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

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Surface tension and neutron reflection measurements have been used to study the surface composition of aqueous solutions of mixtures of sodium dodecyl sulfate (SDS) and *n*-dodecyl-β-D-maltoside (C_{12}maltoside) and C_{12}maltoside and *n*-dodecyl-*N,N'*-dimethylamino betaine (C_{12}betaine). From measurements of surface tension and mixed critical micelle concentrations (cmc) the pseudo-phase separation model has been used to calculate values of the interaction parameters in the micelle, β^M, and at the surface, β^σ. SDS/C_{12}maltoside mixtures behave nonideally and both β^M are negative, indicating attractive interactions between the two surfactants, but the C_{12}maltoside/C_{12}betaine mixtures are closer to being ideal. Direct measurements of the surface excess using neutron reflection on isotopic mixtures of the surfactants are shown to be consistent with the surface tension measurements using the integrated form of the Gibbs equation. These direct values of the surface excess were found to agree with predictions from the partial phase separation model in the case of the nonideal pair, SDS/C_{12}maltoside, but were different for the ideal pair, C_{12}maltoside/C_{12}betaine. It is suggested that this may result from the relatively large errors in the partial phase separation model when the mixture is very unsymmetrical (very different cmc's coupled with weak interaction). The C_{12}maltoside/C_{12}betaine mixture was found to behave regularly in that β^σ showed negligible variation with either surface pressure or composition. On the other hand for the nonideal pair, SDS/C_{12}maltoside, the magnitude of β^σ decreased with surface pressure, consistent with reduced interaction as the molecules are more widely spaced, and also decreased with higher SDS fraction in the layer, consistent with an increasing contribution from electrostatic repulsion.

Introduction

The optimization of mixtures of surfactants in aqueous solution is an important part of the formulation of many commercial cleaning products. There are many examples in the literature showing that binary mixtures of different types of surfactant are nonideal in such a way that important properties of the mixture are quite different from those of the individual species.[1−19] One of the keys to the successful use of mixtures in commercial formulations is to take advantage of this synergy, but the prediction of the properties of such strongly interacting systems is not trivial.

For mixtures of surfactants in aqueous solutions at concentrations up to and just above the critical micelle concentration (cmc) strong interactions are only likely to be significant in aggregates such as micelles and adsorbed layers, for which the important properties are the cmc, surface excess, and surface pressure. First thermodynamic treatments of mixtures focused on ideal mixing. Thus, Shinoda[20] showed that the cmc's of binary mixtures of sodium alkyl carboxylates of different alkyl chain length could be modeled using a formalism based on Raoult's law which relates the cmc of the mixture of any composition to the harmonic mean of the values for the individual species. In Shinoda's work and that of most others, the micelle or surface layer is treated explicitly as a separate phase with a composition distinct from that of the bulk. Lange and Beck[21] and Clint[22] extended this approach to include prediction of monomer activities in the bulk and the micelle composition above the cmc.

Rubingh,[7] Rosen,[2] and others[15,23,24] have treated nonideal binary mixtures using the pseudo-phase separation model (PPS), where nonideality is included in the form of activity coefficients of each surfactant in the bulk phase. Evaluation of these activity coefficients then becomes the important step. The excess free energy in the form of the activity coefficients can generally be expressed as a series expansion, but in all the models so far devised only the first term is taken, which means that the excess free energy is constrained to be symmetrical with respect to micellar composition. It has been suggested that this implies that only enthalpic effects contribute to the nonideality,[7,8] and this has led to the name regular solution theory (RST) for this model, in analogy to the assumption of ideal entropy in the regular solution model of bulk solutions.[25] Adsorbed mixed surfactant layers have been similarly treated by Rosen[1] and Holland.[26] In both cases existing ideal thermodynamic treatments, by Goodrich[27] and Butler,[28] have been modified to include activity coefficients evaluated using the same first-order approximation as above. In this way, surface tension lowering

and individual surface excesses can be estimated for nonideal binary mixtures.

The pattern of the model described above is that the variation of the cmc of a binary mixture is accounted for by the cmc's of the pure components and a single empirical interaction parameter. To the extent that a whole set of data can be fitted in terms of these parameters, the model is judged to be successful or not. However, the model also predicts a composition for the micelle, and a further, more severe, test is to compare the prediction with observed measurements of micelle composition. Thus, it is conceivable that the PPS model could account perfectly for the variation of cmc with composition but would fail to predict the correct compositions. However, it is experimentally difficult to determine micellar compositions; only neutron small angle scattering can do it directly and then only at higher concentrations,[18] where deviations even from ideal behavior become weaker. Similar considerations apply to layers adsorbed at the air/solution interface except that, instead of the cmc, the bulk concentration of the mixture at a given surface pressure is accounted for in terms of an empirical surface interaction parameter and the bulk concentrations of the individual surfactants at the same surface pressure. Once again, the surface composition is predicted, but this prediction is rarely tested.[1,29] In this case, the composition is, in principle, accessible to surface tension measurements, but the accuracy is poor, the experiment is tedious, and the measurements are limited to the sub-CMC region. In this paper we explore the limits of applicability of the present models by comparison of predicted phase compositions with those measured directly by neutron reflection for two mixtures, one of a zwitterionic and nonionic surfactant and the other of an anoinic and nonionic surfactant. Although the hydrophilic head groups are all different, the hydrophobe is a dodecyl chain for all three species considered. The anionic surfactant is sodium dodecyl sulfate (SDS), the zwitterionic is *n*-dodecyl-*N*,*N*′-dimethylamino acetate (C_{12}betaine), an alkyl carboxy group with one CH_2 group separating the charges, and the nonionic is *n*-dodecyl-*β*-D-maltoside (C_{12}maltoside). The latter is of the alkyl saccharide type, a group that is gaining popularity both for research and in commercial formulations. It is expected that the zwitterionic/nonionic mixture should be close to ideal, while the charge shielding from the nonionic and reduction in steric repulsion from the anionic should introduce interactions which will lead to nonideality in the anionic/nonionic system.

Neutron reflection is now a well-established method for probing adsorbed layers and is particularly well suited to the study of mixed systems because it is straightforward, by isotopic substitution, to make the neutrons sensitive to only one adsorbed species at a time.[17,18,30-35] Surface excesses directly measured by neutrons may be integrated according to the Gibbs equation to yield value of the surface tension lowering at any given concentration.[36] Comparison with the observed value of the surface tension at a concentration where there are no uncertainties in the surface tension (e.g. at the cmc) provides an essentially model independent check for consistency.

Thermodynamic Treatment of Binary Surfactant Mixtures

The results in this and a subsequent paper show some discrepancies from PPS predictions, and it is useful to have an outline of the key thermodynamic results for later reference. In a micelle containing two surfactants mixing ideally, the situation may be described by a form of Raoult's Law:[37]

$$\ln a_i = \ln a_i^0 + \ln x_i \qquad (1)$$

where a_i is the activity of species i in the bulk solution and a_i^0 is the activity of i in a solution where it is the only species present. When dealing with nonideality in a micelle a_i^0 will represent the cmc of pure single surfactant species i, and for nonideality in a mixed adsorbed layer at a given surface pressure Π, it will represent the concentration of species i required to attain the same value of Π when i is the only surface active species present. For nonionic surfactants, where there is no counterion activity to be included, and at the cmc, eq 1 may be written in terms of the cmc's of the pure components and that of the mixture at a given micellar composition, x_i,

$$\alpha_i c_{mix}^M = x_i c_i^M \qquad (2)$$

where α_i is the mole fraction of surfactant i in the surfactant mixture and c^M denotes a cmc. Since the x_i must sum to unity,

$$\frac{1}{c_{mix}^M} = \sum_{i=1}^{n} \frac{\alpha_i}{c_i^M} \qquad (3)$$

which is Shinoda's result for the ideal case.[20]

Nonideality may be included by modifying the values of the cmc's by activity coefficients f_i,

$$\frac{1}{c_{mix}^M} = \sum_{i=1}^{n} \frac{\alpha_i}{f_i c_i^M} \qquad (4)$$

which are then described by a series expansion with respect to the composition of the micellar pseudophase,[38]

$$RT \ln f_i = \sum_i x_2^2 A_i [(1 - 2x_2)^{(i-1)} + 2(1 - x_2)(i - 1)(1 - 2x_2)^{(i-2)}] \qquad (5)$$

If the expression 5 is limited to the first-order term, it becomes, for a binary system,

$$RT \ln f_1 = A x_2^2 \qquad (6)$$

with an analogous expression for f_2. The adjustable parameter A is usually divided by RT and written as β^M, the nonideality parameter for micellization.[1,2,7] The numerical value of β^M may be found by iterative solution of the equation resulting from substitution of equation 6 into (3) with the activity coefficient included;

$$\beta^M = \frac{1}{x_2^2} \ln \left[\frac{\alpha_1 c_{mix}^M}{x_1 c_i^M} \right] = \frac{1}{x_1^2} \ln \left[\frac{\alpha_1 c_{mix}^M}{x_2 c_2^M} \right] \qquad (7)$$

subject to the conditions

$$\alpha_2 = 1 - \alpha_1 \qquad (8)$$

$$x_2 = 1 - x_1$$

The form of eq 6 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

$$G^E = \beta^M RT x_1 x_2 \qquad (9)$$

In the regular solution theory of bulk solutions the nonideality is attributed entirely to enthalpic contributions when

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$$\beta^{M} = \frac{N(W_{11} + W_{22} - 2W_{12})}{RT} \qquad (10)$$

where W_{ii} are the self interaction enthalpies and W_{12} is the interaction enthalpy between species 1 and 2. The same physical interpretation of β^{M} has been given by Rubingh.[7] In a system where the first-order fit accounts for the activity coefficients β^{M} will clearly be invariant with composition and the values of c_{mix}^{M} and the micellar composition can be predicted for all bulk-phase compositions from the value of β^{M}.

The above model, the pseudo-phase separation (PPS) model, takes no account of the degree of association of ionic surfactant species in the micelle with their counterions. The apparent success of the model in explaining systems which include charged surfactants (e.g. refs 3−7, 9, 14, 18) does not necessarily imply that electrolyte effects are unimportant but may simply be a result of the fact that such measurements are subject to large experimental error.

Nonideality at the interface can be treated analogously to give an equation similar to (7),[1]

$$\beta^{\sigma} = \frac{1}{(x_2^{\sigma})^2}\ln\left[\frac{\alpha_1 c_{mix}}{x_1^{\sigma} c_1^{\sigma}}\right] = \frac{1}{(x_1^{\sigma})^2}\ln\left[\frac{\alpha_2 c_{mix}}{x_2^{\sigma} c_2^{\sigma}}\right] \qquad (11)$$

where c_1^{σ} and c_2^{σ} are the concentrations of surfactant species 1 and 2 that individually produce a layer of the same surface pressure as that of the mixture of bulk composition α_i and total concentration c_{mix}. Rosen's approach is based on that of Goodrich,[27] in which the surface is taken to consist only of ideally mixed surfactant molecules and can therefore be treated essentially as a two-dimensional gas with the application of the condition that $\Gamma_{solvent} = 0$. Holland[26] has given a treatment parallel to that of Rosen but applying the approximations to the treatment of the ideal surface made by Lucassen-Reynders[39] which stems from the treatment of Butler.[28] The Butler model allows for the inherent heterogeneity of the Gibbs dividing plane by including an additional potential depending on the prevailing surface tension, which adds an extra force field term to the chemical potential. We do not discuss this further except to note that Holland's interaction parameter, which we denote β^{s}, is not equivalent to Rosen's β^{σ}. In this paper we calculate surface compositions using the Rosen formulation of nonideal mixing. In the region below the cmc, β^{σ} is reasonably accessible and does not require assumptions about extra parameters, such as the partial molar areas, which are required for β^{s}.

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

$$\kappa = \frac{4\pi}{\lambda}\sin\theta \qquad (12)$$

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

$$R(\kappa) = \frac{16\pi^2}{\kappa^2}|\hat{\rho}(\kappa)|^2 \qquad (13)$$

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

$$\hat{\rho}(\kappa) = \int_{-\infty}^{+\infty}\exp(-i\kappa z)\rho(z)dz \qquad (14)$$

TABLE 1: Neutron Scattering Lengths for the Different Components

component	$\sum b_i \times 10^3/$Å
H_2O	−0.0168
D_2O	0.1919
hSDS	0.12
dSDS	2.62
hC_{12}betaine	0.04
dC_{12}betaine	2.64
hC_{12}maltoside	0.51
dC_{12}maltoside	2.85

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[42] 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 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[43] for a simple structural model. 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

$$\rho = \sum n_i b_i \qquad (15)$$

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

$$A = \frac{1}{\Gamma N_a} = \frac{b}{\rho\tau} \qquad (16)$$

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 ± 2 Å^2 at 50 Å^2. It is also straightforward to extend eq 16 to the determination of surface excesses for binary mixtures, when it becomes

$$\rho = \frac{1}{\tau}\left[\frac{b_1}{A_1} + \frac{b_2}{A_2}\right] \qquad (17)$$

where the subscripts 1 and 2 refer to the two components. Ideally the evaluation of the adsorbed amounts should be made with the nondeuteriated component having zero scattering length because eq 17 then becomes identical with eq 16. 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

$$A_d' = A_d\left[1 + \frac{b_p A_d}{b_d A_p}\right] \qquad (18)$$

where the subscripts now refer to the deuteriated and protonated components, A_d' is the corrected area per molecule, and A_d has been evaluated using eq 16. A sufficiently accurate value of A_p is obtained from the reverse contrast situation. Even better is to use three combinations, dA/hB, hA/dB, and dA/dB all in NRW, where dA, etc., denotes that surfactant A is deuteriated. The use of the three combinations rather than just the first two gives a means to check the total coverage.

Experimental Details

The preparation and purification of protonated and deuteriated analogues of SDS and C_{12}betaine have already been described.[44,45] The preparation of dC_{12}maltoside was carried out according to a scheme modified from that suggested for C_{12}-glucoside by Havlinova et al.[46] A mixture of alcohol-free chloroform (40 mL), yellow mercury(II) oxide (5.2 g), mercury-(II) bromide (0.1 g), and Drierite (10 g) was added to a 250 mL round-bottomed flask and deuteriated n-dodecanol (3 g) and heptaacetyl-1-bromomaltose (50% molar excess) were added with stirring at room temperature and with exclusion of moisture. The extent of reaction was followed with TLC. The mixture was filtered, and the solids washed with fresh chloroform. The combined filtrate and washings were then extracted with aqueous 1 M KBr until the aqueous phase no longer became cloudy (in order to remove mercury salts). After washing with water, the organic solution was concentrated by rotary evaporation before the residue was dissolved in toluene, and this solution was filtered through a thin layer of activated silica gel. Following evaporation of solvent from the filtrate, the product was recrystallized from a small quantity of n-hexane to yield n-dodecylheptaacetylmaltoside. The acetyl groups were then removed by trans esterification using a methanol/sodium methoxide mixture at room temperature (followed by TLC). Dowex 50W (H) ion-exchange resin was added, after which the solution was filtered and concentrated. The product was recrystallized from acetone and purified on a silica column in acetone/ethanol. The proportion of ethanol in the solvent was progressively increased to ensure elution of the product after passage of the more hydrophobic impurities.

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 mN m^{-1} for three successive readings.

The neutron reflection measurements were made using the reflectometer SURF at ISIS (Rutherford Appleton Laboratory,
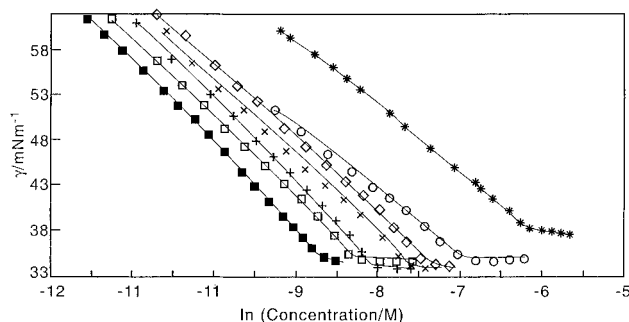

Figure 1. Surface tensions of C_{12}betaine/C_{12}maltoside mixtures as a function of ln c_{total}. The mole fractions of C_{12}betaine are (■) 0, (□) 0.3, (+) 0.5, (×) 0.7, (◇) 0.8, (○) 0.9, and (∗) 1.0.
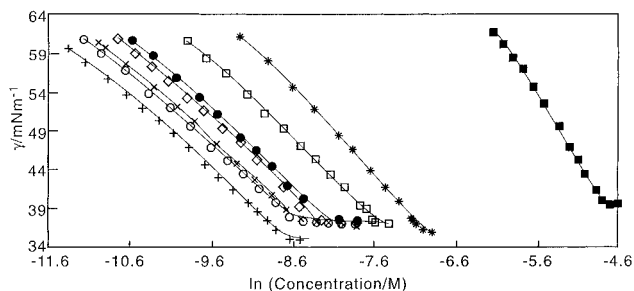

Figure 2. Surface tensions of SDS/C_{12}maltoside mixtures as a function of c_{total}. The mole fractions of SDS are (+) 0, (○) 0.2, (×) 0.3, (◇) 0.5, (●) 0.7, (□) 0.8, (∗) 0.9, and (■) 1.0.

TABLE 2: Cmc and Surface Tension Values for Each Bulk Composition (α Is the Fraction of First Named Surfactant)

	SDS/C_{12}maltoside		C_{12}betaine/C_{12}maltoside	
α	cmc/mM	γ_{cmc}/mN m^{-1}	cmc/mM	γ_{cmc}/mN m^{-1}
0	0.17	35.4	0.17	35.4
0.2	0.18	37.4		
0.3	0.17	37.3	0.23	35.5
0.5	0.20	37.5	0.31	34.6
0.7	0.26	38.1	0.47	35.0
0.8	0.45	37.2	0.62	35.2
0.9	0.82	36.9	0.94	35.3
1.0	7.95	39.6	2.05	38.7

Chilton, Didcot, U.K.). The instrument and the sample containers have been described previously.[47,48] 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 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 in Figures 1 and 2 for C_{12}betaine/C_{12}maltoside mixtures and SDS/C_{12}maltoside, respectively. Also shown are the corresponding plots for the pure species. The criterion of maximum adsorbed amount was used to determine the position of the discontinuity corresponding to the cmc, the maximum slope being calculated using a nonlinear least-squares fit. The values of the mixed cmc's are given in Table 2 together with values of γ at the cmc and are plotted as a function of α (the fraction of either SDS or C_{12}betaine) in Figures 3 and 4.

One of the features of the PPS model is that it relates each value of the mixed cmc to a value of the nonideality parameter
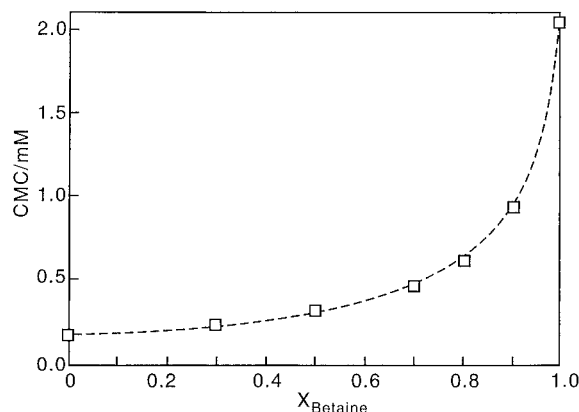
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Figure 3. Critical micelle concentrations of C_{12}betaine/C_{12}maltoside mixtures as a function of composition. The dashed line is calculated for ideal mixing.
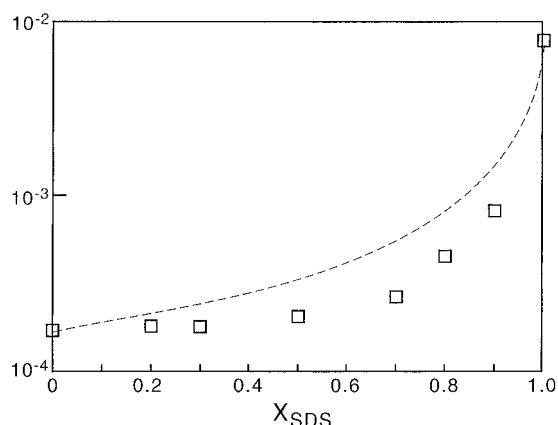

Figure 4. Critical micelle concentrations of SDS/C_{12}maltoside mixtures as a function of composition. The dashed line is calculated for ideal mixing.

TABLE 3: Calculated Values of β^M and x_i for Each Bulk Composition Studied (α Is the Fraction of First Named Surfactant)

	SDS/C_{12}maltoside		C_{12}betaine/C_{12}maltoside	
α	β^M	x_1	β^M	x_1
0		0.0		0.0
0.2	−4.0	0.11		
0.3	−4.6	0.17	0.03	0.04
0.5	−4.8	0.23	0.01	0.07
0.7	−5.0	0.28	−0.01	0.15
0.8	−3.5	0.29	−0.08	0.26
0.9	−2.8	0.33	-−0.02	0.43
1.0		1.0		1.0

β^M by eqs 7 and 8. The values of β^M derived by this means at each composition are given in Table 3 together with values of the predicted micellar composition. If mixing in the micelle is ideal, β^M should be zero (equivalent to the activity coefficients being unity), and this is evidently the case for the C_{12}betaine/C_{12}maltoside mixture since all the $|\beta^M|$ are less than about 0.1. This is confirmed by the comparison of the calculated values of the mixed cmc's according to the ideal model (eq 3) with the observed values, the calculated values being shown as a dashed line in Figure 3. Rosen[4] obtained a small value of β^M for the system C_{12}BMG/C_{12}E$_8$, which is a mixture of a zwitterionic similar to C_{12}betaine and the nonionic octaethylene glycol monododecyl ether. C_{12}betaine is electrically neutral at a pH of 7 so there are no electrostatic interactions, and since the two molecules have a similar head group cross section, they would be expected to mix ideally.

The two head groups in SDS and C_{12}maltoside are quite different and SDS is negatively charged, so it is not difficult to envisage that these two surfactants will mix nonideally. That this is the case is shown both by the values derived for β^M in Table 3 and by the large difference between the curve for ideal mixing and the observed values of the mixed cmc's in Figure 4. There is a large negative deviation from ideal mixing, corresponding in enthalpic terms to an attractive interaction between the two surfactants. This is consistent with the deviations observed for the similar SDS/C_{12}E$_8$, for which Holland gives a value of β^M of −3.9,[10] based on the data of Lange and Beck,[21] and for which Rosen gives a value of −2.7.[3] It is also consistent with the values of −2.4 obtained for SDS/C_{12}E$_3$/0.1 M NaCl and −2.7 for SDS/C_{12}E$_6$/0.1 M NaCl by small angle neutron scattering.[17,18] If the PPS model is correct, a set of data should be fitted by a single value of β^M, and Table 3 shows that this is not quite the case for the SDS/C_{12}maltoside system, although the spread in our values is only comparable with the difference between the values above for the system SDS/C_{12}E$_8$. The charge on the SDS molecules will tend to ensure that they are as widely spaced as possible, a situation that does not correspond with the random mixing that is supposedly required for the regular solution model to hold, which could contribute to the deviations in β^M. It is also possible to use the same model (eqs 11 and 8) to calculate values of the surface interaction parameter β^σ and the composition of the interface at various surface pressures. The composition of the interface is accessible from experiment either via the Gibbs equation or, more directly, from neutron reflection measurements. As we have discussed elsewhere, the calculation of surface excess from surface tension data for a single surfactant is generally less accurate than from neutron reflection, and this is even more so at concentrations further below the cmc. For an impure sample, surface tension data will generally give a misleading result because the presence of impurities has the consequence that it is impossible to write the correct Gibbs equation for the analysis, whereas neutron reflection will measure the true amount at the surface. A clear test of purity is therefore that the surface tension and neutron measurements should give the same value of the surface excess. The difficulty with this comparison is the low accuracy of the excess derived from the surface tension at lower concentrations where the slope $d\gamma/d \ln c$ starts to vary significantly. A much better test, which utilizes the high accuracy of the neutron measurements, is to integrate the neutron coverages using the Gibbs equation to yield changes in the surface tension over a given concentration range. These can then be compared directly with the surface tension measurements. Thus, for a single nonionic surfactant

$$\Delta\gamma = -RT\int_{\ln c_1}^{\ln c_2}\Gamma d \ln c \qquad (19)$$

and for a monovalent ionic surfactant

$$\Delta\gamma = -2RT\int_{\ln c_1}^{\ln c_2}\Gamma d \ln cf_{\pm} \qquad (20)$$

where $f_{\pm}$ is the mean activity coefficient. For a mixture of two surfactant species

$$\Delta\gamma = -RT[\sum_i\int_{\ln c_1}^{\ln c_2}2\Gamma_i d \ln cf_{\pm} + \sum_n\int_{\ln c_1}^{\ln c_2}\Gamma_n d \ln c] \qquad (21)$$

where i and n refer to ionic and nonionic species, respectively. Thus, for the SDS/C_{12}maltoside there would be one term of each type, and for C_{12}betaine/C_{12}maltoside there would be two terms of the second nonionic type.
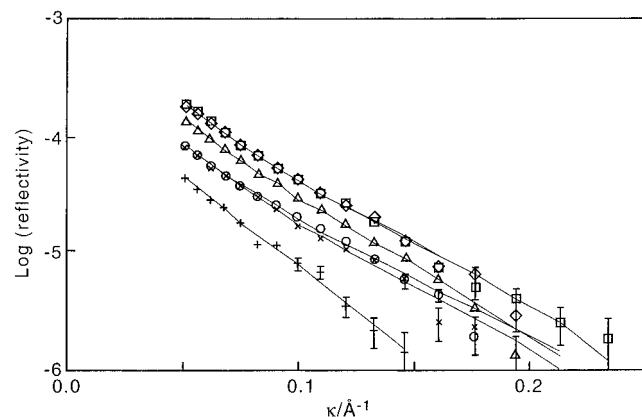
Figure 5. Neutron reflectivity profiles of deuteriated SDS in null reflecting water at various concentrations: (+) 0.6, (×) 0.9, (○) 1.15, (△) 3.6, (□) 8, and (◇) 15 mM. The continuous lines are the best fits of a single uniform layer model.
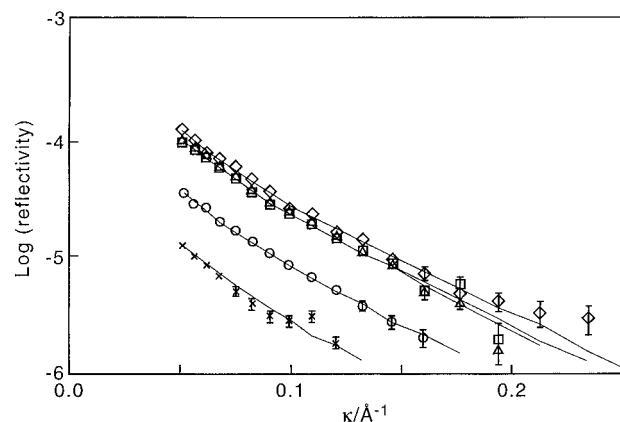

Figure 6. Neutron reflectivity profiles of chain deuterated C_{12}betaine in null reflecting water at various concentrations: (×) 0.01, (○) 0.05, (△) 0.5, (□) 1, and (◇) 2 mM. The continuous lines are the best fits of a single uniform layer model.
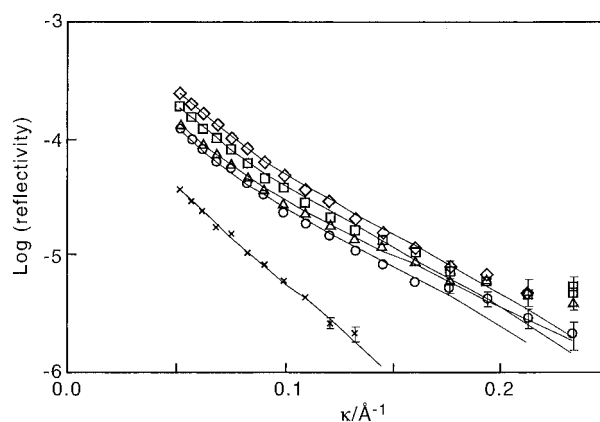

Figure 7. Neutron reflectivity profiles of chain deuterated C_{12}maltoside in null reflecting water at various concentrations: (×) 0.01, (○) 0.075, (□) 0.15, and (◇) 0.2 mM. The continuous lines are the best fits of a single uniform layer model.

Figures 5, 6, and 7 show neutron reflectivity profiles for the three surfactants on their own at different concentrations with the best fits of a single uniform layer shown as continuous lines. The data are fitted with two parameters, the thickness of the surfactant layer and its scattering length density, from which the area per molecule or the surface excess may be calculated using eq 16. The limiting values of these parameters at the cmc are given in Table 4. Values at the other compositions
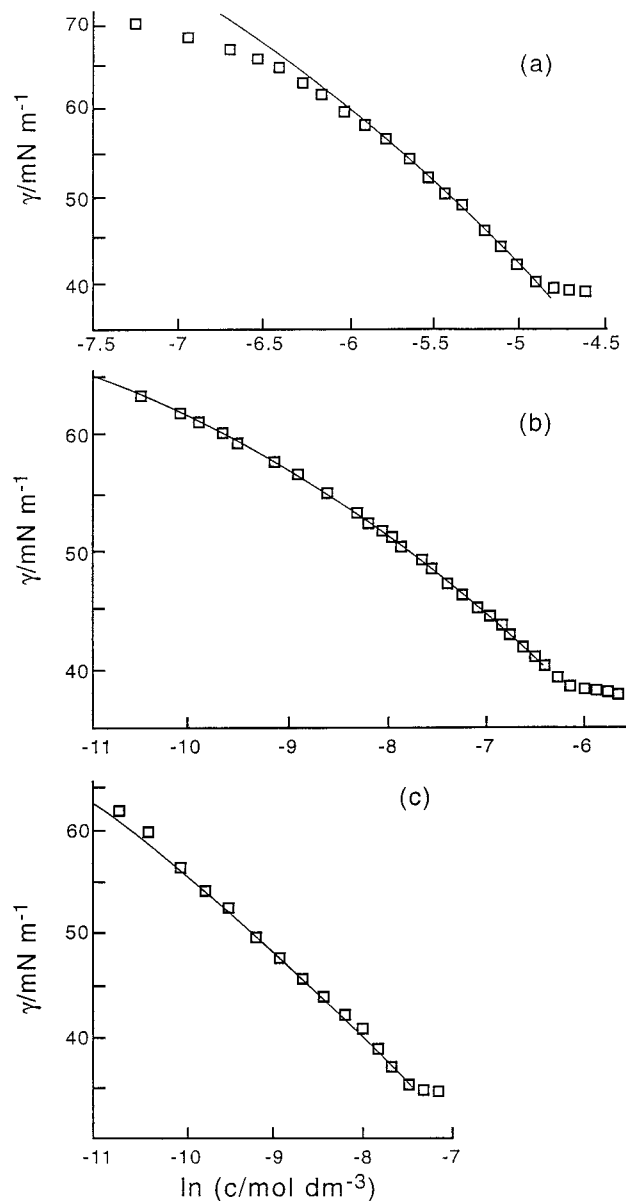

Figure 8. γ/ln c plots calculated from neutron reflection surface excesses compared with the direct measurement for (a) SDS, (b) C_{12}-betaine and (c) C_{12}maltoside.

TABLE 4: Properties of Single Surfactant Layers from Neutron Reflection

	$\rho \times 10^6/\text{Å}^2$	$\tau \pm 2/\text{Å}$	$\Gamma_{cmc}/\mu\text{M m}^{-2}$	$A_{cmc} \pm 3/\text{Å}^2$
SDS	3.42	18	3.9	43
C_{12}betaine	3.21	15.5	3.1	53
C_{12}maltoside	3.30	20.5	3.8	42

and concentrations are not listed but are used in the calculation described below.

The surface excesses obtained from neutron reflection were plotted against ln c and fitted to a quadratic equation. This was then integrated, using the appropriate equation, either (19) and (20), and an integration constant determined by the extrapolated value of ln c when $\Gamma = 0$, for which the tension should be that of pure water. The results are plotted in Figure 8 for each of the three surfactants. For SDS the predicted line agrees with the observed data down to a concentration of about 2 mM ($\gamma = 62$ mN m^{-1}) but then deviates above the observations. This deviation is consistent with trace amounts of divalent ions such as Ca^{2+} being present either as impurities or from the glassware. Clearly, the amount must be small

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TABLE 5: Surface Excesses and Compositions of C$_{12}$Betaine/ C$_{12}$Maltoside Solutions at the cmc Determined from Neutron Reflection (α Is the Fraction of First Named Surfactant)

α	mixture	$\rho \times 10^6/\text{Å}^{-2}$	$\tau/\text{Å}$	$\Gamma_{cmc} \pm 0.15/\mu\text{M m}^{-2}$	$A_{cmc}/\text{Å}^2$	x^{σ}_{Bet}
0.2	dB/hM	0.6	16 ± 4	0.6	275 ± 40	0.10
	hBdM	3.2	18.0 ± 2	3.4	48 ± 3	
	dBdM	3.6	16.5 ± 2	3.6	46 ± 3	
0.5	dB/hM	0.8	19	1.0	170	0.24
	hB/dM	2.6	19.0	2.9	58	
	dB/dM	3.4	18.5	3.8	44	
0.8	dB/hM	1.4	20	1.7	96	0.39
	hB/dM	2.2	17.0	2.2	75	
	dB/dM	3.5	17.0	3.6	47	

TABLE 6: Surface Excesses and Compositions of SDS/ C$_{12}$Maltoside Solutions at the cmc Determined from Neutron Reflection (α Is the Fraction of First Named Surfactant)

α	mixture	$\rho \times 10^6/\text{Å}^{-2}$	$\tau/\text{Å}$	$\Gamma_{cmc} \pm 0.15/\mu\text{M m}^{-2}$	$A_{cmc}/\text{Å}^2$	x^{σ}_{SDS}
0.2	dS/hM	0.6	19 ± 5	0.7	240 ± 40	0.14
	hSdM	3.3	15.5 ± 2	3.0	55 ± 4	
	dSdM	3.7	15.0 ± 2	3.3	50 ± 3	
0.5	dS/hM	0.5	21	0.7	250	0.17
	hS/dM	3.3	15.5	3.0	55	
	dS/dM	3.5	16.5	3.5	47	
0.8	dS/hM	0.9	20	1.1	150	0.21
	hS/dM	3.1	16.0	2.8	58	
	dS/dM	3.8	15.5	3.6	47	

because the deviation does not occur until a low concentration of SDS is reached. This is an example where the simple Gibbs equation (20) will not give the true surface excess because it does not include terms involving the divalent ions, which would lead to a prefactor in the equation of less than 2. Deviations of this type have been discussed previously and have been much larger than the one observed here.[35,49] For the zwitterionic and nonionic surfactants the agreement is very good over the whole range. Both were fitted by eq 19, which shows that the zwitterionic is behaving as a neutral species. Since it is extremely unlikely that the nonionic C$_{12}$maltoside would be affected by any trace ionic species present in the solution, the good agreement in this case establishes the validity of the comparison between neutrons and surface tension.

The partial coverages for the mixtures were determined by measuring the reflectivities of the three combinations dA/hB, hA/dB, and dA/dB all in NRW, where dA, etc., denotes that surfactant A is deuteriated. We do not show the large number of profiles obtained (each pair at three surfactant compositions, six overall concentrations, and three isotopic species). The results obtained by fitting a one-layer model to the data at the cmc and then applying eqs 16 to obtain the individual coverages are given in Tables 5 and 6. In all cases numerical integration of the Gibbs equation was performed on the quadratic curve of the best fit to the plots of Γ against $\ln c$ using eq 21. Figures 9 and 10 show the results of this consistency check on all three compositions used for the mixtures C$_{12}$betaine/C$_{12}$maltoside and C$_{12}$maltoside/SDS, respectively. Since the adsorption of C$_{12}$-betaine and C$_{12}$maltoside individually gives results completely consistent between surface tension and neutron reflection, good agreement of the results for their binary mixtures, as observed, gives further support to the validity of the surface tension/neutron comparison. More importantly it shows that the accurate and relatively easily obtained neutron surface excesses can be used to test models of surfactant mixing. Even for the SDS/C$_{12}$maltoside case, where the consistency for SDS on its own was not perfect, the calculated lines fit the data reasonably well over the whole range of the measurements. The only deviations occur for low concentrations when SDS is the
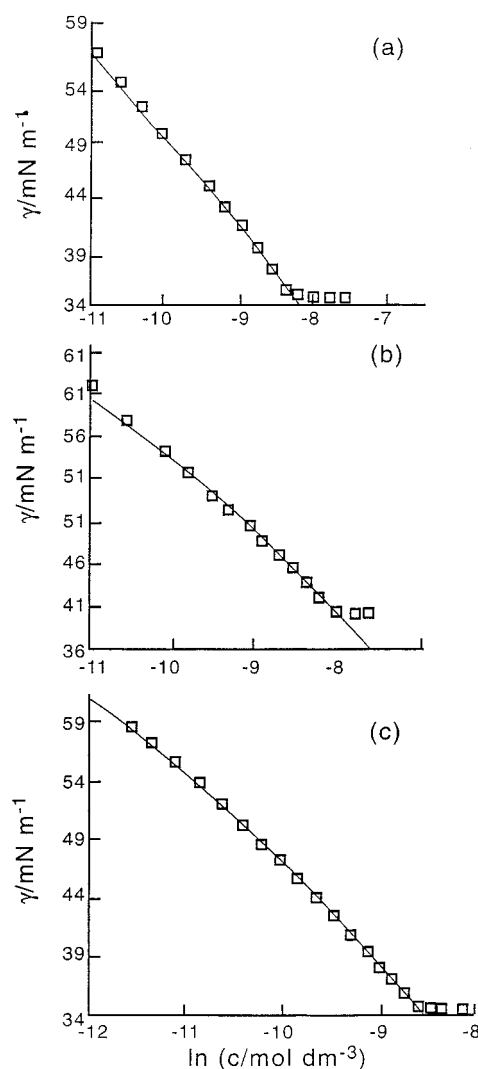
Figure 9. $\gamma/\ln c$ plots calculated for C$_{12}$betaine/C$_{12}$maltoside mixtures from neutron reflection surface excesses compared with the direct measurement for composition ratios of (a) 20:80, (b) 50:50, and (c) 80:20 (betaine to maltoside).

dominant component. This analysis demonstrates that the surface excesses determined by surface tension and neutron reflection agree, but because the experimental errors in determining surface excess from surface tension are generally larger than those from neutron reflection, the latter values are more useful for testing theories of surfactant mixing.

Table 7 compares the compositions of the C$_{12}$betaine/C$_{12}$-maltoside layer determined from neutron reflection with those calculated from the PPS model using values of the concentrations at the appropriate surface pressure. The neutron values have been determined by interpolation from the experimental curves. The calculations suggest that mixing at the surface is approximately ideal, which is similar to that in the micelles, but the directly determined compositions are more symmetrical in terms of composition. Indeed, if the directly measured compositions are used to calculate β^{σ}, a value of -1.7 is obtained for all compositions and surface pressures greater than 15 mN m^{-1} and a value of -1.4 at 15 mN m^{-1}. As expected from the direction of the deviations from ideal mixing, this suggests an attractive interaction between C$_{12}$betaine and C$_{12}$-maltoside, although not a very large one. The constancy of the compositions as a function of surface pressure implies that the excess area of mixing is zero, which could be taken as an indicator of ideal behavior. We return to a discussion of the discrepancy after considering the SDS/C$_{12}$maltoside results.
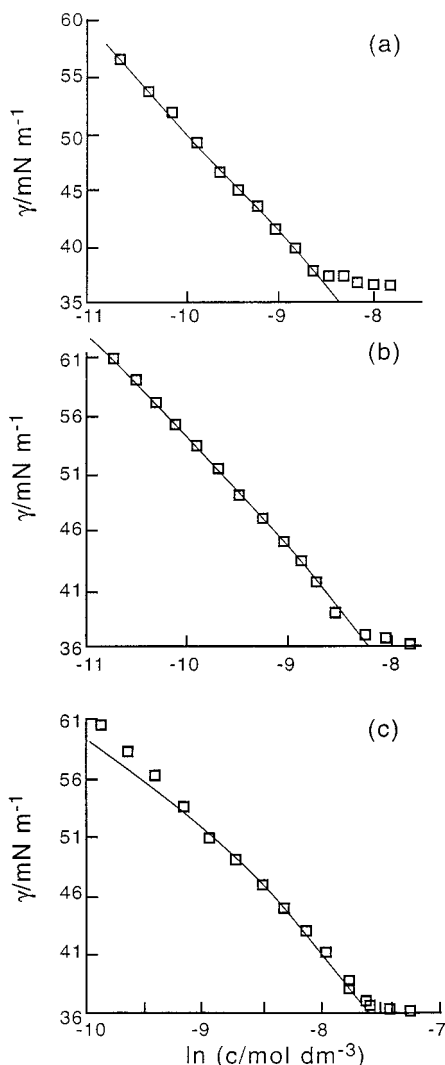
Figure 10. $\gamma/\ln c$ plots calculated for SDS/C$_{12}$maltoside mixtures from neutron reflection surface excesses compared with the direct measurement for composition ratios of (a) 20:80, (b) 50:50, and (c) 80:20 (SDS to maltoside).

TABLE 7: Predicted (Pseudo-Phase Separation Model) and Observed (Neutron Reflection) Compositions and Interaction Parameters (PPS) for the C$_{12}$Maltoside/C$_{12}$Betaine Layer at Various Bulk Compositions and Surface Pressures

Π/mN m^{-1}	β^{σ}	x_B^{σ}(PPS)	x_B^{σ}(N)	$\Gamma \times 10^{10}$/mol cm^{-2}
		20 Betaine/80 Maltoside		
30	−0.08	0.03	0.10	3.1
25	−0.04	0.02	0.09	2.9
20	0.01	0.02	0.10	2.7
15	−0.05	0.02	0.08	
		50 Betaine/50 Maltoside		
30	−0.01	0.07	0.21	3.7
25	−0.03	0.08	0.20	3.4
20	0.01	0.07	0.20	3.2
15	−0.01	0.07	0.19	2.7
		80 Betaine/20 Maltoside		
30	0.01	0.23	0.39	3.3
25	−0.01	0.23	0.39	3.1
20	0.0	0.23	0.40	2.9
15	−0.01	0.23	0.40	2.6

The equivalent set of results is shown for the SDS/C$_{12}$-maltoside system in Table 8. Comparison with the behavior of the cmc's suggests that the system will be nonideal with a negative interaction parameter, and this is indeed found for both calculated and directly measured compositions, which are now

TABLE 8: Predicted (Pseudo-Phase Separation Model) and Observed (Neutron Reflection) Compositions and Interaction Parameters (PPS) for the SDS/C$_{12}$Maltoside Layer at Various Bulk Compositions and Surface Pressures

Π/mN m^{-1}	β^{σ}	x_B^{σ}(PPS)	x_B^{σ}(N)	$\Gamma \times 10^{10}$/mol cm^{-2}
		20 SDS/80 Maltoside		
30	−4.0	0.09	0.11	3.7
25	−3.7	0.06	0.07	3.4
20	−3.3	0.04	0.04	3.4
15	−3.0	0.03	<0.01	
		50 SDS/50 Maltoside		
30	−3.8	0.16	0.16	4.2
25	−3.5	0.13	0.13	3.9
20	−3.3	0.10	0.10	3.6
15	−3.1	0.08	0.07	3.3
		80 SDS/20 Maltoside		
30	−2.9	0.23	0.21	4.7
25	−2.7	0.19	0.18	4.1
20	−2.5	0.15	0.15	3.4
15	−2.3	0.12	0.11	3.1

in good agreement. The size and magnitude of β^{σ} is comparable with values obtained by neutron specular reflection for β^s for SDS/C$_{12}$E$_3$/0.1 M NaCl ($\beta^s = -3.4$) and for SDS/C$_{12}$E$_6$ /0.1 M NaCl ($\beta^s = -2.5$).[17,18] The value of β^{σ} is comparable in magnitude with β^M and varies with both surface pressure and composition. The steady decrease of β^{σ} with surface pressure is intuitively reasonable in that any interaction between the two surfactants must become weaker as the surface concentration decreases. The negative excess area of mixing is what would be expected for an ionic/nonionic mixture where the ionic head group is smaller than that of the nonionic. Both directly measured and calculated values of β^{σ} show a systematic decrease as the overall SDS concentration increases, as does β^M. This can be attributed to the increasing electrostatic repulsion in the layer, or micelle, as the fraction of SDS increases.

The strong attractive interaction between SDS and C$_{12}$-maltoside has the effect of reducing the impact of the large difference in the two cmc's on the calculated compositions. This suggests that a possible cause of the large discrepancy between calculated and observed values of the surface compositions for the C$_{12}$betaine/C$_{12}$maltoside system results from the differences in the two cmc's being very large. This might simply be because of error because Hoffman and Pössnecker have shown that errors in the evaluation of the activity coefficients using the first-order term in the expansion (eq 6) become larger as the composition moves away from the ratio 1:1.[19] In this respect it is interesting that the generally good agreement reported by Rosen and Hua[1] for binary mixtures of ethoxylated alcohols and for mixtures of these with anionic and cationic surfactants was for systems whose cmc's were much less skewed in favor of one component.

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