A Study of the Interactions in a Ternary Surfactant System in Micelles and Adsorbed Layers

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Surface tension and neutron reflection measurements have been used to study the micellization and interfacial adsorption of ternary surfactant mixtures containing sodium dodecyl sulfate (SDS), *n*-dodecyl-*N,N*-dimethylaminoacetate (C_{12}Betaine or C_{12}B), and *n*-dodecyl-β-D-maltoside (C_{12}M). Critical micelle concentrations (cmc) for the ternary mixtures are compared with values predicted using a multicomponent extension to the pseudophase separation model for nonideal mixing. Although the observed cmcs may be up to 50% different from those predicted, the errors resulting from inadequacies in the binary model mean that the results are the same within error. Values of the surface excesses at the air/solution interface at the cmc were determined directly using neutron reflection and isotopic substitution. They are found to be quite different from those predicted using the binary interaction parameters determined by surface tension. However, if the apparent binary interaction parameters obtained from directly measured compositions in the binary systems are used, the agreement between prediction and experiment is much improved. This suggests that prediction of the properties of ternary surfactant mixtures may be relatively straightforward once mixing in binary mixtures is properly characterized.

Introduction

It is well-known that mixing in surfactant systems can radically alter aspects of their behavior which are important in many industrial applications. Accordingly, prediction of properties such as the interfacial tension and critical micelle concentration (cmc) of novel mixtures is consequently a key issue in formulation science. Considerable effort has been devoted to finding adequate theoretical descriptions of mixing in these often highly nonideal systems.[1–16] For mixed surfactants in relatively dilute aqueous solution, interactions between solute molecules are only significant when they condense into interfacial layers or aggregates in bulk solution, e.g. micelles. Models for nonideal mixing therefore concentrate on properties of the system which are directly affected by the changes in the interactions in these pseudophases. Such properties of interest include the ability to lower the interfacial tension at a given total concentration, the lowering of the limiting tension above the cmc, or the formation of the micelles themselves.

The pseudophase separation model proposed by Rubingh[5] and utilized by many other workers[6–12,15,16] to describe interactions in nonideal mixed systems is based upon the first term in an expansion for the activity coefficients inserted into the standard thermodynamic model for ideal mixing.[2,3] The first-order approximation introduces many restrictions into the model with respect to the possible form that the mixing function can adopt,

the most well-known of these being the so-called regular solution approximation[19] where the symmetry implied by the first-order approximation for activity coefficients is the same as the restriction in bulk regular solutions to an ideal entropy of mixing. This approximation therefore neglects other entropic contributions to the free energy of mixing. We have shown that this may lead to fundamental problems within the model when it comes to the prediction of the properties of binary systems.[20,21]

This paper is concerned with the extension of models of mixing to mixtures of more than two surfactants. Holland and Rubingh[11] have produced a general multicomponent treatment, which describes interactions in the mixture in terms of each of the pairwise interactions in the system. Consequently, all the approximations already required in the binary model are also part of this more general treatment, with the additional assumption that only pairwise interactions are important; i.e., there is no modification of the interaction between a pair of surfactants by the presence of other components. There is some parallel here with the central assumption of the binary model that activity coefficients are well described by the first-order term in an expansion of the free energy, which also assumes that only nearest-neighbor interactions are important. Thus, binary systems well described by this model may be equally well modeled by the more general treatment when they are mixed in more complicated ways.

The ternary surfactant system that we have chosen for study is one in which strong nonideal interactions are possible. An anionic surfactant, sodium dodecyl sulfate (SDS) is mixed with

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a nonionic surfactant, *n*-dodecyl-β-D-maltoside ($C_{12}M$) and a zwitterionic surfactant, dodecyldimethylaminoacetate ($C_{12}B$). All three binary mixtures have been investigated previously,[20-22] and these investigations have shown that strong electrostatic interactions exist between SDS and $C_{12}B$ and that less nonideal interactions are also present in the SDS/$C_{12}M$ system. Mixtures of $C_{12}B$ and $C_{12}M$, on the other hand, were found to mix almost ideally in both micelles and mixed adsorbed layers.[22] In addition, the combination of surface tension and neutron reflection experiments in a consistent manner showed that deviations from ideality in the SDS/$C_{12}B$ system are particularly poorly described by the regular solution model of surfactant mixing.[20,21] Although one of the binary systems has already been shown to deviate from the predictions of the binary model, it is interesting to attempt to isolate errors in the ternary predictions from those that are a consequence of the failure of the binary model.

We have studied various compositions within the ternary system using both surface tension measurement and neutron reflection at the air/solution interface so that mixing in both micelles and interfacial layers could be investigated. As far as we know, the only attempt so far to predict the properties of a ternary system has been to fit the cmcs of a ternary system to the set of β^M parameters from the binaries;[11] no attempt has been made to account for surface composition in the same way. The main difficulty has been that this would require a more extensive set of surface tension measurements than most researchers are prepared to make. Neutron reflection, however, is now acknowledged to be a valid and powerful tool for studying the composition of mixed adsorbed layers as well as their structure.[23-31] The effectiveness of the technique is especially clear when dealing with multicomponent mixtures of adsorbing species because it is relatively straightforward to extract the surface excess of each individual surfactant, a process that would be extremely time consuming and error prone to do via surface tension measurements and the Gibbs isotherm.

Thermodynamic Treatment of Ternary Surfactant Mixtures

For a binary mixture of nonionic surfactants, where there is no counterion activity to be included, the following relationship can be derived for the cmcs of the pure components and that of the mixture at a given micellar composition, x_i:

$$\frac{1}{c^M_{mix}} = \frac{\alpha_1}{f_1 c^M_1} + \frac{\alpha_2}{f_2 c^M_2} \tag{1}$$

where α_i is the mole fraction of surfactant i in the surfactant mixture, f_i is its activity coefficient in the micelle, and c^M denotes a cmc. When the surfactants behave ideally in the micelle, this result becomes identical with that derived by Shinoda,[1] Clint,[2] and Lange and Beck.[3] A similar relation holds for the composition of an adsorbed layer but with c^M_i replaced by c^π_i which represents the bulk concentration at which the surface pressure has the value π. The derivation of eq 1 rests on the validity of assuming pseudophase behavior of both micelle and adsorbed layer (see, e.g. ref 32). The activity coefficients are described by a series expansion with respect to the composition of the micellar pseudophase,[33] which, taking just the first-order term, simplifies to

$$\ln f_1 = \beta^M x_2^2 \tag{2}$$

with an analogous expression for f_2. The interaction parameter

β^M, the nonideality parameter for micellization, can be evaluated empirically from a suitable set of data and should be invariant with composition.[1,2,7] The numerical value of β^M may be found by iterative solution of the equation resulting from substitution of eq 2 into (1):

$$\beta^M = \frac{1}{x_2^2} \ln\left[\frac{\alpha_1 c^M_{mix}}{x_1 c^M_i}\right] = \frac{1}{x_1^2} \ln\left[\frac{\alpha_2 c^M_{mix}}{x_2 c^M_2}\right] \tag{3}$$

subject to the conditions

$$\alpha_2 = 1 - \alpha_1$$

$$x_2 = 1 - x_1 \tag{4}$$

A similar equation holds for an adsorbed layer but with c^π replacing c^M and, of course, a different interaction parameter, which we designate β^σ. An alternative approach to the adsorbed layer removes the restriction to concentrations at constant surface pressure by including a force field term.[9,10] Also, the pseudophase separation model takes no account of the degree of association of ionic surfactant species in the micelle with their counterions. The changes to the equations resulting from inclusion of either of these effects have been discussed elsewhere.[12,20] The effects of the former can be avoided by working within the constant π restriction and, although we will be dealing with a charged system, we will neglect the effects of the latter. We have discussed this issue in detail elsewhere.[20] The main effect of the incorporation of charge into the pseudophase is to shift the value of the interaction parameter without breaking the symmetry in the behavior of the excess thermodynamic functions with composition. In comparison with the discrepancies between prediction and experiment that we will describe below the effect of including charge is insignificant.

The form of eq 2 leads to a symmetrical distribution of the excess free energy with respect to micellar composition, which may be written in terms of the nonideality parameter as

$$G^E = \beta^M RT x_1 x_2 \tag{5}$$

and this is often explained as resulting from a combination of an ideal entropy of mixing and an enthalpy of mixing given the same expression as in the regular solution theory for bulk solutions. These are not, however, necessary assumptions.

When there are more than two surfactants eq 1 may be generalized to give

$$\frac{1}{c^M_{mix}} = \sum_i \frac{\alpha_i}{f_i c^M_i} \tag{6}$$

and the activity coefficients expressed as[11]

$$\ln f_i = \sum_{j \neq i} \beta_{ij} x_j^2 + \sum_{j \neq i}\sum_{k \neq j} (\beta_{ij} + \beta_{ik} - \beta_{jk}) x_j x_k \tag{7}$$

where β_{ij} represents the pairwise interaction between i and j. This model assumes that the interactions in a multicomponent system are just the sum of all the binary interactions, and the binary interaction parameters are assumed to be unchanged from their values in the binary system. The mixed cmcs (or c^π) may then be calculated from the solution of the set of simultaneous equations obtained by substitution of each of the activity

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TABLE 1: Neutron Scattering Lengths for the Different Components

component	$\sum b_i \times 10^{-3}$
H_2O	-0.0168
D_2O	0.1919
hSDS	0.12
dSDS	2.62
$hC_{12}B$	0.04
$dC_{12}B$	2.64
$hC_{12}M$	0.51
$dC_{12}M$	2.85

coefficients in turn into eq 6. In this paper we use the Nelder−Mead simplex routine for function minimization.[34]

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

$$\kappa = (4\pi/\lambda)\sin\theta \qquad (8)$$

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 across an interface, $\rho(z)$, by

$$R(\kappa) = (16\pi^2/\kappa^2)|\hat{\rho}(\kappa)|^2 \qquad (9)$$

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

$$\hat{\rho}(\kappa) = \int_{-\infty}^{+\infty} \exp(-i\kappa z)\,\rho(z)\,dz \qquad (10)$$

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[35] to calculate the reflectivity for any given model of the interface, and this is the method we use in the present paper.

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 others 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 for a simple structural model.[25] 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

$$\rho = \sum n_i b_i \qquad (11)$$

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

$$A = \frac{1}{\Gamma N_a} = \frac{b}{\rho\tau} \qquad (12)$$

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. We have shown elsewhere that, although the thickness and scattering length density may have typical uncertainties of $\pm 15\%$, these errors largely compensate each other in the determination of A. When account is taken of other errors arising from misalignment of either the sample or the D_2O calibration run, or incorrect background subtraction, A can be determined with an accuracy of about ± 2 Å^2 at 50 Å^2. For surfactant mixtures, eq 12 becomes

$$\rho = (1/\tau)\sum(b_i/A_i) \qquad (13)$$

Ideally, the evaluation of the adsorbed amounts should be made with the nondeuterated component having exactly zero scattering length because eq 13 then becomes identical with eq 12. In practice, it is more convenient to use the protonated form and this will give rise to a small contribution to the reflectivity but, provided that measurements have been made of the coverage of both components, this small correction may be made using

$$A'_{di} = A_{di}\left[1 + \sum_{j\neq i}\frac{b_{pj}A_{dj}}{b_{dj}A_{pj}}\right] \qquad (14)$$

where the subscripts now refer to the deuterated and protonated components, A'_{di} is the corrected area per molecule for molecule i, and A_{di} has been evaluated using eq 12. A sufficiently accurate value of A_{pj} is obtained from the reverse contrast situation. A further improvement in the accuracy is also obtained by overdetermination of the coverages using such combinations as d−A/d−B/h−C, where d−A etc. denote that surfactant A is deuterated. The neutron scattering lengths of the relevant species are given in Table 1.

Experimental Details

The preparation and purification of protonated and deuterated analogues of all three surfactants have already been described.[20,22] Water used for surface tension measurement 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. 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.

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.[36] 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 0.5−6.5 Å and was calibrated by using the known reflectivity
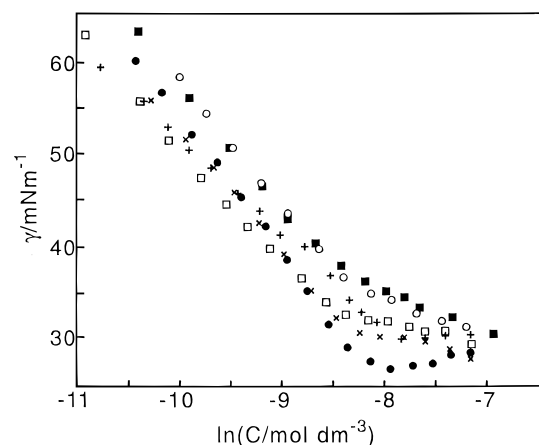
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Figure 1. Surface tension for ternary mixtures of SDS/C_{12}B/C_{12}M of composition (mole fraction) 25/25/50 (+), 25/50/25 (□), 50/25/25 (○), 33/33/33 (■), 40/40/20 (×), and 45/45/10 (●).

TABLE 2: Observed and Predicted Cmcs for Ternary Mixtures Studied

bulk composition SDS/C_{12}B/C_{12}M	cmc$_{obs}$/mM	cmc$_{pred}$/mM[a]
25/25/50	0.275	0.15−0.33
25/50/25	0.225	0.18−0.63
50/25/25	0.261	0.18−0.66
33/33/33	0.275	0.17−0.52
40/40/20	0.236	0.11−0.33
45/45/10	0.235	0.12−0.32
100/0/0	7.9	
0/100/0	2.05	
0/0/100	0.167	

[a] The values of β^M were taken to be the average of a spread of values consistent with the variation of the β^M with concentration and were β^M_{12}(SDS/CB)$_{12}$ = −10.3 ± 1.0, β^M_{13}(SDS/C_{12}M) = −4.1 ± 0.8, and β^M_{23}(C_{12}B/C_{12}M) = 0.0 ± 0.0.

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

Plots of surface tension, γ, against log of the total surfactant concentration, ln c, at 298 K are shown for each ternary system in Figure 1. The cmcs were calculated from the surface tension plots of Figure 1 using the criterion of maximum slope and the point of inflection,[37] the maximum slope being calculated using a nonlinear least-squares fit. The values of the mixed cmcs are compared with values predicted using eq 6 and the previously determined binary interaction parameters in Table 2. The values for the binary interaction parameters had been found to vary with composition in the binary mixtures[20,22] and the following average values were used for the calculations in Table 2: β^M_{12}(SDS/C_{12}B) = −10.3 ± 1.0, β^M_{13}(SDS/C_{12}M) = −4.1 ± 0.8, and β^M_{23}(C_{12}B/C_{12}M) = 0.0 ± 0.0, where we have included a spread of values consistent with the variation of the β^M with concentration. The values at any given surface concentration were determined to a much higher accuracy than these apparent standard deviations.

At first sight, extension of the pseudophase model to the ternary system using the method of Holland, i.e., eq 7, would not seem to be very accurate, some of the predicted cmcs being in error by as much as 50%. However, the errors resulting from the stated errors in the β^M values given above, and given in the
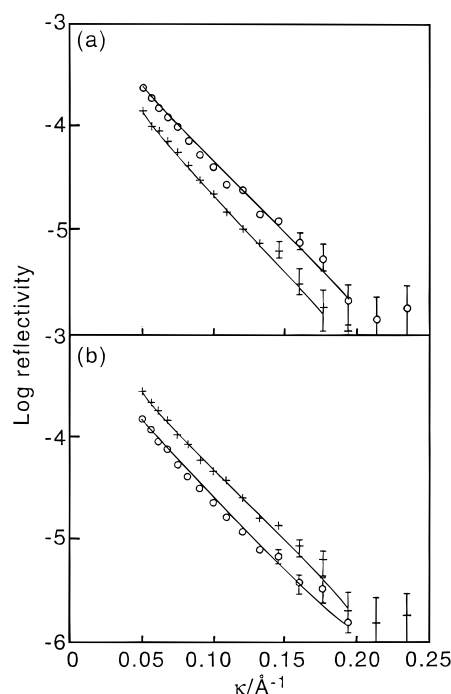

Figure 2. Neutron reflectivity profiles for SDS/C_{12}B/C_{12}M mixtures in the mole fraction ratio 25/25/50 and at an overall concentration of 0.275 mM: (a) hSDS/dC_{12}B/dC_{12}M (○) and dSDS/hC_{12}B/dC_{12}M (+), (b) dSDS/dC_{12}B/hC_{12}M (○) and dSDS/dC_{12}B/dC_{12}M (+). Temperature 313 K. The continuous lines are the best fits to the data using the compositions given in Table 3, the scattering lengths given in Table 1, and thicknesses in the range 22−24 ± 3 Å.

last column of Table 2, are such that calculated and observed cmcs agree within the rather large error. The errors in the β^M values represent an attempt to allow for the failure of the assumption of using only the first-order term in the expansion for the activity coefficients (eq 2). We have already shown that this is not valid for the strongest interacting system, SDS/ C_{12}B.[20] It is not possible to separate errors arising from this source from errors in Holland's expression for the activity of each component in the ternary system, eq 7.

Figures 2−4 show the neutron reflectivity from three bulk compositions of the ternary system, where four different isotopic compositions have been studied for each bulk composition; hSDS/dC_{12}B/dC_{12}M, dSDS/hC_{12}B/dC_{12}M, dSDS/dC_{12}B/hC_{12}M, and dSDS/dC_{12}B/dC_{12}M,hSDS, all in null reflecting water. The measurements were all made at 313 K at the appropriate mixed cmc. The observed compositions for each mixture are compared with the values predicted using eqs 6 and 7 in Table 3. The values of β^σ used for the predictions were β^σ_{12}(SDS/C_{12}B) = −14.3, β^σ_{13}(SDS/C_{12}M) = −3.8, and β^σ_{23}(C_{12}B/C_{12}M) = 0.0. There are large differences between the observed and predicted compositions. However, this failure is not necessarily the result of errors in the assumption that the interactions in the ternary system can be represented in terms of the binary interactions by eq 7 because large discrepancies were also observed in two of the binary mixtures.

An alternative to calculating β^σ and the x_i from surface tension data is to calculate β and the surface tension of the mixture from the measured surface mole fractions. This can only be done when there is a direct measure of the surface compositions of the binary mixtures, such as is available from neutron reflection. We designate the value of β calculated by this route, β^{NR}. These values will reflect the strength of the interaction genuinely resulting from pairwise compositional interactions, rather than including other, less well-defined contributions to
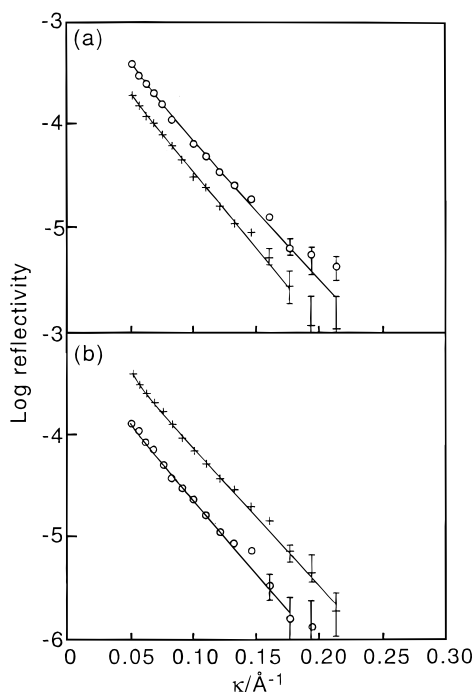
Figure 3. Neutron reflectivity profiles for SDS/C_{12}B/C_{12}M mixtures in the mole fraction ratio 25/50/25 and at an overall concentration of 0.225 mM: (a) hSDS/dC_{12}B/dC_{12}M (O) and dSDS/hC_{12}B/dC_{12}M (+), (b) dSDS/dC_{12}B/hC_{12}M (O) and dSDS/dC_{12}B/dC_{12}M (+). Temperature 313 K. The continuous lines are the best fits to the data using the compositions given in Table 3, the scattering lengths given in Table 1, and thicknesses in the range 22−23 ± 3 Å.
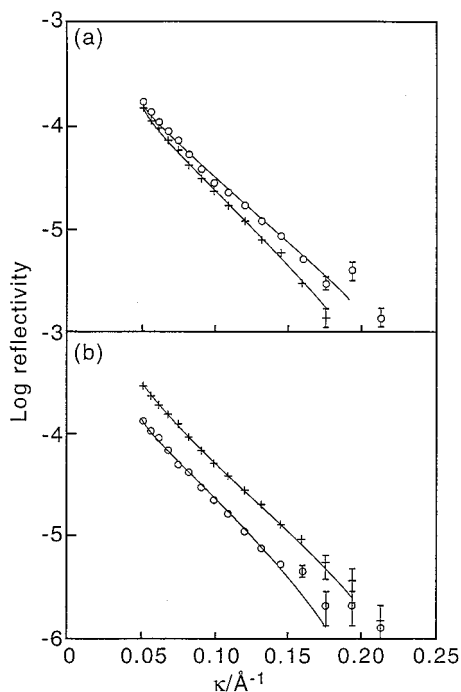
Figure 4. Neutron reflectivity profiles for SDS/C_{12}B/C_{12}M mixtures in the mole fraction ratio 50/25/25 and at an overall concentration of 0.261 mM: (a) hSDS/dC_{12}B/dC_{12}M (O) and dSDS/hC_{12}B/dC_{12}M (+), (b) dSDS/dC_{12}B/hC_{12}M (O) and dSDS/dC_{12}B/dC_{12}M (+). Temperature 313 K. The continuous lines are the best fits to the data using the compositions given in Table 3, the scattering lengths given in Table 1, and thicknesses in the range 21−24 ± 3 Å.

the surface tension. For SDS/C_{12}B we find β^{NR} is only −1.6,[20] whereas β^{σ} is −14.3, and for C_{12}B/C_{12}M β^{NR} is −2.0[22] whereas β^{σ} is 0.0. Importantly, when the compositions of the ternary

mixtures are calculated using these values of β^{NR} in eq 7 a much improved agreement with the observed compositions is obtained at the two lower SDS concentrations studied, and at all three compositions the order of composition agrees with experiment. These results are given in Table 3. The main observation, that the SDS fraction in the layer is small, could not occur given the values of β^{σ} calculated, but is a natural consequence of the much smaller value of β^{NR} for the interaction of SDS and C_{12}Betaine.

The first result is that the predictions using the surface tension data in combination with the pseudophase separation model and Holland's approximation for the ternary interactions (eq 7) give results that barely resemble the direct measurements of the surface excess. Since the pseudophase separation model also fails seriously for one of the binary mixtures and significantly for one of the others, this catastrophic failure may be a result of either of the two main assumptions. That the problem may lie with the pseudophase separation model is indicated by the following considerations. We recall that the directly observed surface excesses in the SDS/C_{12}B binary mixtures indicate a much weaker interaction than that predicted in the pseudophase separation model. In addition, in the C_{12}B/C_{12}M system, the observed compositions indicate a significant interaction, while the model predicts ideality. Both of these differences lie well outside experimental error and, indeed, they are reproduced in the ternary systems. In the 25/25/50 and 25/50/25 mixtures (see Table 3) the observed SDS composition is low and this can only be explained if it interacts relatively weakly with both the other components. The strong interaction between SDS and C_{12}B that is obtained from the pseudophase separation model must always have the effect of increasing the SDS surface excess well beyond that expected from the values of the respective cmcs and leads to the anomalously high values for the SDS excess in the third column of Table 3. Conversely, a stronger interaction between C_{12}B and C_{12}M will raise the C_{12}B concentration above the pseudophase prediction, as observed for the first two compositions in Table 3. It is clear that any progress in this area will require one or other of the two approximations being used to be bypassed and such an approach has been developed by Blankschtein and co-workers for a ternary system,[18] although so far they have only considered micellar mixing.

The second result from the work is that the use of β^{NR} from neutron reflection data allows much better predictions of compositions than use of β^{σ} from surface tension data. It must be recognized that β^{NR} is an empirically derived parameter and such an approach is not of direct value in constructing a better theoretical model. However, that the values of β^{NR} for the three binary mixtures are obtained from a direct fit to the surface excess for the binary mixtures (i.e., β^{NR} is correct for the binaries almost by definition) and that their combination in the Holland approximation (eq 7) leads to a tolerable explanation of the ternary surface excesses indicates that the problem is probably due to contributions to the excess free energy of mixing in the binaries other than those resulting directly from pairwise interaction. We have argued elsewhere[20] that these anomalies may be due to an excess entropic term resulting from changes in the hydration of adsorbed layers on mixing. It would seem from the use of the "correct" neutron values of β^{NR} for the binaries that, once these anomalies are accounted for in the binaries, eq 7 may be a reasonably accurate approximation.

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TABLE 3: Predicted and Observed Surface Compositions for Ternary Surfactant Systems at 313 K and at the Mixed Cmc (see Table 2)

bulk composition SDS/C_{12}B/C_{12}M	obsd composn/mol %	using β^σ values derived from surface tension[a]	surface composn/mol % using β^{NR} derived from neutron reflection[b]
25/25/50	$7 \pm 3/26 \pm 5/67 \pm 5$	15/9/76	5.5/18/76.5
25/50/25	5/42/53	31/39/30	5.5/29.5/65
50/25/25	27/32/40	34/29/37	16.5/20.5/63

[a] β^σ used were the best experimental values from the application of the pseudophase separation model to the surface tension data from the binary mixtures -14.3 (SDS/C_{12}B), -3.8 (SDS/C_{12}M), and 0 (C_{12}B/C_{12}M). [b] β^{NR} values used were obtained from directly measured compositions of the binary mixtures -1.6 (SDS/C_{12}B), -3.6 (SDS/C_{12}M) and -2.0 (C_{12}B/C_{12}M).

References and Notes

(1) Shinoda, K.; and others. In *Colloidal Surfactants*; Academic Press: New York, 1963.

(2) Clint, J. H. *J. Chem. Soc. Faraday Trans.* 1 **1975**, *71*, 946, 1327.

(3) Lange, H.; Beck, K. H. *Kolloid Z. Z. Polym.* **1973**, *251*, 424.

(4) Lucassen-Reynders, E. H. *J. Colloid Interface Sci.* **1972**, *41*, 156.

(5) Rubingh, D. N. In *Solution Chemistry of Surfactants*, Mittal, K. L., Ed.; Plenum: New York, **1979**, Vol. 1, p 337.

(6) Rosen, M. J.; Hua, X. Y. *J. Colloid Interface Sci.* **1982**, *86*, 164.

(7) Rosen, M. J.; Hua, X. Y.; *J. Colloid Interface Sci.* **1982**, *90*, 212.

(8) Rosen, M. J.; Zhu, B. Y.; *J. Colloid Interface Sci.* **1984**, *99*, 435.

(9) Holland, P. M. *Adv. Colloid Interface Sci.* **1986**, *26*, 111.

(10) Holland, P. M. *Colloids Surf.* **1986**, *19*, 171.

(11) Holland, P. M.; Rubingh, D. N. *J. Phys. Chem.* **1983**, *87*, 1984.

(12) Hall, D. G.; Huddleston, R. W. *Colloids Surf.* **1985**, *13*, 209.

(13) Puvvada, S.; Blankschtein, D. *J. Chem. Phys.* **1990**, *92*, 3710.

(14) Puvvada, S.; Blankschtein, D. *J. Chem. Phys.* **1992**, *96*, 5579.

(15) Sarmoria, C.; Puvvada, S.; Blankschtein, D. *Langmuir* **1992**, *8*, 2690.

(16) Jost, F.; Leiter, H.; Schwuger, M. J. *Colloid Polym. Sci.* **1988**, *266*, 554.

(17) Shiloach, A.; Blankschtein, D. *Langmuir*, **1998**, *14*, 4105.

(18) Shiloach, A.; Blankschtein, D. *Langmuir*, **1998**, *14*, 1618.

(19) Hildebrand, J. H.; Scott, R. L.; *Regular Solutions*; Prentice Hall: New York 1962.

(20) Hines, J. D.; Thomas, R. K.; Garrett, P. R.; Rennie, G. K.; Rennie, A. R. *J. Phys. Chem.*, in press.

(21) Hines, J. D.; Fragneto, G.; Thomas, R. K.; Garrett, P. R.; Rennie, G. K.; Rennie, A. R. *J. Colloid Interface Sci.* **1997**, *89*, 259.

(22) Hines, J. D.; Thomas, R. K.; Garrett, P. R.; Rennie, G. K.; Rennie, A. R. *J. Phys. Chem.* **1997**, *101*, 9215.

(23) Penfold, J.; Thomas, R. K. *J. Phys. Cond.* M*att.* **1990**, *2*, 1369.

(24) Lu, J. R.; Lee, E. M.; Thomas, R. K. *Acta Crystallogr.* 1996, *A52*, 11.

(25) Lu, J. R.; Thomas, R. K. In *Surfactant Adsorption and Surface Solubilization*; Sharma, R., Ed.; ACS Symposium Series; American Chemical Society: Washington, DC, 1996; Vol. 615, p 342.

(26) Thomas, R. K.; Penfold, J. *Curr. Opinion Colloid Interface Sci.* **1996**, *1*, 23.

(27) Lu, J. R.; Hromadova, M.; Simister, E. A.; Thomas, R. K.; Penfold, J. *Physica B* **1994**, *198*, 120.

(28) Lu, J. R.; Li, Z. X.; Smallwood, J.; Thomas, R. K.; Penfold, J. *J. Phys. Chem.* **1995**, *99*, 233.

(29) Lu, J. R.; Li, Z. X.; Thomas, R. K.; Staples, E. J.; Thompson, L.; Tucker, I.; Penfold, J. *J. Phys. Chem.* **1994**, *98*, 6659.

(30) Lu, J. R.; Purcell, I. P.; Lee, E. M.; Simister, E. A.; Thomas, R. K.; Rennie, A. R.; Penfold, J. *J. Colloid Interface Sci.* **1995**, *174*, 441.

(31) An, S. W.; Lu, J. R.; Thomas, R. K.; Penfold, J. *Langmuir* **1996**, *12*, 2446.

(32) Butler, J. A. V. *Proc. R. Soc.* **1932**, *A135*, 348.

(33) Guggenheim, E. A. *Trans. Faraday Soc.* **1937**, *33*, 151.

(34) Nelder, J. A.; Mead, R. *Comput. J.* **1965**, *7*, 308.

(35) Heavens, O. S. *Optical Properties of Thin Films*; Dover: New York, 1955.

(36) Penfold, J.; Richardson, R. M.; Zarbakhsh, A.; Webster, J. R. P.; Bucknall, D. G.; Rennie, A. R.; Jones, R. A. L.; Cosgrove, T.; Thomas, R. K.; Higgins, J. S.; Fletcher, P. D. I.; Dickinson, E.; Roser, S. J.; McLure, I. A.; Hillman, R.; Richards, R. W.; Staples, E. J.; Burgess, A. N.; Blake, T. D.; White, J. W. *J. Chem. Soc.* **1997**, *93*, 3899.

(37) Phillips, J. N. *Trans. Faraday Soc*. **1955**, *51*, 561.

(38) Hines, J. D., manuscript in preparation.