

Surface Adsorption in Ternary Surfactant Mixtures above the Critical Micelle Concentration: the Effects of Asymmetry on the Composition Dependence of the Excess Free Energy

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Abstract

The composition of the adsorbed layer of a ternary surfactant mixture at the air-water interface has been studied by neutron reflectivity. The adsorption of the ternary mixture of octaethylene monododecyl ether, $C_{12}E_8$, sodium dodecyl 6-benzene sulfonate, LAS, and sodium dioxyethylene glycol monododecyl sulphate, SLES, and of each of the binary mixtures, at solution concentrations greater than the mixed critical micelle concentration (CMC) are highly non-ideal. In the ternary mixture the surface adsorption is dominated by the $C_{12}E_8$ and LAS, and there is little SLES at the interface. The departure from ideality in the binary mixtures can be quantitatively described by applying the pseudo-phase approximation with quadratic and cubic terms in the excess free energy of mixing (G_E) both at the surface and in the micelles. The same parameters that describe the binary interactions give a quantitative fit to the adsorbed fractions in the ternary mixture over a wide range of composition. A similar analysis is effective for the mixture when SDS replaces SLES. Of the set of six G_E required to fit the ternary data one is ideal (SLES-LAS) and three, LAS- $C_{12}E_8$ (micelle) and $C_{12}E_8$ -SLES (micelle and surface), have minima occurring at a composition (mole fraction) of the anionic species of 1/3.

Introduction

The diverse domestic, industrial and technological applications of surfactants in home and personal care products, foods, pharmaceuticals, dyeing, mineral flotation, and paints and other surface coatings, invariably involve mixtures. Different types of surfactants are mixed to optimise different aspects of product performance, usually making use of synergistic interactions between the different surfactant components. Such surfactant mixtures also offer

greater flexibility in processing and formulation. In addition, the surfactants used commercially are usually already mixtures of different isomeric forms with polydispersity in their alkyl chain length and headgroup and variability in the headgroup structures. Hence surfactant mixing in solution, micelles and at interfaces has been extensively studied experimentally and theoretically, e.g. references (1) - (5).¹⁻⁵ The synergistic effects observed in mixed surfactants have been described in terms of non-ideal mixing, where the basic assumption used to rationalize the mixing is that the micelles or the surface layer behave as separate phases (pseudo-phases) to which the Gibbs-Duhem equation can be applied.¹⁻³ This assumption is then usually supplemented by further assuming that the free energy of mixing in the micelle or layer obeys the regular solution approximation, in which the departure from ideality is described by a single parameter. Although the pseudo-phase approximation is a significant assumption,⁶ it has been shown that for typical micelle dimensions the pseudo-phase and the alternative mass action approaches are essentially equivalent.^{7,8} An entirely different method of quantifying surfactant mixing, which uses molecular thermodynamics has also been extensively developed, e.g. by Nagarajan^{9,10} and Blankschtein et al.¹¹⁻¹³

The theoretical models so far used are applicable at any concentration. Experiment is much more limited. Thus, mixing in micelles can be studied using values of the mixed critical micelle concentration (CMC), which can be determined accurately in a number of ways, but a much more rigorous test of models would be to use values of both the CMC and micelle compositions in the vicinity of the CMC. However, the latter are largely inaccessible at present. This means that experimental data can only realistically be interpreted in terms of the regular solution model, in which the excess free energy of mixing, G_E , is characterized by the single parameter, B_m , with a minimum at the equimolar composition. Only direct measurement of the composition can confirm the accuracy of this assumption. Before the advent of neutron reflection (NR) surface tension (ST) measurements were effectively the only source of experimental data for surface mixing. The composition of the layer can be determined using the Gibbs adsorption equation and information about the free energy of the

surface, equivalent to the CMC, can also be obtained from the ST itself. The latter can be handled in a number of ways, e.g. the concentration at which a given ST is reached,¹⁴ use of surface pressure–area terms to compare different surfactants,³ and fitting of the Szyskowski equation to obtain surface activity coefficients.¹⁵ The combination of the two measurements can be used to probe the shape of G_E more accurately. However, ST measurements can only give values of the surface composition *below the CMC*, whereas most practical applications use concentrations *above the CMC*. Neutron reflection (NR) can be used to determine compositions of mixed monolayers equally well above and below the CMC and we have shown that in the region just above the CMC adsorption at the surface becomes sensitive not just to the G_E for mixing in the layer but also to the CMC and the composition of the micelle.¹⁶ This behaviour had been predicted theoretically¹⁷ and is also predicted by the pseudophase approximation. Apart from the more direct relevance to applications, such measurements above the CMC have the potential to probe deviations of G_E for both micelles and surface from the symmetry of the regular solution assumption, and hence to explore possible contributions from factors such as differences in size and charge between the components of a mixture.¹⁸

The properties of a wide range of different binary surfactant mixtures have been studied.^{1,3,19} Bearing in mind the limitations described above, the results are usually consistent with the pseudophase–regular solution model.^{1–3,19} More recent applications making use of neutron scattering techniques have identified some of the limitations of these two assumptions, mostly in binary mixtures.^{20–22} Although the two assumptions adequately describe mixtures in which the departure from ideality is not large, effects of changes in packing, significantly strong interactions and the effects of changes in hydration are often apparent. This is particularly the case when the components have very different preferred curvatures or are subject to different packing constraints, such as in the non-ionic surfactant mixture of monododecyl triethylene glycol ($C_{12}E_3$) and monododecyl octaethylene glycol ($C_{12}E_8$)¹⁶ or mono and di-rhamnose rhamnolipid mixtures,²³ where the discrepancies with model calculations

can be large.

Reports on the experimental behaviour of ternary and multicomponent mixtures are much less frequent. Holland and Rubingh² and Graciaa et al.²⁴ have used the pseudophase approximation to treat the mixed CMCs of a range of ternary mixtures of non-ionic–cationic–anionic, nonionic–cationic and non-ionic–anionic surfactants. They found that the binary interaction parameters could satisfactorily explain the ternary behaviour. Cui et al. have used CMCs and applied the Szyskowski equation to interpret ST data of ternary mixtures of some anionic–cationic–nonionic ternary mixtures of commercial surfactants.¹⁵ They similarly found that the ternary behaviour could be interpreted in terms of the binary parameters, and also showed that the data could be interpreted in terms of a pseudo-binary system based on the regular solution model. Moulik et al. probed the micellisation and solution properties in binary and ternary mixtures of C₁₆pyridinium chloride, C₁₆TAB and Brij-56, using a variety of methods and made a similar study of ternary mixtures of alkyltriphosphonium halides, mainly drawing only semiquantitative conclusions about the mixing.^{25,26} Similarly, Szymczyk and Janczuk obtained only qualitative information about ternary mixtures of C₁₆TAB with two commercial nonionic surfactants.²⁷ Das et al. studied the CMCs and adsorption of mixtures of three cationic surfactants using tensiometry and conductimetry and concluded that the “Rubingh-Holland” model gave unexpected results for their ternary system.²⁸ Hines et al.²⁹ used NR and ST to study the interactions in the ternary mixture of sodium dodecyl sulphate (SDS)–*n*-dodecyl- β -D-maltoside and *n*-dodecyl-N,N-dimethylamino betaine in micelles and in adsorbed layers. Hines et al. showed that there could be large differences between the mixing parameters obtained from the surface compositions directly determined by NR and those derived from ST. However, the compositions of ternary mixed layers were well explained using the summation of the pairwise interactions. Finally, Staples et al.³⁰ used NR to study the adsorption of multicomponent mixtures of non-ionic–anionic mixtures containing dodecanol of up to six components. They attempted to apply the pseudophase regular solution model but found that the behaviour of dodecanol deviated too far from

normal micellization to be included in such a calculation. Theoretical calculations have been more successful in assessing whether pair interactions will give an adequate description of ternary mixtures. Thus Coret et al. have presented CMC predictions for the ternary surfactant mixture sodium octyl sulphate, sodium dodecyl diethylene glycol sulphate (SLES), and penta-ethyleglycol monodecyl ether ($C_{10}E_5$) in which they used molecular thermodynamics to calculate the binary interaction parameters and then combined these in a pseudophase calculation of the CMC and obtained close agreement with experiment.³¹ A similarly successful prediction for a wider range of surfactants has been done by Shiloach and Blankschtein.³²

The focus of this study is the ternary surfactant mixture of $C_{12}E_8$, sodium dodecyl 6-benzene sulfonate (LAS), and sodium dodecyl diethylene glycol sulphate (SLES). This mixture is currently the base formulation for a wide range of home and personal care products. NR and ST are used to probe the surface properties over the whole ternary composition parameter space. The NR measurements provide a direct measure of the variation in the surface composition at a fixed surfactant concentration above the mixed CMC, and at a fixed composition as a function of solution concentration. The NR and ST data are analysed using both the extension of the pseudophase model to ternary mixtures and using cubic terms in the expansion of the activity coefficients.

Experimental Details

Surface Tension

The surface tension measurements were made on a Krüss K10T maximum pull digital tensiometer, using a Pt–Ir du Nouy ring. Measurements were made at $25 \pm 0.1^\circ\text{C}$ with the temperature controlled using a Haake K15 water bath with a manual D30 circulator connected to the water bath. All surface tension values were referred to a value of $71.5 \pm 0.1 \text{ mN m}^{-1}$ at $25 \pm 0.1^\circ\text{C}$ for ultrapure water. To achieve temperature equilibrium, the solutions were contained in a glass vessel (48 mm diameter and 30 mm depth) and kept in the instrument for 10 min. before the surface tension was measured. The most concentrated solution

was measured first, approximately $8 \times \text{CMC}$, and subsequent concentrations were obtained by dilution with ultrapure water containing 10^{-6} M NaOH, with all subsequent volumes added verified by weight. The average of three consecutive surface tension measurements was taken and in between measurements the Pt/Ir ring was washed in ultrapure water and flame dried immediately before further use.

Neutron Reflectivity

In the kinematic approximation²² the neutron reflectivity R depends on κ , the wave vector transfer in the direction perpendicular to the surface (z) and the square of the Fourier transform of the scattering length density perpendicular to the surface. The wave vector transfer is given by $\kappa = 4\pi(\sin \theta)/\lambda$, where θ is the grazing angle of incidence and λ is the neutron wavelength. The scattering length density ρ_z is given by $\rho_z = \sum_i b_i n_{iz}$ where n_{iz} is the number density of species i and b_i its neutron scattering length. For neutrons ρ_z can be manipulated using D-H isotopic substitution, where the scattering lengths of H and D are respectively -3.75×10^{-6} and 6.67×10^{-5} Å. A 92 : 8 mole % H₂O:D₂O mixture, null reflecting water (NRW), has a scattering length density of zero, and hence a refractive index the same as air. For a monolayer of deuterium labelled surfactant adsorbed at the interface the reflectivity then arises only from the adsorbed layer, in which case the reflectivity can be expressed exactly as

$$R(\kappa) = \frac{64\pi^2}{\kappa^4} \rho^2 \sin^2 \left(\frac{\kappa d}{2} \right) \quad (1)$$

where d and ρ are the thickness and scattering length density of the adsorbed layer. For a single surfactant species at the interface the area per molecule A is related to the product $d \times \rho$ and the $\sum b$ value (see Table 1) of the surfactant such that

$$A = \frac{\sum b}{d\rho} \quad (2)$$

and the surface excess, Γ , is given by $\Gamma = 1/N_a A$. This approach has been extensively used to study surfactant and mixed surfactant adsorption at the air-water interface.²² For a ternary mixture Eqn (2) becomes

$$d\rho = \frac{\sum b_1}{A_1} + \frac{\sum b_2}{A_2} + \frac{\sum b_3}{A_3} \quad (3)$$

Thus by making a series of NR measurements with each of the three components deuterium labelled in turn, a set of simultaneous equations are obtained, which can be solved to determine the adsorbed amounts of each component. The $\sum b$ values for the different surfactants studied here are summarised in Table 1.

Table 1: Scattering lengths for deuterated (d) and hydrogenous (h) surfactants used in the ternary mixture. In the deuterated surfactants only the hydrocarbon chain is deuterated at a level of 98% deuterium.

compound	$\sum b \times 10^3 \text{ \AA}$	compound	$\sum b \times 10^3 \text{ \AA}$
dC ₁₂ E ₈	2.82	hC ₁₂ E ₈	0.22
dLAS	3.48	hLAS	0.35
dSLES	2.88	hSLES	0.24

For the binary and ternary mixtures measurements were made for the isotopic combinations of dd, dh, and hd and for ddd, dhh, hdh, and hhd respectively in NRW, where d and h refer to the deuterium labelled and hydrogenous surfactant components. In both cases the system is over determined and the sets of 3 or 4 simultaneous equations based on Eqns (2) and (3) were solved using the subroutine MB11a from the Harwell subroutine library,³³ which uses a simplex algorithm to solve a series of over-determined linear equations.

The NR measurements were made on the SURF and INTER reflectometers at ISIS^{34,35} and on FIGARO at the ILL.³⁶ In each case the measurements were made at a fixed glancing angle of incidence θ using a range of wavelengths sorted by time of flight, to measure $R(\kappa)$. On SURF the measurements were made at $\theta = 1.5^\circ$ and neutron wavelengths $0.5 - 6.8 \text{ \AA}$ to cover a κ range $0.048 - 0.5 \text{ \AA}^{-1}$. On INTER the equivalent κ range was $0.03 - 0.5 \text{ \AA}^{-1}$

using $\theta = 2.3^\circ$ and a λ range $0.5 - 15 \text{ \AA}$. On FIGARO the angle of incidence was 3.6° with neutron wavelengths $2 - 30 \text{ \AA}$ giving a κ range $\approx 0.02 - 0.39 \text{ \AA}^{-1}$. The reflected intensity was normalised to the direct beam and the absolute reflectivity values were calibrated by reference to the reflectivity from the surface of D_2O . The samples were contained in sealed Teflon troughs held at 298K and containing a sample volume of $\approx 25 \text{ mL}$. Each individual NR measurement took 15 to 30 minutes and the measurements were made in sequence in a 5, 6 or 7 position sample changer.

Materials

C_{12}E_8 was obtained from Nikkol and used as supplied. The hydrocarbon for the h-LAS was synthesised in Oxford, sulphonated at Unilever, and purified as previously described.³⁷ The hSLES and deuterated chain, dSLES, were synthesised in Oxford. The ethylene glycol monododecyl ether was first purified by medium pressure liquid chromatography (MPLC) and the sulfonated SLES was purified by recrystallization from ethanol–propanol mixtures as described by Xu et al.³⁸ The alkyl chain deuterated C_{12}E_8 , $\text{d-C}_{12}\text{E}_8$, was also synthesised in Oxford and purified by MPLC. The fully deuterated LAS, dLAS, was synthesised and purified using the same procedures as the hLAS. SDS and dSDS were synthesised in Oxford and recrystallized from ethanol as described elsewhere.³⁹ The measurements were all made in 10^{-6} M NaOH at a theoretical pH of 8, to correspond to the alkaline pH conditions of many commercial detergent formulations. However due to atmospheric CO_2 all the solutions were measured to be at a $\text{pH} \approx 6.5 \pm 0.5$. The NaOH pellets were obtained from Sigma, and D_2O (99.9 %) was obtained from Fluorochem. High purity water (Elga Ultrapure) was used throughout. The purity of the surfactants was assessed by ST. All glassware and Teflon troughs were cleaned in dilute Decon90 solution and rinsed in ultrapure water, ethanol, and acetone, and dried under nitrogen gas flow.

Measurements

The NR measurements were made for the binary mixtures of $C_{12}E_8$ –SLES and LAS–SLES using the isotopic combinations dd, dh, and hd, and for the ternary mixtures $C_{12}E_8$ –LAS–SLES using the isotopic combinations ddd, dhh, hdh, and hhd. The data for $C_{12}E_8$ –LAS were taken from Penfold et al.³⁷ All the measurements were made in NRW. The compositions at which the measurements were made at a total fixed surfactant concentration of 2 mM are marked in Figure 1. NR measurements were also made at a fixed composition for $C_{12}E_8$:LAS:SLES at the mole ratio 0.125:0.125:0.75 and surfactant concentrations of 0.5, 1.0 and 2.0 mM. Some additional NR measurements were made for the ternary mixture $C_{12}E_8$:LAS:SDS, where SLES was replaced by SDS, at a surfactant concentration of 2 mM and at solution compositions of 0.375:0.375:0.25 and 0.125:0.125:0.75.

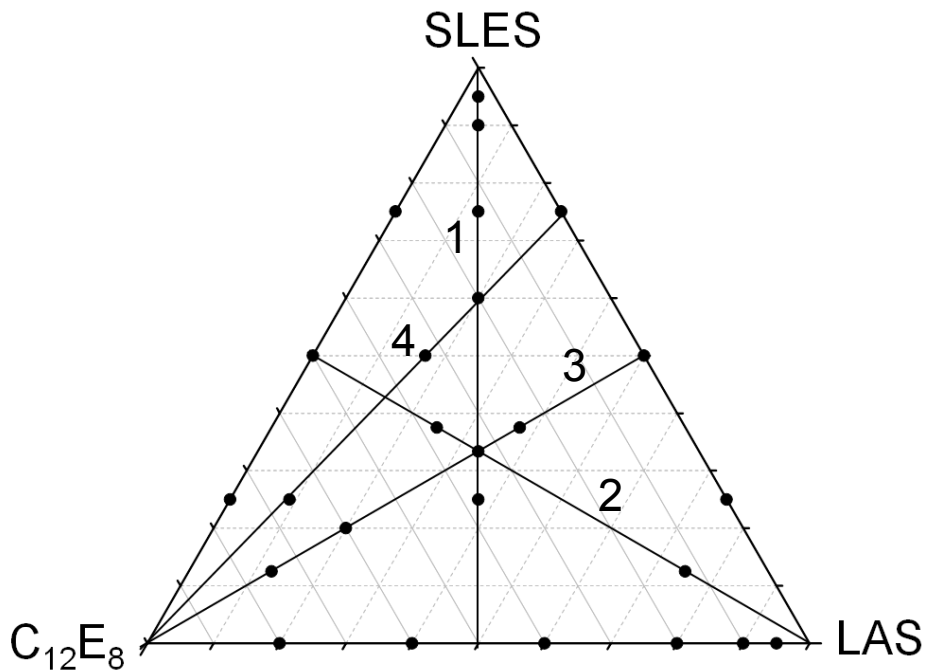


Figure 1: Ternary diagram for a SLES–LAS– $C_{12}E_8$ mixture, indicating the composition at which NR measurements were made at an overall surfactant concentration of 2 mM. ST measurements were made for the binary mixtures of SLES–LAS, LAS– $C_{12}E_8$, $C_{12}E_8$ –SLES and for the ternary mixture of SLES–LAS– $C_{12}E_8$ at a fixed solution composition of 0.75: 0.125: 0.125 mole ratio.

Thermodynamics

The pseudophase assumption means that at equilibrium the chemical potentials of the components of pseudophases (micelle, solution, surface layer) are equal. Equating the chemical potentials of a surfactant component in the bulk solution to that in the micelles^{1,3,19,40} gives the fundamental equation,

$$x_i = \frac{c_i^{mon}}{f_i^\mu c_i^\mu} \quad (4)$$

where x_i is the mole fraction of component i in the micelle, c_i^{mon} the monomer concentration of i in the bulk solution, f_i^μ its activity coefficient in the micelle (the activity coefficient in the bulk is taken to be 1), and c_i^μ its CMC. At the CMC $c_i^{mon} = \alpha_i c_{mix}^\mu$ where α_i is the mole fraction of monomer in solution and c_{mix}^μ is the mixed CMC. The use of this relation to derive the equations necessary for the analysis of a binary mixture including quadratic and cubic contributions to the activity has been given in a previous paper¹⁸ and here we only give the equivalent equations for a ternary mixture.

From the sum of the micellar mole fractions in a ternary mixture, which must equal unity, Eqn (4) gives

$$\frac{1}{c_{mix}^\mu} = \frac{\alpha_1}{f_1 c_1^\mu} + \frac{\alpha_2}{f_2 c_2^\mu} + \frac{\alpha_3}{f_3 c_3^\mu} \quad (5)$$

The activity coefficients are derived from the excess free energy of mixing, G_E , which in an expansion including only quadratic and cubic terms is^{2,18,41,42}

$$G^E = x_1 x_2 B_{12} + x_2 x_3 B_{23} + x_3 x_1 B_{31} + x_1 x_2 (x_1 - x_2) C_{12} + x_2 x_3 (x_2 - x_3) C_{23} + x_3 x_1 (x_3 - x_1) C_{31} \quad (6)$$

where B_{ij} and C_{ij} are the binary interaction constants. The importance of this expansion is that it is consistent with the Gibbs–Duhem equation, which itself is a requirement of the pseudophase approximation. In the regular solution approximation the C coefficients are

zero and the activity coefficients then depend only on the quadratic terms in x_i and are^{19,43}

$$\begin{aligned}
RT \ln f_1 &= x_2^2 B_{12} + x_2 x_3 (B_{12} - B_{23} + B_{31}) + x_3^2 B_{31} \\
RT \ln f_2 &= x_3^2 B_{23} + x_3 x_1 (B_{23} - B_{31} + B_{12}) + x_1^2 B_{12} \\
RT \ln f_3 &= x_1^2 B_{31} + x_1 x_2 (B_{31} - B_{12} + B_{23}) + x_2^2 B_{23}
\end{aligned} \tag{7}$$

In the analysis that follows we will also include cubic terms^{2,42}

$$\begin{aligned}
RT \ln f_1 &= [2x_1 x_2 (1 - x_1 + x_2) - x_2^2] C_{12} + 2x_2 x_3 (x_3 - x_2) C_{23} \\
&\quad - [2x_3 x_1 (1 - x_1 + x_3) - x_3^2] C_{31} \\
RT \ln f_2 &= [2x_2 x_3 (1 - x_2 + x_3) - x_3^2] C_{23} + 2x_3 x_1 (x_1 - x_3) C_{31} \\
&\quad - [2x_1 x_2 (1 - x_2 + x_1) - x_1^2] C_{12} \\
RT \ln f_3 &= [2x_3 x_1 (1 - x_3 + x_1) - x_1^2] C_{31} + 2x_1 x_2 (x_2 - x_1) C_{12} \\
&\quad - [2x_2 x_3 (1 - x_3 + x_2) - x_2^2] C_{23}
\end{aligned} \tag{8}$$

A total activity coefficient f_i is the product of the quadratic and cubic contributions to f_i . The importance of introducing the cubic terms is that the interaction between any pair of surfactants is not constrained to be a maximum or a minimum at the equimolar composition. The effects of asymmetry, which are highly likely to occur, especially from packing or charge interactions, can therefore be identified.

The general difficulty with CMC data is that the composition of the micelles, i.e. the x_i , is not known experimentally and mixed CMC data have to be analysed by using an iterative solution of some combination of Eqns (7) and (5). We have shown that this can be done effectively for binary mixtures by use of the function $\ln(f_2/f_1)$ introduced by Redlich and Kister,⁴⁴ which reduces the degree of the equation by 1. Using Eqn (4) at the CMC gives

$$\ln \left(\frac{f_2}{f_1} \right) = \ln \left[\frac{x_1 c_1^\mu \alpha_2}{x_2 c_2^\mu \alpha_1} \right] \tag{9}$$

For ternary mixtures there is an additional independent Redlich–Kister function, $\ln(f_3/f_2)$, which is obtained by rotating the subscripts sequentially. When Eqns (7) and (8) are substituted into the left hand side of Eqn (9) we obtain

$$\begin{aligned} & B_{12}(x_1 - x_2) + x_3(B_{23} - B_{31}) + [(x_1 - x_2)^2 - 2x_1x_2] C_{12} \\ & + x_3(2x_2 - x_3)C_{23} + x_3(2x_1 - x_3)C_{31} - \ln \left[\frac{x_1 c_1^\mu \alpha_2}{x_2 c_2^\mu \alpha_1} \right] = 0 \end{aligned} \quad (10)$$

where again the second equation of the pair is obtained sequentially. Given that all the terms in Eqn (10) can be differentiated, the two Redlich–Kister equations can be satisfactorily solved using the Newton-Raphson method.⁴⁵ The above analysis applies to both the CMCs and adsorption at the surface. For the latter the CMCs are replaced either by a concentration at which a certain surface pressure is reached, c^π , or by a CMC corrected for the different limiting surface pressures of the components, following a procedure given by Holland.³ The B and C parameters will generally not be the same for surface and micelle.

Above the CMC the calculation is quite different and the basic equation is obtained by mass balance and substitution of Eqn (4) to give two independent equations¹

$$\begin{aligned} x_1 &= \frac{\alpha_1 c - f_1 x_1 c_1^\mu}{c - f_1 x_1 c_1^\mu - f_2 x_2 c_2^\mu - f_3 x_3 c_3^\mu} \\ x_2 &= \frac{\alpha_2 c - f_2 x_2 c_2^\mu}{c - f_1 x_1 c_1^\mu - f_2 x_2 c_2^\mu - f_3 x_3 c_3^\mu} \end{aligned} \quad (11)$$

Elimination of $x_3 = 1 - x_1 - x_2$ then gives the following pair of equations

$$\begin{aligned} (f_3 c_3^\mu - f_1 c_1^\mu) x_1^2 + (f_3 c_3^\mu - f_2 c_2^\mu) x_1 x_2 + (c + f_1 c_1^\mu - f_3 c_3^\mu) x_1 - \alpha_1 c &= 0 \\ (f_3 c_3^\mu - f_2 c_2^\mu) x_2^2 + (f_3 c_3^\mu - f_1 c_1^\mu) x_1 x_2 + (c + f_2 c_2^\mu - f_3 c_3^\mu) x_2 - \alpha_2 c &= 0 \end{aligned} \quad (12)$$

Writing $A_{31} = f_3c_3^\mu - f_1c_1^\mu$ and $A_{32} = f_3c_3^\mu - f_2c_2^\mu$ these reduce to

$$\begin{aligned} A_{31}x_1^2 + A_{32}x_1x_2 + (c - A_{31})x_1 - \alpha_1c &= 0 \\ A_{32}x_2^2 + A_{31}x_1x_2 + (c - A_{32})x_2 - \alpha_2c &= 0 \end{aligned} \quad (13)$$

where

$$A_{ji} = f_jc_j^\mu - f_ic_i^\mu \quad (14)$$

Once again the Eqns (13), (7) and (8) have to be solved iteratively. Again the Newton–Raphson method can be used because all the relevant functions can be differentiated but the iteration has to be handled with some care. This was achieved by plotting out the pair of functions, e.g. the two Redlich-Kister functions, and checking that the iteration produced the correct intersection point. All this and the data were analysed using our own programs written in Java. The compositions of the micelle are the output and the corresponding monomer concentrations are obtained by applying Eqn (4) to each of the three x_i values.

Results and Discussion

There are four types of data, each with a different dependence on the interactions between the surfactants, (i) the values of the mixed CMC, (ii) the variation of the adsorbed mole fractions of the binary mixtures with bulk composition (the edges of Figure 1), (iii) the variation of adsorbed fraction with composition of the ternary mixtures (the lines running across Figure 1), and (iv) the variation of composition with total concentration of the ternary mixtures, not shown by Figure 1. All four depend on G_E^μ , where μ designates the micelle, and all except the first also depend on G_E^s for the surface. The sensitivity of the different types of data to G_E depends on the region of micelle or surface composition that is probed. In what follows we discuss each type of data separately, but for the model that includes both B and C parameters, which we refer to as the BC model, we show the fit of a single set of values of twelve B and C parameters.

Surface Tension and CMC

The ST was measured for each of the binary surfactant mixtures SLES–LAS, LAS–C₁₂E₈, C₁₂E₈–SLES, and the variation in the mixed CMC with composition is summarised in Tables S1 (a)–(c) in the Supporting Information. Figure 2 shows the variation in CMC with solution composition for the three binary mixtures. The binary equivalents of Eqns (10) and (5) were used to fit three different models to the data, ideal mixing ($B = C = 0$), regular solution mixing ($C = 0$), and the BC model. For the BC model the fit uses the same values of B and C as used for all the later data fitting, which means that the fit shown in Figure 2 for this model may not be the optimum fit to the CMC data alone. The SLES–LAS mixture is ideal and in the other two cases there are small differences in the values of the minimum in G_E fits for the regular solution and the BC models, although the BC model gives a quite different composition dependence for G_E . Thus, the minimum in the regular solution G_E occurs at $x_{anionic} = 0.5$, where $x_{anionic}$ is the mole fraction of the anionic surfactant in the micelle, but it occurs at approximately $x_{anionic} = 1/3$ in the BC model for LAS–C₁₂E₈. The points at which the minima occur are marked in Figure 2 (b) and (c), and draw attention to the fact that basically only one half of G_E is being probed by the experimental data, which is itself a result of the large difference in CMC for the two components. For a fixed value of the minimum in G_E the effect of a shift in x_{min} from 0.5 to 0.37 is to shift the non-ideal stabilization towards lower bulk composition and hence a smaller minimum value of G_E is required to fit the data, e.g. for LAS–C₁₂E₈ G_{Emin} changes from $-0.97RT$ to $-0.72RT$. Although Figure 2 indicates that the use of the more elaborate BC model to fit the CMC data is barely justifiable, we will show that, unlike the B only model, it is consistent with the whole set of data.

The ST of the ternary SLES–LAS–C₁₂E₈ mixture was measured for one composition at a mole ratio of 0.125:0.125:0.75 and the data are plotted in Figure S2 in the Supporting Information. The mixed CMC was found to be 0.34 ± 0.05 mM and the ST at the CMC was 39.3 ± 0.2 mN m⁻¹. The full form of Eqns (10) and (5) was used to calculate the mixed

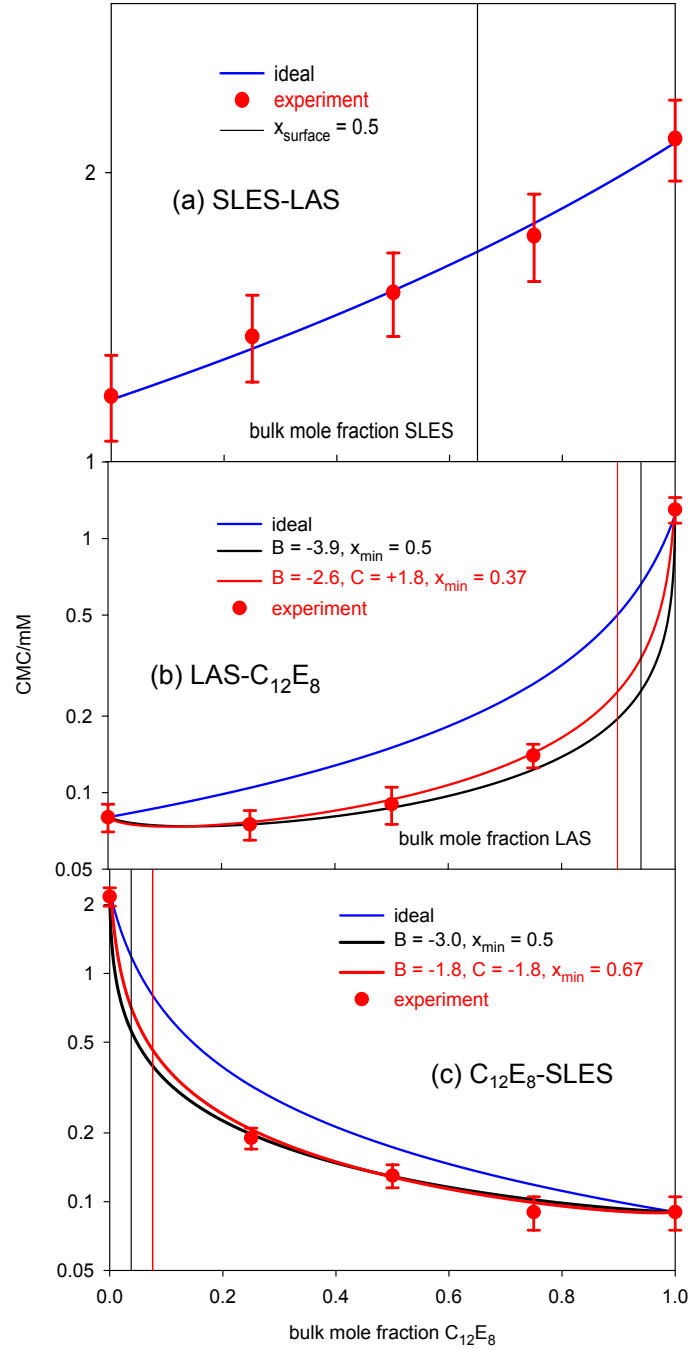


Figure 2: CMC variation with solution composition for (a) SLES–LAS, (b) LAS– C_{12}E_8 and (c) C_{12}E_8 –SLES. The lines in blue are the best fits for ideal mixing, those in black the best fits for the regular solution model with a single parameter B and those in red for an excess free energy of mixing, G_E , characterized by both quadratic (B) and cubic (C) parameters. The vertical lines in black mark a micellar mole fraction of 0.5, which is also the composition of minimum excess free energy for the regular solution model, and those in red mark the mole fraction at the minimum of G_E in the BC model.

CMC for this ternary mixture using the values for the three binary mixtures in Figure 2. The ideal value was 0.55 mM, the regular solution model gave 0.27 mM and the BC model gave 0.32 mM, here an improvement over the regular solution value and within error of the experimental result. The calculated composition of the micelle at the CMC was 0.25 SLES using the regular solution model and this dropped to 0.19 for the BC model, again indicating the key role of the extra C parameter on the asymmetry of G_E .

Neutron Reflectivity

Neutron reflectivity (NR) measurements were made for the binary mixtures $C_{12}E_8$ -SLES and LAS-SLES at the air-water interface and measurements have previously been reported for $C_{12}E_8$ mixtures.³⁷ In each case measurements were made for the three differently labelled combinations of surfactants, dd, dh and hd. NR measurements were also made for the ternary SLES-LAS- $C_{12}E_8$ mixtures at the ternary compositions marked in Figure 1. In the ternary mixtures four differently labelled combinations of surfactants, ddd, dhh, hdh, and hhd, were measured. Some typical reflectivity data are shown in Figure 3 for the mole ratio 0.125 : 0.125 : 0.75 $C_{12}E_8$:LAS:SLES and the results of the basic analysis in terms of a single layer are given in Table 2.

Table 2: Key model parameters for a single layer model fit to the reflectivity data for the ternary mixture $C_{12}E_8$:LAS:SLES at a total concentration of 2 mM and a molar ratio of 0.125:0.125:0.75.

contrast	$d \pm 2 \text{ \AA}$	$10^6 \times \rho \pm 0.1$	$10^5 \times d\rho \pm 0.2$
ddd	27	2.3	6.0
dhh	30	0.9	2.5
hdh	23	0.9	2.0
hhd	16	0.9	1.4

The reflectivity data and the model parameters are consistent with a thin monolayer of surfactant at the interface, with a thickness of $\approx 20 \pm 2 \text{ \AA}$. For the determination of the area per molecule (A) and the adsorbed amount (Γ) it is the product $d\rho$ that is important, as can

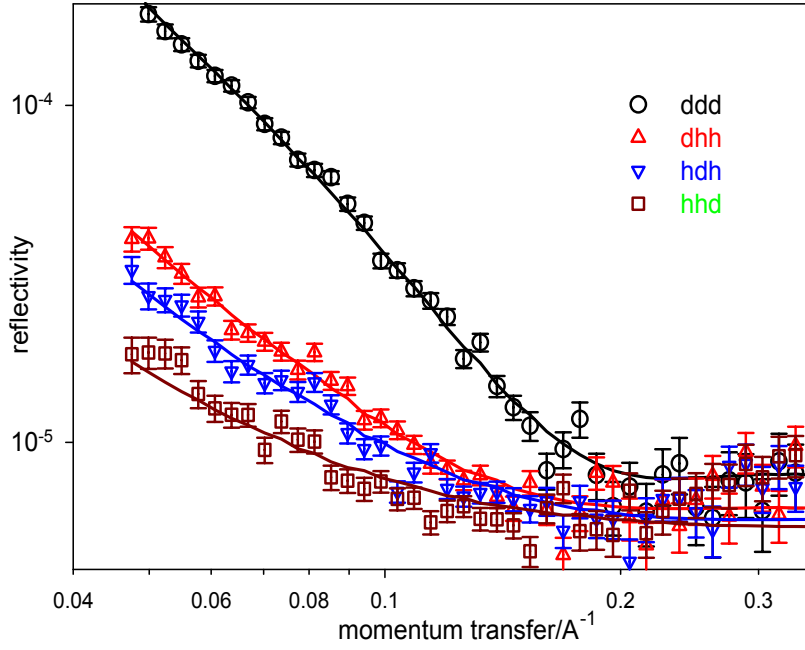


Figure 3: Neutron reflectivity for the ternary mixture $C_{12}E_8$:LAS:SLES in the molar ratio 0.125:0.125:0.75 at a total concentration of 2 mM (above the CMC). The isotopic compositions are ddd, dhh, hdh, and hhd as marked in the figure, where d indicates a perdeuterated hydrophobic unit. The solid lines are profiles calculated using the parameters in Table 2 for a single monolayer.

be seen from Eqns (2) and (3). Three or four simultaneous equations were obtained from the measurements at the different contrasts, and were solved using a simplex algorithm for over determined sets of linear equations. The surface composition and total adsorption data for a fixed total concentration of 2 mM are given in Table 3. The data for LAS-C₁₂E₈ are taken from Penfold et al.³⁷ However, in the course of doing the present fits it was noticed that the fraction of LAS at a bulk mole fraction of 0.40 was inconsistently high when compared with the data in Figure 2 of the Supplementary Information. This was traced to a typographical error of 2.0 instead of 2.8 in the value of $d\rho$ in Table 4a of the Supplementary Information of that paper. The value has been corrected in the present Table.

Table 3: Variation in surface composition and total adsorption at a total concentration of 2 mM for SLES-LAS, LAS-C₁₂E₈ (data from Penfold et al.³⁷) and C₁₂E₈-SLES. The data marked * has been modified from the original paper (see text).

SLES-LAS (right hand edge of Figure 1)		
mole fraction SLES	surface mole fraction SLES	$10^6 \times \Gamma_{total} \pm 0.05 \text{ mol m}^{-2}$
0.25	0.21	3.68
0.50	0.36	3.31
0.75	0.52	3.23
0.90	0.60	3.17
LAS-C ₁₂ E ₈ (base of Figure 1)		
mole fraction LAS	surface mole fraction LAS	$10^6 \times \Gamma_{total} \pm 0.05 \text{ mol m}^{-2}$
0.20	0.32	3.00
0.40	0.48*	2.70*
0.60	0.54	2.90
0.80	0.68	2.90
0.90	0.71	3.20
0.95	0.79	3.10
C ₁₂ E ₈ -SLES (left hand edge of Figure 1)		
mole fraction C ₁₂ E ₈	surface mole fraction C ₁₂ E ₈	$10^6 \times \Gamma_{total} \pm 0.05 \text{ mol m}^{-2}$
0.1	0.52	2.88
0.25	0.64	2.65
0.5	0.74	2.59
0.75	0.95	2.50

The data in Table 3 were fitted with the ideal, regular solution model and the *BC* model. The calculation requires two steps. First, Eqn (11) is used to obtain the monomer composi-

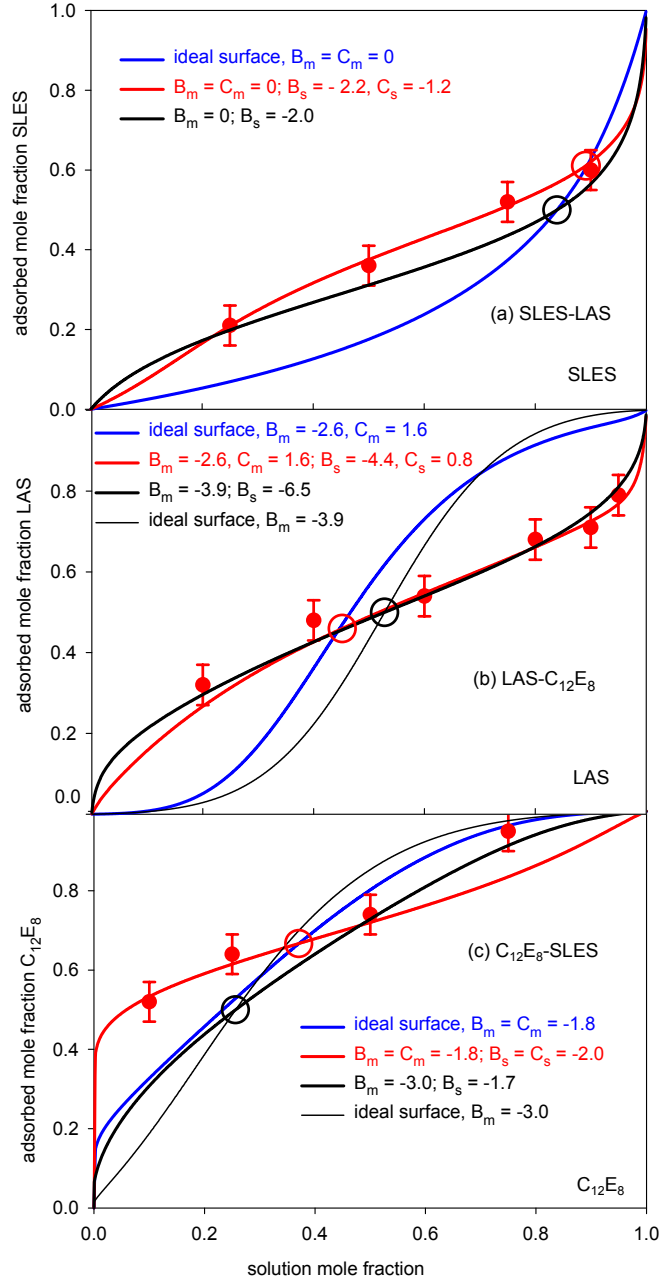


Figure 4: Variation of adsorbed mole fraction with bulk mole fraction for the three binary mixtures (a) SLES–LAS, (b) LAS–C₁₂E₈ and (c) C₁₂E₈–SLES. The lines in blue are for ideal mixing in the surface layer with the best fit for the BC model for the micelles from Figure 2. The lines in black use the regular solution model for the micelle with B from Figure 2 and either ideal surface adsorption (thin line) or the regular solution model (thick line). The red lines are for the BC model for both micelle and surface with values of the B and C parameters optimized to fit the binary mixtures here and the ternary mixtures shown in later figures. The circles mark the points of intersection of each ideal adsorption with its related regular solution model (black) and the BC model (red). The significance of these points is discussed in the text.

tion in the solution, which is then used in a slightly modified form of Eqn (10) to calculate the adsorption. The modification uses the Holland approach for the basic adsorption,³ which assumes that a monolayer is reached at the CMC and therefore adsorption of each component depends on its CMC after correction for the differing limiting STs at the CMC. This surface pressure correction depends on the known limiting areas at the CMC and the STs of the individual components and of the mixture. The limiting values for A for the individual components are 46, 57 and 62 Å² for SLES, LAS and C₁₂E₈ respectively, determined using NR, and the corresponding measured limiting STs are 43, 35 and 36 mN m⁻¹. The ST of all the mixtures was taken to be 39 mN m⁻¹, as observed for the single measurement mentioned in the previous section. The corrected CMCs replace the actual CMCs in Eqn (10). Although the ST of the mixtures does vary, the variation is sufficiently small that the use of a fixed ST affects the final fits at a level much smaller than those caused by variations in the four BC parameters. The ideal calculation assumes ideality just for the surface adsorption, but uses the BC parameters for the micelle to calculate the monomer composition. The regular solution calculation uses the regular solution model for calculating the monomer composition with the regular solution value of B from Figure 4, and the BC calculation uses the same set of four BC parameters that best fits *all* the data including both the CMC data of Figure 2 and the ternary data. The full set of parameters fitted using both BC and regular solution models is given in Table 4. Before discussing the fits we introduce some important results that greatly help the analysis of the data and which appear not to have been identified previously.

The Redlich–Kister function for a binary mixture is¹⁸

$$\ln \left(\frac{f_2}{f_1} \right) = B(x_1 - x_2) \quad (15)$$

When $x_1 = x_2 = 0.5$, f_1 and f_2 therefore become identical independently of the value of B , i.e. this result occurs for both an ideal solution and a regular solution, the difference

being that $f_1 = f_2 = 1$ for the ideal solution at all bulk concentrations but $f_1 = f_2 \neq 1$ for a regular solution at just one bulk concentration. Plots of ideal adsorption and regular solution adsorption against bulk composition, e.g. such as in Figure 4, will therefore intersect when the surface composition, x_1^{ideal} , is 0.5, and we will refer to this point as the *ideal point*. This simple result can be used as a direct test of the validity of the regular solution model for a particular system by comparing the calculated ideal adsorption curve with the experimental data to obtain an approximate value of x_1^{ideal} . The surfactant pair, SLES–LAS, in Figure 4(a), is a particularly clear example. The intersection of the ideal curve (in blue) with the experimental points occurs at close to $x_1^{ideal} = 0.6$. This suggests that the regular solution model is not suitable for the surface adsorption in this system and this is supported by the poor fit of the regular solution model (black line) and its lower intersection with the ideal line, marked by a black circle. However, although this conclusion would be definite for adsorption below the CMC where the bulk composition is known from experiment, this is not quite the case for adsorption above the CMC, because the monomer composition used to calculate the ideal curve itself has to be calculated and therefore relies on the accuracy of the parameters used to fit the CMC curve in Figure 2. This should not be a problem unless mixing in the micelle deviates strongly from either ideality or the regular solution.

The ideal point for the regular solution occurs at the composition where G_E^s is a minimum. There are comparable conditions when the higher cubic terms of Eqns (9) and (10) are included in Eqn (15). Thus, for $C = -B$, $x_1^{ideal} = 1/3$ and for $B = C$ $x_1^{ideal} = 2/3$, each coinciding with the minimum in G_E^s . Intermediate values of C between 0 and $\pm B$ indicate shifts of the minimum in G_E^s from $x_1^{ideal} = 0.5$ towards either $1/3$ or $2/3$. Thus, if a set of experimental measurements of the surface composition can be interpolated to obtain the point of intersection with the ideal adsorption curve the resulting value of x_1^{ideal} directly gives the position of the minimum in G_E^s , i.e. the composition at the minimum can be determined without any assumptions about its shape or depth. Similar conditions also hold for the quartic interaction, which is not given here, but can be found in the appropriate

references.^{18,41,42} Thus, in Figure 4 the observed values of x_1^{ideal} for SLES-LAS and C₁₂E₈-SLES, obtained by comparison of the ideal (blue) line with the experimental points in each case, gives values of x_1^{ideal} that are closer to 2/3 rather than 1/2. They suggest that the cubic terms are important for the surface layers of these two surfactants and that B and C are similar in both systems. The result is particularly striking for C₁₂E₈-SLES where the lowest experimental value of the surface C₁₂E₈ composition is 0.52 at a bulk mole fraction of 0.1, which is outside the range that the regular solution model could possibly give. In this case the simple analysis therefore shows that the regular solution model is not only inappropriate for the surface adsorption but is also inappropriate for the micelle. This suggests two general results. First, the identification of the value of x_1^{ideal} from the combination of ideal adsorption and experimental observations does not depend on any particular pattern of behaviour of the monomer concentration and is therefore applicable both below and above the CMC. Secondly, if the parameters used to fix the mixing in the micelle are incorrect, fitting surface adsorption measurements above the CMC becomes a route for making a more accurate analysis of the parameters for micellar mixing than possible simply from CMC measurements. A similar conclusion was reached by Li et al. using slightly different arguments.¹⁸

The conclusions from the simple analysis above are confirmed with the fitting. The best fits of the BC model to the three sets of data in Figure 4 are shown as red lines in the Figure and use the same values of B and C as used to fit the CMC data in Figure 2 and the ternary mixture data in Figures 5 and 6. For comparison the best fits from the regular solution model are shown as thick black lines and these also use the regular solution model for the micelles with values of B_m determined from Figure 2. The thin black lines use the regular solution model for the micelles and ideal mixing for the surface. Thus, the intersection to obtain the ideal point for this model is the black circle in the Figure. This is a very poor fit to the data for SLES-LAS and C₁₂E₈-SLES and also fails to fit the ternary data, as will be discussed below. For LAS-C₁₂E₈ both the regular solution and BC models fit the data satisfactorily, i.e. the value of C is much smaller in magnitude than that of B , as can be seen

from the set of fitted parameters collected in Table 4. In this table we have also included the calculated values of G_{min} and $x_{min}(=x_1^{ideal})$ since, as we have argued elsewhere,¹⁸ these give a clearer physical picture of G_E .

The values of the total adsorbed amounts Γ are also given in Table 3. For C₁₂E₈, LAS and SLES these are respectively 2.7, 2.9 and $3.6 \pm 0.05 \times 10^{-6}$ mol m⁻². For all three mixtures the total adsorption is approximately constant across the composition range with average values of 2.7, 3.3 and 3.5×10^{-6} mol m⁻² for C₁₂E₈-SLES, LAS-C₁₂E₈ and SLES-LAS respectively. The mixtures in which C₁₂E₈ is most dominant have the lowest total adsorption, and the LAS-SLES mixture the highest.

Table 4: Parameters determining the excess free energy of mixing for the three binary pairs of surfactants and C₁₂E₈-SDS. The primary parameters are B_{ij} and C_{ij} , from which G_{min} (BC) and x_{min} are derived, or G_{min} (regular) for the regular solution. This set of six independent parameters B_{ij} and C_{ij} were used to fit all the data shown. The sign of C is defined with component 1 being the first named component in each pair. Taking Figure 1 in a clockwise direction corresponds to the pairs in the table. The units are RT except for x , which is a mole fraction.

system	phase	B_{ij}	C_{ij}	G_{min} (BC)	x_{BC}	B	G_{min} (regular)
SLES-LAS	micelle	0	0	-	-	0	-
SLES-LAS	surface	-2.2	-1.2	-0.59	0.61	-2.0	-0.50
LAS-C ₁₂ E ₈	micelle	-2.6	1.8	-0.72	0.37	-3.9	-0.98
LAS-C ₁₂ E ₈	surface	-4.4	0.8	-1.11	0.46	-6.5	-1.63
C ₁₂ E ₈ -SLES	micelle	-1.8	-1.8	-0.53	0.67	-3.0	-0.75
C ₁₂ E ₈ -SLES	surface	-2	-2	-0.59	0.67	-1.7	-0.43
C ₁₂ E ₈ -SDS	micelle	-1.0	-1.0	-0.30	0.67	-	-
C ₁₂ E ₈ -SDS	surface	-3	-3	-0.89	0.67	-	-

For the ternary mixtures, two different types of measurement were made. The main set of results was obtained at the fixed total composition of 2 mM. The compositions and total adsorption at the points marked in Figure 1 are given in Table 5. A small set of measurements were made at the fixed composition of 0.125:0.125:0.75 C₁₂E₈:LAS:SLES but at three different total concentrations 0.5, 1.0 and 2.0 mM and these are given in Table 6.

The results of varying the overall concentration are particularly interesting because they show how the closeness of the system to the CMC has a large effect on the monomer com-

Table 5: Surface composition and total adsorbed amount for C₁₂E₈–LAS–SLES mixtures at a total concentration of 2 mM and for the lines of solution composition variation indicated in Figure 1.

total mole fraction			surface mole fraction ± 0.05			$10^6 \times \Gamma_{total} \pm 0.05$
$x_{C12E8} = x_{LAS}$ (line 1)						
C ₁₂ E ₈	LAS	SLES	C ₁₂ E ₈	LAS	SLES	
0.025	0.025	0.95	0.33	0.17	0.50	3.16
0.05	0.05	0.90	0.37	0.24	0.40	3.00
0.125	0.125	0.75	0.41	0.35	0.25	2.86
0.20	0.20	0.60	0.45	0.39	0.18	2.85
0.33	0.33	0.33	0.49	0.46	0.05	2.81
0.375	0.375	0.25	0.47	0.46	0.07	2.72
$x_{C12E8} = x_{SLES}$ (line 2)						
0.125	0.75	0.125	0.27	0.72	0.01	2.80
0.20	0.60	0.20	0.34	0.65	0.01	2.88
0.33	0.33	0.33	0.49	0.47	0.04	2.81
0.375	0.25	0.375	0.50	0.35	0.15	2.84
$x_{SLES} = x_{LAS}$ (line 3)						
0.75	0.125	0.125	0.82	0.17	0.01	2.60
0.60	0.20	0.20	0.76	0.23	0.01	2.80
0.33	0.33	0.33	0.49	0.47	0.04	2.81
0.25	0.375	0.375	0.39	0.51	0.10	2.75
(line 4)						
0.66	0.09	0.25	0.84	0.12	0.04	2.54
0.33	0.17	0.50	0.54	0.33	0.13	2.75
0.20	0.20	0.60	0.45	0.39	0.18	2.85

Table 6: Surface composition and total adsorbed amount for 0.125:0.125:0.75 C₁₂E₈:LAS:SLES mixtures at total concentrations of 0.5, 1.0 and 2.0 mM.

concentration/mM	surface mole fraction ± 0.05			$10^6 \times \Gamma \pm 0.05 \text{ mol m}^{-2}$
	C ₁₂ E ₈	LAS	SLES	
0.5	0.66	0.22	0.13	2.79
1.0	0.53	0.28	0.19	2.96
2.0	0.41	0.34	0.25	2.86

position. This has been demonstrated and discussed several times for binary mixtures but we believe this is the first such demonstration for a ternary mixture. The results from Table 6 are plotted in Figure 5(c). The three different concentrations were fitted using exactly the same set of BC parameters as used to fit the binary mixtures in Figure 4 together with Eqns (12) and (10). To show how the adsorption is affected by micellization we have included the calculated micelle and monomer compositions in Figure 5(a) and (b). Considering the various approximations and assumptions the calculation of the coverage fits well, especially the change with increasing total concentration. Figure 5(a) shows the expected high dominant fraction of the low CMC $C_{12}E_8$ at the CMC and the onset of its slow decline towards an overall mole fraction of 0.125. SLES is the least surface active component and, again as expected, its mole fraction in the micelle near the CMC is much lower than its overall mole fraction, to which it then gradually increases with concentration. It is, however, the monomer concentration that determines the adsorption. At high concentrations the bulk of the surfactant is in the micelles and this must eventually conform to the bulk composition of 0.125:0.125:0.75. However, the relatively small amount of free monomer, which makes a negligible contribution to the overall composition, is not constrained and the mole fraction of SLES tends to a limit higher than its overall mole fraction, while the $C_{12}E_8$ tends to a lower limit. These trends lead to an increase in the adsorbed fraction of SLES with concentration and a decrease in the adsorbed $C_{12}E_8$. Although the fraction of SLES monomer is some 5 times higher than that of $C_{12}E_8$, the relative intrinsic strengths of adsorption, which vary in the opposite direction to the CMCs, are such that $C_{12}E_8$ still adsorbs more strongly. Adjustment of the BC parameters shows that, apart from the intrinsic adsorption characteristics, an increase in the attractive interaction between any two components has the effect of excluding the third from the surface. The strongest interaction is between LAS and $C_{12}E_8$ and with the other parameters set to 0 this is strong enough to squeeze more or less all the SLES off the surface. That SLES adsorbs significantly is crucially dependent on the fact that its surface interaction with LAS is also strong and attractive.

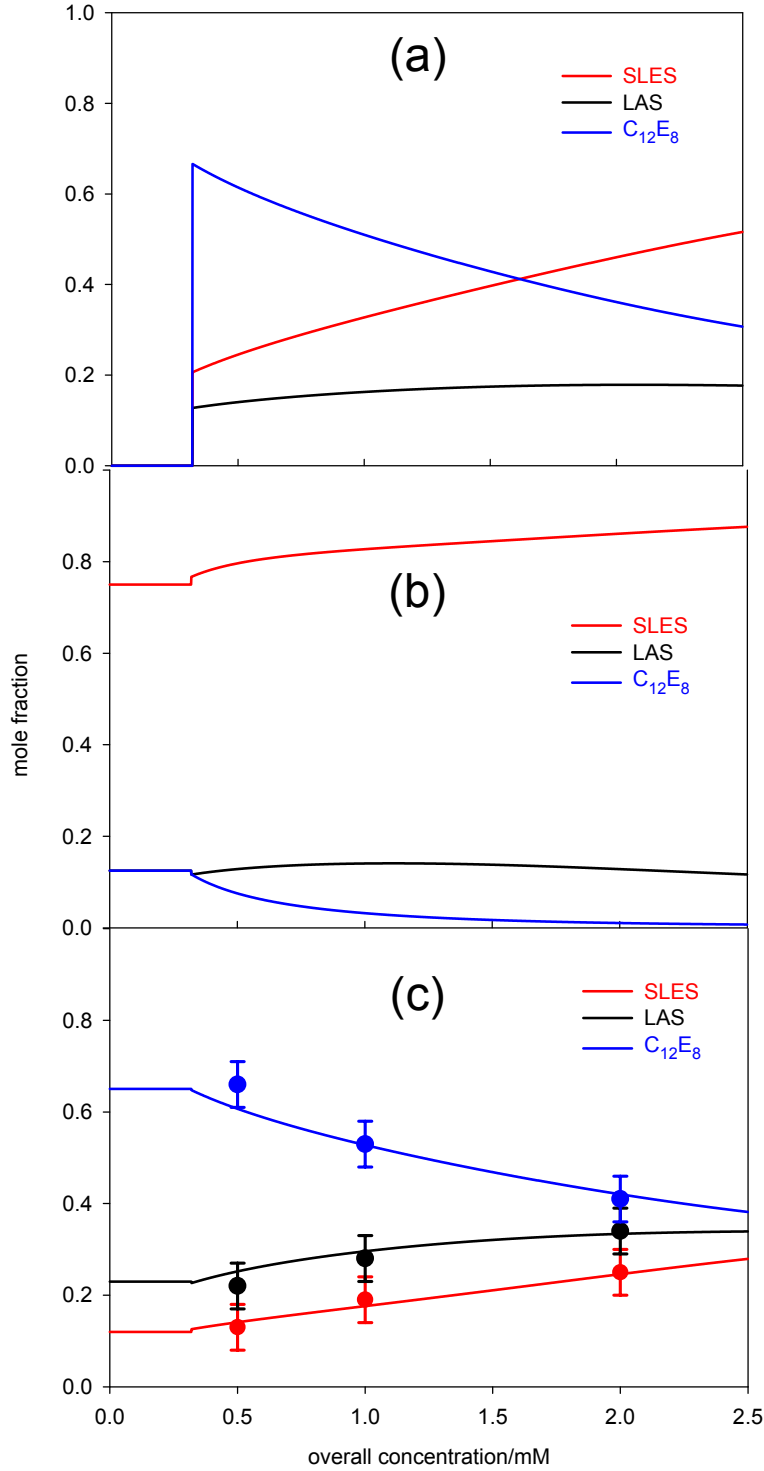


Figure 5: Fit of the BC interaction model to the ternary 0.75:0.125:0.125 SLES:LAS: $C_{12}E_8$ mixture at three different overall concentrations, using the 6 B and C parameters in Table 4 and an ST of 39 mN m^{-1} . (a) shows the calculated micelle composition, (b) the monomer composition and (c) the calculated and observed compositions. The monomer concentrations, which are not shown, are the product of the mole fraction and the concentration. In the immediate vicinity of the CMC the iterative solution becomes uncertain and leads to the small kinks at this point.

The compositions of the adsorbed mixtures along the lines 1-3 of Figure 1 are given in Table 5 and shown in Figure 6 together with the fits using the same set of BC parameters and the same equations as for Figure 5. Despite the very wide range in adsorption patterns between the three different conditions used the fits are consistently good and, taken together with the good fits to the binary data, show that the assumption that only binary interactions are required to fit the mixing in more complex mixtures is sound.

The question then arises as to whether the data for the ternary mixtures can also be accounted for accurately by use of just the regular solution model. We test this initially by attempting to fit the data of part of Figure 6 to the optimum B values obtained in Figure 4 and this fit is shown in Figure 7. This calculates the adsorption of $C_{12}E_8$ and LAS to be the opposite way round from that observed. This turns out to be a direct consequence of the poor fit of the regular solution model to the binary adsorption for the $C_{12}E_8$ –SLES pair, as shown in Figure 4(c). As stated above, reduction of the attractive interaction between any pair of components in a micelle will reduce the fractions of those two components in the micelle and enhance the fraction of the third component. This can be approximately achieved by a reduction of B_{31} for the micelle formed by the $C_{12}E_8$ –SLES pair. However, such a reduction results in a very poor fit to the CMC data in Figure 2(c), i.e. it is not possible to obtain a good fit to all the data using the regular solution model. This is a direct result of the inability of the regular solution model to account for the adsorption in Figure 4(c) which, as already discussed above, can only result from the regular solution model giving an incorrect value of the free monomer in solution above the CMC.

Although the relative inability of SLES to compete with $C_{12}E_8$ and LAS for the surface is explained by the analysis presented above it was unexpected when the experiments were performed, and the corresponding mixtures with SDS instead of SLES were therefore also examined in the hope of obtaining some explanation. The structure of SDS is related to that of SLES, but the introduction of the ethylene oxide groups between the alkyl chain and sulphate headgroup is expected to make the headgroup of SLES more hydrophilic. Thus,

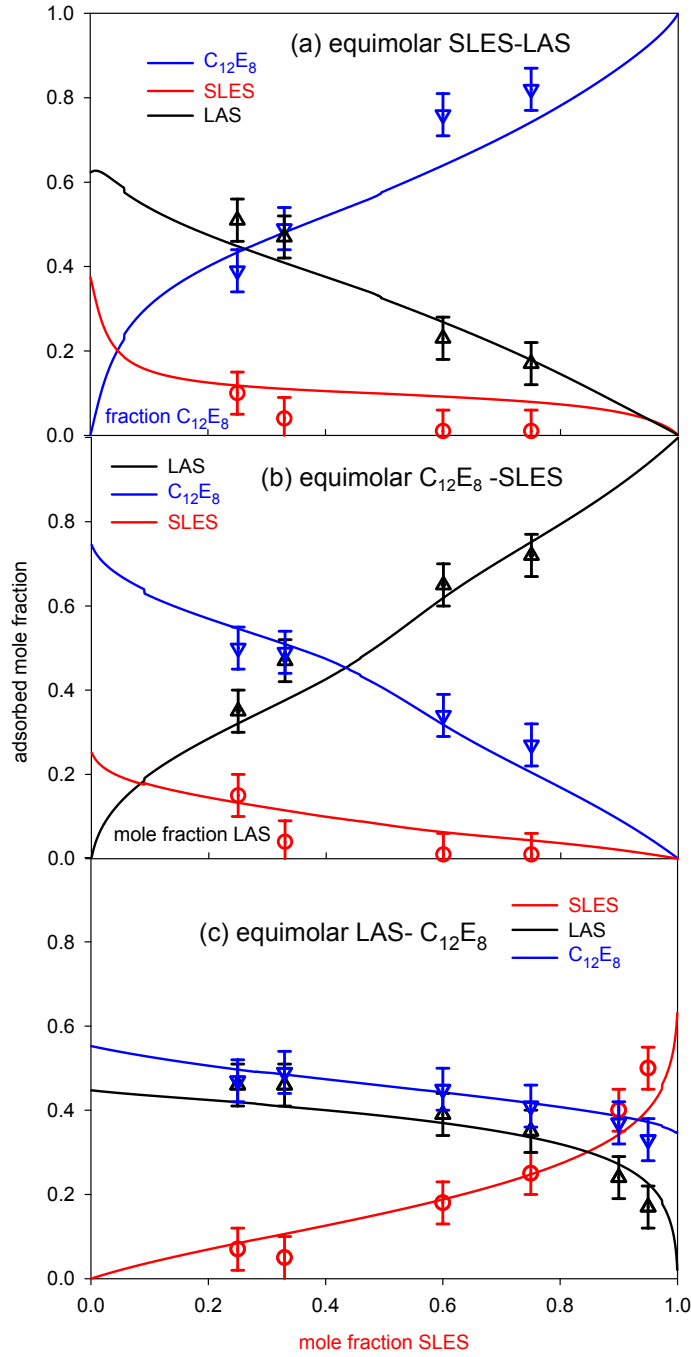


Figure 6: Fit of the BC model to the composition of the adsorbed layer of three different ternary mixtures of SLES:LAS: $C_{12}E_8$ above the CMC at 2 mM. Two surfactants are kept equimolar while the third is varied, with the third surfactant being (a) $C_{12}E_8$, (b) LAS and (c) SLES. The calculation used the set of 6 B and C parameters in Table 4 and an ST of 39 mN m^{-1} . In the immediate vicinity of the CMC the iterative solution becomes uncertain and leads to the small kinks at this point.

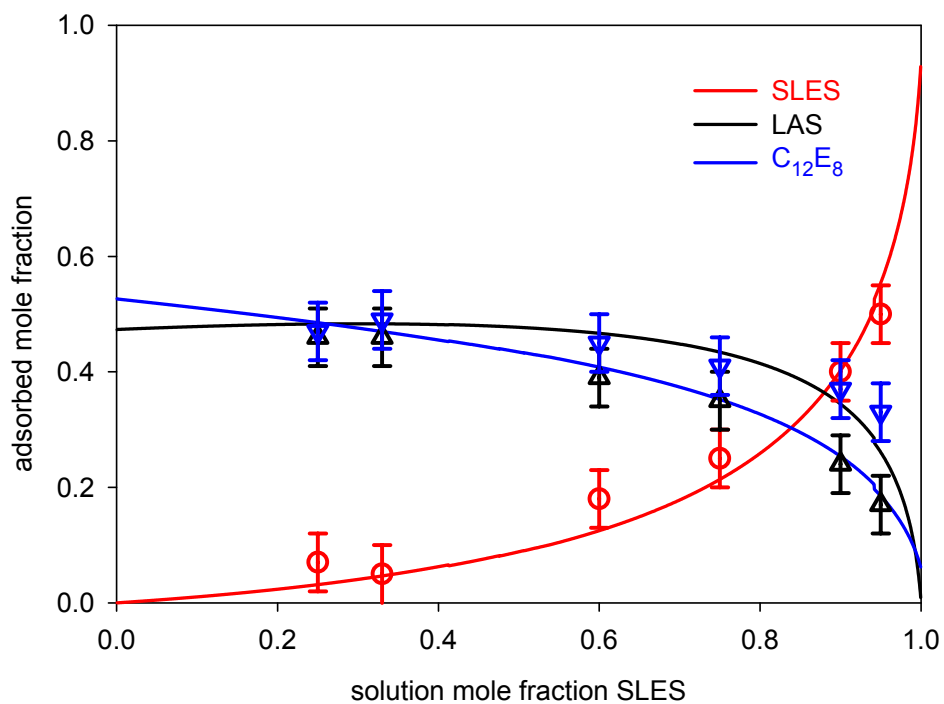


Figure 7: Fit of the regular solution model to the composition of the adsorbed layer of the ternary mixture of SLES:LAS:C₁₂E₈ above the CMC at 2 mM with LAS and C₁₂E₈ equimolar. The calculation used the set of 6 B parameters in Table 4 and an ST of 39 mN m⁻¹.

the CMC of SLES is lower at 2.2 mM. Measurements were made at two different solution compositions, 0.125:0.125:0.75 and 0.375:0.375:0.25, and the results are summarised in Table 7. The general trend observed with SLES is also present with SDS, i.e. SLES and SDS both only weakly compete with $C_{12}E_8$ and LAS for the surface with the SDS being even less surface active than SLES, which is qualitatively consistent with the relative CMC values of SLES and SDS. However, this is accompanied by a marked increase in the amount of $C_{12}E_8$ adsorbed relative to LAS, especially at high SDS concentrations, although the adsorbed SDS is consistently lower than adsorbed SLES at comparable compositions. Much of the ternary adsorption pattern is accounted for simply by retaining the same BC parameters for SDS as for SLES. However, a substantially better fit to the data is obtained by increasing the strength of the surface attraction between SDS and $C_{12}E_8$ relative to SLES and $C_{12}E_8$, which approximately increases both of their adsorption at the expense of the LAS, and by decreasing the corresponding micellar attraction, which causes a further relative increase in the adsorption of $C_{12}E_8$ relative to LAS. In both cases the same composition asymmetry in G_E , i.e. $B = C$, was found to be a necessary part of fitting the data. Both of these are probably the result of the higher degree of ionization of SDS compared with SLES. This increases the attractive interaction between the nonionic and SDS but may also enhance the repulsion between SDS in the more closely packed micelle. The fit is shown in Figure 8 and the fitting parameters are shown in Table 4.

Table 7: Surface composition and total adsorbed amount for two $C_{12}E_8$ –LAS–SDS mixtures at a total concentration of 2 mM with the corresponding data for $C_{12}E_8$ –LAS–SLES incuded from Table 5.

total mole fraction			surface mole fraction ± 0.05			$10^6 \times \Gamma_{total} \pm 0.05$
$C_{12}E_8$	LAS	SDS	$C_{12}E_8$	LAS	SDS	
0.125	0.125	0.75	0.56	0.27	0.17	3.08
0.375	0.375	0.25	0.57	0.39	0.04	2.96
$C_{12}E_8$	LAS	SLES	$C_{12}E_8$	LAS	SLES	
0.125	0.125	0.75	0.41	0.35	0.25	
0.375	0.375	0.25	0.47	0.46	0.07	2.72

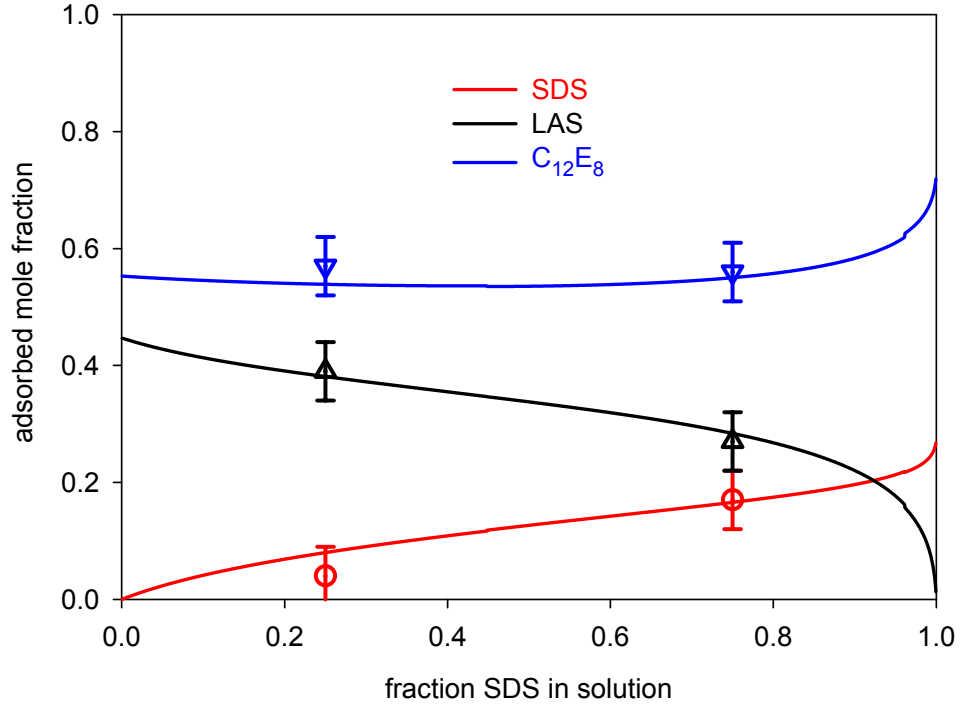


Figure 8: Fit of the BC model to the composition of the adsorbed layer of the ternary mixture of SDS:LAS:C₁₂E₈ CMC at 2 mM with LAS and C₁₂E₈ equimolar. The parameters used were those given in Table 4 except that the C₁₂E₈-SLES parameters were replaced by different values for C₁₂E₈-SDS of $B = C = -3.0$, compared with $B = C = -2.0$ for SLES for the surface adsorption and $B = C = -1.0$ compared with $B = C = -1.8$ for SLES for the micelle. The ST of both mixtures was taken to be 39 mN m⁻¹.

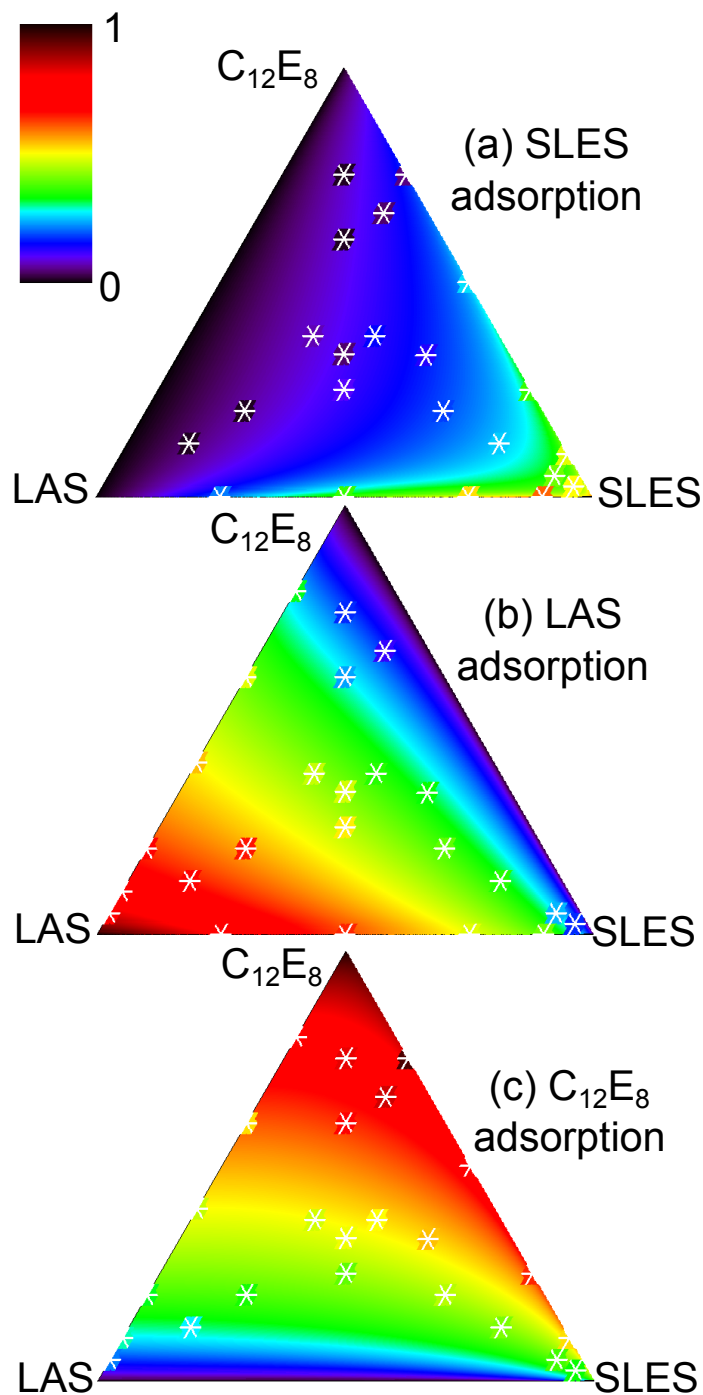


Figure 9: Fit of the BC model to the composition of the adsorbed layer of the ternary mixture of SLES:LAS: $C_{12}E_8$ at 2 mM. Each triangular diagram represents the adsorbed fraction of one of the components, (a) SLES, (b) LAS and (c) $C_{12}E_8$. The level of fractional adsorption from 0–1 is represented by the colours shown in the rectangular palette. The experimental points, which include all the ternary and binary measurements, are marked by white stars with the appropriate surrounding colour from the colour palette so that, if the calculated and observed points agree exactly, only the white asterisk shows. The parameters used were those given for the *BC* model in Table 4 with an ST of 39 mN m⁻¹.

Not all of the ternary data can be analysed using a 2D plot and a more complete representation of the data can only be made using a triangular plot. The observed fractions of each component are compared with the calculated BC model in the three triangular diagrams in Figure 9. The calculated adsorption is represented as a colour contour plot with the colour scale shown on the rectangular palette. The points are marked by the white asterisks. The values of the experimental values of the adsorption are indicated by the colour immediately surrounding the lines of the white asterisks, using the same colour scale as for the calculated values. This colour becomes invisible if there is good agreement between calculated and observed adsorption, i.e. only the white asterisk is seen when there is a good match between calculated and observed points. Overall, these triangular plots confirm the excellent agreement between the BC model and the data with the advantage that the complete set of data can be shown in a single plot. This is the first presentation of the fit of the pseudophase approximation to a set of experimentally adsorbed amounts determined above the CMC for a ternary mixture, and it may well be the first for any ternary mixture.

Discussion

The results have a number of interesting features. The first is that the use of directly measured compositions using NR allows a much more precise characterization of the surfactant interactions than possible by other means. In a recent paper we showed that the reason for this is essentially that the composition of the layer or micelle is much more sensitive to the interaction than the values of the CMC (or c^π).¹⁸ While it is in principle possible to use the gradient of the CMC variation with concentration to obtain the composition of the micelle this demands an accuracy in the data that is almost impossible to achieve experimentally. This was illustrated clearly by Hoffmann and Possnecker who concluded that it can only be done when the CMCs are more or less the same.⁴⁶ The second feature is that the pseudophase approximation in conjunction with the regular solution model is in principle applicable only to nonionic mixtures and corrections that include dissociation are not compatible with the

inclusion of odd terms in the expansion of G_E .⁴⁷ However, neglect of the ionization and inclusion of a cubic term in G_E evidently describes the three binary mixtures in this paper extremely well in a situation already more complicated than normally considered, i.e. above the CMC. The further interesting feature is that the set of binary interaction parameters including cubic terms accurately explains the mixing in the ternary system, again in the more complex situation above the CMC. That the set of binary interactions should explain the ternary mixing behaviour is not a surprise because ternary interactions between molecules are known to be weak. However, if the binary interaction parameters have been obtained using an inappropriate model, one could expect that false ternary interactions might be needed to fit the data, but this is not the case here. The set of results therefore suggests that the level of ionization in both the surface layer and the micelle is sufficiently low that its effect can be incorporated as part of the cubic terms in G_E . In this connection it is interesting that the degree of ionization of an anionic surfactant in a mixed aggregate with a nonionic surfactant decreases with its mole fraction in the aggregate.⁴⁸ It is then interesting to examine whether the asymmetry in G_E for the three pairs of surfactants follows any particular trend.

Asymmetry in the composition dependence of the interaction between a pair of surfactants could be expected to arise from electrostatic interactions, differences in packing requirements, and/or changes of hydration on mixing.⁴⁷ Patist et al. have made the empirical observation that the ratio 1:3 in surfactant mixtures is often associated with enhancement of typical surfactant properties.⁴⁹ Reif and Somasundaran showed that electrostatic screening in SDS–nonionic surfactant mixtures leads to a minimum in G_E at a mole fraction of SDS of about 0.3.⁵⁰ In an ordered 2D mixture of charged and uncharged species the simplest lattice arrangement for minimizing the repulsion while keeping the mixing ratio high is 2:1 non-ionic:ionic. This is as observed for SLES- $C_{12}E_8$ and SDS- $C_{12}E_8$ both at the surface and in the micelle. SDS is expected to be more dissociated than SLES because of the extra screening by the EO groups in SLES but this evidently has no significant influence. These two

also agree with the calculations of Reif and Somasundaran above. SLES, SDS and $C_{12}E_8$ have identical single hydrophobic chains but LAS has a double chain that is significantly shorter than the SDS hydrophobic unit and packing differences would be expected to play a role. In the mixed micelle the minimum in G_E is at a fraction of LAS of 1/3, consistent with the same electrostatic effect as for SLES mixtures, but the minimum occurs at about 1/2 at the surface, i.e. the electrostatic effect is either reduced or dominated by packing considerations at the surface. $C_{12}E_8$ with its large head group prefers curved structures (low packing parameter) whereas LAS with a hydrophobic group of much larger cross section prefers lamellar structures (large packing parameter). The inclusion of LAS in the micelle is therefore disfavoured, which reinforces the electrostatic effect, but its adsorption in the surface layer is strongly enhanced and dominates the electrostatic effect. LAS is expected to be slightly more dissociated than SLES and the packing parameter of SLES will be intermediate between those of LAS and $C_{12}E_8$. Both electrostatic and packing effects are therefore weaker for SLES-LAS than for LAS- $C_{12}E_8$ and this weakness is reflected in the values of B and C being zero. At the surface the minimum in G_E occurs at a LAS fraction of 0.39. This is close to that expected from an electrostatic effect (LAS charged) but is the opposite of an effect determined by the packing parameter. In this mixture there is the further consideration that SLES packs more closely at the surface ($A = 46$ and 57 \AA^2 for SLES and LAS respectively), which evidently offsets the packing parameter or curvature advantage.

Conclusions

The surface composition of ternary and binary mixtures of $C_{12}E_8$, LAS, and SLES adsorbed at the air-water interface has been measured directly using neutron reflection over a wide range of compositions at concentrations above the CMC. At these concentrations adsorption depends on the intrinsic adsorption, the excess free energy of mixing, G_E^s , at the surface, and the monomer concentration of each component in the bulk solution. Since the last of these depends on the individual CMCs and the excess free energy of mixing in the micelle, G_E^m , the

measurements are sensitive to mixing both in the micelles and at the surface. Application of the pseudophase approximation with the regular solution model fitted two of the binary mixed pairs but not the third (C₁₂E₈–SLES). The data could, however, all be fitted by including cubic terms in G_E^s and G_E^m . This shows that the composition dependence of G_E^s is strongly asymmetric for two of the binary mixtures and for two of the binary mixtures (not the same ones). The mixed adsorption in the ternary mixtures was quantitatively fitted with the same set of G_E . This confirms the expected result that a ternary system depends only on binary interactions, i.e. ternary interactions are insignificant. It also confirms that the assumptions made in applying the pseudophase model to mixing in charged systems can be accommodated within a two parameter model for G_E . Finally, the observed asymmetry in the composition dependence of the various G_E can be explained mainly in terms of the optimum shielding of the anionic species by the nonionic species, although there are also clear additional effects of the packing parameter/preferential curvature.

Supporting Information

The Supporting Information contains a table of the variation in critical micelle concentration (CMC) and limiting surface tension at the CMC (γ_{CMC}) for the binary mixtures SLES–LAS, LAS–C₁₂E₈ and C₁₂E₈, and a diagram showing the surface tension behaviour of a ternary mixture of the three surfactants.

Acknowledgements

The provision of beam time at ISIS and the ILL, and the invaluable help and expertise of the Instrument Scientists, Max Skoda, and Arwell Hughes at ISIS, Richard Campbell at the ILL, and the technical support of the two institutions is acknowledged. The studentship for Jessica Liley was a CASE award, part funded by Unilever research, Port Sunlight, and part by the EPSRC, UK.

References

- (1) Rubingh, D. N. *Solution Chemistry of Surfactants*, Editor K. L. Mittal; Plenum Press: new York, 1979; pp 337–354.
- (2) Holland, P. M.; Rubingh, D. N. Nonideal Multicomponent Mixed Micelle Model. *J. Phys. Chem.* **1983**, *87*, 1984–1990.
- (3) Holland, P. M. Nonideal Mixed Micellar Solutions. *Adv. Colloid and Interface Sci.* **1986**, *26*, 111–129.
- (4) Ogino, K., Abe, M., Eds. *Mixed Surfactant Systems*; Marcel Dekker Inc.: New York, 1993.
- (5) Abe, M., Scamehorn, J. F., Eds. *Mixed Surfactant Systems: Surfactant Science Series 124*, 2nd ed.; Marcel Dekker Inc.: New York, 2005.
- (6) Letellier, P.; Turmine, M. Non-Applicability of the Gibbs–Duhem Relation in Nonextensive Thermodynamics. Case of Micellar Solutions. *J. Phys. Chem. B* **2015**, *119*, 4143–4154.
- (7) Kamrath, R. F.; Franses, E. I. Mass-action Model of Mixed Micellisation. *J. Phys. Chem.* **1984**, *88*, 1642–1648.
- (8) Nikishido, N. In *Mixed Surfactant Systems*; Ogino, K., Abe, M., Eds.; Marcel Dekker Inc.: New York, 1993; pp 23–61.
- (9) Nagarajan, R. Micellization, Mixed Micellization, and Solubilization: the Role of Interfacial Interactions. *Adv. Colloid Interface Sci.* **1986**, *26*, 205–264.
- (10) Nagarajan, R.; Ruckenstein, E. Theory of Surfactant Self -Assembly: A Predictive Molecular Thermodynamic Approach. *Langmuir* **1991**, *7*, 2934–2969.

- (11) Sarmoria, C.; Puwada, S.; Blankschtein, D. Prediction of Critical Micelle Concentrations of Nonideal Binary Surfactant Mixtures. *Langmuir* **1992**, *8*, 2690–2697.
- (12) Shiloach, A.; Blankschtein, D. Predicting Micellar Solution Properties of Binary Surfactant Mixtures. *Langmuir* **1998**, *14*, 1618–1636.
- (13) Shiloach, A.; Blankschtein, D. Measurement and Prediction of Ionic–Nonionic Mixed Micelle Formation and Growth. *Langmuir* **1998**, *14*, 7166–7182.
- (14) Rosen, M. J. Purification of Surfactants for Studies of their Fundamental Surface Properties. *J. Colloid Interface Sci.* **1981**, *79*, 587–588.
- (15) Cui, Z. G.; Canselier, P.; Zhou, X. Q. Mixed Adsorption and Surface Tension Prediction of Nonideal Ternary Surfactant Systems. *Colloid Polym. Sci.* **2005**, *283*, 539–550.
- (16) Penfold, J.; Staples, E. J.; Thompson, L.; Tucker, I. The Composition of Non-ionic Surfactant Mixtures at the Air/Water Interface as Determined by Neutron Reflectivity. *Colloids Surfaces A* **1995**, *102*, 127–132.
- (17) Nikas, Y. J.; Puvvada, S.; Blankschtein, D. Surface Tensions of Aqueous Nonionic Surfactant Mixtures. *Langmuir* **1992**, *8*, 2680–2689.
- (18) Li, P. X.; Ma, K.; Thomas, R. K.; Penfold, J. Analysis of the Asymmetric Synergy in the Adsorption of Zwitterionic-Ionic Surfactant Mixtures at the Air-Water Interface below and above the Critical Micelle Concentration. *J. Phys. Chem.* **2016**, *120*, 3677–3691.
- (19) Holland, P. M.; Rubingh, D. N. Mixed Surfactant Systems: An Overview. *ACS Symposium Series* **1992**, *501*, 2–30.
- (20) Penfold, J.; Thomas, R. K. Mixed Surfactants at the Air–Water Interface. *Annu. Rep. Prog. Chem. C* **2010**, *106*, 14–35.
- (21) Penfold, J.; Thomas, R. K. The Limitations of Models of Surfactant Mixing at Interfaces as Revealed by Neutron Scattering. *Phys.Chem. Chem. Phys.* **2013**, *15*, 7017–7027.

- (22) Lu, J. R.; Thomas, R. K.; Penfold, J. Surfactant Layers at the Air/Water Interface: Structure and Composition. *Adv. Colloid Interface Sci.* **2000**, *84*, 143–304.
- (23) Chen, M. L.; Penfold, J.; Thomas, R. K.; Smyth, T. J. P.; Perfumo, A.; Marchant, R.; Banat, I. M.; Stevenson, P.; Parry, A.; Tucker, I. et al. Solution Self-Assembly and Adsorption at the Air-Water Interface of the Monorhamnose and Dirhamnose Rhamnolipids and Their Mixtures. *Langmuir* **2010**, *26*, 18281–18292.
- (24) Graciaa, A.; Ben Ghoulam, M.; Marion, G.; Lachaise, L. Critical Concentrations and Compositions of Mixed Micelles of Sodium Dodecylbenzenesulfonate, Tetradecyltrimethylammonium Bromide, and Polyoxyethylene Octylphenols. *J. Phys. Chem., Vol. 93, No. 10, 1989* **1989**, *93*, 4167–4173.
- (25) Chakraborty, T.; Ghosh, S.; Moulik, S. P. Micellization and Related Behavior of Binary and Ternary Surfactant Mixtures in Aqueous Medium: Cetyl Pyridinium Chloride (CPC), Cetyl Trimethyl Ammonium Bromide (CTAB), and Polyoxyethylene (10) Cetyl Ether (Brij-56) Derived System. *J. Phys. Chem. B* **2005**, *109*, 14813–14823.
- (26) Ray, G. B.; Ghosh, S.; Moulik, S. P. Ternary Mixtures of Alkyltriphenylphosphonium Bromides (C₁₂TPB, C₁₄TPB and C₁₆TPB) in Aqueous Medium: their Interfacial, Bulk and Fluorescence Quenching Behaviour. *J. Chem. Sci.* **2010**, *122*, 109–117.
- (27) Szymczyk, K.; Janczuk, B. A Study of the Interactions of Ternary Surfactant Systems at the Water-Air Interface. *Langmuir* **2010**, *26*, 2491–2496.
- (28) Das, C.; Chakraborty, T.; Ghosh, S.; Das, B. Physicochemistry of Mixed Micellization: Binary and Ternary Mixtures of Cationic Surfactants in Aqueous Medium. *Colloid J.* **2010**, *72*, 788–798.
- (29) Hines, J. D.; Thomas, R. K.; Garrett, P. R.; Rennie, G. K.; Penfold, J. A Study of the Interactions in a Ternary Surfactant System in Micelles and Adsorbed Layers. *J. Phys. Chem. B* **1998**, *102*, 9708–9713.

- (30) Staples, E. J.; Thompson, L.; Tucker, I.; Penfold, J. Effect of Dodecanol on Mixed Non-ionic and Nonionic–Anionic Surfactant Adsorption at the Air/Water Interface. *Langmuir* **1994**, *10*, 4136–4141.
- (31) Coreta, J.; Shiloach, A.; Bergera, P.; Blankschtein, D. Critical Micelle Concentrations of Ternary Surfactant Mixtures: Theoretical Prediction with User-Friendly Computer Programs and Experimental Design Analysis. *J. Surfactants Detergents* **1999**, *2*, 51–58.
- (32) Shiloach, A.; Blankschtein, D. Prediction of Critical Micelle Concentrations of Nonideal Ternary Surfactant Mixtures. *Langmuir* **1998**, *14*, 4105–4114.
- (33) Harwell Subroutine Library. <http://www.hsl.rl.ac.uk>.
- (34) Penfold, J.; Richardson, R. M.; Zarbakhsh, A.; Webster, J. R. P.; Bucknall, D. G.; Jones, A. R.; Cosgrove, T.; Thomas, R. K.; Higgins, J. S.; Fletcher, P. D. I. et al. Recent Advances in the Study of Chemical Surfaces and Interfaces by Specular Neutron Reflection. *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 3899–3917.
- (35) Webster, J. R. P.; Langridge, S.; Dalglish, R. M.; Charlton, T. R. Reflectometry Techniques on the Second Target Station at ISIS: Methods and Science. *Eur. Physical J. Plus* **2011**, *126*, 112.
- (36) Campbell, R. A.; Wacklin, H. P.; Sutton, I.; Cubitt, R.; Fragneto, G. FIGARO: the New Horizontal Neutron Reflectometer at the ILL. *Eur. Physical. J. Plus* **2011**, *126*, 107.
- (37) Penfold, J.; Thomas, R. K.; Dong, C. C.; Tucker, I.; Metcalfe, K.; Golding, S.; Grillo, I. Equilibrium Surface Adsorption Behavior in Complex Anionic–Nonionic Surfactant Mixtures. *Langmuir* **2007**, *23*, 10140–10149.
- (38) Xu, H.; Penfold, J.; Thomas, R. K.; Petkov, J. T.; Tucker, I.; Webster, J. P. R. The Formation of Surface Multilayers at the AirWater Interface from Sodium Polyethylene

- Glycol Monoalkyl Ether Sulfate/ AlCl_3 Solutions: The Role of the Size of the Polyethylene Oxide Group. *Langmuir* **2013**, *29*, 11656–11666.
- (39) Lu, J. R.; Marrocco, A.; Su, T. J.; Thomas, R. K.; Penfold, J. Adsorption of Dodecyl Sulfate Surfactants with Monovalent Metal Counterions at the Air–Water Interface Studied by Neutron Reflection and Surface Tension. *J. Colloid Interface Sci.* **1993**, *158*, 303–316.
- (40) Holland, P. M. Modelling Mixed Surfactant Systems: Basic Introduction. *ACS Symposium Series* **1992**, *501*, 31–44.
- (41) Rowlinson, J. S.; Swinton, F. L. *Liquids and Liquid Mixtures*, 3rd ed.; Butterworth-Heinemann Ltd: London, 1982.
- (42) Barker, J. A. Determination of Activity Coefficients from Total Pressure Measurements. *Australian J. Chem.* **2005**, *6*, 207–210.
- (43) Porter, A. W. On the Vapour Pressures of Mixtures. *Trans. Faraday Soc.* **1920**, *16*, 336–345.
- (44) Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345–348.
- (45) Hoffman, J. D. *Numerical methods for Engineers and Scientists*, 2nd ed.; Marcel Dekker Inc: New York, 2001.
- (46) Hoffmann, H.; Possnecker, G. The Mixing Behavior of Surfactants. *Langmuir* **1994**, *10*, 381–389.
- (47) Hines, J. D.; Thomas, R. K.; Garrett, P. R.; Rennie, G. K.; Penfold, J. Investigation of Mixing in Binary Surfactant Solutions by Surface Tension and Neutron Reflection: Strongly Interacting Anionic/Zwitterionic Mixtures. *J. Phys. Chem. B* **1998**, *102*, 8834–8846.

- (48) Penfold, J.; Tucker, I.; Thomas, R. K.; Staples, E.; Schuermann, R. Structure of Mixed Anionic/Nonionic Surfactant Micelles: Experimental Observations Relating to the Role of Headgroup Electrostatic and Steric Effects and the Effects of Added Electrolyte. *J. Phys. Chem. B* **2005**, *109*, 10760–10770.
- (49) Patist, A.; Devi, S.; Shah, D. O. Importance of 1:3 Molecular Ratio on the Interfacial Properties of Mixed Surfactant Systems. *Langmuir* **1999**, *15*, 7403–7405.
- (50) Reif, I.; Somasundaran, P. Asymmetric Excess Free Energies and Variable Interaction Parameters in Mixed Micellization. *Langmuir* **1999**, *15*, 3411–3417.

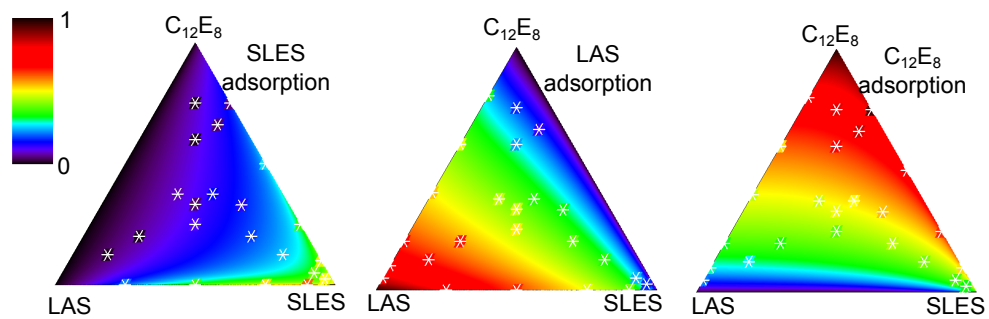


Figure 10: TOC Graphic.