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Molecular Theory for Mixed Micelles

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Received December 4, 1984. In Final Form: February 12, 1985

A molecular theory for the formation of mixed micelles is developed here as an extension of our earlier theory for single-component micelles. The theory permits the calculation of the cmc, the average micelle size, and the average micelle composition as well as the size and the composition distribution of micelles in mixed surfactant systems. Central to the theory is an explicit molecular thermodynamic expression for the Gibbs energy of formation of the mixed micelle. This Gibbs energy of micelle formation, which is composition dependent, can be decomposed into bulk and interfacial components. The bulk component includes the free energy contributions arising from the transfer of the surfactant tail from water to the micelle. The interfacial component includes the free energy contributions due to the micellar core-water interfacial energy, the steric repulsions between the head groups at the micelle surface, and the electrostatic repulsions between the head groups at the micelle surface. If the Gibbs energy of micelle formation is a linear function of the micelle composition, then the excess Gibbs energy is zero and the surfactant mixture behaves ideally. On the other hand, if the Gibbs energy of micelle formation has a nonlinear dependence on the micelle composition, then the excess Gibbs energy is nonzero and the surfactant mixture displays nonideal micellization behavior. It is shown that the bulk component of the Gibbs energy of micelle formation depends linearly on the micelle composition and hence does not account for any nonideal behavior displayed by the mixed micelles. In contrast, the interfacial component has a nonlinear dependence on the composition of the mixed micelle and thus constitutes the source of the observed nonidealities in mixed micellar systems. Therefore, surfactant mixtures displaying markedly nonideal micellization behavior are those for which the interfacial interactions show significant composition dependence. Illustrative results based on this molecular theory are obtained for a number of binary mixtures and are compared against the available experimental data.

Introduction

Surfactant molecules self-associate in dilute aqueous solutions to generate aggregates of various types, shapes, and sizes such as small globular micelles, large cylindrical micelles, and spherical vesicles. The characteristics of the aggregates formed are determined by the molecular structure of the surfactant as well as by the solution conditions such as concentration, temperature, ionic strength, etc. Elucidating the relation between aggregation and various molecular features of the surfactant solution is central to our understanding of surfactant self-assembly.¹⁻³ Toward this end, a pioneering contribution was made by Tanford, who presented an intuitively appealing as well as simple phenomenological expression for the free energy change associated with micelle formation.^{1,4} Using this free energy expression, Tanford was able to calculate the size, shape, and the size distribution of surfactant aggregates. In recent years, alternate free energy expressions based on statistical thermodynamics have been developed which permit a priori, quantitative predictions of surfactant self-assembly.^{5,6} These allow one to calculate the critical micelle or vesicle concentration, the size distribution and the average size of the aggregates, the conditions under which a transition occurs from spherical micelles to cylindrical micelles and/or vesicles, and also the conditions for the coexistence of more than one kind of aggregate.

The molecular thermodynamic treatments describing the self-assembly in single-component surfactant solutions have remained unexplored for their ability to describe the aggregation behavior of binary and multicomponent surfactant mixtures. Current approaches to describing mixed

micelles are based on the use of formal classical thermodynamic relations.⁷⁻¹⁷ Assuming ideal mixing behavior, and given the properties of the pure components, they can be used to calculate the critical micelle concentration and the composition of micelles as a function of the composition of the singly dispersed surfactant. Obviously, predictive calculations are not possible with this approach for the more interesting systems exhibiting nonideality. For such systems, one can at best describe the measured experimental data by assuming one or another model for the system nonideality. The model parameters reflecting nonideality can then be evaluated through a fitting of the experimental data. The regular solution theory has commonly been used to describe the nonideality in available studies of mixed micellization. In addition to their lack of predictive power, the above treatments cannot provide any information about the aggregation number of mixed micelles as a function of the mixture composition, whether the mixture is ideal or nonideal.

The main goal of this paper is to present a molecular thermodynamic theory for mixed micelle formation based on our earlier^{5,6} treatment of aggregation in single-component surfactant solutions. The expression for the free energy change of micellization given in our previous paper has, however, been recast in a form analogous to the in-

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tuitively more appealing expression formulated by Tanford.^{1,4} Illustrative calculations have been carried out for various types of binary surfactant mixtures to show that the cmc, micelle size, micelle composition, and the relation between the micelle composition and that of the singly dispersed surfactant can all be determined without introducing any new parameters in the theory. The calculated cmc values are found to be in satisfactory agreement with the available experimental data for various binary mixtures investigated in this study. Additional interesting results on how the micellar size varies with the composition of the surfactant mixture and on the occurrence of azeotropy (namely, identical compositions for micelles and monomers at all total concentrations) are also presented. Further, the nonideality exhibited by the mixed surfactants has been traced to its source in the various molecular interactions.

Although the illustrative calculations presented here refer only to binary mixtures of surfactants, the theory is applicable to multicomponent mixtures as well. Further, in the present paper, results for only hydrocarbon surfactants are presented. The nonideal mixtures of hydrocarbon and fluorocarbon surfactants can also be described by the present theory, and the results for such systems will be discussed in a later paper.

Theory

Classical Thermodynamic Approach. The principal results obtained from the classical thermodynamic description of the micellization of binary surfactant mixtures are briefly summarized here. Considering a mixture of surfactants A and B, the critical micelle concentration (cmc) of the mixture X_T^* as a function of the composition is given by the expression

$$X_T^* = \left(\frac{\alpha_{AT}}{f_{Am}X_A^*} + \frac{\alpha_{BT}}{f_{Bm}X_B^*} \right)^{-1} \quad (1)$$

Here, X_T^* is expressed in units of mole fraction in the total solution. α_{AT} and α_{BT} are the mole fractions of A and B in the total surfactant mixture. X_A^* and X_B^* are the cmc values of pure surfactants A and B, respectively, both in mole fraction units. f_{Am} and f_{Bm} are the activity coefficients of surfactants A and B in the mixed micelle. Further, one may calculate the mole fraction X_{Am} of surfactant A in the mixed micelle from the relation

$$X_{Am} = \frac{\alpha_{AT}f_{Bm}X_B^*}{\alpha_{AT}f_{Bm}X_B^* + \alpha_{BT}f_{Am}X_A^*} \quad (2)$$

In eq 1 and 2, if the activity coefficients f_{Am} and f_{Bm} are taken equal to unity, one obtains the expressions for ideal mixed micelles. For nonideal mixed micelles, the nonideality can be described by various expressions for the activity coefficients, borrowing from the thermodynamic treatments of liquid mixtures. One of the simplest expressions arises from the regular solution theory and involves only one model parameter

$$f_{Am} = \exp[\beta_{12}(1 - X_{Am})^2] \quad (3a)$$

$$f_{Bm} = \exp[\beta_{12}(1 - X_{Bm})^2] \quad (3b)$$

The parameter β_{12} is composition independent and its magnitude can be evaluated by fitting the experimental X_T^* vs. surfactant composition data to eq 1.^{13,15,16} Obviously, $\beta_{12} = 0$ for ideal mixed micelles.

In developing eq 1 and 2, the pseudophase approximation of micelles is invoked. Alternately, one can develop corresponding expressions based on monomer-micelle equilibrium or multiple-equilibria models. While the re-

sulting equations are thermodynamically consistent, they have little predictive power because the molecular features of the system are not explicitly incorporated into these treatments. Equations 1-3, or other essentially similar equations, summarize the theoretical descriptions of mixed micellization currently available in the literature. In the following section, we briefly review our molecular theory of micellization for a single-surfactant system. Subsequently, we present an extension of the treatment to binary-surfactant mixtures.

Molecular Theory of Micellization. A surfactant solution is made up of singly dispersed surfactant molecules, micelles of various sizes, and the solvent water. The micelles are spherical for small values of the aggregation number g . As the aggregation number increases to $g = g_s$, the radius of the sphere becomes equal to the extended length of the surfactant tail. Beyond this aggregation number g_s , the micelles are considered to be cylinders with hemispherical ends. The geometrical properties of the micelles and their dependence on the aggregation number g are given in the Appendix.

Aggregates of different types and sizes are considered as distinct chemical species each characterized by its own standard chemical potential. The solution is dilute, and, therefore, the mutual interactions between the species are considered negligible.

The minimization of the Gibbs energy of the total surfactant solution results in the following expression for the size distribution of micelles:^{1,3,18}

$$X_g = X_1^g \exp[-(\mu_g^\circ - g\mu_1^\circ)/kT] \quad (4)$$

Here, X_g is the mole fraction of aggregates of size g and X_1 is the mole fraction of the singly dispersed surfactant molecules. μ_1° and μ_g° are the standard Gibbs energies of the singly dispersed surfactant molecule and of the micelle of size g . The standard states are defined to correspond to infinitely dilute solution conditions. k is the Boltzmann constant, and T is the absolute temperature. The term $(\mu_g^\circ - g\mu_1^\circ)$ refers to the change in standard Gibbs energy when g isolated surfactant molecules are transferred from water to the micelle. Using an explicit expression for this Gibbs energy difference, one can calculate the size distribution of the micelles, the cmc, and all the size-dependent solution properties.

In our earlier studies on micellization,^{5,6} an expression for $(\mu_g^\circ - g\mu_1^\circ)$ has been developed by using a statistical thermodynamic approach and by taking into account all the important changes accompanying the transfer of the surfactant molecule from water to the micelle. The expression is presented below in a somewhat altered form paralleling the phenomenological expression introduced by Tanford:

$$[(\mu_g^\circ - g\mu_1^\circ)/kT] = g\Delta\mu_{HC/W}^\circ/kT + g\Delta\mu_{enth}^\circ/kT - g \ln(\Omega_{mic}/\Omega_{HC}) + g\sigma(a - a_0)/kT - g \ln(1 - a_p/a) + (g_{ion}^2 e^2 \beta / 2\epsilon k T r) [(1 + \kappa a_i)/(1 + \kappa a_i + \kappa r)] \quad (5)$$

The first term refers to the free energy change associated with the transfer of the hydrocarbon tail of the surfactant from water to a liquid hydrocarbon phase. However, the interior of the micelle is not identical with that of a bulk liquid hydrocarbon since there is some ordering of the tails inside the micelle. This is because the polar head group of the surfactant is constrained to remain at the micelle-water interface in contrast to a hydrocarbon chain whose both end segments are free to occupy any location in its bulk liquid phase. Free energy corrections for this ordering effect inside the micelle are represented by the second and the third terms. While the second term accounts for the

Table I. Some Molecular Constants for Surfactants

molecular formula	symbol	$a_p, \text{\AA}^2$	$a_0, \text{\AA}^2$	$a_i, \text{\AA}$	$\delta, \text{\AA}$
$\text{C}_{10}\text{H}_{21}(\text{CH}_3)_2\text{PO}$	C_{10}PO	44	21	0	0
$\text{C}_{10}\text{H}_{21}(\text{CH}_3)\text{SO}$	C_{10}SO	37	21	0	0
$\text{C}_{12}\text{H}_{25}(\text{CH}_2\text{CH}_2\text{O})_8$	C_{12}E_8	36	21	0	0
$\text{C}_8\text{H}_{17}\text{SO}_4\text{Na}$	SOS	17	17	1	2.3
$\text{C}_{10}\text{H}_{21}\text{SO}_4\text{Na}$	SDeS	17	17	1	2.3
$\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$	SDS	17	17	1	2.3
$\text{C}_{14}\text{H}_{29}\text{SO}_4\text{Na}$	STS	17	17	1	2.3
$\text{C}_7\text{H}_{15}\text{COOK}$	KC_8	11	11	1.35	1
$\text{C}_9\text{H}_{19}\text{COOK}$	KC_{10}	11	11	1.35	1
$\text{C}_{10}\text{H}_{21}\text{COOK}$	KC_{11}	11	11	1.35	1
$\text{C}_{11}\text{H}_{23}\text{COOK}$	KC_{12}	11	11	1.35	1
$\text{C}_{13}\text{H}_{27}\text{COOK}$	KC_{14}	11	11	1.35	1

enthalpic effects associated with the ordering, the third term represents the entropic effects. Here, Ω_{HC} and Ω_{mic} refer to the number of chain configurations possible when both ends of the chain are free as in liquid hydrocarbon (Ω_{HC}) and when one end is fixed as in a micelle (Ω_{mic}).

The fourth term represents the free energy of formation of an interface between the hydrocarbonaceous micellar core and water. σ is the macroscopic hydrocarbon-water interfacial tension, a is the surface area of the micellar core per amphiphile, and a_0 is the core area per amphiphile that is shielded from contact with water because of the presence of the polar head group.

Further, the formation of the micelle involves bringing the polar head groups of the surfactant into close proximity of one another at the micelle surface. Consequently, steric and electrostatic interactions among the head groups have to be considered. The steric repulsions are estimated by the fifth term which is written in a form suggested by the van der Waals equation of state. Here a_p is the effective cross-sectional area of the polar head group and is determined by its molecular geometry.

The last term accounts for the electrostatic interactions among the head groups at the micelle surface. It is written as equal to the work of charging a sphere of radius r with g_{ion} net charges and invoking the Debye-Hückel approximation. Obviously, $g_{\text{ion}} = 0$ for nonionic surfactants and $g_{\text{ion}} = g$ for ionic surfactants. In this term, e is the electronic charge, ϵ is the dielectric constant of water, r is the radius of the micelle surface where charges are located, κ is the reciprocal Debye length, a_i is the radius of the counterion of the surfactant, and β is an empirical constant which corrects for the overestimation of the electrostatic interactions by the Debye-Hückel approximation (see discussion below). The expression for calculating the interionic interactions in cylindrical micelles is given in the Appendix.

One may observe that the Gibbs energy of formation of micelles (eq 5) can be decomposed into interfacial and bulk components. The interfacial component includes the micellar core-water interfacial energy, the steric repulsions between head groups, and the electrostatic repulsions between head groups. The bulk component includes the remaining terms associated with the transfer of the surfactant tail from water to the micelle. The present theory explicitly shows that the size of the equilibrium micelles is determined by the interfacial component of the Gibbs energy while the cmc is determined by both the interfacial and the bulk components.^{19,20}

Estimation of Model Parameters. The values for various molecular constants involved in eq 5 are given in Table I for a number of surfactants. In addition to them, one needs estimates of the different parameters appearing

in eq 5. The magnitude of $\Delta\mu_{\text{HC/W}}^\circ$ is known from independent experimental data on the solubility of hydrocarbons in water.^{1,21-23} For an aliphatic hydrocarbon tail of length n_c with $(n_c - 1)$ methylene groups and a terminal methyl group, at 25 °C,

$$\Delta\mu_{\text{HC/W}}^\circ/kT = -(2.05 + 1.49n_c) \quad (6)$$

The enthalpic and entropic corrections accounting for the ordering inside the micelle are difficult to estimate precisely. Some rough estimation is possible on the basis of various approximate methods.^{5,6} Here, eq 7 is used to calculate this free energy correction for all surfactants with hydrocarbon tails. This equation ensures that the calculated incremental variation in the cmc of a homologous family of surfactants is in agreement with the measurements. At 25 °C,

$$[(\Delta\mu_{\text{enth}}^\circ/kT) - \ln(\Omega_{\text{mic}}/\Omega_{\text{HC}})] = (-0.5 + 0.24n_c) \quad (7)$$

The micellar core-water interfacial tension is similar to the interfacial tension between aliphatic hydrocarbons and water. Therefore, σ is taken to be 50 dyn/cm. The surfactant tail (which has a cross-sectional area of 21 Å²) is effectively shielded from water if the polar head group of the surfactant has a cross-sectional area a_p larger than 21 Å². In this case, the area a_0 equals 21 Å². If a_p is smaller than 21 Å², then the polar group shields only a part of the cross-sectional area of the tail. In this case $a_0 = a_p$.

As is well-known, the estimation of the electrostatic interaction energy among the ionic head groups at the micelle surface in the Debye-Hückel approximation is clearly unsatisfactory.^{1,4} On the other hand, the use of nonlinear Poisson-Boltzmann equation along with the consideration of discrete distribution of charges at the micelle surface requires involved numerical computations. Moreover, the unknown parameters present in such calculations contribute as much uncertainty in the estimates as that introduced by the Debye-Hückel approximation. Tanford noted that a self-consistent interpretation of experimental data is obtained, if one assumes the actual value of the electrostatic interaction energy to be about one-half the value given by the Debye-Hückel approximation.¹ Therefore, in order to calculate the interionic interaction energy the simple Debye-Hückel approximation may be used with the empirical constant β assigned a value close to 0.5. In the present paper, β is taken equal to 0.46. One may note that the equation used here (incorporating β) to calculate the interionic interaction energy is not built on the physical model of ion binding at the micelle surface. Therefore, it does not require any information on the fractional dissociation of ionic groups at the micelle surface. Neither is the equation capable of estimating this degree of dissociation.

The above treatment of single surfactant molecules has been used to calculate the cmc, the average micelle size, and the size distribution of micelles for about 40 single- and double-tailed surfactants with nonionic, anionic, cationic, and zwitterionic head groups.⁶ The calculated cmc's and the average micelle sizes are in satisfactory agreement with experimental data reported in the literature. Also, the calculated size distributions of micelles conform to the qualitative trends observed experimentally.⁶

Molecular Theory of Mixed Micellization. We consider an aqueous solution containing different types of surfactant molecules A, B, C, etc. In this solution, singly

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dispersed surfactant molecules of all the components and aggregates of all possible sizes as well as compositions are present. As before, the small aggregates are considered to be spherical while the larger ones are assumed to be cylindrical with hemispherical ends. Aggregates of different sizes and compositions are treated as distinct chemical species each characterized by its own standard chemical potential. The entire solution is dilute and hence the interactions among the various species present in the solution are negligible. The minimization of the Gibbs energy of the solution leads to the following equation for the size and the composition distribution of the multi-component mixed micelle:

$$X_g = X_{A1}^{g_A} X_{B1}^{g_B} X_{C1}^{g_C} \dots \exp[-(\mu_g^\circ - g_A \mu_{A1}^\circ - g_B \mu_{B1}^\circ - g_C \mu_{C1}^\circ - \dots)/kT] \quad (8)$$

In the above equation g is the aggregation number of the mixed micelle containing g_A, g_B, g_C, \dots molecules of type A, B, C, etc. ($g = g_A + g_B + g_C + \dots$). X_g is the mole fraction of the mixed micelle of size g in the total solution while X_{A1}, X_{B1}, X_{C1} , etc. are the mole fractions of the singly dispersed surfactant molecules. $\mu_g^\circ, \mu_{A1}^\circ, \mu_{B1}^\circ, \mu_{C1}^\circ$, etc. are the standard Gibbs energies of the mixed micelle of size g and the singly dispersed surfactants A, B, C, etc., defined at infinitely dilute solution conditions.

For a binary mixture of surfactants A and B, the micelle size and composition distribution can be calculated from the relation

$$X_g = X_{A1}^{g_A} X_{B1}^{g_B} \exp[(\mu_g^\circ - g_A \mu_{A1}^\circ - g_B \mu_{B1}^\circ)/kT] \quad (9)$$

Various averages of interest can be calculated from X_g . The average aggregation number $\langle g \rangle$ of the binary mixed micelle is

$$\langle g \rangle = \frac{\sum_{g_A, g_B} g X_g}{\sum_{g_A, g_B} X_g} \quad (10)$$

Note that both g and X_g are dependent on g_A and g_B . The average mole fraction of component A in the mixed micelles is calculated from

$$\langle X_{Am} \rangle = \frac{\sum_{g_A, g_B} g_A X_g}{\sum_{g_A, g_B} g X_g} \quad (11)$$

On the basis of the above two average quantities, one can estimate the average numbers of A and B molecules in the mixed micelle.

$$\langle g_A \rangle = \langle X_{Am} \rangle \langle g \rangle \quad (12)$$

$$\langle g_B \rangle = \langle g \rangle - \langle g_A \rangle \quad (13)$$

The total mole fraction α_{AT} of surfactant A in the binary surfactant mixture is given by

$$\alpha_{AT} = (X_{A1} + \sum_{g_A, g_B} g_A X_g) / (X_{A1} + \sum_{g_A, g_B} g_A X_g + X_{B1} + \sum_{g_A, g_B} g_B X_g) \quad (14)$$

The mole fraction of surfactant A in the singly dispersed surfactant molecules is denoted by α_{A1} and is

$$\alpha_{A1} = X_{A1} / (X_{A1} + X_{B1}) \quad (15)$$

Given an explicit expression for the standard Gibbs energy difference ($\mu_g^\circ - g_A \mu_{A1}^\circ - g_B \mu_{B1}^\circ$), one can calculate the cmc of the binary mixture, the average micellar size, the average micellar composition, and the size as well as the composition distribution of the mixed micelles, as a function of the composition variable α_{AT} or α_{A1} .

The physical factors contributing to the Gibbs energy of formation of the mixed micelle are the same as those associated with the formation of a single-component micelle. In the case of binary mixed micelles, the hydrocarbon tails of surfactants A and B are removed from water

and transferred to the nonpolar core of the mixed micelle. A hydrocarbon core-water interface is generated. The polar head groups of the two kinds of surfactants interact sterically as well as electrostatically at the micelle-water interface. All these contributions have been considered before for single-component surfactant systems. The only new contribution arises due to the mixing of two different kinds of surfactant molecules in mixed micelles. Taking into account all the above contributions, one may write an extension of eq 5 for binary mixed micelles:

$$\begin{aligned} [(\mu_g^\circ - g_A \mu_{A1}^\circ - g_B \mu_{B1}^\circ)/kT] = & g_A [\Delta \mu_{HC/W}^\circ/kT + \Delta \mu_{enth}^\circ/kT - \ln(\Omega_{mic}/\Omega_{HC})]_A + g_B [\Delta \mu_{HC/W}^\circ/kT + \Delta \mu_{enth}^\circ/kT - \ln(\Omega_{mic}/\Omega_{HC})]_B + g\sigma[a - (g_A a_{0A} + g_B a_{0B})/g]/kT - g \ln[1 - (g_A a_{pA} + g_B a_{pB})/ga] + \\ & [g_{ion}^2 e^2 \beta / 2 \epsilon k T r] [(1 + \kappa a_i)/(1 + \kappa a_i + \kappa r)] + [g_A \ln (g_A v_{0A}/(g_A v_{0A} + g_B v_{0B})) + g_B \ln (g_B v_{0B}/(g_A v_{0A} + g_B v_{0B}))] \quad (16) \end{aligned}$$

In eq 16, the first two terms account for the transfer from water to the micellar core of g_A and g_B hydrocarbon tails of surfactants A and B, respectively. The third term represents the micellar core-water interfacial energy. The steric repulsions among the polar head groups are accounted for by the fourth term. The electrostatic interactions among the charged head groups at the micelle surface are estimated by the fifth term. In this term, g_{ion} refers to the net number of charges at the micelle surface as was the case in eq 5 for single surfactants. One may note that for nonionic A-nonionic B mixtures, $g_{ion} = 0$. For nonionic A-ionic B mixtures, $g_{ion} = g_B$. For anionic A-anionic B mixtures and for cationic A-cationic B mixtures, $g_{ion} = g_A + g_B = g$. For anionic A-cationic B mixtures, g_{ion} is equal to the difference between g_A and g_B . Only the last term in eq 16 is an additional term not present in the case of single-component micelles. This term accounts for the entropy of internal mixing between the two components inside the micelle. Here v_{0A} and v_{0B} are the respective molecular volumes of the hydrocarbon tails of the surfactants A and B. Though the entropy of mixing is written here in terms of the respective volume fractions (Flory-Huggins estimate), the conventional expression involving the mole fractions can be used as well. For most surfactant mixtures examined in this paper v_{0A} and v_{0B} are of comparable magnitudes and hence the use of mole fractions or volume fractions provide practically equal estimates of the entropy of mixing.

Illustrative results based on the present theory are provided in the following section for various binary surfactant mixtures. It should be emphasized once again that eq 7 (which corrects the transfer free energy to account for the ordering of tails inside the micelle) and the constant β (which modifies the Debye-Hückel estimate of interionic interactions) are the only two empirical elements introduced in the theory for single-component micelles. Even they display remarkable generality in the sense that eq 7 is valid for all hydrocarbon surfactants while β is a single-valued constant equal to 0.46 independent of any surfactant. No new parameters are introduced in the theory for mixed micelles.

Results and Discussion

For all the binary mixtures examined in this study, the calculations reveal certain common characteristics related to the composition distribution of the mixed micelles. It is found that the extent of dispersion in the composition distribution of the mixed micelles is very small. This implies that for any given total concentration and overall

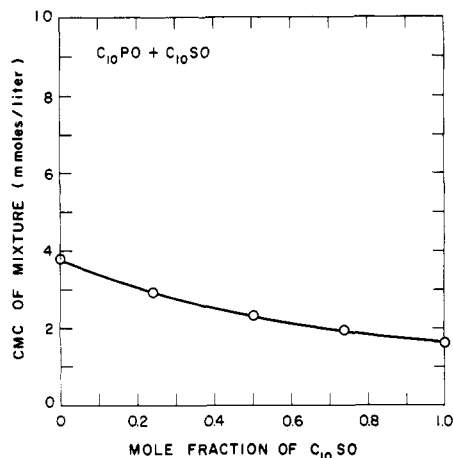


Figure 1. Cmc's of mixtures of $C_{10}PO$ and $C_{10}SO$. The plotted points are experimental data.¹⁵ The solid line represents the results from the molecular theory. The solid line also corresponds to the mixed micelle equation, eq 1, with $\beta_{12} = 0$.

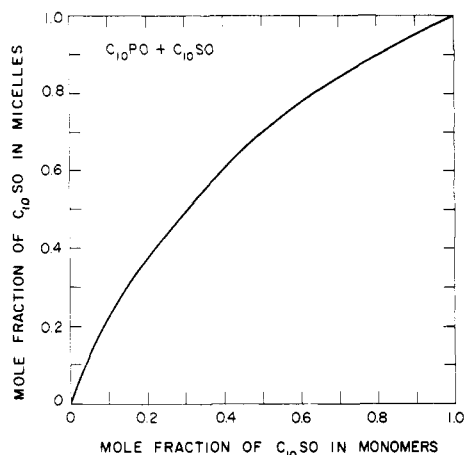


Figure 2. The composition of the mixed micelle as a function of the composition of the singly dispersed surfactant molecules for $C_{10}PO$ and $C_{10}SO$ mixtures. The solid line is the prediction of the molecular theory and it also corresponds to the mixed micelle equation, eq 2, with $\beta_{12} = 0$.

composition of the surfactant mixture, all the mixed micelles are of practically identical composition. Further, the average composition of the mixed micelles calculated using eq 11 has only a weak dependence on the total concentration of the surfactant mixture. For concentrations between the cmc and 100 times the cmc, the calculated variation in the average micelle composition $\langle X_{Am} \rangle$ is less than 0.02. The results reported here on the average micelle compositions correspond to surfactant concentrations of about 10 cmc. For all the binary mixtures examined, the calculated micelle size distributions are very narrow. Also, the average aggregation numbers increase by less than 4% in the concentration range between the cmc and 100 times the cmc. The results reported here on the average aggregation numbers correspond to surfactant concentrations of about 10 times cmc. Specific results obtained for various binary surfactant mixtures are discussed below.

Nonionic A-Nonionic B Mixtures. The aggregation behavior of binary mixtures of decyl methyl sulfoxide, $C_{10}SO$ (A), and decyl dimethyl phosphine oxide, $C_{10}PO$ (B), has been investigated and the results are presented in Figures 1-4. The two nonionic surfactants have identical hydrocarbon tails and differ only in the size of their polar head groups. The cmc of the mixture as a function of the total composition is plotted in Figure 1. The calculated cmc's agree very well with the available¹⁵ experimental

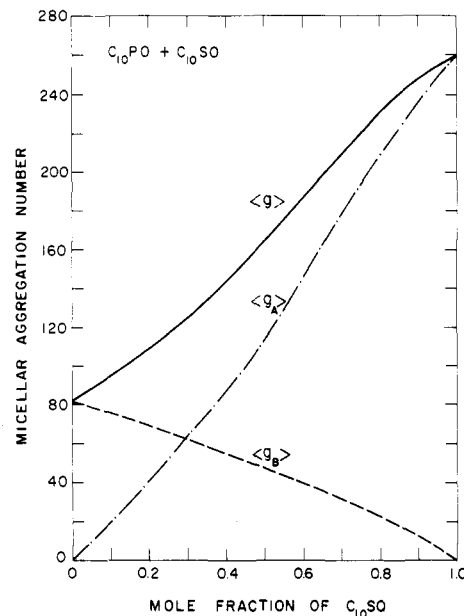


Figure 3. Average aggregation number $\langle g \rangle$ of the mixed micelle and the average numbers $\langle g_A \rangle$ and $\langle g_B \rangle$ of the constituent $C_{10}SO$ (A) and $C_{10}PO$ (B) molecules calculated from the molecular theory.

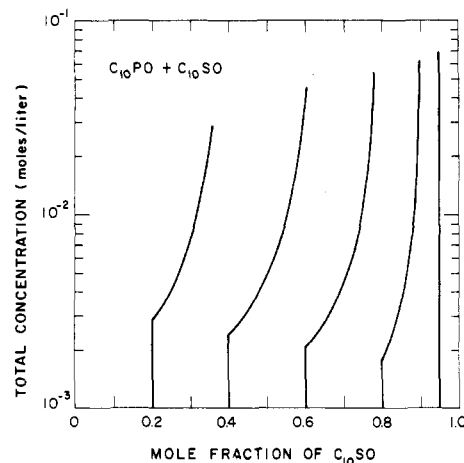


Figure 4. Loci of constant composition of singly dispersed molecules in the total concentration vs. total composition space for $C_{10}PO$ - $C_{10}SO$ mixtures. The lines represent the results from the molecular theory.

data. The mixture cmc's have also been calculated on the basis of the classical thermodynamic relation (eq 1) and assuming ideality, i.e., $f_{Am} = f_{Bm} = 1$. The results for the ideal mixture model coincide with the results of the present molecular theory.

In Figure 2, the average composition of the mixed micelle is related to the composition of the monomers in equilibrium with it. Again the results from the present theory and those obtained from the classical thermodynamic relation (eq 2) for ideal mixtures coincide. The average aggregation number $\langle g \rangle$ of the mixed micelle and the average numbers $\langle g_A \rangle$ and $\langle g_B \rangle$ of the constituent surfactant molecules have been calculated from the present theory and the results are shown in Figure 3 as a function of the composition of the singly dispersed surfactants. It is seen that the average aggregation numbers $\langle g \rangle$, $\langle g_A \rangle$, and $\langle g_B \rangle$ change approximately linearly with composition. In Figure 4, the overall composition α_{AT} of the surfactant mixture in equilibrium with a given composition α_{A1} of the singly dispersed surfactant is shown for various total concentrations of the surfactant mixture. Each line in the figure corresponds to a fixed composition of the singly

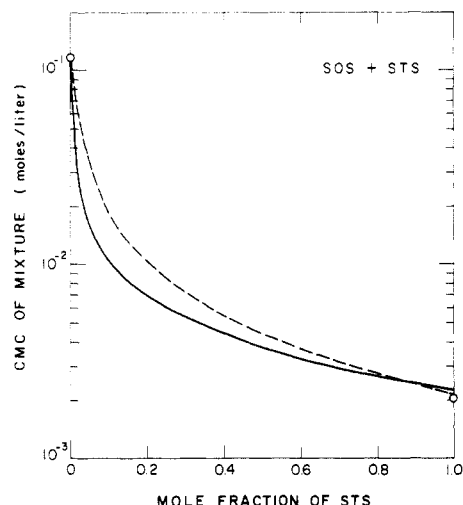


Figure 5. Cmc's of mixtures of SOS and STS. The solid line is calculated from the molecular theory and the dotted line is calculated for the ideal mixed micelle (eq 1 with $\beta_{12} = 0$).

dispersed molecules. At concentrations below the cmc, the total concentration is identical with the concentration of the monomeric molecules. Hence, the total composition α_{AT} is the same as the monomeric composition α_{AI} . Given any total concentration and overall composition of the mixture, one can find the composition α_{AI} of the singly dispersed molecules from this figure. Corresponding to this value of α_{AI} , the cmc of the mixture can be found from Figure 1, the average micellar composition from Figure 2, and the average size of the micelle from Figure 3.

One may note that at $\alpha_{AT} = 0.95$, the composition of the monomers and of the total surfactant system remain identical for all total concentrations of the surfactant mixture, $\alpha_{AI} = \alpha_{AT} = \langle X_{Am} \rangle = 0.95$. This composition corresponds to the so-called azeotropic condition.^{14,17} One may note that the occurrence of azeotropy implies some nonideality in the mixed micellar system. Although such nonideality is not revealed by the mixture cmc data, its presence is evident from the results shown in Figure 4. The small nonideality arises from the difference in the sizes of the polar head groups of the two surfactants. Currently, no experimental data on the size of the mixed micelles and on the azeotropic composition are available for comparison against the theoretical predictions. Such data, which could be obtained on the basis of known experimental techniques, would be very useful for the development and testing of molecular theories.

Ionic A-Ionic B Mixtures. The micellization behavior of sodium tetradecyl sulfate, STS (A), and sodium octyl sulfate, SOS (B), mixtures have been calculated and the results are presented in Figures 5-7. The cmc of the mixture calculated from this molecular theory is compared in Figure 5 against that calculated from eq 1 for ideal mixtures. In Figure 6, the micellar composition is plotted as a function of the composition of the monomeric surfactant in equilibrium with it. Also shown for comparison is the corresponding relation obtained from eq 2 for ideal mixtures. The composition of the total surfactant mixture in equilibrium with a given composition of the monomeric surfactant is shown in Figure 7 at various total concentrations of the surfactant mixture. Both Figures 6 and 7 show that the micelles incorporate a larger proportion of the more surface active (i.e., lower cmc) STS molecules when compared to the composition of the monomers in equilibrium with the micelles.

In addition to the STS and SOS mixtures, binary mixtures of two other alkyl sulfates, sodium decyl sulfate

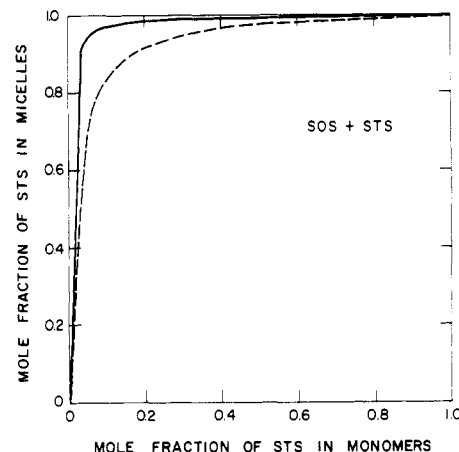


Figure 6. The composition of the mixed micelle as a function of the composition of the singly dispersed molecules for the SOS/STS mixtures. The solid line is calculated by the molecular theory while the dotted line is calculated for the ideal mixed micelle (eq 2 with $\beta_{12} = 0$).

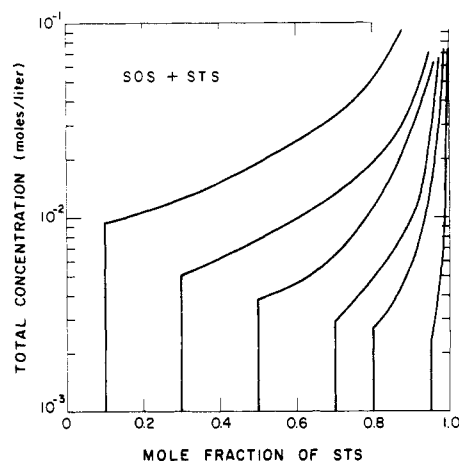


Figure 7. Loci of constant monomeric composition in the total concentration vs. total composition space for the SOS-STS system. The lines are computed from the molecular theory.

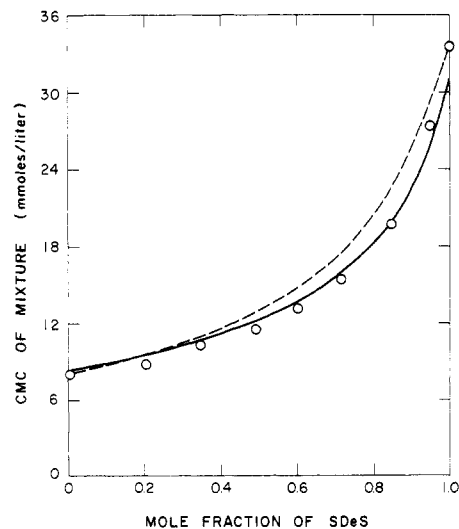


Figure 8. Cmc's of mixtures of SDeS and SDS. The plotted points are experimental data²⁴ and the solid line corresponds to the present theory. The dotted line is calculated for ideal mixed micelles, taking $\beta_{12} = 0$ in eq 1.

(SDeS) and sodium dodecyl sulfate (SDS), have been investigated. In Figure 8, the cmc values predicted by the present theory are compared against the experimental data of Mysels and Otter.²⁴ These authors used their con-

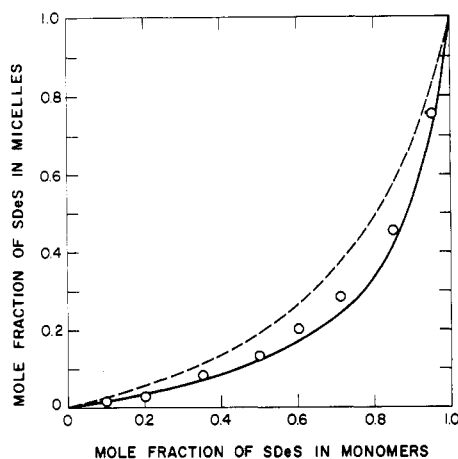


Figure 9. Average composition of mixed micelles as a function of the composition of the singly dispersed surfactant for SDeS-SDS mixtures. The continuous line is calculated from the present theory while the dotted line represents the ideal mixed micelle equation, eq 2, with $\beta_{12} = 0$. The points are estimates obtained by Mysels and Otter,²⁴ using their measured conductivity data.

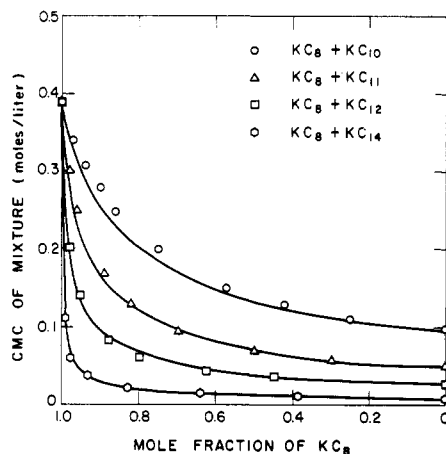


Figure 10. Cmc's of mixtures of various potassium soaps. The plotted points are experimental data⁸ and the solid lines are predicted by the present molecular theory.

ductivity data to also estimate the average composition of the mixed micelles. Their estimates are compared in Figure 9 to the results yielded by the present theory. Also shown in Figures 8 and 9 are the results anticipated for ideal mixed micelles. One may observe that some nonideality is exhibited by the binary mixture of SDeS and SDS even though the two molecules differ from one another by merely two methylene groups. The results obtained from the present theory are in satisfactory agreement with the experimental cmc as well as micelle composition data.

The calculated and measured⁸ cmc values of binary mixtures of potassium soaps are compared in Figure 10. Mixtures of potassium octanoate (KC_8) with potassium decanoate (KC_{10}), potassium undecanoate (KC_{11}), potassium dodecanoate (KC_{12}), and potassium tetradecanoate (KC_{14}) have been considered in this comparison. Evidently, the agreement between the measured cmc values and the values calculated from the present molecular theory is satisfactory.

Ionic-Nonionic Mixtures. In the homoionic systems considered above, the deviations from ideality exhibited by the mixture cmc values are not very large. But large deviations occur in systems of molecules containing polar heads of differing ionic characteristics. The aggregation

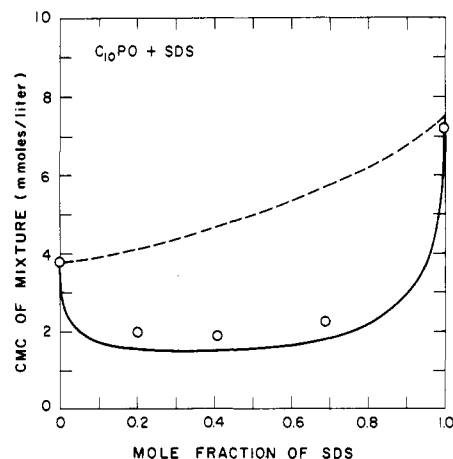


Figure 11. Cmc's of mixtures of SDS and $C_{10}PO$ in the presence of 1 mM Na_2CO_3 . The plotted points are measured data¹⁵ and the solid line corresponds to the predictions from the present theory. The dotted line is calculated for an ideal mixed micelle, $\beta_{12} = 0$ in eq 1. Equation 1 has been shown to describe the experimental data well if the regular solution model parameter $\beta_{12} = -3.7$.¹⁵

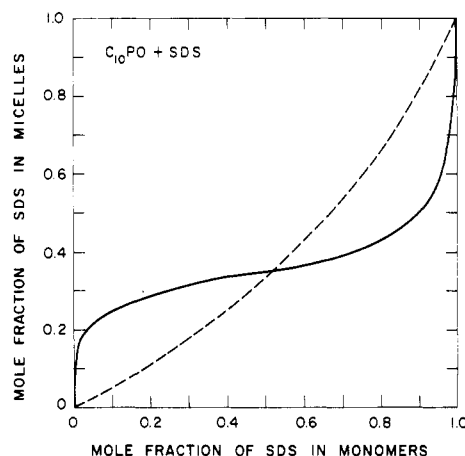


Figure 12. Composition of the mixed micelles as a function of the composition of the monomeric surfactant for the SDS- $C_{10}PO$ system. The solid line is based on the molecular theory while the dotted line is for ideal mixed micelles.

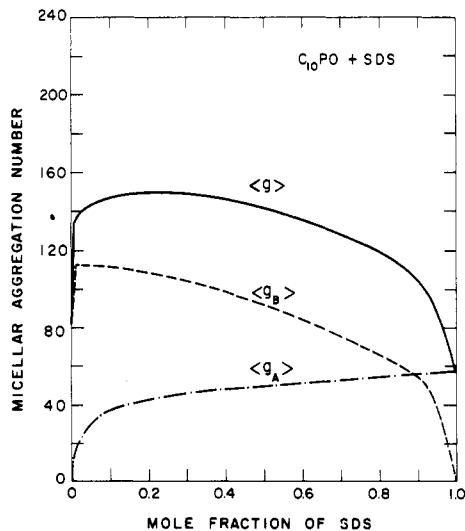


Figure 13. Average aggregation number (\bar{g}) of mixed micelles and the average numbers (\bar{g}_A) and (\bar{g}_B) of the components SDS (A) and $C_{10}PO$ (B). All the lines are based on the present theory.

properties of mixtures of anionic sodium dodecyl sulfate, SDS (A), and nonionic decyldimethylphosphine oxide,

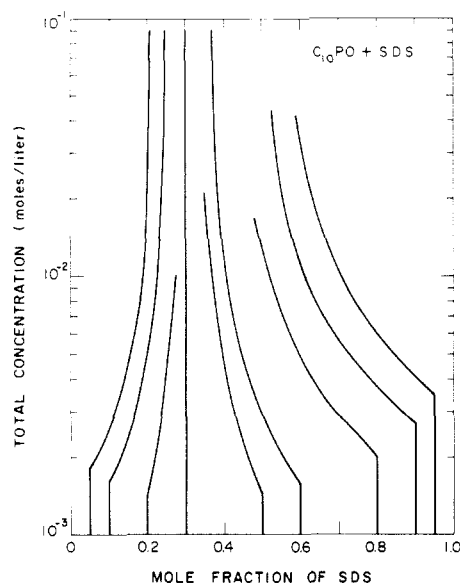


Figure 14. Computed loci of constant composition of singly dispersed molecules in the space of total concentration vs. total composition for the $C_{10}PO$ -SDS system.

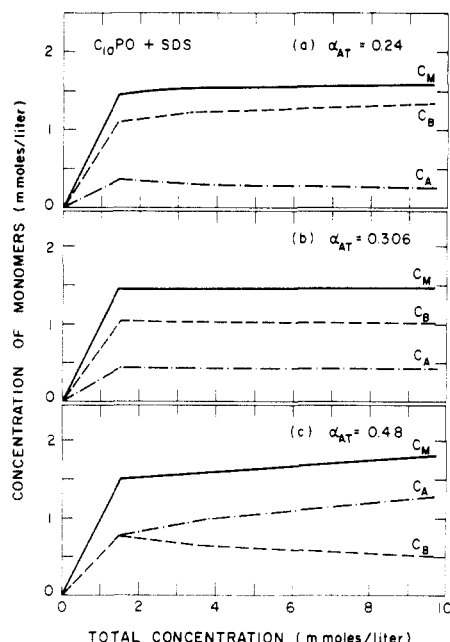


Figure 15. Calculated dependence of the concentration of singly dispersed molecules on the total surfactant concentration for the $C_{10}PO$ -SDS system. C_A refers to the concentration of SDS, C_B to that of $C_{10}PO$, and $C_M = C_A + C_B$. Plot b corresponds to the azeotropic composition for this binary mixture.

$C_{10}PO$ (B), have been calculated and the results are summarized in Figures 11–15. The cmc's of the mixture calculated from the present theory are closer to the measured¹⁵ values compared to the cmc's calculated from eq 1 for ideal mixtures (Figure 11). The data show that significant nonideality is exhibited by this binary mixture. Figure 12 shows the average composition of the micelle as a function of the composition of the monomers in equilibrium with it. The average aggregation number of the mixed micelle is plotted in Figure 13 as a function of the composition of the singly dispersed surfactant molecules in equilibrium. The results are in marked contrast to those seen in Figure 3. For this ionic-nonionic mixture, the size of the mixed micelles over most of the composition range is larger than that of the two pure component micelles. This results from the fact that in mixed micelles, the in-

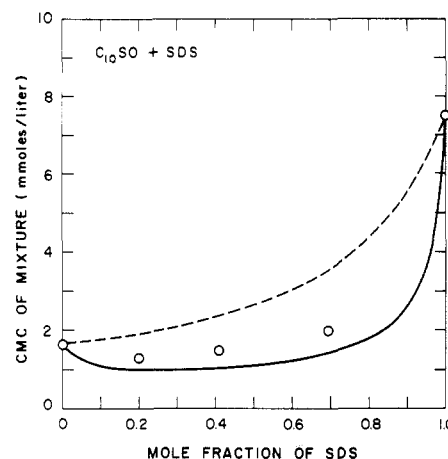


Figure 16. Cmc's of mixtures of $C_{10}SO$ and SDS in 1 mM Na_2CO_3 . The plotted points are experimental data.¹⁵ The solid line is predicted by the present molecular theory. The dotted line corresponds to the ideal mixed micelle equation, eq 1, with $\beta_{12} = 0$. The experimental data are described well by eq 1 if $\beta_{12} = -2.4$.¹⁵

corporation of SDS results in decreased steric interactions compared to pure $C_{10}PO$ micelles. Similarly, the incorporation of $C_{10}PO$ results in decreased electrostatic interactions compared to pure SDS micelles. As a result of the reduction in the repulsive head group interactions occurring at the micellar surface, the mixed micelles can be of larger size than either of the pure component micelles and the mixture cmc can be lower than that of either of the pure components, for a considerable range of mixture composition. Figure 14 shows lines of constant monomeric composition in the total concentration vs. total surfactant composition diagram. An azeotropic condition is revealed at a composition of $\alpha_{AI} = \alpha_{AT} = \langle X_{Am} \rangle = 0.306$, where A refers to the anionic SDS. The variation of the monomeric surfactant concentrations as a function of the total surfactant concentration is shown in Figure 15 for the azeotropic composition as well as for two other total compositions lying on either side of the azeotropic composition. For the azeotropic composition the concentrations of monomeric A, monomeric B, and the total monomers remain constants when the total surfactant concentration is increased beyond the mixture cmc. For the other two compositions, the monomeric concentrations either increase or decrease as the total surfactant concentration is increased beyond the mixture cmc.

Similar results are shown for the binary mixture sodium dodecyl sulfate, SDS (A), and decyl methyl sulfoxide, $C_{10}SO$ (B), in Figures 16–18 and for the binary mixture sodium dodecyl sulfate, SDS (A), and dodecyl octaethylene oxide, $C_{12}E_8$ (B), in Figures 19–21. The mixture cmc values displaying large nonideality are shown in Figures 16 and 19. For both binary surfactant systems, there is reasonable agreement between the measured^{11,15} cmc values and the values predicted by the molecular theory. The cmc values computed on the basis of the ideal mixed micelle equation (eq 1) deviate quite substantially from the experimental data. Figures 17 and 20 show the composition of the mixed micelles in equilibrium with a given composition of the singly dispersed surfactants for the two binary mixtures. The relation between the total surfactant composition and the composition of the monomeric surfactants at various total surfactant concentrations is plotted in Figures 18 and 21 for the two anionic-nonionic mixtures. One may observe the existence of an azeotropic composition at $\alpha_{AT} = 0.20$ for the SDS- $C_{10}SO$ and at $\alpha_{AT} = 0.04$ for the SDS- $C_{12}E_8$ system.

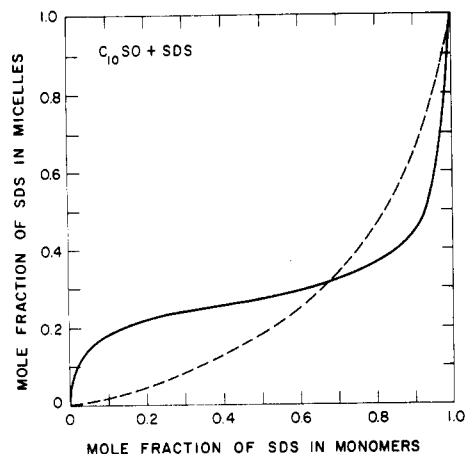


Figure 17. Composition of the mixed micelle as a function of the composition of the singly dispersed molecules for the $C_{10}SO$ -SDS system. The solid line corresponds to the molecular theory and the dotted line is calculated for the ideal mixed micelle.

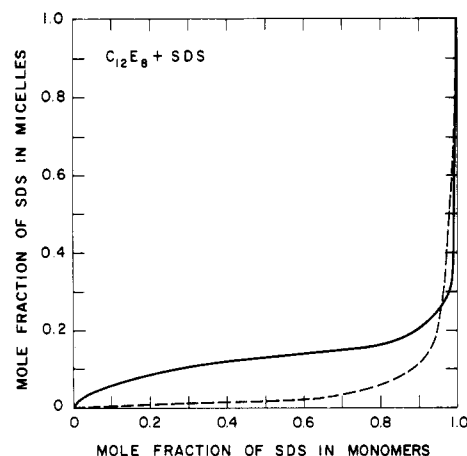


Figure 20. Composition of the mixed micelle as a function of the composition of the singly dispersed molecules for the $C_{12}E_8$ -SDS mixtures. The solid line corresponds to the results from the molecular theory while the dotted line is for ideal mixed micelles.

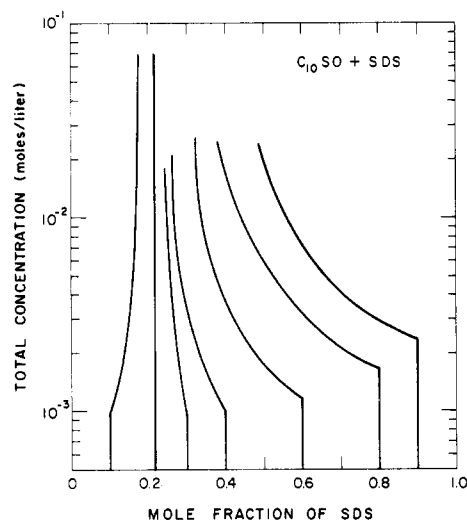


Figure 18. Calculated loci of constant composition of singly dispersed molecules in the total concentration vs. total composition space for the $C_{10}SO$ -SDS system.

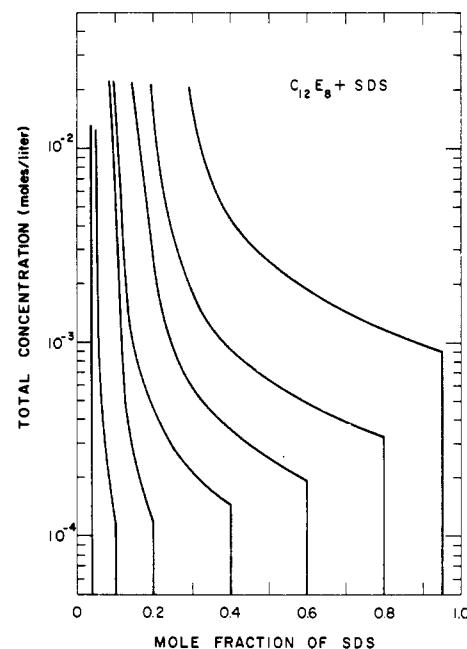


Figure 21. Calculated loci of constant composition of singly dispersed molecules in the total concentration vs. total composition space for the $C_{12}E_8$ -SDS system.

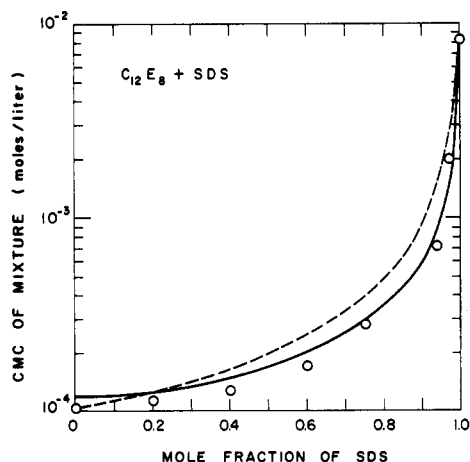


Figure 19. Cmc's of mixtures of $C_{12}E_8$ and SDS. The plotted points are experimental data¹¹ and the solid line shows the predictions of the molecular theory. The dotted line corresponds to the ideal mixed micelle equation, eq 1, with $\beta_{12} = 0$.

Origin of Nonideality. In the framework of the present theory, a molecular interpretation of the nonideal behavior exhibited by the binary surfactant mixtures can be provided. The Gibbs energy of formation of a mixed

micelle consists of an interfacial component and a bulk component. The interfacial component includes the micellar core-water interfacial energy, the steric repulsions among head groups, and the electrostatic interactions among the head groups. The bulk component involves the transfer of the surfactant tail from water to the micelle interior. In addition, there is a contribution due to the entropy of internal mixing in the micelles. Therefore, one may decompose the Gibbs energy of formation of a mixed micelle of components A and B into

$$\Delta\mu_{A+B}^{\circ} = \Delta\mu_{A+B}^{\circ}(\text{bulk}) + \Delta\mu_{A+B}^{\circ}(\text{interface}) + \Delta\mu_{A+B}^{\circ}(\text{entropy of mixing}) \quad (17)$$

The Gibbs energy of formation of a mixed micelle can also be written in terms of the Gibbs energies of formation of the two pure component micelles and an excess free energy accounting for nonidealities, in addition to the above mentioned entropy of mixing contribution,

$$\Delta\mu_{A+B}^{\circ} = X_{Am}\Delta\mu_A^{\circ} + X_{Bm}\Delta\mu_B^{\circ} + \Delta\mu_{A+B}^{\circ}(\text{entropy of mixing}) + \Delta\mu_{A+B}^{\circ}(\text{excess}) \quad (18)$$

If the Gibbs energy of formation of the mixed micelle (excluding the contribution due to entropy of internal mixing) is a linear combination of the Gibbs energies of formation of single-component micelles weighted by the micellar composition, then the excess free energy of formation of the mixed micelle is zero. Consequently, the micellization behavior of the surfactant mixture is that of an ideal mixture. Any deviation in the Gibbs energy of formation of the mixed micelle from the composition-weighted, linear additive estimate is an excess free energy and accounts for the nonideality of the mixed micellar system. One may observe from eq 16 that the bulk component of the Gibbs energy of formation of the mixed micelle is a linear combination of the bulk components of the Gibbs energies of formation of the single-component micelles.

$$\Delta\mu^\circ_{A+B}(\text{bulk}) = X_{Am}\Delta\mu^\circ_A(\text{bulk}) + X_{Bm}\Delta\mu^\circ_B(\text{bulk}) \quad (19)$$

Therefore, the bulk component does not account for any nonideal behavior exhibited by the mixed micellar systems. In contrast, the interfacial component of the Gibbs energy of formation of the mixed micelle is a nonlinear function of the micelle composition and hence is the source of the excess free energy:

$$\Delta\mu^\circ_{A+B}(\text{interface}) = X_{Am}\Delta\mu^\circ_A(\text{interface}) + X_{Bm}\Delta\mu^\circ_B(\text{interface}) + \Delta\mu^\circ_{A+B}(\text{excess}) \quad (20)$$

It is this excess energy arising from the interfacial component that gives rise to the observed nonideal behavior of mixed surfactant systems. On this basis, one can now interpret the micellization behavior of all binary surfactant mixtures examined in this paper.

When two nonionic surfactants have identical tail lengths, but differ in the size of the polar head groups ($C_{10}PO-C_{10}SO$), the steric interactions among the head groups at the micellar surface are altered as a function of the composition of the micelle. Also depending upon the size of the polar groups there can be a variation in the micellar core-water interfacial energy as well (though not for $C_{10}PO$ and $C_{10}SO$ both of which have head group areas a_p larger than 21 \AA^2 and hence areas a_0 equal to 21 \AA^2). These give rise to an excess free energy of formation of the mixed micelle. However, the excess free energy due to steric interactions is very small for this system. Therefore, the extent of nonideality is hardly perceptible for the $C_{10}PO-C_{10}SO$ mixtures.

When two surfactants with identical polar heads and different tail lengths are considered (STS-SOS), the volume of the mixed micelle at any total aggregation number changes as a function of the micelle composition. This implies that the interfacial area per amphiphile depends upon the composition of the micelle. The variation in the area with micelle composition gives rise to changes in all the interfacial interactions and hence in the interfacial component of the Gibbs energy of formation of the mixed micelle. As mentioned before, the interfacial component has a nonlinear dependence on the micelle composition and thus gives rise to an excess free energy and the nonideal behavior of the mixed micellar system. This is seen in the case of the STS-SOS system. Since the electrostatic interaction energy is larger in magnitude compared to the steric interaction energy, the excess free energy for the STS-SOS mixture is larger than the excess free energy arising from steric interactions in the nonionic $C_{10}PO-C_{10}SO$ mixture. Consequently, the nonideal behavior of the STS-SOS system is more pronounced compared to that of the $C_{10}PO-C_{10}SO$ system.

When binary mixtures of ionic and nonionic surfactants having the same hydrocarbon tails are considered, the

volume of the mixed micelle and hence the surface area per amphiphile do not change when the composition of the micelle is altered. The anionic SDS-nonionic $C_{12}E_8$ mixture is a typical example. However, the fraction of ionic head groups at the micellar surface decreases as the fraction of the ionic surfactant in the micelle is decreased. This causes considerable alteration in the magnitude of the electrostatic interaction energy. In addition, if the polar groups have different cross-sectional areas, then the steric interaction energy as well as the micellar core-water interfacial energy are modified by changes in the micellar composition. All these account for the excess free energy in this type of binary mixture. Since the electrostatic interaction energy is significantly modified by the changes in the fraction of ionic head groups at the micelle surface, the magnitude of the excess free energy is quite substantial in this case compared to the previous example of the STS-SOS system. Consequently, the deviation from ideality is larger for the SDS- $C_{12}E_8$ mixture. In ionic-nonionic mixtures like SDS- $C_{10}SO$ and SDS- $C_{10}PO$, in addition to the effects discussed above, the volume of the mixed micelle and hence the area per amphiphile is also dependent on the composition of the micelle. Therefore, the excess free energy in this case is augmented by this additional factor compared to the SDS- $C_{12}E_8$ system. As a result, very pronounced nonideal micellization behavior is exhibited by these binary mixtures.

Conclusions

No theory is available in literature to calculate a priori the properties of mixed surfactant systems, even with the knowledge of the properties of the single-component surfactants. In this paper, a molecular theory for mixed micelles is developed which allows one to calculate the mixed cmc and the size and the composition distribution of the micelles as well as the average size and the average composition of the micelles. The theory is built on an explicit expression for the Gibbs energy of formation of the mixed micelle derived from molecular thermodynamic considerations. The composition dependence of this Gibbs energy governs the nature of nonideality displayed by the mixed surfactants. The Gibbs energy of micelle formation can be decomposed into bulk and interfacial components. The bulk component arises from the transfer of the surfactant tail from water into the micelle. This component is shown to be linearly dependent on micelle composition and hence with no influence on the nonideal behavior of mixed micelles. In contrast, the interfacial component, which arises from the micellar core-water interfacial energy as well as the steric and electrostatic repulsions between head groups at the micelle surface, has a nonlinear dependence on the micelle composition. This interfacial component thus solely contributes to the excess Gibbs energy and thereby determines the extent of nonideality in the aggregation properties of surfactant mixtures. Illustrative calculations have been performed for various types of binary mixtures, viz., mixtures of two nonionic surfactants, mixtures of two ionic surfactants, and mixtures of an ionic and a nonionic surfactant. The calculations show that the composition dependence of the interfacial interactions is most significant for the ionic-nonionic binary mixtures. Consequently, the nonideal behavior of such mixtures is very pronounced. The results predicted by the present molecular theory are found to be in satisfactory agreement with the available experimental data.

Appendix

Geometrical Properties of Mixed Micelles Containing g_A Molecules of A and g_B Molecules of B. For

single-component micelles, let $g_B = 0$. For spherical micelles

$$r_0 = [3(g_A v_{0A} + g_B v_{0B})/4\pi]^{1/3}$$

$$r_0 \leq (g_A l_{0A} + g_B l_{0B})/(g_A + g_B) \quad a = 4\pi r_0^2/(g_A + g_B)$$

$$r = r_0 + \delta$$

For cylindrical micelles

$$r_0 = (g_A l_{0A} + g_B l_{0B})/(g_A + g_B)$$

$$L = (g_A v_{0A} + g_B v_{0B} - 4\pi r_0^3/3)/\pi r_0^2$$

$$a = (4\pi r_0^2 + 2\pi r_0 L)/(g_A + g_B) \quad r = r_0 + \delta$$

Electrostatic Interactions for Cylindrical Micelles.

For single-component micelles, let $g_B = 0$. For spheres of radius r and containing g_{ion} charges on the surface

$$[(\mu_g^\circ - g_A \mu_{A1}^\circ - g_B \mu_{B1}^\circ)/kT]_{\text{electrostatic}} = \left(\frac{g_{ion}^2 e^2 \beta}{2\epsilon k T r} \right) \left(\frac{1 + \kappa a_i}{1 + \kappa a_i + \kappa r} \right)$$

For infinite cylinders (with flat ends) of length L , radius r , and containing g_{ion} charges on the surface

$$[(\mu_g^\circ - g_A \mu_{A1}^\circ - g_B \mu_{B1}^\circ)/kT]_{\text{electrostatic}} = \left(\frac{g_{ion}^2 e^2 \beta}{\epsilon k T L} \right) \left[\frac{K_0(\kappa r)}{\kappa r K_1(\kappa r)} + \ln \left(1 + \frac{a_i}{r} \right) \right]$$

K_0 and K_1 are modified Bessel functions of order 0 and 1, respectively.

One may note that the electrostatic interaction energy per molecule on a spherical surface is different from that on an infinite cylindrical surface.

(a) For spherical micelles, the equation for spheres is used.

(b) For large cylindrical micelles ($L/2r_0 > 3$) with hemispherical ends, the equation for the infinite cylinder is used for the cylindrical part of the micelle while the equation for the sphere is used for the two hemispherical ends of the micelle.

(c) For cylindrical micelles which are not much larger than the largest spherical micelle, the equation for infinite cylinders will be inappropriate for the cylindrical part because of the sharp discontinuity in the estimates for spheres and for infinite cylinders. Therefore, in order to calculate the electrostatic interaction energy for small cylinders ($L/2r_0 < 3$), the equation for spheres is used with the understanding that the surface area of this equivalent sphere will be identical with the surface area of the small cylinder with hemispherical ends.

$$[(\mu_g^\circ - g_A \mu_{A1}^\circ - g_B \mu_{B1}^\circ)/kT]_{\text{electrostatic}} = \left(\frac{g_{ion}^2 e^2 \beta}{2\epsilon k T r_{\text{eqv}}} \right) \left(\frac{1 + \kappa a_i}{1 + \kappa a_i + \kappa r_{\text{eqv}}} \right)$$

where

$$r_{\text{eqv}} = \left[\frac{1}{4\pi} (4\pi r^2 + 2\pi r L) \right]^{1/2}$$

The length to diameter ratio of 3 chosen to differentiate between small and large cylinders is arbitrary. Other

values (say 0.5 and above) can be used for this ratio, without affecting any of the results discussed in this paper.

Notations and Definitions

a	surface area of the micellar core per amphiphile
a_p	cross-sectional area of the polar head group of the surfactant
a_0	surface area per molecule of the micelle shielded from contact with water by the polar head group
a_i	radius of the counterion for an ionic surfactant
C_1	molar concentration of the singly dispersed ionic surfactant
C_{add}	molar concentration of any added electrolyte
e	electronic charge ($=4.8 \times 10^{-10}$ esu)
f_{Am}	activity coefficient of A in the mixed micelle
f_{Bm}	activity coefficient of B in the mixed micelle
g	aggregation number of the micelle
g_s	aggregation number of the largest spherical micelle
g_{ion}	net number of ionic groups at the micellar surface
k	Boltzmann constant ($=1.38 \times 10^{-16}$ erg/K)
l_0	length of the hydrocarbon tail of the surfactant ($=1.50 + 1.26n_c$ Å)
L	length of the cylindrical portion of cylindrical micelles with hemispherical ends
n_c	number of CH_2 and CH_3 groups in the hydrocarbon tail of surfactant
r_0	radius of the hydrocarbon core of the micelle
r	radius of the micelle surface at which ionic charges are located ($=r_0 + \delta$)
T	absolute temperature ($=298^\circ\text{K}$ in the present calculations)
v_0	molecular volume of the hydrocarbon tail of the surfactant ($=27 \text{ Å}^3$ for the CH_2 group and 54 Å^3 for the CH_3 group)
X_A^*	cmc of pure surfactant A in mole fraction units
X_B^*	cmc of pure surfactant B in mole fraction units
X_T^*	cmc of the binary surfactant mixture of A and B in mole fraction units
X_{A1}	mole fraction of monomeric A molecules
X_{B1}	mole fraction of monomeric B molecules
X_{Am}	mole fraction of A molecules in the mixed micelle ($=g_A/g$)
X_{Bm}	mole fraction of B molecules in the mixed micelle ($=g_B/g$)
α_{A1}	fraction of A molecules in the singly dispersed surfactant
α_{AT}	fraction of A molecules in the total surfactant mixture
β	a constant which modifies the Debye-Hückel estimate of interionic interaction energy ($=0.46$)
β_{12}	regular solution model parameter
δ	distance of separation between the micellar core and the surface at which ionic charges are located
ϵ	dielectric constant of water ($=80$)
κ	reciprocal Debye length ($= (C_1 + C_{\text{add}})^{1/2} / (3.08 \times 10^{-8}) \text{ cm}^{-1}$ at 25°C)
σ	macroscopic hydrocarbon-water interfacial tension ($=50 \text{ dyne/cm}$)
$\Delta\mu^\circ$	standard Gibbs energy of formation of the micelle
μ°	standard chemical potential of specie referred to infinitely dilute solution conditions