon mixtures. On the basis of these group contributions, we calculate the solubility parameter of the SPFO tail to be approximately  $9.5\text{MPa}^{1/2}$ . Computed results are presented later utilizing both these estimates. It may be mentioned that improved accounting of the interactions between hydrocarbon and fluorocarbon chains would be necessary to improve the quantitative accuracy of our predictions.



Of the molecular constants needed for the calculations, there can be some small uncertainty in estimating  $a_p$  for nonionic,  $a_p$  and  $\delta$  for ionic and  $a_p$  and  $d$  for zwitterionic surfactants. Reasonable estimates for these constants can be obtained from knowledge of various bond lengths and atomic or ionic radii. To improve the estimates, information about conformation and orientation of the polar heads will be necessary. It is this factor which is responsible for the small uncertainty in the estimated molecular constants. Although the estimates employed in our calculations (Table I) could be revised, the molecular constants are not adjustable parameters. Indeed, the requirement that the same value of the molecular constant be used to predict the cmc, micelle size and the influence of salt and temperature for pure micelles, and also the micelle composition of mixed micelles, solubilization behavior, etc., provides an unusually stringent test.

**Nonionic Hydrocarbon-Nonionic Hydrocarbon Mixtures.** The aggregation behavior of binary mixtures of decyl methyl sulfoxide,  $C_{10}SO$  and decyl dimethyl phosphene oxide,  $C_{10}PO$  at  $24^\circ C$  has been examined and the results are presented in Figures 3 and 4. In Figure 3, the cmc values are plotted against the composition of the micelles and the composition of the singly dispersed surfactant. Note that when the total surfactant concentration is equal to the cmc, the amount of micelles present is small and hence, one can practically equate the composition of the monomers to the composition of the total surfactant. Also shown for comparison are the experimental data obtained by Holland and Rubingh [33] based on surface tension measurements. Figure 4 presents the average aggregation numbers predicted by the theory as a function of the composition of the mixed micelle and that of the monomers. No experimental data are available for comparison. The size of the mixed micelle is approximately linear with composition but one can discern a slight s-shaped curve as was observed in the experiments of Warr et al. [5] for another binary mixture of nonionic surfactants.

It has been shown that the cmc of this mixed surfactant system could be calculated from the cmc values of the individual surfactants by assuming the phenomenological ideal mixed micelle model [33]. In the framework of the free energy model presented here, nonidealities in this binary mixture can arise from the fact that the two surfactants have somewhat differing head group cross sectional areas while possessing identical tails. Since there are no volume differences between the hydrophobic tails of the two surfactants, for any aggregation number, the area per molecule of the mixed micelle is independent of the micelle composition. However, the steric interactions between head groups at any aggregation number is a nonlinear function of the micelle composition. This is the source of mixture nonideality. Nevertheless, the deviation from ideal mixing conditions are rather small, thus allowing the phenomenological ideal mixed micelle model

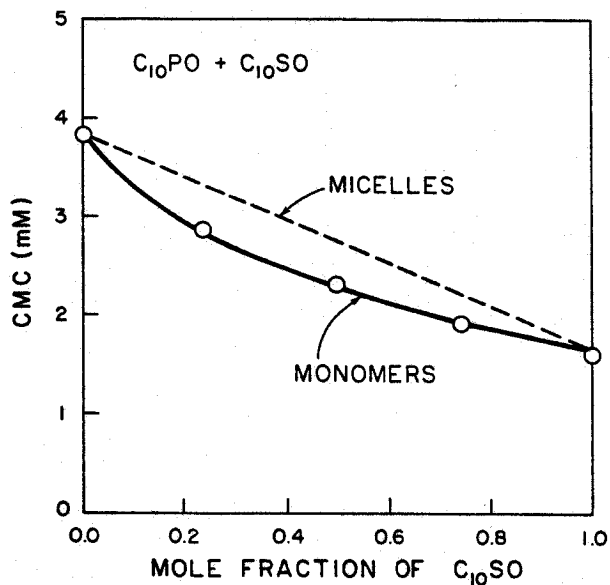


Figure 3. The cmc of  $C_{10}PO + C_{10}SO$  mixtures as a function of the composition of micelles (dotted line) and that of singly dispersed surfactants (continuous line) at  $24^{\circ}C$ . The experimental data are from ref. [33].

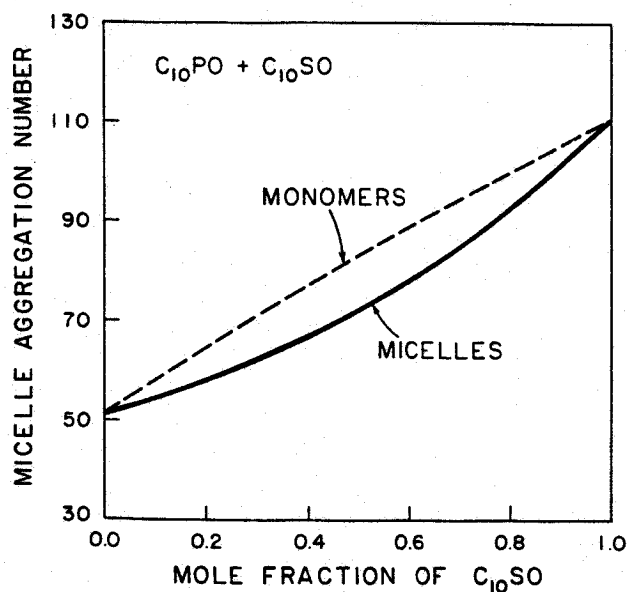


Figure 4. The average aggregation number of  $C_{10}PO + C_{10}SO$  mixed micelles at the cmc as a function of the composition of micelles (continuous line) and that of the singly dispersed surfactants (dotted line) for the conditions specified in Figure 3.

to predict the mixture cmc satisfactorily. The small nonideality, however, is reflected in the micelle aggregation number in terms of the slight nonlinear dependence of the aggregation number on the micelle composition.

**Ionic Hydrocarbon-Ionic Hydrocarbon Mixtures.** The micellization behavior of mixtures of two anionic surfactants having the same head group has been examined. The surfactants are sodium dodecyl sulfate, SDS and sodium decyl sulfate, SDeS which differ from one another in their hydrocarbon tail lengths. The predicted cmc values are plotted against the composition of the singly dispersed surfactant in Figure 5. Also shown are the experimental data obtained by Mysels and Otter [34] using conductivity measurements and the data of Shedlowsky et al. [35] based on e.m.f. measurements. The predicted mixed micelle compositions as a function of the composition of the singly dispersed surfactants are compared in Figure 6 with the experimental data obtained by Mysels and Otter [34] using conductivity measurements.

In these binary mixtures, one source of nonideality arises from the volume differences between the hydrophobic tails of the two surfactants. Consequently, at any given aggregation number, the area per molecule of the mixed micelle is a nonlinear function of the micelle composition and hence, all the free energy contributions reflect this nonlinear dependence. The other source of nonideality is the change in ionic strength of the solution as the composition is modified. In the absence of any added salt, the ionic strength is determined by the concentration of the singly dispersed surfactants. This concentration changes with composition, thus modifying the ionic interactions at the micelle surface nonlinearly with respect to composition. Given the importance of the ionic interactions to the free energy of micellization, the nonideality is more perceptible in these binary mixtures. The predicted micelle aggregation numbers shown in Figure 7 reflect the nonideality arising from the change in ionic strength of the surfactant solution. Since the ionic strength has a significant influence on the ionic interactions between the head groups, the aggregation numbers are larger for the mixed micelles than for the pure component micelles over most of the composition.

Somewhat contrasting behavior is shown by the mixtures of cationic surfactants, dodecyl trimethyl ammonium bromide, DTAB and decyl trimethyl ammonium bromide, DeTAB. This mixture is similar to the SDS-SDeS mixture with respect to the tail lengths of the two surfactants. However, the trimethyl ammonium bromide head group has a very large area  $a_p$  compared to that of the anionic sulfate head group. The predicted cmc values as a function of the micelle and the monomer compositions are presented in Figure 8. For comparison, experimental cmc data obtained by Garcia-Mateos et al. [36] using electrical conductivity measurements are also presented. One can observe the large cmc changes in DTAB-DeTAB mixtures as the composition is altered which also affects the ionic strength of

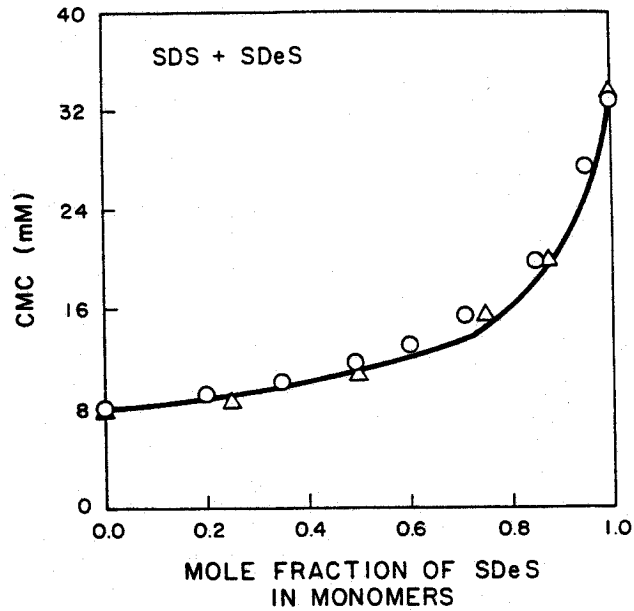


Figure 5. The cmc of SDS + SDeS mixtures as a function of the composition of singly dispersed surfactants. The experimental data shown by circles are from ref. [34] while the data shown by triangles are from ref. [35].

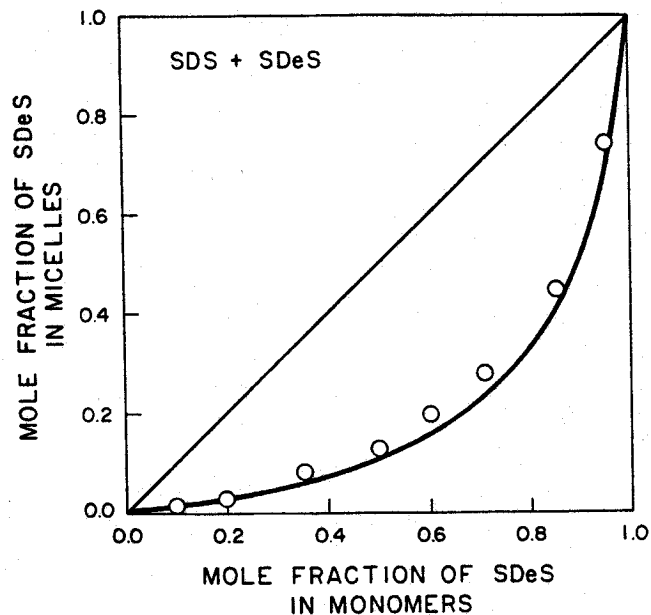


Figure 6. The composition of SDS + SDeS mixed micelles as a function of the composition of singly dispersed surfactants. The experimental data shown by circles are from ref. [34].

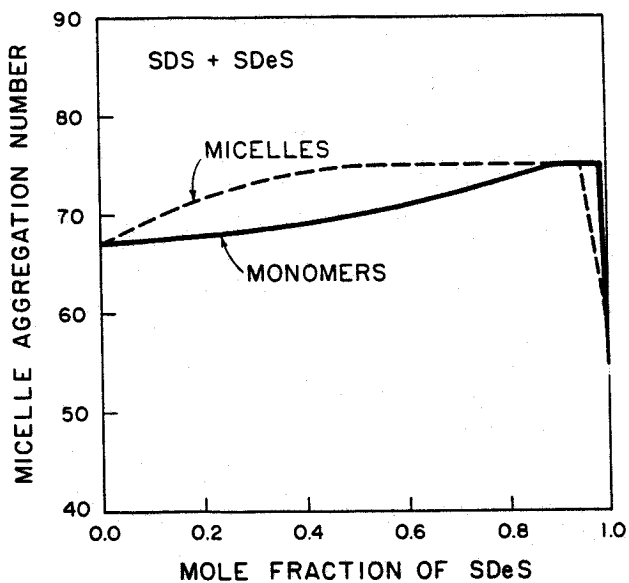


Figure 7. The average aggregation number of SDS + SDeS mixed micelles as a function of the composition of the micelles (dotted line) and that of singly dispersed surfactants (continuous line).

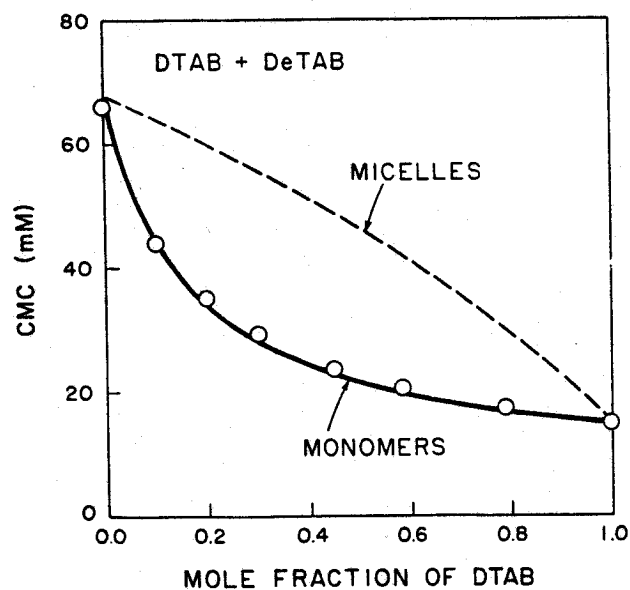


Figure 8. The cmc of DTAB + DeTAB mixtures as a function of the composition of the micelles (dotted line) and that of singly dispersed surfactants (continuous line). The experimental data are from ref. [36].

the solution. Nevertheless, the predicted micelle aggregation numbers plotted in Figure 9 do not show any growth above that of pure component micelles. This differing behavior is a direct consequence of the larger steric repulsions in the case of these cationic surfactants with their bulky head groups when compared to the sulfate head groups of SDS-SDeS.

To explore the consequences of significant variations in the hydrophobic tail lengths, we have computed the micellization behavior of mixtures of anionic potassium alkanoates, namely, potassium tetradecanoate,  $KC_{14}$ —potassium octanoate,  $KC_8$  and potassium decanoate,  $KC_{10}$ —potassium octanoate,  $KC_8$  at 25°C. The calculated cmc, micelle composition and micelle aggregation numbers are shown in Figures 10 to 12 as a function of the composition of the monomers. Also shown in Figure 6 are the experimental cmc data [37] obtained by Shinoda using dye solubilization measurements. One can observe from Figure 11 that the less hydrophobic  $KC_8$  is almost completely excluded from the micelles in  $KC_8 + KC_{14}$  mixtures because of the comparatively much stronger hydrophobicity of  $KC_{14}$ . This contrasts against the behavior displayed by  $KC_8 + KC_{10}$  mixtures.

**Ionic Hydrocarbon-Nonionic Hydrocarbon Mixtures.** In contrast to the two kinds of binary mixtures considered above where nonidealities were relatively small, mixtures of ionic and nonionic surfactants display significant nonideal behavior. We consider mixtures of anionic sodium dodecyl sulfate, SDS and nonionic decyl methyl sulfoxide,  $C_{10}SO$  at 24°C and in the presence of 1 mM  $Na_2CO_3$ . The calculated cmc values are shown in Figure 13 while the aggregation numbers are presented in Figure 14, both as functions of the monomer composition. The experimental cmc data based on surface tension measurements [33] are also provided for comparison. The results show that considerable nonideality is exhibited by this binary mixture. The cmc values of the mixed system are substantially smaller than those expected for ideal mixed micelles. Thus, a negative deviation from ideal behavior is observed.

The two surfactants differ somewhat in their hydrophobic tail lengths and in the sizes of the polar head groups. Similar variations occurred in the case of nonionic-nonionic mixtures considered before but by themselves, they do not give rise to significant nonidealities. However, in the present case, one component is ionic while the other is nonionic. This results in a large variation in the ionic interaction energy at the micelle surface as the micelle composition is modified. This free energy contribution is thus responsible for most of the nonideal behavior exhibited by this system.

We also present the model predictions for binary mixtures of anionic sodium dodecyl sulfate, SDS and nonionic  $\beta$ -dodecyl maltoside, DM that has been experimentally investigated by Bucci et al. [6]. In this system, the two surfactants have identical hydrophobic parts and hence, all the

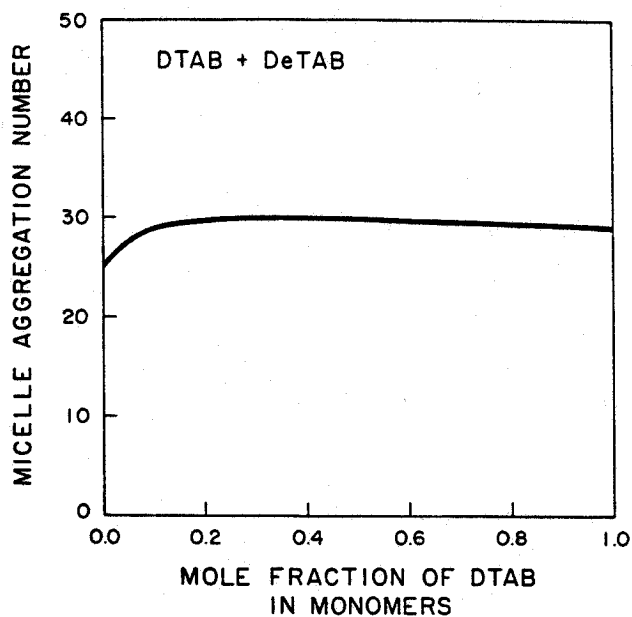


Figure 9. The average aggregation number of DTAB + DeTAB mixed micelles as a function of the composition of singly dispersed surfactants.

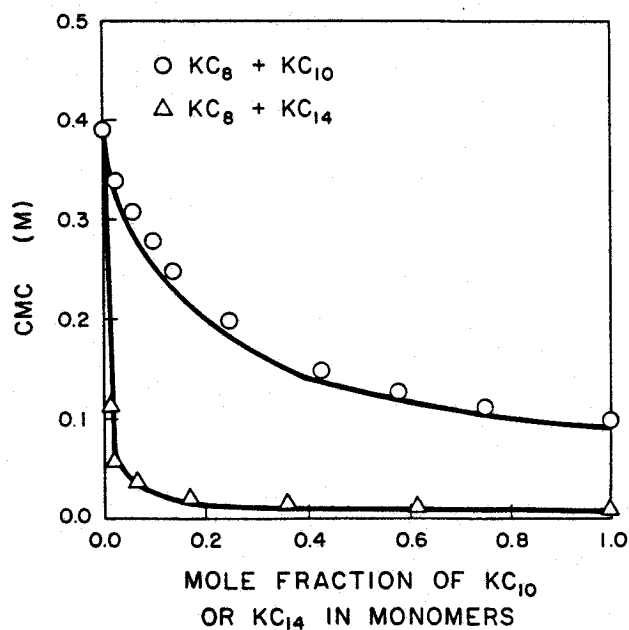


Figure 10. The cmc of  $KC_8 + KC_{10}$  mixtures and  $KC_8 + KC_{14}$  mixtures as a function of the composition of singly dispersed surfactants. The experimental data are from ref. [37].

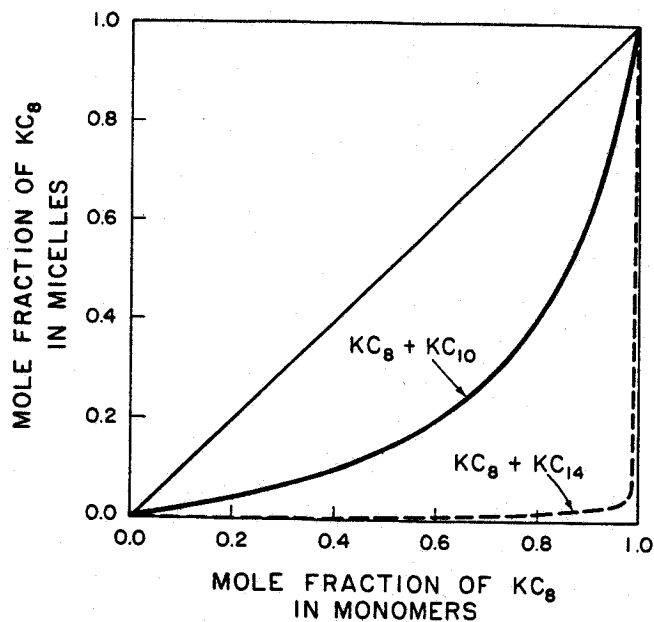


Figure 11. The composition of  $KC_8 + KC_{10}$  mixed micelles and  $KC_8 + KC_{14}$  mixed micelles as a function of the composition of singly dispersed surfactants.

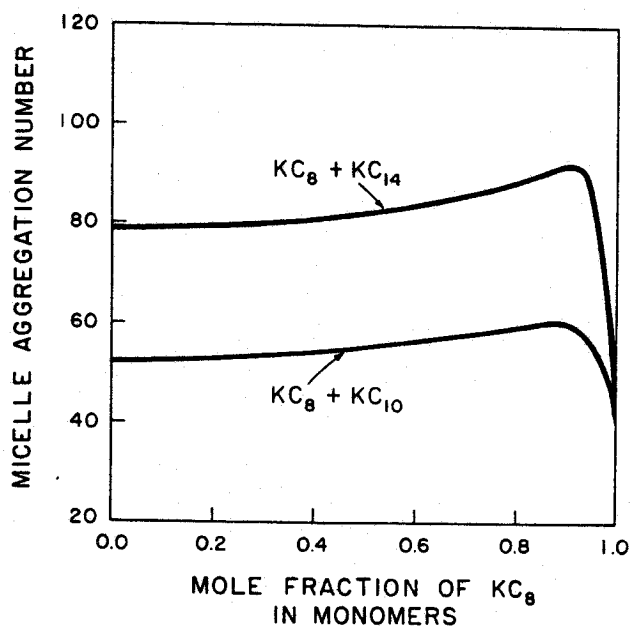


Figure 12. The average aggregation number of  $KC_8 + KC_{10}$  mixed micelles and  $KC_8 + KC_{14}$  mixed micelles as a function of the composition of singly dispersed surfactants.



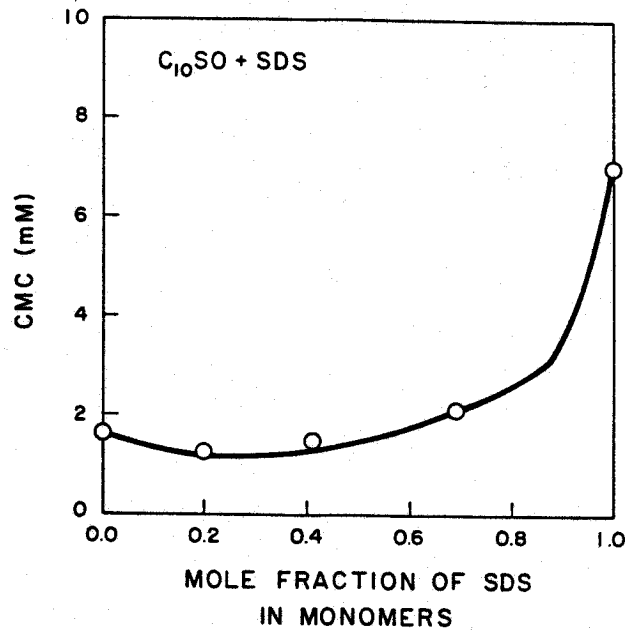


Figure 13. The cmc of SDS + C<sub>10</sub>SO mixtures as a function of the composition of singly dispersed surfactants. The experimental data are from ref. [33].

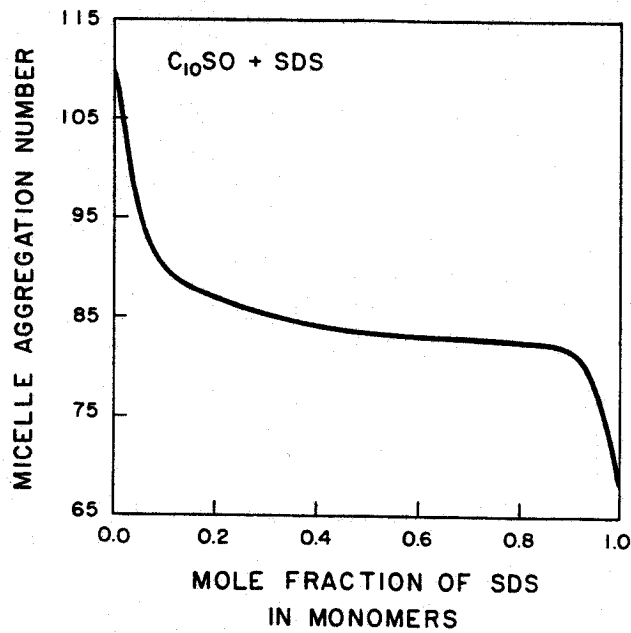


Figure 14. The average aggregation number of SDS + C<sub>10</sub>SO mixed micelles as a function of the composition of monomers.

nonideality emerges from the differences in the size and charge of the two head groups. The calculated average aggregation numbers and those estimated from neutron scattering measurements [6] are shown in Figure 15 in solutions with and without added salt. The average aggregation numbers and the average micelle compositions are estimated at a total surfactant concentration of 50 mM and at 25°C. Figures 16 and 17 present respectively, the cmc and micelle composition, as functions of the composition of the singly dispersed surfactant at two concentrations of added electrolyte, NaCl. One can see the preferential incorporation of nonionic DM molecules in the micelles over most of the composition range. In the absence of any added electrolyte, this preference is stronger since the presence of anionic SDS in micelles will give rise to a positive free energy contribution. Obviously, in the presence NaCl, the electrostatic repulsions between ionic head groups are reduced and hence a larger number of SDS molecules are incorporated into the mixed micelles.

**Anionic Hydrocarbon-Cationic Hydrocarbon Mixtures.** Anionic and cationic surfactants when present together are expected to form ion pairs with no net charge and thereby undergo a decrease in their aqueous solubility resulting in precipitation. This phenomenon is widely observed [38,39]. But depending upon their hydrophobic parts, these surfactant mixtures can also exhibit the formation of mixed micelles or mixed spherical bilayer vesicles in certain concentration and composition domains. As discussed earlier, depending upon the location of the charges on the anionic and the cationic surfactants, one may associate a permanent dipole moment with each ion pair. Consequently, these surfactant mixtures can behave as part ionic single chain molecules and a part zwitterionic paired chain molecules. We have calculated the aggregation properties of binary mixtures of decyl trimethyl ammonium bromide, DeTAB and sodium decyl sulfate, SDeS and the results are presented in Figures 18 and 19. The calculated and experimental [33] cmc values are shown in Figure 18 while information on the micelle composition is found from Figure 19. The formation of rodlike mixed micelles is indicated over the entire composition range. The micelle composition data show that the mixed micelles contain approximately equal numbers of the two types of surfactants over the entire composition space. Indeed, the small deviation from the micelle composition value of 0.5 arises because of the differing sizes of the polar head groups. The formation of spherical bilayer vesicles from binary mixtures of this type will be examined in a latter paper.

**Anionic Fluorocarbon-Nonionic Hydrocarbon Mixtures.** We consider the aggregation behavior of nonionic alkyl-N-methyl glucamines (MEGA-n) and anionic sodium perfluorooctanoate (SPFO) mixtures that have been experimentally studied by Wada et al. [40]. In such mixtures, the nonideality associated with the mixing of hydrocarbon and fluorocarbon surfactant tails

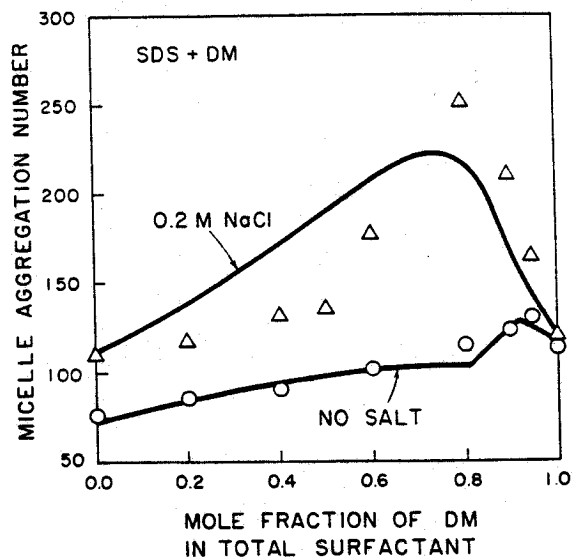


Figure 15. The average aggregation number of SDS + DM mixed micelles as a function of the total surfactant composition at a total surfactant concentration of 50 mM. The experimental data are from ref. [6] where the circles refer to micelle sizes in the absence of any added salt while the triangles correspond to a 0.2 M concentration of added NaCl.

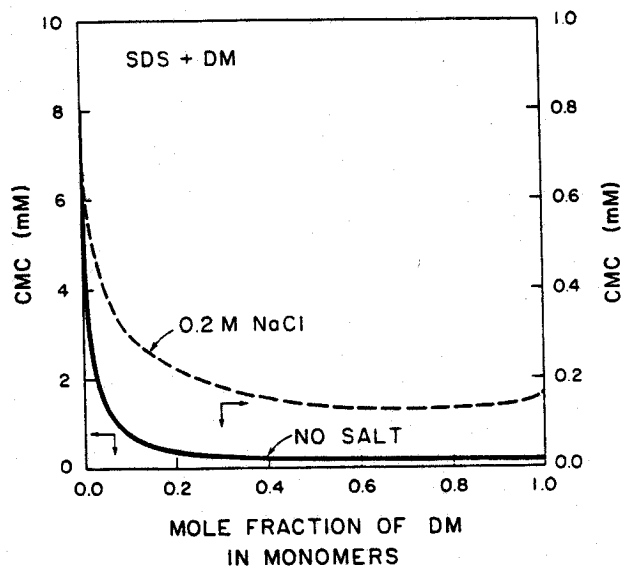


Figure 16. The cmc of SDS + DM mixtures as a function of the composition of monomers. The conditions correspond to those in Figure 15.

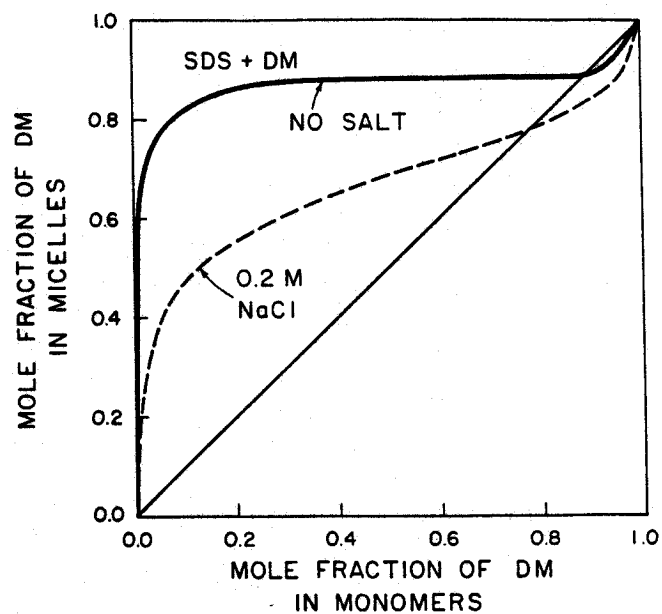


Figure 17. The composition of mixed micelles of SDS + DM as a function of the composition of monomers. The conditions correspond to those in Figure 15.

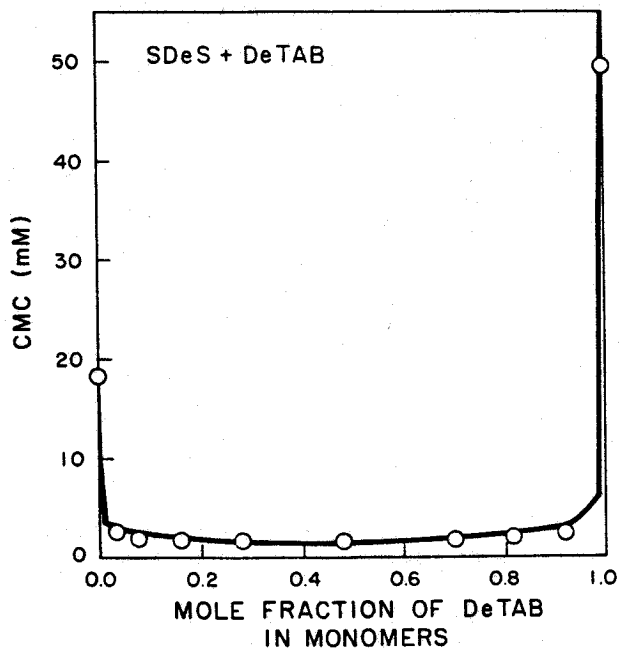


Figure 18. The cmc of SDeS + DeTAB mixtures as a function of the composition of singly dispersed surfactants. The experimental data are from ref. [33].

is superimposed on another type of nonideality associated with the mixing of anionic and nonionic headgroups. For such polar head group mixtures in hydrocarbon surfactants, our earlier calculations revealed considerable negative deviations from ideality. For mixtures of hydrocarbon and fluorocarbon tails we anticipate strong positive deviations from ideality. Thus, for the mixtures under study, both negative and positive deviations from ideality occur, partially compensating one another. As a result, these binary mixtures exhibit reduced nonideality. Figures 20 and 22 present the calculated cmc values as a function of the composition of the monomers. The calculations have been performed with two alternate values for the solubility parameter of SPFO, one determined from pure fluorocarbon properties ( $12.3\text{MPa}^{1/2}$ ), and the other determined from fluorocarbon-hydrocarbon mixture properties ( $9.5\text{MPa}^{1/2}$ ). The cmc values calculated using these two solubility parameter estimates are found to provide bounds for the measured cmc. We note that the cmc values of pure MEGA-*n* surfactants determined by Wada et al. [40] using surface tension measurements are 10 to 20 percent lower than those estimated from their light scattering measurements. All the mixture measurements have been made using the surface tension technique and it is therefore, conceivable that the actual cmc values may be somewhat larger than those indicated by the experimental points in Figures 20 and 22. Both MEGA-8-SPFO and MEGA-9-SPFO mixtures display the same qualitative behavior. Miscibility between the two surfactants is promoted because of the head group interactions and a single kind of mixed micelles exists in solution. This is seen in the micelle composition data shown in Figures 21 and 23 for MEGA-8-SPFO and MEGA-9-SPFO mixtures, respectively.

**Anionic Hydrocarbon-Anionic Fluorocarbon Mixtures.** We have calculated the micellization behavior of sodium perfluorooctanoate, SPFO and sodium decyl sulfate, SDeS mixtures and the results are shown in Figures 24 and 25. The cmc values are compared with available experimental data [40] in Figure 24 where the composition of the mixed micelle is also shown. One can observe positive deviations in cmc in contrast to the negative deviations seen for all the binary mixtures discussed previously. This positive deviation is a direct consequence of the nonideality in the interactions between the hydrocarbon and fluorocarbon tails. This positive deviation which was also present in SPFO-MEGA-*n* mixtures was compensated partially by the negative deviations due to head group interactions in those systems. Such compensating negative head group interactions are absent in SPFO-SDeS mixtures. The calculated micelle composition data show the interesting feature that over a composition domain two types of micelles coexist. One can observe the hydrocarbon rich and the fluorocarbon rich micelles with the average compositions of  $\alpha_{\text{eA}} = 0.32$  and  $0.79$ , in coexistence. Phenomenological models of mixed micelles employing regular solution concept are not capable of predicting such asymmetry in the compositions of

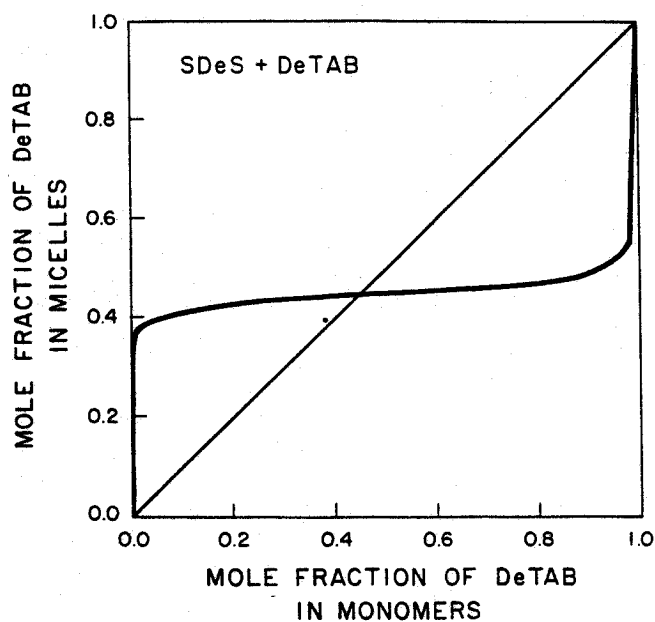


Figure 19. The average composition of SDeS + DeTAB mixed micelles as a function of the composition of monomers.

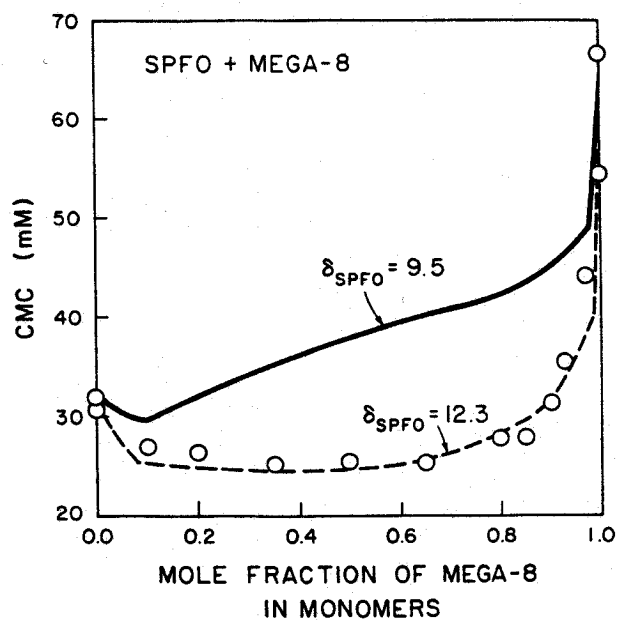


Figure 20. The cmc of MEGA-8 + SPFO mixtures as a function of the composition of singly dispersed surfactants. The calculated results are presented for two limiting values of the solubility parameter of the SPFO tail. The experimental data are from ref. [40].

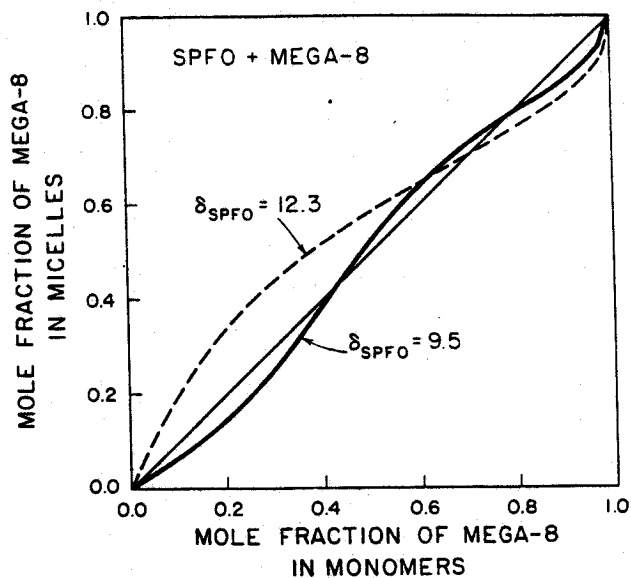


Figure 21. The average composition of MEGA-8 + SPFO mixed micelles as a function of the composition of monomers. The conditions correspond to those described in Figure 20.

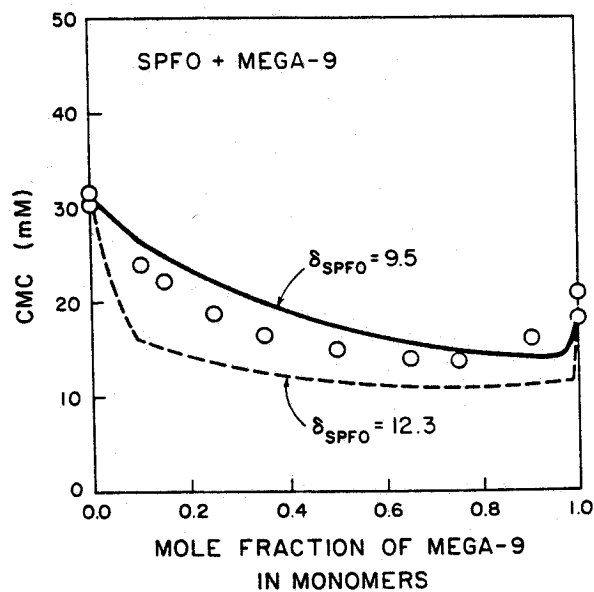


Figure 22. The cmc of MEGA-9 + SPFO mixtures as a function of the composition of singly dispersed surfactants. The calculated results are presented for two limiting values of the solubility parameter of the SPFO tail. The experimental data are from ref. [40].

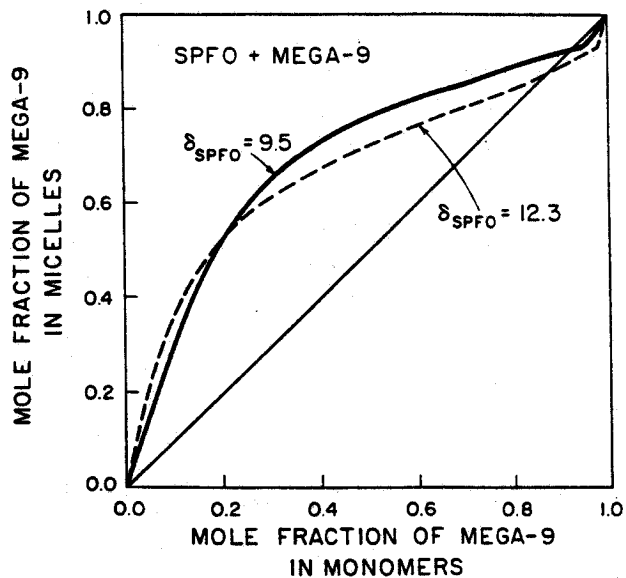


Figure 23. The average composition of MEGA-9 + SPFO mixed micelles as a function of the composition of monomers. The conditions correspond to those described in Figure 22.

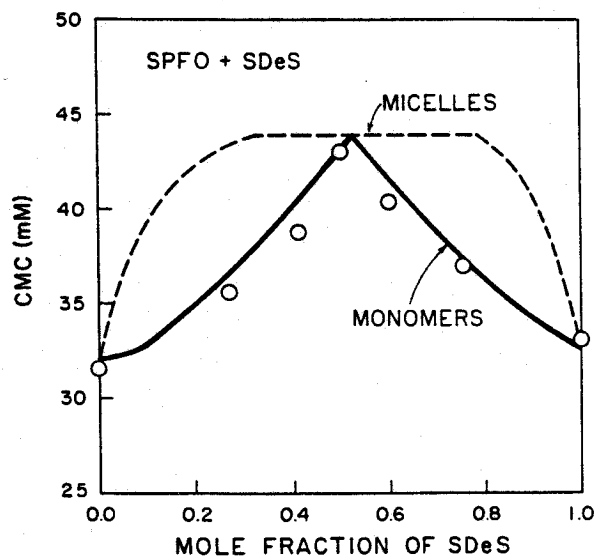


Figure 24. The cmc of SDeS + SPFO mixtures as a function of the composition of micelles (dotted line) and that of singly dispersed surfactants (continuous line). The experimental data are from ref. [40]. The experimental and calculated results indicate the coexistence of two micelle populations.



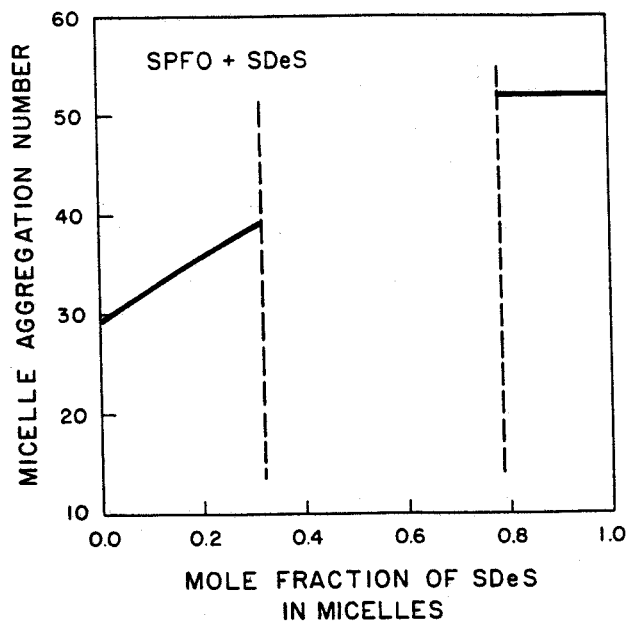


Figure 25. The average aggregation number of SDeS + SPFO mixed micelles as a function of the composition of micelles. Two distinct micelle sizes corresponding to the two coexisting micelle populations are indicated.

the coexisting micelle populations. The average aggregation numbers of the mixed micelles have been predicted and these results are shown in Figure 25. The micelles that are fluorocarbon and hydrocarbon rich are found to have distinctly different aggregation numbers.

### Conclusions

A molecular thermodynamic treatment of binary surfactant mixtures in aqueous media is developed in this paper. The model allows the prediction of the size and the composition distribution of spherical, globular and rodlike mixed micelles. Central to the model are the expressions for various contributions to the free energy of formation of mixed micelles. These expressions are obtained by extending the theory for single surfactants developed recently by us.

The present model improves upon our earlier treatment of mixed micelles in a number of ways. Of special importance are the analytical expressions for the free energy of deformation of the surfactant tails associated with the molecular packing requirements within the micelle core. Also, ionic interactions are calculated using an approximate analytic solution to the Poisson-Boltzmann equation available in the literature. The free energy of mixing of surfactant tails within the micelle core is estimated on the basis of Hildebrand's solubility parameter approach. Further, the

free energies of transfer of the surfactant tails from water into micelles and other variables are given as explicit functions of temperature. The model is now strictly predictive in the sense that the empirical factors present in our earlier treatment of mixed micelles are all entirely replaced.

The theory is used to predict the micellization behavior of various binary surfactant mixtures differing in both the hydrophobic tails and the polar head groups. Negative and positive deviations from ideal behavior are observed for the surfactant systems considered. For hydrocarbon-hydrocarbon surfactant mixtures, close to ideal behavior is observed for nonionic-nonionic mixtures. Negative deviations from ideality become significant in the order ionic-ionic, ionic-nonionic and anionic-cationic mixtures. For hydrocarbon-fluorocarbon surfactants, with ionic-ionic head groups, positive deviation from ideal behavior is observed. Of interest is the observed coexistence of two populations of mixed micelles one rich in fluorocarbon and the other in hydrocarbon. In contrast, when ionic-nonionic head groups are considered, the micelles become miscible with a single type of mixed micelle being present.

The thermodynamic model allows an interpretation of the observed ideal and nonideal behavior of mixed micelles in terms of bulk and surface components of the free energy of micelle formation as well as the free energy of mixing. In general, the surface component leads to negative deviations from the ideal behavior. The bulk component contributes weakly or not at all to nonideality. The free energy of mixing contributes to a positive deviation from ideality for hydrocarbon-fluorocarbon mixtures.

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