Investigation of Mixing in Binary Surfactant Solutions by Surface Tension and Neutron Reflection: Strongly Interacting Anionic/Zwitterionic Mixtures

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Aqueous solutions of the strongly interacting anionic/zwitterionic surfactant mixture of sodium dodecyl sulfate (SDS) and dodecyl dimethylamino acetate (C_{12}betaine) have been studied by means of surface tension and neutron reflection. The mixed critical micelle concentrations (cmc) were used to derive the interaction parameter β^M for micellization, which was found to be large and negative. It was also found to be composition dependent and therefore not to obey the first-order approximation for the activity coefficients in the pseudo-phase separation approximation. The temperature dependence of the mixed cmc gave the thermodynamic excess functions for micellization; S^E was found to be positive over most of the composition range. Application of the pseudo-phase separation model to surface tension data was used to show that the interaction parameter β^σ in the surface layer is similarly large and negative. However, direct measurement of the surface concentrations using neutron reflection disagree with the predictions of the pseudo-phase separation model and indicate that β^σ, although negative, is much smaller in magnitude. The structure of the mixed layer was determined at three compositions and found to be significantly dehydrated in comparison with layers of the single surfactants, which may explain the positive excess entropies observed for both micellization and surface mixing. It is also suggested that changes of hydration on mixing invalidate the use of the pseudo-phase separation model and may be responsible for the deviations from the first-order model observed for both micellization and surface interaction.

Introduction

Nonideality in surface mixtures has been observed in micelles and at interfaces for several different interacting species. Important properties, such as surface tension, micellization, and interaction with substrates and additives, may be modified by mixing to optimize solution properties with respect to a given application. Although accurate prediction of these effects is crucial to the continued development of formulations, some of the most advantageous systems, which display the largest deviations from ideality, are not well described by current models.

We have shown already that the techniques of neutron reflection and surface tension can be combined with excellent consistency of data to yield definitive information about interfacial mixing of surfactants.[1,2] Previous work was restricted to the study of weakly or noninteracting systems with the purpose of verifying the validity of the investigative method. In this paper, we present the results of a study of a strongly interacting binary surfactant mixture consisting of the anionic surfactant, sodium dodecyl sulfate (SDS), and the zwitterionic *n*-dodecyl-*N*,*N*′-dimethylamino acetate (C_{12}betaine). Large deviations from ideality may be anticipated for these surfactants because of the strong electrostatic interactions possible between the headgroups, and nonideal mixing has already been observed for this system at the hydrophobic solid/solution interface[2] and for similar mixtures in micelles.[3−5]

The results are presented in three sections. In the first, measurements of the critical micelle concentration (cmc) using surface tension at both 298 and 313 K are combined using a second-order expansion for surface activity coefficients to reveal the separate contributions of entropy and enthalpy to the excess free energy of micellization, G^E. The widely used current model for nonideal surfactant mixing assumes that the free energy of mixing is symmetric in the composition,[6−8] and we will show that this assumption is not correct in the case of this strongly interacting system. The second set of results concerns mixing at the air/solution interface, for which surface compositions measured directly using neutron reflection are compared with those predicted using RST. The results indicate errors in the model consistent with the omission of a significant excess free energy. Finally, neutron reflection is used to obtain structural information about the mixed layer adsorbed at the air/water interface. Using neutron reflection it is possible to determine the relative position of the two surfactants in the layer, as well as their position in relation to the solvent and the solvent distribution.[9−12] Analysis of the structural data indicates a

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possible molecular origin for the discrepancies between the measured coverages and those derived indirectly from RST.

Mixing in Micelles Mixing

Mixing in surfactant systems can be considered to be important only in condensed pseudo-phases such as micelles or interfacial adsorbed layers. Deviations from ideality are therefore generally measured as a function of their effects on properties associated with the formation of these pseudo-phases, such as micellization or lowering of the surface tension. An account of the thermodynamics of these systems has been presented in the previous paper.[1] For micelles, the cmc of any binary mixture can be written in terms of the bulk mole fraction of surfactant i in the mixture α_i and the cmc's c_i^M of the pure components. For the ideal case[13-15]

$$\frac{1}{c_{mix}^M} = \frac{\alpha_1}{c_1^M} \frac{\alpha_2}{c_2^M} \tag{1}$$

Nonideality is incorporated by modifying the values of the cmc's by activity coefficients f_i for the micellar subphase[6,8]

$$\frac{1}{c_{mix}^M} = \frac{\alpha_1}{f_1 c_1^M} \frac{\alpha_2}{f_2 c_2^M} \tag{2}$$

Nonideal models seek to evaluate the activity coefficients given in eq 2 and then use them to solve for the values of the mixed cmc. This is generally accomplished using the first term in a series expansion[16] to yield a single nonideality parameter for micellar mixing β^M, which is related to the activity coefficients by[6,8]

$$RT \ln f_1 = \beta^M (1 - x_1)^2 \tag{3}$$

where x_1 is the mole fraction of component 1 in in the micelle. The numerical value of β^M may be found by iterative solution of the following pair of equations[6,8]

$$\beta^M = \frac{1}{x_2^2} \ln \left[\frac{\alpha_1 c_{mix}^M}{x_1 c_1^M} \right] = \frac{1}{x_1^2} \ln \left[\frac{\alpha_2 c_{mix}^M}{x_2 c_2^M} \right] \tag{4}$$

subject to the constraints

$$\alpha_2 = 1 - \alpha_1 \tag{5}$$

$$x_2 = 1 - x_1$$

The form of eq 3 leads to a symmetrical distribution of the excess free energy with respect to the composition of the micellar pseudo-phase. The nonideality parameter may be written in terms of the excess free energy of mixing as

$$G^E = \beta^M RT x_1 x_2 \tag{6}$$

In this approximation, as the composition of the pseudo-phase approaches 1:1 stoichiometry, so G^E necessarily increases in magnitude, which is the same result as that of the regular solution model,[17] which explicitly assumes that the only contribution to G^E is the excess enthalpy. In the standard model, β^M is[6]

$$\beta^M = \frac{N(W_{11} + W_{22} - 2W_{12})}{RT} \tag{7}$$

where W_{ii} are the self-interaction enthalpies and W_{12} is the interaction enthalpy between species 1 and 2. The physical interpretation of β^M in terms of eq 7 is not a prerequisite for the use of a single fitting parameter for activity coefficients but merely an attempt to ascribe a physical meaning to it. In a system where the first-order fit correctly estimates the activity coefficients, the value of β^M will be invariant with bulk composition. Thus given the values of the pure cmc's and one mixed cmc value at known bulk composition the values of the mixed cmc and micellar composition may be predicted for all bulk phase compositions.

In terms of micellar mixing this pseudo-phase approach has been used with some success to described the behavior of many binary surfactant systems.[1,3-8,18-28] The approach is strictly only applicable to nonionic surfactant mixtures since no account is taken of the degree of association of ionic surfactant species in the micelle with their counterions and hence the effect of ionic strength upon the micellar activity coefficients is not included. This apparent limitation has, however, not prevented the use of this method to describe, again with some success, nonionic and ionic systems.[1,3,4,6,24-28] The degree to which this success implies that electrolyte effects are unimportant in determining the net behavior of aggregating surfactant mixtures is not clear; the available experimental evidence is often subject to large errors and a degree of interpretation.

Hall and Huddleston[29] define a quantity, k, as the degree of association (or association constant) of surfactant i and counterions j in the micelle

$$k = N_j/N_i \tag{8}$$

where N_i and N_j are the number of each species associated with the micelle. The situation for an ionic surfactant at the cmc may be described in the same way as that of a nonionic using Raoult's Law in the form

$$\ln a_i = \ln x_i + \ln a_i^0 \tag{9}$$

where a_i is the activity of ionic species i in the mixture at its cmc and x_i is its mole fraction in the pseudo-phase. In this case, however, a_i^0 may not be equated with the cmc of the pure surfactant because the activity of the counterion must be accounted for. For a single counterion species j with activity a_j, mass action gives

$$\ln a_i^0 + k \ln a_j = \ln a_i^* + k \ln a_j^* \tag{10}$$

where a_i^* and a_j^* are the activities of i and j in a solution containing only those ionic species at its cmc, a_{ij}^*. Hence when the counterion is not in excess

$$a_i^* = a_j^* = a_{ij}^* \tag{11}$$

and it follows that

$$\ln a_i^* + k \ln a_j^* = (1 + k) \ln a_{ij}^* \tag{12}$$

Substituting this result into eq 9 yields for an ionic surfactant species i with single counterion species j in a mixture at the cmc

$$\ln a_i = (1 + k) \ln a_{ij}^* - k \ln a_j + \ln x_i \tag{13}$$

Nonideality can be introduced as before by introducing micellar activity coefficients

$$\ln a_i(1 + k) \ln a_{ij}^* - k \ln a_j + \ln x_i + \ln f_i \quad (14)$$

This micellar activity coefficient can be evaluated to a first-order approximation in the same way as the nonionic case (eq 3)

$$\ln a_i = (1 + k) \ln a_{ij}^* - k \ln a_j + \ln x_i + \beta^M (1 - x_i)^2 \quad (15)$$

In the limit of vanishing x_i, this relationship may be written as

$$\lim_{x_i \to 0} \ln \frac{a_i}{x_i} = (1 + k) \ln a_{ij}^* - k \ln a_j + \beta^M \quad (16)$$

With this relationship, the dependence of the nonideality parameter upon the charged nature of the micellar phase may be examined. Since any ionic surfactant ions in a largely nonionic micelle (i.e., when x_i is very small) should not be expected to bind counterions any more than in the monomeric state, the left-hand side of eq 16 should be independent of both the nature of the counterion and its activity. The nonideality parameter must therefore be redefined in this case so as to be a function of temperature and pressure only.

It is possible to define β^{M*} as the nonideality parameter for micellar mixing in ionic systems

$$\beta^{M*} = \lim_{x_i \to 0} \ln \frac{a_i}{x_i} - (1 + k) \ln a_{ij}^* \quad (17)$$

where the relationship between β^M and β^{M*} is

$$\beta^M = k \ln a_j + \beta^{M*} \quad (18)$$

At the cmc in the case where an ionic component (surfactant 1) has only one counterion and there is no excess electrolyte and assuming that the activity coefficient of the electrolyte may be ignored

$$a_i = a_j = \alpha_1 c_{mix}^M \quad (19)$$

Hence, by modification of the nonionic case, nonideal expressions may be written to include explicitly the effect of a charged micellar phase. For a binary system with no added electrolyte where surfactant species 1 is a 1:1 ionic and surfactant species 2 is nonionic

$$\ln (\alpha_1 c_{mix}^M) = (1 + k) \ln c_1^M + \ln x_1 - k(1 - x_2^2) \ln c_1^M + \beta^{M*} x_2^2 \quad (20)$$

$$\ln (\alpha_2 c_{mix}^M) = \ln c_2^M + \ln x_2 + x_1^2 k \ln c_1^M + \beta^{M*} x_1^2 \quad (21)$$

In addition, it is possible to account for bulk ionic interaction by incorporating Debye–Huckel activity coefficients, $\gamma_\pm$, into the bulk concentrations.[30] In most cases for dilute surfactant systems (at or near the cmc), log $\gamma_\pm$ will tend to zero and eq 20 and eq 21 may be used without modification.

It is apparent that in the case of a mixture containing only nonionic surfactants, the value of k is zero and eqs 20 and 21 reduce to the standard nonionic expressions, where $\beta^{M*} = \beta^M$. The same reduction occurs in the limiting case of $x_i = 0$, where the micelle contains only nonionic surfactant and is not charged. Equally evident is the fact that the value of β^{M*} obtained from eqs 20 and 21 when k is nonzero will not match β^M obtained from the standard calculation and hence previously obtained values may not be substituted into this model.

The physical relationship between β^{M*} and β^M is given by eq 18. Thus, while β^M will be dependent on both the nature and activity of the counterion species j, β^{M*} is a function only of T and P. β^{M*} will still be related to G^E, although not in the simple manner of β^M. An important consequence of this is that the possiblity of further expansion of activity coefficients to higher orders (and hence the use of more "nonideality param eters") is severely restricted by this model. Only the first-order case, and selected higher orders where the excess thermodynamic functions remain symmetric with respect to composition, may be solved. In any other case, the limiting condition of $x_i \to 0$, which is required to define the parameters of nonideality in the charged system, is not tractable because higher order terms of the expansion for the activity coefficients will collapse (see Appendix for proof). Values for k may be obtained experimentally from the gradient of a plot of $\ln a_i^0$ against $\ln a_r$ for the single ionic surfactant i at its cmc, where a_r is the activity of the only counterion species r and in which there are varying amounts of nonsurface active co-ions.

Mixing at Surfaces

Mixing in layers adsorbed at interfaces has been treated by the simpler of the two models described in the previous section by both Rosen[7,19,20] and Holland.[18,31] Descriptions of both these models have already been presented.[1] Extension in this case to include ionic charge effects is hampered by the difficulty in defining and measuring counterion binding at surfaces.

In this paper the predictions of both the standard and charged approaches for micellar mixing are calculated and it is shown that the inclusion of counterion binding does not significantly improve the fit of the model. For the results of the surface investigations only the standard model is used, and here Rosen's model,[7,19,20] derived from the equations of Goodrich,[32] is preferred to Holland's model.[18,31] Holland's model includes a surface pressure term, but since we will be considering data below the cmc, we can choose to compare data at a fixed surface pressure and hence eliminate this term. The Rosen model then offers the flexibility of allowing the value of the surface interaction parameter, β^σ, to vary with surface pressure.[1]

Theory of Neutron Reflection

In a neutron reflection experiment, the specular reflection, R, is measured as a function of the wave vector transfer, κ, perpendicular to the reflecting surface, where

$$\kappa = \frac{4\pi}{\lambda} \sin \theta \quad (22)$$

θ is the glancing angle of incidence and λ the wavelength of the incident neutron beam. $R(\kappa)$ is related approximately to the scattering length density profile across an interface $\rho(z)$ by

$$R(\kappa) = \frac{16\pi^2}{\kappa^2} |\hat{\rho}(\kappa)|^2 \quad (23)$$

where $\hat{\rho}(\kappa)$ is the one-dimensional Fourier transform of $\rho(z)$,

$$\hat{\rho}(\kappa) = \int_{-\infty}^{+\infty} \exp(-i\kappa z) \, \rho(z) \, dz \quad (24)$$

These approximate relations show that there is a direct relation between reflectivity and structure, but it is often more convenient to use the exact optical matrix method[33] to calculate the reflectivity for any given model of the interface, and this is the method we use in the present paper.

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TABLE 1: Neutron Scattering Lengths for the Different Components Component

component	$\sum b_i \times 10^4$/nm	$V \times 10^3$/nm^3
H_2O	−0.0168	30
D_2O	0.1919	30
$C_{12}H_{25}$	−0.137	325
$C_{12}D_{25}$	2.47	325
SO_4^-	0.26	60
$N(CH_3)_2CH_2CO_2$	0.176	165

The sensitivity of neutron reflectivity to the presence of surfactant is greatest if the isotopic composition of the water is chosen to contain D_2O:H_2O in the molar ratio 0.088:1. At this composition the water has a scattering length density of zero and therefore contributes nothing at all to the reflected signal. We refer to this as null reflecting water (NRW). Thus if the solution contains deuterated surfactant in NRW the only reflected signal is from the deuterated layer of surfactant at the surface. The composition of most surfactants is such that when they are fully protonated their scattering lengths are close to zero (see Table 1) and so there is only a very small reflected signal from a layer of protonated surfactant at the surface of NRW. For the determination of the surface excess of one surfactant in a mixture at the air/aqueous solution interface the reflectivity is therefore measured for a mixture where one surfactant is deuterated and the other protonated in NRW. The signal is then almost entirely from the adsorbed layer of surfactant 1 at the interface, and the procedure for determining the surface concentration is to fit this reflectivity profile by comparing it with a profile calculated using the optical matrix method.[34] Typically, it is sufficient to assume that the surfactant profile across the interface is a single layer of homogeneous composition. The parameters obtained from such a fit are the scattering length density of the layer, ρ, defined by

$$\rho = \sum n_i b_i \tag{25}$$

and its thickness, τ. The area per molecule is then

$$A = \frac{1}{\Gamma N_a} = \frac{b}{\rho \tau} \tag{26}$$

where b is the scattering length of the surfactant molecule, A is the area per molecule, Γ is the surface excess, and N_a is Avogadro's number. If the only errors are errors arising from the neutron measurement itself, such as misalignment of either the sample or the D_2O calibration run, or incorrect background subtraction, then it is straightforward to determine A with an accuracy of about ±0.02 nm^2 at 0.50 nm^2. It is also straightforward to extend eq 26 to the determination of surface excesses for binary mixtures, when it becomes

$$\rho = \frac{1}{\tau}\left[\frac{b_1}{A_1} + \frac{b_2}{A_2}\right] \tag{27}$$

where the subscripts 1 and 2 refer to the two components. Ideally the evaluation of the adsorbed amounts should be made with the nondeuterated component having zero scattering length because eq 27 then becomes identical with eq 26. In practice it is more convenient to use the protonated form and this will give rise to a small contribution to the reflectivity (see Table 1), but, provided that measurements have been made of the coverage of both components, this small correction may be made using

$$A_d' = A_d\left[1 + \frac{b_p A_d}{b_d A_p}\right] \tag{28}$$

where the subscripts now refer to the deuterated and protonated components, A_d' is the corrected area per molecule, and A_d has been evaluated using eq 26. A sufficiently accurate value of A_p is obtained from the reverse contrast situation. Even better is to use three combinations, d-A/h-B, h-A/d-B, and d-A/d-B all in NRW, where d-A etc denotes that surfactant A is deuterated. The use of the three combinations rather than just the first two gives a means to check the total coverage.

For a mixed surfactant layer the primary structural features of interest that are accessible to the neutron experiment are the relative positions of the two surfactants along the direction normal to the surface, their positions relative to water w, and the widths of their distributions normal to the interface. The most direct method of analysis of the data is to use the kinematic approximation, where fairly realistic analytic distributions of the individual fragments are fitted to the data from several isotopes. This has been the method that we have used on previous mixtures. The limitation of this method is that it is desirable to be able to vary the labeling on all the fragments whose structure is to be analyzed, and this is not easy for the present binary mixture. Even when some data is missing it may be possible to make sound deductions about the structural data, and we have already done this in the case of C_{12}betaine and SDS on their own. However, the alternative method of analyzing reflectivity data is to divide the interfacial layer into as many layers as are thought necessary for an adequate description and to calculate the reflectivity exactly using the optical matrix method. We have found for other surfactant layers that division into two layers is sufficient for the calculation, one containing only hydrocarbon and air and the other being a space-filling layer containing the headgroups, water, and the residual fraction of hydrocarbon chain. This approach has the advantage for the present work that it gives the number of water molecules associated with the average surfactant molecule, i.e., the hydration number, directly, and this will be shown to be relevant to the thermodynamics of mixing. While the kinematic method has some conceptual advantages, another technical reason for preferring the layer method is that, at the low coverages of the individual surfactants that are characteristic of mixtures, systematic errors in the determination of partial structure factors used in the kinematic approach become very difficult to avoid.[9,35]

Experimental Details

The synthesis and purification of SDS and C_{12}betaine have been described previously.[36,37] Water used for the surface tension measurements was doubly distilled, once from a strong solution of $KMnO_4$ and once under nitrogen. Water used for neutron reflection measurements was purified using an Elga purification apparatus, and D_2O was from Sigma.

The surface tension measurements were made on a thermostated Krüss K12 tensiometer using a platinum Wilhelmy plate.[38] The plate was cleaned with chromic acid and distilled water and flamed before each measurement. Measurement of the surface tension of pure water at 298 K was used to calibrate the tensiometer and to check the cleanliness of the glassware. The surface of each solution was cleaned by suction immediately before the measurement. Each measurement was repeated automatically every 90 s until the result was invariant to within 0.01 mN m^{-1} for three successive readings.
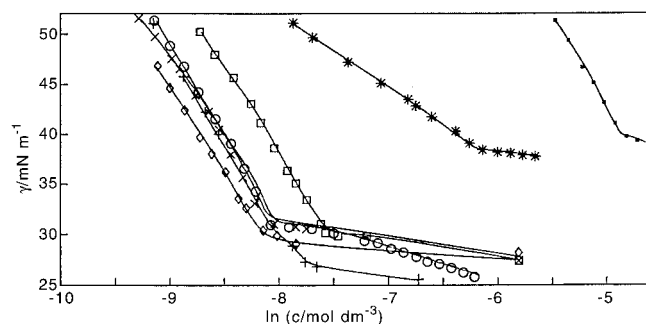
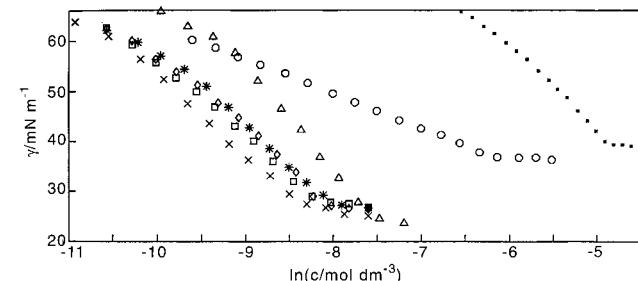**8838** *J. Phys. Chem. B, Vol. 102, No. 44, 1998*

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Figure 1. Surface tensions of SDS/C_{12}betaine mixtures at 298 K as a function of n c_{total}. The mole fractions of SDS are ($*$) 0, ($\bigcirc$) 0.1, ($\diamondsuit$) 0.2, ($\times$) 0.3, ($+$) 0.5, ($\square$) 0.8, and ($\blacksquare$) 1.0.

Figure 2. Surface tensions of SDS/C_{12}betaine mixtures at 313 K as a function of ln c_{total}. The mole fractions of SDS are ($\bigcirc$) 0, ($\diamondsuit$) 0.1, ($\times$) 0.2, ($\square$) 0.3, ($*$) 0.5, ($\triangle$) 0.8, and ($\blacksquare$) 1.0.

TABLE 2: Cmc and Surface Tension Values for Each Bulk Composition

	298 K		313 K	
α_{SDS}	cmc/mM	γ_{cmc}/mN m^{-1}	cmc/mM	γ_{cmc}/mN m^{-1}
1.0	7.95	39.6	7.87	40.0
0.8	0.52	30.2	0.51	25.5
0.5	0.37	28.0	0.33	27.4
0.3	0.29	31.2	0.28	27.8
0.2	0.27	30.7	0.22	27.9
0.1	0.31	31.0	0.29	27.7
0.0	2.1	38.7	2.0	34.0

The neutron reflection measurements were made using the reflectometer SURF at ISIS (Rutherford Appleton Laboratory, Chilton, Didcot, U.K.). The instrument and the sample containers have been described previously.[39] The samples, contained in Teflon troughs, were thermostated to ±1 K. The reflectivity was measured at a fixed angle of 1.5° using a wavelength range of 0.05−0.65 nm and was calibrated by using the known reflectivity profile of D_2O. A flat incoherent background resulting from scattering by the bulk solution was determined by extrapolation to high momentum transfer and subtracted from each measured profile.

Results and Discussion

Micellar Mixing. Plots of surface tension, γ, against log of the total surfactant concentration, ln c, are shown in Figures 1 and 2 for SDS/C_{12}betaine mixtures at 298 and 313 K, respectively. In each case mixtures of various total surfactant composition were studied. Also shown are the corresponding plots for the pure species. The cmc's were calculated from these plots using the criterion of maximum adsorption and the point of inflection on the curve of γ/ln c,[40] and the values are given in Table 2. For all measurements α designates the bulk mole fraction of SDS. The mixed cmc values are appreciably lower than those of either pure component over the entire range of composition studied, suggesting strong interactions. In addition,
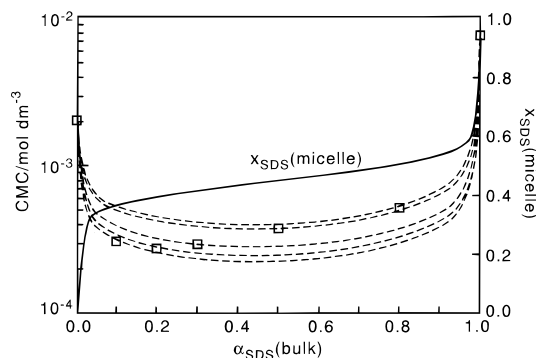

Figure 3. Values of the cmc of SDS/C_{12}betaine mixtures over the whole composition range calculated from the value of β^{M*} obtained for each experimental composition. $\square$ indicates the observed cmc at each composition.

TABLE 3: Calculated Values of β^M and β^{M*} for Each Bulk Composition Studied

	β^M		β^{M*}	
α_{SDS}	298 K	313 K	298 K	313 K
0.8	−9.1	−9.1	−5.6	−5.6
0.5	−9.4	−9.7	−5.9	−6.2
0.3	−10.5	−10.6	−7.0	−7.0
0.2	−11.1	−11.8	−7.5	−8.3
0.1	−11.4	−11.5	-7.9	−8.0

significant lowering of the surface tension at the cmc because of mixing in the surface layer is observed. Both of these properties are characteristic of strongly interacting systems with a significant deviation from ideality. It is precisely this behavior that makes such mixtures particularly useful in many commercial and industrial applications.

Values of the nonideality parameters for micellar mixing calculated from the pseudo-phase separation model are given for each composition in Table 3. Where a system is well described by this model, the values of β^M or β^{M*} should be invariant with composition, so all points should fall on the same line. A previously determined value for k_{SDS} of 0.73[41] was used in calculating β^{M*}.

At both temperatures studied, and using either model, the value of the interaction parameter varies with a clear trend across the composition range. Although the values derived for interaction parameters are always subject to significant error, the clear trend observed shows that the excess free energy G^E is not a symmetrical function with respect to the micellar composition. Thus, the single-parameter fit for the activity coefficients does not produce a consistent result for β^M or β^{M*}. The effect of this variation in the nonideality parameter upon the predictive capability of the model is shown in Figure 3, where the value of the cmc is calculated for all bulk phase compositions from each experimental result in turn at 298 K. The calculated value of the cmc for a bulk composition of 0.8 SDS:0.2 C_{12}betaine can be more than a factor 2 in error if calculated using the experimental c^M_{mix} from a zwitterionic rich bulk phase, and vice versa.

Despite the evident shortcomings of the model, the large negative values of the nonideality parameters consistently indicate strong electrostatic attractions between the two surfactants. Furthermore, the values for β^M obtained here are of the same order as those derived by Tajima[3] who used the nonionic model for the related system, SDS/C_{12}glycine, for which he obtained a β^M value of −14.1, although he gave no indication as to whether there was any variation in β^M with composition.

Where a single-parameter fit for the activity coefficients does not adequately describe the excess free energy of mixing, it is
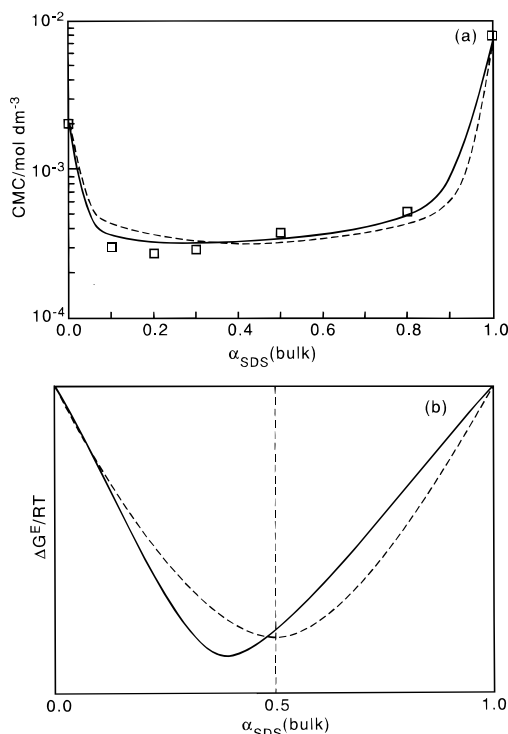
Figure 4. (a) Fit of the pseudo-phase separation model to the observed cmcs for SDS/C$_{12}$betaine mixtures using first-(dashed line) and second-order expansions for the activity coefficients. (b) Excess free energies of mixing corresponding to the first- and second-order fits in (a).

helpful to include higher terms in the approximation for the activity coefficients. The general form of the series expansion required for this type of calculation is[16]

$$RT \ln f_i = \sum_i x_2^2 A_i \left[(1 - 2x_2)^{(i-1)} + 2(1 - x_2)(i-1)(1 - 2x_2)^{(i-2)} \right] \quad (29)$$

Equation 3 results from the solution of eq 29 in the limit of $i = 1$. If $i = 2$ is taken as the limit, the activity coefficients, and hence G^E, are not necessarily symmetrical with respect to micellar composition. The second-order parameters may then be obtained by nonlinear fitting of the experimental values of the cmc's using the analogue of eq 4 which results from the substitution of a second-order activity coefficient expansion into eq 2. The result of the second-order fit using first and second-order nonideality parameters of $A_1 = -11.9$ and $A_2 = 19.9$ is shown in Figure 4a, which compares the mean first and second-order fits at 298 *K*. The asymmetry in G^E is reflected in a skew in the plot of predicted c_{mix}^M against α, which cannot be accounted for by the standard first-order treatment. The use of the higher order approximation for the activity coefficients clearly enhances the fit of the standard pseudo-phase separation model to the data. While the procedure does not add any predictive value because it is a direct fit to experiment, the results are of interest for the energetics of mixed micellization. The excess free energy G^E can be evaluated from the micellar pseudo-phase composition at the cmc and the nonideality parameters, A_1, A_2,

$$G^E = x_1 x_2 [A_1 + A_2(2x_1 - 1)] \quad (30)$$

Figure 4b shows that the relationship between the composition of the pseudo-phase and the excess free energy of mixing for the first- and second-order models. Unfortunately, the use of a
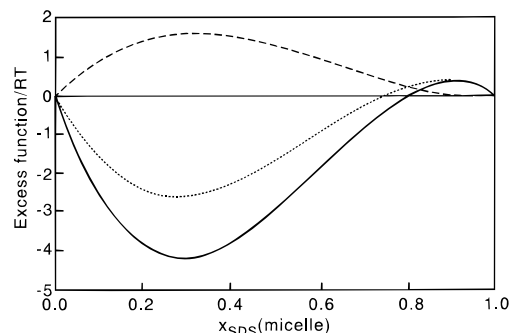
Figure 5. Micellar excess mixing functions for the SDS/C$_{12}$betaine system, G^E (continuous line), H^E (dotted line), and TS^E (dashed line).

TABLE 4: Second-Order Parameters for SDS/C$_{12}$betaine Data Presented in Table 2

	A_1	A_2
298 K	-12.0	19.9
313 K	-12.2	20.2

binding constant to account for ionic micelles, as in the charged pseudo-phase model, precludes the subsequent use of more than one parameter to describe the activity coefficients. This is a result of the change in the relationship between the free energy of mixing, the activity coefficients, and the nonideality parameter. The above second-order analysis is therefore, strictly speaking, limited to nonionic mixtures. We have nevertheless fitted the cmc data from the SDS/C$_{12}$betaine system at both 298 and 313 K using the second-order model because there are reasons for believing that the charged pseudo-phase model does not affect the comparative analysis significantly and such an analysis proves very revealing.

Applying the Gibbs–Helmholtz equation to the expression for G^E, eq 30, gives the following expressions for the excess enthalpy and entropy of mixing, H^E and S^E

$$H^E = x_1 x_2 \left(\frac{\partial (A_1/T)}{\partial (1/T)} \right)_P + (2x_1^2 x_2 - x_1 x_2) \left(\frac{\partial (A_2/T)}{\partial (1/T)} \right)_P \quad (31)$$

$$S^E = x_1 x_2 \left(\frac{\partial A_1}{\partial T} \right)_P + (2x_1^2 x_2 - x_1 x_2) \left(\frac{\partial A_2}{\partial T} \right)_P \quad (32)$$

The second-order ideality parameters A_1 and A_2, calculated using the cmc results given in Table 2, are presented in Table 4, and these parameters have been used to determine G^E, H^E, and S^E, respectively, using eqs 30, 31, 32. The excess mixing functions are shown as a function of micellar composition in Figure 5. Although the second-order expansion improves the fit considerably, the A_2 term is somewhat insensitive to the data. In hindsight this could have been partially overcome by concentrating data points at the extremes of the range, where the gradient, $dC_{mix}/d\alpha$, is changing more rapidly.

Figure 5 emphasizes some interesting aspects of the micellar mixing in this system. A single-parameter fit for activity coefficients implies that H^E is the dominant excess function, simply because of the analogy with bulk regular solution theory.[3–8,18–28] In the present case, this requires the intuitively reasonable result that H^E is negative. In the second-order model a negative excess enthalpy is also obtained, but its magnitude is not sufficient to explain the whole of the excess free energy observed and it has a very marked asymmetry. The largest enthalpic interactions occur when the mole fraction of SDS in the micelle is less than 0.5. In the region of high mole fraction of SDS, the micelle will be a more highly charged species and

will tend to oppose the addition of further SDS molecules by electrostatic repulsion. This will then favor the inclusion of more C_{12}betaine molecules in the micelle, correspondingly altering the composition. Enthalpically the most favored composition has an SDS mole fraction of approximately 0.3, which is significantly lower than the optimum of 0.5 required by the first-order model. It is important to note that the largest reduction in cmc occurs when the bulk composition corresponds to this favored micellar composition, as shown in Figure 4. Another interesting feature of Figure 5 is the change of G^E to positive values at high x_{SDS}. In such a situation, the system favors micellization even less than would be predicted by assuming ideality. Assuming that this is not an artifact of the analysis, which is difficult to assess, this would mean that at high α_{SDS} the presence of a small amount of C_{12}betaine inhibits micellization.

The most interesting feature of Figure 5 is the entropic contribution to the excess free energy, which represents a significant step back from the validation of the unnecessary assumption about the origins of β^M, which is often implied in the standard single-order model.[1,3-8,18-28] The source of the entropic contribution is not immediately obvious because a strong specific interaction between the two species should lead to greater ordering and an attendant loss in entropy. The major driving force for the micellization of surfactant species at a given bulk concentration in water is the hydrophobic effect, which is generally accepted to be entropic,[42,43] although the origin of this entropy has not yet been clearly identified. The entropic benefit could be associated with the greater freedom of water molecules in bulk water rather than when associated with hydrocarbon chains, and/or the increased freedom of hydrocarbon chains in the oily center of a micelle. For there to be an entropic gain over and above ordinary micellization, an additional benefit from mixing other than micellization in general must be found. For the present system increased ordering of the chains is suggested by the results of sum frequency spectroscopy experiments at the flat solid/liquid interface,[44] which in turn implies a reduction in entropy. However, it may be that it is this increased ordering that holds the key to the origin of a possible entropic benefit upon mixing. Since the headgroup of a surfactant molecule is generally hydrated, when such a molecule enters a micelle (or the surface pseudo-phase) it can only take up a particularly energetically favored position if there is an associated release of associated water of hydration, and this could lead to a substantial gain in entropy. Although we are not able to show this directly for the micelles, we will show below that the formation of the mixed monolayer at the air/water interface is associated with a significant decrease in the number of water molecules in the layer.

Mixing in Adsorbed Layers. Nonideality in mixed adsorbed layers has been treated in much the same way as micelles by the introduction of activity coefficients, typically evaluated at first order, into the appropriate thermodynamic surface equations of state.[7,18-20] Here we use the model produced by Rosen,[7,19-20] based upon the ideal equations of Goodrich.[32] Quantitative analysis of nonideality at the air/solution interface can then be made using surface tension measurements. Rosen has identified and separated two parameters for interfacial nonideality: synergy in the efficiency and effectiveness of surface tension reduction.[19-20] The former descibes the ability of an interacting mixture to lower the surface tension of the solution at a given concentration below that of either of the pure components, while the second defines limiting surface tension values in the micellar

solution. Mixtures of SDS with C_{12}betaine exhibit marked deviations from ideality in both of these respects (see Figures 1 and 2), but only the efficiency of surface tension reduction is dealt with here.

We have shown previously that excellent agreement can be obtained between surface tension measurements and integrated surface excesses derived from neutron reflection data.[1,37] The advantage of this method over the Hutchinson partial excess determination[45] used by Rosen[7] is that neutron reflection is an independent and direct method for the determination of surface excess and composition and is more accurate than the results from the application of the Gibbs equation to surface tension measurements. Figures 6, 7, and 8 show neutron reflectivity measurements made at 313 K for mixtures of SDS and C_{12}-betaine in the bulk mole ratios 20:80, 50:50, and 80:20, respectively, all in null reflecting water (NRW). For each mixture at each total surfactant concentration, three isotopic contrasts were used, dSDS/hC_{12}betaine, hSDS/dC_{12}betaine, and dSDS/dC_{12}betaine, so that the individual excesses of each adsorbed species, as well as the total surface excess, could be determined.

Compositions derived directly by neutron reflection can be compared with those predicted from the pseudo-phase separation model and the appropriate surface tension measurements. However, it is important to investigate the limits within which this comparison can be made in terms of the consistency between neutron reflection and Gibbs surface excesses. This consistency check has already been made for pure SDS and pure C_{12}betaine,[1,37] and in both cases satisfactory agreement was obtained between surface tension and neutron reflection measurements. This method also confirmed that the zwitterionic surfactant C_{12}betaine is correctly described using the Gibbs equation with a prefactor of 1, as appropriate for nonionic surfactant species. Figure 9 shows plots of total surface excess at 313 K versus ln c for each bulk composition studied together with the best least-squares quadratic fit. The fitted lines at the two temperatures were integrated in the same way as for single surfactants to yield the change in surface tension over a given concentration range using the Gibbs equation appropriate for a binary mixture of surfactant species of ionic and nonionic surfactant,

$$\Delta\gamma = -RT[\sum_i \int_{\ln c_1}^{\ln c_2} 2\Gamma_A \, d \ln a_A + \Gamma_B \, d \ln a_B] \quad (33)$$

Figure 10 shows the integrated surface tension lines for each SDS/C_{12}betaine mixture studied together with the experimental values of the surface tension over the same concentration range at 313 K. At 298 K the line predicted by the neutron reflection results for the 50:50 mixture (the only one measured) agrees satisfactorily with the values of the surface tension, but at the higher temperature of 313 *K* the two curves increasingly diverge at lower concentrations.

Each of the two components, as well as mixtures of each surfactant with the nonionic surfactant C_{12}maltoside, yielded totally self-consistent results.[1] The major difference between this mixture and those studied previously with C_{12}maltoside is the extent to which the anionic component is present in the interfacial layer. In mixtures with C_{12}betaine, SDS is still the minor component at the interface, but the combination of the strong interaction and relatively similar surface activities both mean that the proportion of SDS at the interface is greater than that in its mixtures with C_{12}maltoside. In addition the bulk concentration of SDS at the surface pressures of interest is much lower than that for pure SDS. There is evidence that trace
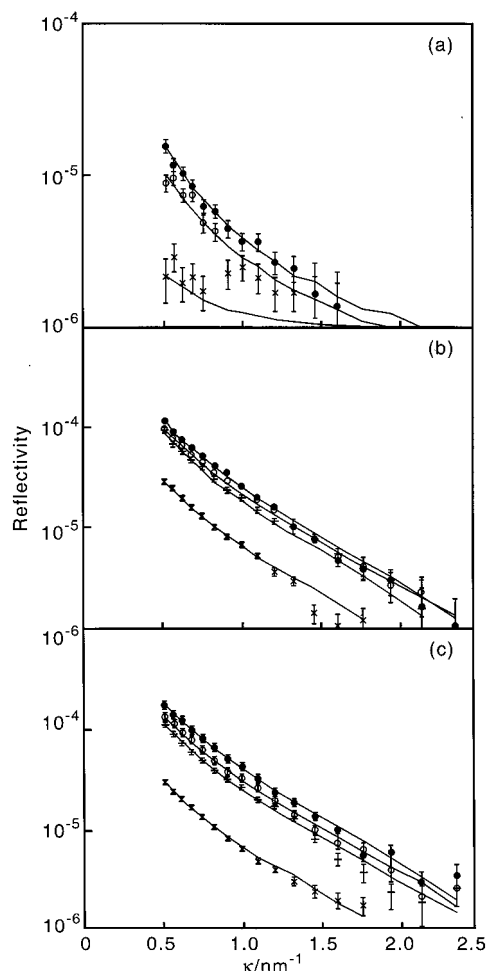
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Figure 6. Neutron reflectivity profiles of SDS/C$_{12}$betaine mixtures (20: 80) at overall concentrations of (●) 0.4 mM, (○) 0.2 mM, (+) 0.1 mM, and (×) 0.03 mM (a) dSDS/hC$_{12}$betaine, (b) hSDS/dC$_{12}$betaine, and (c) dSDS/dC$_{12}$betaine. The continuous lines are best fits to the data. All the measurements were made at 313 K.

Figure 7. Neutron reflectivity profiles of SDS/C$_{12}$betaine mixtures (50: 50) at overall concentrations of (●) 0.4 mM, (○) 0.2 mM, (+) 0.1 mM and (×) 0.03 mM (a) dSDS/hC$_{12}$betaine, (b) hSDS/dC$_{12}$betaine, and (c) dSDS/dC$_{12}$betaine. The continuous lines are best fits to the data. All the measurements were made at 313 K.

divalent metal ion impurity is very difficult to eliminate from SDS[36,46] and from other anionic surfactants[47,48] and that it becomes increasingly problematical as the concentration is lowered and/or as the surface activity of the pure material falls. This is because the divalent species in combination with the surfactant ion will be much more surface active than the monovalent species. However, since it is only present in trace amounts, it can only start to adsorb at the surface when the adsorption of the monovalent species drops significantly from its saturation value, either because its bulk concentration is low or because it does not have a high surface activity. The present behavior is consistent with this explanation in that the surface excess in the mixed monolayer is much higher at 298 K than at 313 K. It would seem that the change in temperature has lowered the surface activity of the mixture to a point where, at low concentrations, the effects of trace amounts of ions of higher valency may become significant. Thus, any inconsistencies between the measurements and the theoretical predictions may be unreliable at 313 K if the surface pressure is less than about 30 mN m^{-1}. At this pressure the consistency between surface tension and neutron reflection is within 10% in the value of dγ/d ln c. There should, however, be no such difficulties with the data at 298 K. In any case, it should be noted that the neutron measurement gives the actual coverage of the surfactant ion or neutral surfactant species in the case of a nonionic. The extent to which this may be different from the result that would
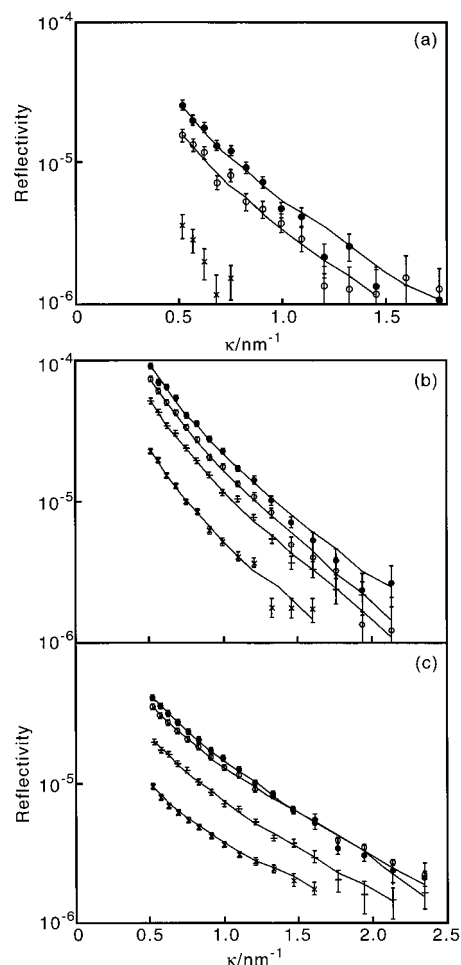
have been obtained if the system were not contaminated seems to vary from system to system. For example, for AOT, the neutron surface excess is always much closer to the true value whereas for the perfuorooctanoates the opposite is true.[47,48]

It might be thought that the discrepancy could be explained by association of SDS and C$_{12}$betaine in the bulk, which would have the effect of introducing nonnegligible values of the activity coefficients for both species and hence would affect the implementation of the Gibbs equation. Such an association is plausible given the strong interaction already observed in the micelles. However, the effect would increase rapidly with concentration, which is the reverse of what is observed here. This possibility can therefore be discarded.

Tables 5 and 6 compare interfacial compositions predicted with values of β^σ obtained from the pseudo-phase separation model at a series of surface pressures with experimental values obtained by interpolation between directly observed points. When the bulk SDS fraction is low, the pseudo-phase separation model substantially overestimates adsorption of SDS in the interfacial layer at all surface pressures. When the bulk fraction of SDS is 0.5 the overestimate is not as large but is still significant at both temperatures. Only at an SDS bulk fraction of 0.8 do the predicted and observed values approximately agree. However, this composition is closest to the ratio of the concentrations of the pure species required to reach a surface pressure of 30 mN m^{-1} (actually 0.85), so the surface composi-
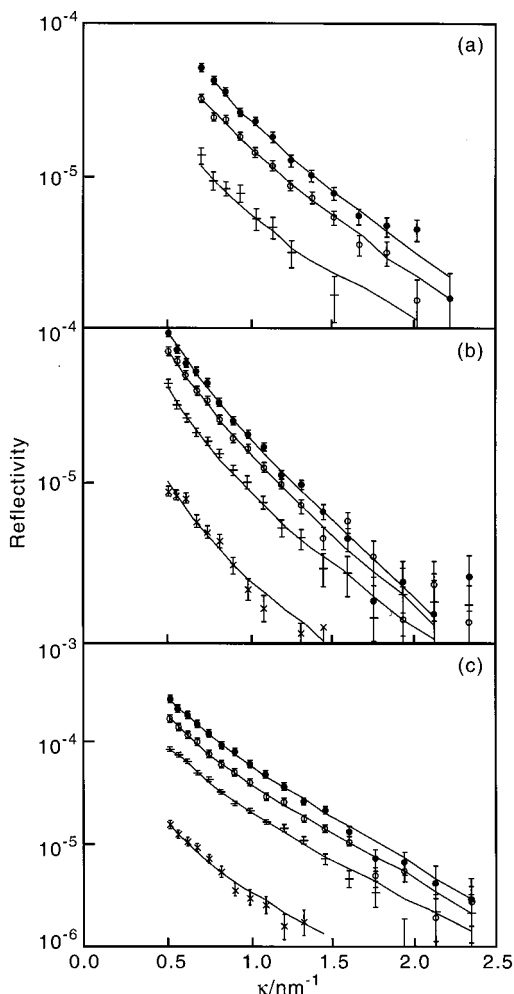
Figure 8. Neutron reflectivity profiles of SDS/C$_{12}$betaine mixtures (80:20) at overall concentrations of (●) 0.4 mM, (○) 0.2 mM, (+) 0.1 mM, and (×) 0.03 mM (a) dSDS/hC$_{12}$betaine, (b) hSDS/dC$_{12}$betaine, and (c) dSDS/dC$_{12}$betaine. The continuous lines are best fits to the data. All the measurements were made at 313 K.
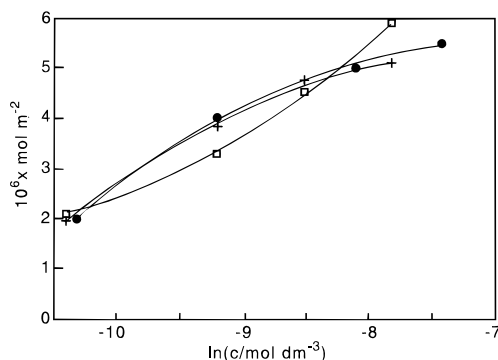

Figure 9. Neutron-derived surface excesses and best fits of a quadratic function to the data for SDS/C$_{12}$betaine at SDS:C$_{12}$betaine ratios of (+) 20:80, (□) 50:50, and (●) 80:20; $T = 313$ K.

tion should be independent of nonideality at this composition. This can be seen clearly in Figure 11 where the effect of variation of β^{σ} on the surface composition is plotted as a function of bulk mole fraction. Near an SDS bulk fraction of 0.8 variation of β^{σ} has almost no effect on the surface composition. At this bulk mole fraction, then, only the ideal model is being tested, not the evaluation of the nonideal activity coefficients. Since this ratio will vary with concentration (as the gradients of the two pure isotherms are different), this result is confirmation that the neutron and surface tension derived data are
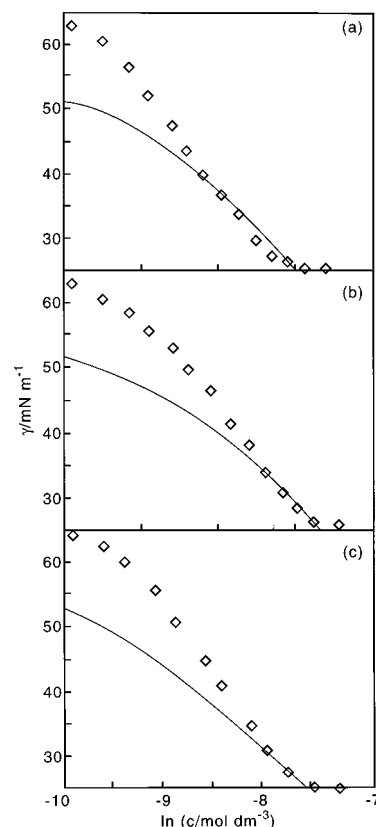

Figure 10. $\partial/\ln c$ plots calculated for SDS/C$_{12}$betaine mixtures from neutron reflection surface excesses compared with the direct measurement for respective compositions of (a) 20:80, (b) 50:50, and (c) 80:20 at 313 K.

TABLE 5: Surface Composition of SDS/C$_{12}$betaine Solutions at 298 K

α_{SDS}	0.5			
Π/mN m^{-1}	32	27	22	17
β^{σ}	−11.5	−10.8	−9.5	−8.3
x_{SDS} (pred.)	0.45	0.42	0.39	0.36
x_{SDS} (obs.)	0.36	0.33	0.32	0.30
$10^6\Gamma$/mol m^{-2}	4.8	4.65	4.45	4.1

consistent at this surface pressure. It is also interesting that the discrepancy was found to be of a similar direction and magnitude for adsorption of this mixture at the solid/liquid interface at the mixed cmc, where trace impurity effects would be negligible.[2]

Figure 11 shows the experimentally observed interfacial composition values (closed circles) plotted against bulk composition along with the curve of least-squares best fit to the pseudo-phase separation model. Although it is not strictly correct to fit a β^{σ} value to the neutron reflection data, we found that a satisfactory fit to the surface compositions could be obtained with a single value of $\beta^{\sigma N}$ of −1.6. The fit to the data is remarkably good. This and the fact that the composition dependence of β^{σ} found from the pseudo-phase separation model on composition is no longer observed suggests that the compositions observed by neutron reflection are not a result of experimental errors; they are internally consistent and lie on a curve that is more consistent with a type of physical behavior than with measurement error. We defer discussion of this large discrepancy between observed and predicted compositions until we have considered the structure of the layer.

Structure of the Mixed Monolayer. Four isotopic compositions of solution were studied for each mixture at the mixed

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TABLE 6: Surface Composition of SDS/C_{12}betaine Solutions at 313 K

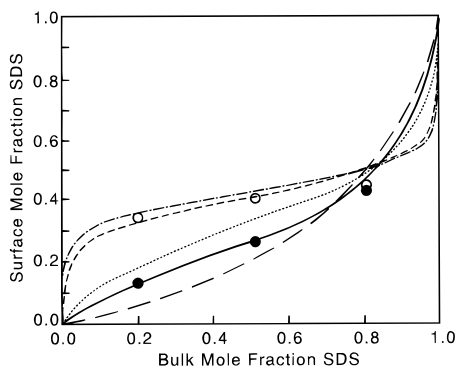| α_{SDS}	0.2				0.5				0.8			
Π/mN m^{-1}	30	25	20	15	30	25	20	15	30	25	20	15
β^σ	−16.7	−15.4	−14.3	−12.4	−14.3	−13.1	−11.9	−10.7	−13.2	−11.9	−10.5	−8.9
x_{SDS} (pred.)	0.34	0.32	0.30	0.27	0.37	0.35	0.33	0.30	0.42	0.40	0.38	0.35
x_{SDS}(obs.)	0.14	0.10	0.07	0.03	0.26	0.22	0.18	0.14	0.37	0.36	0.34	0.32
$10^6\Gamma$/mol m^{-2}	3.20	2.75	2.35	1.95	3.35	2.85	2.45	2.05	3.95	3.65	3.30	3.00

Figure 11. Variation of surface composition with bulk composition for the SDS/C_{12}betaine system for various values of the interaction parameter β^σ calculated using the pseudo-phase separation model. The calculated lines are for $\beta^\sigma = 0$ (small dashes), $\beta^\sigma = -2$ (dots), $\beta^\sigma = -6$ (large dashes), and $\beta^\sigma = -8$ (alternate dashes and dots). The open circles are calculated from the experimental surface tension data using eq 2 with the appropriate values of the three concentrations at a surface pressure of 30 mN m^{-1} replacing the cmc values. The solid circles are the surface compositions observed by neutron reflection. The continuous line is calculated from the pseudo-phase separation model using $\beta^\sigma = -1.6$.

cmc. Thus, to determine the widths of the two surfactant chains and of the headgroup region required the measurements dSDS/ hC_{12}betaine in NRW, hSDS/dC_{12}betaine in NRW, and hSDS/ hC_{12}betaine in D_2O. Although these two isotopic compositions together with those of Figures 6−8 are sufficient to determine the structural parameters of the two-layer model used to fit the data, we also measured the reflectivity profiles from dSDS/dC_{12}-betaine in D_2O in order to ensure that the structural parameters were well determined. The set of reflectivities used to determine the structure of the layer at the 80:20 composition is shown in Figure 12. The full set of profiles at all three bulk compositions was only done at 313 K.

We used a two-layer model to fit the data using the exact optical matrix calculation of the reflectivity and optimizing the fits using least squares. In this two-layer model the outer layer consists of a fraction of the hydrophobic chain, f_C, with thickness, τ_C. The inner layer consists of the headgroup of the surfactant, the remainder of the chains, $(1 - f_C)$, and enough water molecules, n_W, to fill completely any residual space in the layer, whose volume is determined by the thickness of the layer, τ_H, and the area per molecule. The volumes of the various fragments needed for the calculation of n_W have been given in Table 1. For the mixed layer it is more flexible to allow f_C and τ_C to take different values for the individual surfactants. This might be thought to be complicating the structure unnecessarily, but these values are directly determined in the contrast situation of only one surfactant being deuterated in NRW. The fitted structural parameters for the three compositions are given in Table 7, and examples of the fits are given as continuous lines in Figures 12 and 7. Not all the fits are good, and this is probably a consequence either of the model being limited to just two layers or because there are slight variations in the structure with isotopic composition. However, the main conclusions involve structural characteristics large enough not to be
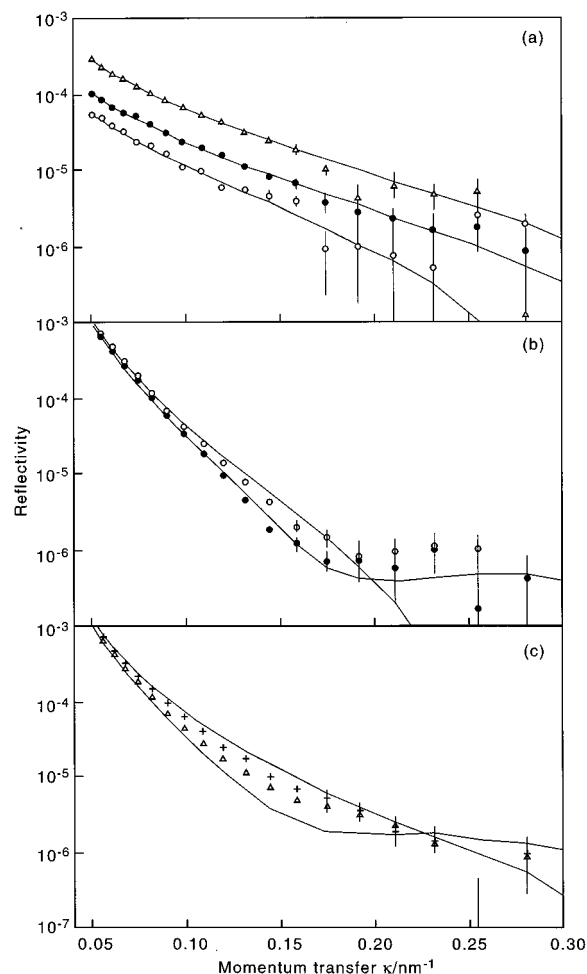

Figure 12. Neutron reflectivity profiles used to determine the structure of 80:20 mixtures of dSDS-dC_{12}betaine (△), dSDS-hC_{12}betaine (●), hSDS-dC_{12}betaine (○), and hSDS-hC_{12}betaine (+) in (a) NRW and (b) and (c) D_2O. The continuous lines are the best fits using the parameters given in Table 7.

affected by minor adjustments to the model; they depend on the coarser features of the reflectivity profiles.

We first note that in terms of the overall coverage the mean area per surfactant molecule hardly varies over the set of measurements. This is shown by the value of the mean area per molecule shown in the fifth column of Table 7. The structure of the mixed layer is seen to be quite different from that of either of the individual surfactants. Thus the fraction of the alkyl chain immersed in the water $(1 - f_C)$ drops from one-third to about one-tenth; i.e., the mixed layer is much more extensively out of the water. This is also seen from the change in the width of the headgroup region, which drops from 1.1 to 0.7 nm in the case of C_{12}betaine and from 0.8 to 0.7 nm in the case of SDS. The other marked change is that the chain region of the betaine is much thicker in the mixed interface, increasing from 0.75 to about 1.1 nm. This is partly as would be expected if chains had been expelled from the aqueous region and partly because the presence of the SDS in the layer clearly forces the

TABLE 7: Structural Parameters of Layers of SDS, Betaine, and the Mixtures

SDS/C$_{12}$B	c/mm	A_{SDS}/nm^2	A_B/nm^2	$\bar{A}$/nm^2	τ_{SDS}/nm^2	τ_B/nm^2	τ_{HG}/nm	f_{HG}	n_W	$\overline{n_W}$ (calc.)
100/0	8.0	0.45		0.45	1.1		0.45	0.3	7	7
0/100	2.0		0.45	0.42		0.45	1.1	0.35	6	6
80/20	0.6	0.88	0.65	0.37	1.2	1.05	0.7	0.1	4	6.5(5.5)
50/50	0.4	1.24	0.64	0.42	1.3	1.10	0.7	0.1	4	6.5(6.0)
20/80	0.4	1.85	0.57	0.435	1.2	1.15	0.7	0.1	4	6.0(6.0)

betaine headgroup out of its vertical orientation. We argued in a previous paper that the reason for the thin hydrocarbon region of the pure betaine layer was that it was forced to be strongly tilted away from the surface normal because the headgroup interactions are optimized if the headgroup alignment is vertical.[37] There is also a small increase in the alkyl chain thickness for SDS, which is consistent with the change in the dimensions of its headgroup region. It is noticeable also that the SDS chain is slightly higher in the layer than the betaine chain, consistent with its negative headgroup being aligned with the positive group in the zwitterionic betaine.

From the point of view of understanding the deviations of the SDS/C$_{12}$betaine behavior from the regular solution model, the most important features are the change in the chain orientation of the betaine, the removal of a significant fraction of hydrocarbon chain from the water, and the evident decrease in the level of hydration of the mixed surfactant layer relative to the individual layers. The last two effects are, of course, not independent. The effect of the alignment of the two chains appears to make the mixed layer more ordered than either of the individual layers. It is dangerous to draw definite conclusions about the consequences of such ordering when dealing with the hydrophobic effect, but it is difficult to see that this could be directly associated with the observed positive excess entropy. On the other hand, the removal of the hydrocarbon from the water could lead to a gain of entropy because of the hydrophobic effect, and the loss of water from the layer would even more certainly give a positive excess entropy of mixing. It would therefore be useful to estimate how much water has effectively been released from the layer. The simplest estimate of what the hydration ought to be is to take the mean of the hydration number of each individual surfactant, although it might be thought to be necessary to make some allowance for any compression of the layer on mixing. Thus for the 80:20 SDS: betaine mixture the simple mean hydration number should be 6.5, but if an allowance is made for the lower mean area of 0.37 nm^2 relative to the value of 0.435 nm^2 for the individual surfactants the predicted mean hydration number would drop to 5.5. These two sets of values are given in the last column of Table 7. For all three compositions it is clear that the hydration of the layer (given to the nearest 0.5 of a molecule), however estimated, has decreased by about 2 molecules. The maximum entropy gain this could represent would be about 50 J K^{-1} mol^{-1} since this is the entropy of fusion of two water molecules. However, the initial freedom of a water molecule in the layer is likely to be higher than that of ice, and the entropy gain should be much less than 50 J K^{-1} mol^{-1}.

Conclusions

We now return to the large difference between the measured surface composition and that predicted by the pseudo-phase separation model. In the calculation of the composition of the surface layer, the pseudo-phase separation model uses two equations, equivalent to eqs 2 and 4 but with the set of three concentrations at a given pressure replacing the values of the cmcs. The former is based on the derivation by Butler[49,50] and

is therefore only appropriate for an interfacial layer of constant volume (the pseudo-phase). The structural measurements show that mixing of SDS and C$_{12}$betaine is accompanied by a significant change of volume. It would be surprising if this was not also accompanied by changes in the entropy of mixing additional to those included in the derivation of eq 2. Lucassen-Reynders[51] has given a more general derivation of the basic equations for mixing, which are not based on pseudo-phase separation and where it is clear that the entropy of mixing should be sensitive to the composition of the interface. It is therefore possible that the discrepancies between neutron reflection and the pseudo-phase separation model result from eq 2 being invalid. However, the structural measurements also indicate that there may be further problems associated with the derivation of the compositions from the activity coefficients based on eqs 3 and 4, the basic assumption here being that the excess free energy of mixing is proportional to x_1x_2. The dehydration of the layer will almost certainly be associated with a large change in free energy. Provided that this is also proportional to x_1x_2 it will be incorporated along with the direct binary interaction energy between the surfactants into β^σ without destroying the validity of the assumptions and regardless of whether the excess free energy is enthalpic or entropic. The structural measurements, however, indicate that the dehydration of the layer is already large at the two more extreme compositions of 20:80 to 80:20. If the free energy of hydration is similarly large at these two compositions then it would not be proportional to x_1x_2 but would show a steeper variation at the high and low-SDS concentration limits. Such a variation, even if the excess free energy were to remain symmetrical with respect to composition, would also invalidate the assumptions used in the derivation of the layer composition in eq 4. In practice, such an effect would be more marked on the low-SDS side of the composition diagram because of the difference in the cmcs. This can be seen in Figure 11, which shows the variation of the composition of the layer calculated for different values of β^σ; the composition at 80 SDS:20 C$_{12}$betaine is relatively insensitive to the value of β^σ.

The arguments of the previous paragraph also hold for the behavior of the mixed cmc with composition, for which we do not have direct measurements for the composition of the micelles. There, however, the impossibility of fitting a single β^M value to the data demonstrates directly the inadequacies of the first-order approximation for the activity coefficients of the SDS/C$_{12}$betaine system. It would be expected from the results on the layer at the air/water interface that dehydration should also be an important factor in the thermodynamics of micelle formation, although the curvature of the micelles might modify its extent. This is borne out by the measurements of the excess functions for micellization in Figure 5 where it can be seen that there is a large positive entropic contribution which is qualitatively consistent with what might be expected for dehydration. A similar treatment of the surface tension data at the two temperatures 298 and 313 K yields a set of excess functions whose overall appearance is similar to those for micellization except that the entropic term is more positive and
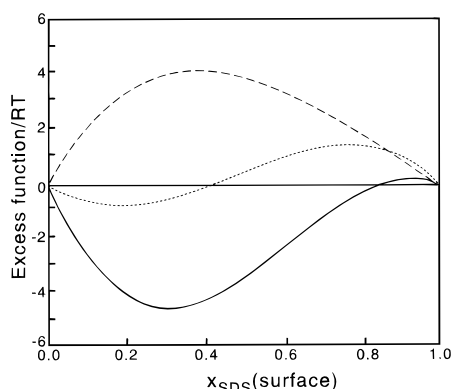
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Figure 13. Surface excess mixing functions derived from surface tension data for the SDS/C$_{12}$betaine system, G^E (continuous line), H^E (dotted line), and TS^E (dashed line).

the enthalpic term less negative (Figure 13), which tends to support the dehydration mechanism. Also, as anticipated from the variation of hydration of the layer with composition, the decrease in G^E is more rapid at low SDS concentrations than would be expected from the simple $x_1 x_2$ dependence of the first-order theory (the changes at high SDS concentrations have less significance as explained earlier). However, the data of Figure 13 should be treated with caution until the uncertainty in the consequences of a change in composition of the layer for the equivalent of eq 2 for the surface tension, from which the basic activity coefficients are derived, is removed.

Appendix

In general the activities of the two surfactants in a nonideal binary mixture are given by

$$\ln a_1 = \ln a_1^0 + \ln x_1 + \ln f_1 \qquad (A1)$$

$$\ln a_2 = \ln a_2^0 + \ln x_2 + \ln f_2 \qquad (A2)$$

where a_1^0 and a_2^0 may be identified with the cmc's of the pure single surfactants for nonionic surfactants. The activity coefficients may be expanded using eq 27 so that in the general case eq A1 may be rewritten

$$\ln a_1 = \ln a_1^0 + \ln x_1 + \sum_i x_2^2 \beta_i^M [(1 - 2x_2)^{i-1} +$$

$$2(1 - x_2)(i - 1)(1 - 2x_2)^{i-2}] \quad (A3)$$

where $\beta_i^M = A_i/RT$ and similarly for eq A2.

In the case of an ionic surfactant, however, a_1^0 must be modified to account for the association of counterions. This is accomplished by eqs 8−12. The general case for a charged surfactant will then be

$$\ln a_1(1 + k) \ln a_{13}^* - k \ln a_3 + \ln + x_1 +$$

$$\sum_i x_2^2 \beta_i^M [(1 - 2x_2)^{i-1} + 2(1 - x_2)(i - 1)(1 - 2x_2)^{i-2}] \quad (A4)$$

where species 3 is the nonsurface active counterion of the surfactant ion, species 1. In this case, however, the β_i^M must be converted to β_i^{M*} (independent of counterion activity) by the procedure described in the main body of the text. The limiting case of $x_i \rightarrow 0$ is used to give

$$\lim_{x_1 \to 0} \ln \frac{a_1}{x_1} = (1 + k) \ln a_{13}^* - k \ln a_3 + \sum_i \beta_i^{M*}(-1)^{i-1} \quad (A5)$$

It is possible at this point to define the β_i^{M*} as independent of counterion activity such that

$$\sum_i \beta_i^{M*}(-1)^{i-1} = \lim_{x_1 \to 0} \ln \frac{a_1}{x_1} - (1 + k) \ln a_{13}^* \quad (A6)$$

Hence

$$\sum_i \beta_i^{M*}(-1)^{i-1} = k \ln a_3 + \sum_i \beta_i^{M*}(-1)^{i-1} \quad (A7)$$

At this point it is clear that while an expansion to $i = 1$ is possible (and thus arrive at eq 18), there is no way to define correctly more than one parameter in this manner. Any further expansion will merely result in a sum of β_i^{M*} with no higher powers of x_2. Clearly, as the number of unknowns in a system increases, the number of relationships involving them must similarly increase if a solution is to be possible. This is not the case here because only one equation will exist (eq A7) regardless of the value of i taken. This problem may be overcome by introducing further relationships between two parameters. However, this is only possible in the special case of lattice theory of mixing, where symmetry is maintained, and is in reality a description of distinct aspects of a single parameter.

References and Notes

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