The structure of mixed surfactant monolayers at the air–liquid interface, as studied by specular neutron reflection

J Penfold†, R K Thomas‡, E Simister‡, E Lee‡ and A Rennie§

† Neutron Science Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK
‡ Physical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, UK
§ Institut Laue–Langevin, BP 156X, 38042 Grenoble Cédex, France

Abstract. The specular reflection of neutrons is now finding widespread application in the study of a range of problems in surface chemistry. In recent studies, using hydrogen–deuterium contrast variation, it has been possible in the investigation of surfactant adsorption at the air–liquid interface to determine both the surfactant surface excess and the detailed surface structure of the surfactant molecules. We present here results that extend these studies to the adsorption of mixed surfactants at the air–liquid interface. For the mixed system sodium dodecyl sulphate and dodecanol, we have determined the surface excess and surface structure of each component in the mixed surface layer.

The specular reflection of neutrons is now established as a technique for the study of surfaces and interfaces [1], and has been applied particularly to problems in surface chemistry [1, 2].

The essence of a neutron reflection experiment is to measure the specular reflection as a function of the wave vector transfer, Q, perpendicular to the reflecting surface. This can be related to the neutron refractive index profile normal to the interface, and is often simply related to the scattering length density, yielding information about the composition and density gradient at surfaces and interfaces.

It has been shown [3] that the reflection of neutrons at interfaces is determined by the same laws as electromagnetic radiation, with the electric vector perpendicular to the plane of incidence. Hence most of the standard formulisms in classical light optics [4] can be used with only minor modification. In particular, the optical matrix method has been used extensively to calculate exactly the neutron reflectivity profile from structural models of interfaces, and is the preferred method of data analysis [5].

The neutron refractive index can be written as

$$n = 1 - (\lambda^2/2\pi)\rho \tag{1}$$

where ρ is the scattering length density given by

$$\rho = \sum_i n_i b_i. \tag{2}$$

n_i is the number density of the ith nucleus, b_i its scattering length, and λ is the neutron wavelength.

For neutrons, isotopic substitution can be used to produce large contrasts in scattering densities, and of particular importance to the study of surface chemistry is the large difference in the scattering powers between hydrogen and deuterium.

In the study of surfactant adsorption at the air–liquid interface, classical measurements such as surface tension can provide information about the amount adsorbed, but give little information about the structure and are difficult to interpret for multicomponent systems. In neutron reflection studies the large contrast in the scattering powers of protons and deuterons can be used to manipulate refractive index profiles. Not only can the amount adsorbed be determined for single and multicomponent systems, but the detailed surface structure can be determined. By choosing the appropriate hydrogen deuterium ratio, an aqueous solvent can be made null reflecting (that is, its refractive index can be matched to air), and if the surfactant is deuterated then any reflection results entirely from the surface adsorbed layer of surfactant. Hydrogen deuterium isotopic substitution can be further used to determine the surface profile of the solvent, and to highlight particular features of the solute molecules, by selective deuteration.

Isotopic substitution has been used to some advantage in the study of absorption of the cationic surfactant decyltrimethyl ammonium bromide (DTAB) at the air–liquid interface [6]. Reflectivity measurements with the chain and headgroups selectively deuterated in solvents of different refractive indices have enabled a detailed structural model to be determined. This study was extended to the anionic surfactant tetramethyl ammonium dodecyl sulphate (TMDS), where by selective deuteration of the counterion it was possible to determine the counterion distribution [7].

We present here recent results on the adsorption of the mixed surfactants sodium dodecyl sulphate (SDS) and dodecanol at the air–water interface. We have determined the surface excesses of both components and compared it with the adsorption of pure SDS. In addition we have been able to determine the detailed surface structure of each surfactant component. The neutron reflectivity measurements have been made on the reflectometer CRISP [8] at the ISIS pulsed neutron source, where the measurements have been made using the fixed geometry while beam time of flight method in the Q-range 0.05 to 0.65 Å^{-1}. The detailed experimental procedures are described elsewhere [9].

A minimum in surface tension measurements can arise from the presence of small amounts of impurity. This often arises for SDS, where small amounts of dodecanol due to the hydrolysis of the SDS can be present. Dodecanol is almost insoluble in water and forms a close packed monolayer at the surface; hence a very small amount in a SDS solution below the SDS critical micellar concentration (CMC) will preferentially adsorb at the surface. Above the CMC the SDS solubilises the dodecanol from the surface into micelles. Since the surface free energy of a monolayer of the SDS is greater than one containing dodecanol, the surface tension will rise at the CMC.

For the case of a deuterated surfactant in null reflecting water, the reflectivity arises solely from the adsorbed surfactant layer at the air–solution interface, and is related directly to the surface excess, Γ, or area per molecule, ahg [2]. If such a reflectivity curve is fitted by a single uniform layer, then the area per molecule is given by [9]

$$ahg = \left(\sum b \right) / \mathrm{d}fNbf \tag{3}$$

where $\sum b$ is the total scattering length of the deuterated surfactant molecule, and df and Nbf are the fitted surface layer thickness and scattering length density.
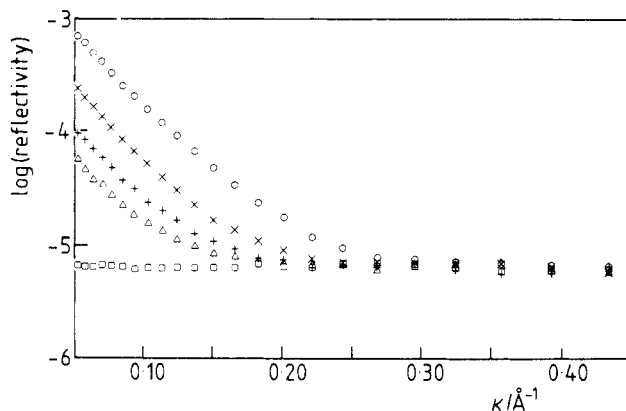
Figure 1. Reflectivity profiles of deuterated dodecanol, sodium dodecyl sulphate (protonated), mixtures in null reflecting water. The highest and lowest reflectivity profiles are respectively for spread dodecanol (○) and 0.009 M SDS (□). The remaining three profiles are for a dodecanol/SDS ratio of 0.00125 and a varying SDS concentration of 0.00675 (×), 0.009 (+) and 0.012 M (△).
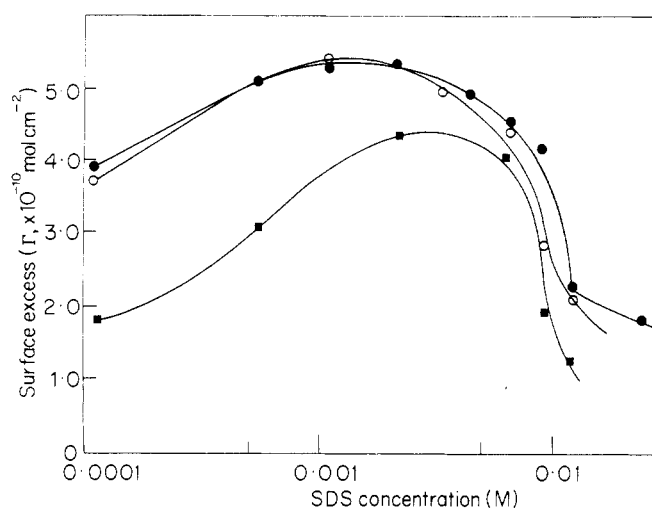

Figure 2. Dodecanol adsorption isotherm for 0.5% dodecanol as a function of SDS concentration for dodecanol/SDS ratios of (□) 0.0005, (○) 0.00125 and (●) 0.002.

In figure 1 we show the reflectivity of the SDS (protonated) in null reflecting water and, as expected, since the surfactant is protonated and the water is index-matched to air, there is no reflectivity. In contrast, a spread deuterated dodecanol layer gives a strong reflectivity. The addition of small amounts of the deuterated dodecanol to the protonated SDS leads to a substantial increase in reflectivity as the dodecanol replaces the SDS at the surface.

By selectively deuterating either the SDS or the dodecanol, we have been able to determine the surface excesses and adsorption isotherms of both components over a range of concentrations. Figure 2 shows the dodecanol absorption isotherm for different
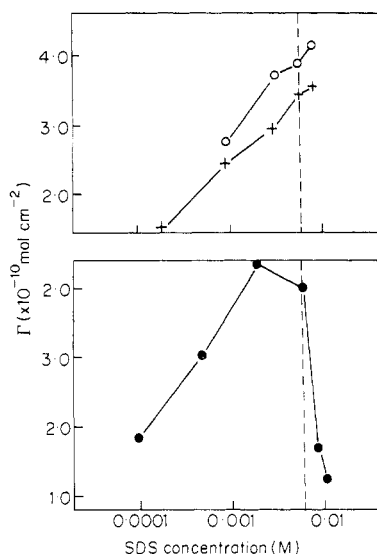
Figure 3. Adsorption isotherms as a function of SDS concentration for (○) pure SDS, (+) SDS for dodecanol/SDS ratio of 0.005 and (●) dodecanol for dodecanol/SDS ratio of 0.005. The dashed line indicates the position of the CMC for pure SDS.

dodecanol concentrations (relative to the SDS concentration), whereas in figure 3 the relative adsorptions of SDS and dodecanol at a fixed dodecanol concentration are shown, and for comparison the adsorption isotherm for pure SDS is included. The dodecanol adsorption has a maximum density which is of the order of 70% of the spread dodecanol monolayer, and the surface adsorption of the dodecanol drops markedly at the SDS CMC.

We have also been able to determine the detailed surface structure of the adsorbed monolayers. The simplest model that is consistent with the reflectivity of absorbed surfactant layers is a two-layer model where the first layer adjacent to the vapour phase contains some fraction $(1 - fhg)$ of the hydrocarbon chains, and the second layer, adjacent to the aqueous subphase, contains the headgroups, some fraction, fhg, of the chains, solvent and bond counterions. The model is then characterized by three structural parameters, ahg, fhg and fc, the extent to which the chains are fully extended, and from known molecular volumes, sizes and scattering lengths it is possible to calculate the extent and scattering densities of the two layers. The fitting procedure adopted then requires that the same model is consistent with the reflectivity from the different refractive index profiles (obtained by isotropic substitution) for the same system.

In figure 4 we show the application of this approach to pure SDS (0.0067 M) where we have measured the reflectivity profiles for deuterated SDS in null reflecting water, deuterated SDS in D_2O and protonated SDS in D_2O: the model parameters for the fits are summarized in table 1. Consistent with other measurements [6, 7], some fraction (of order 20%) of the chains are in the headgroup region. The chains are less than fully extended, and approach full extension as the CMC is approached.

We have determined the structure of SDS and dodecanol in the mixed surface layer in a similar way. From measurements with the SDS only deuterated (for 0.0067 M SDS/ 0.5% dodecanol), compared to the pure SDS structure, the presence of 0.5% dodecanol increases the fraction of chains in the headgroup region and results in the chains being less fully extended, whereas the surface excess is rather similar (see table 2(a)).

From measurements with the dodecanol only deuterated we have also determined the structure of the dodecanol. At a dodecanol concentration of 1.25% and for SDS
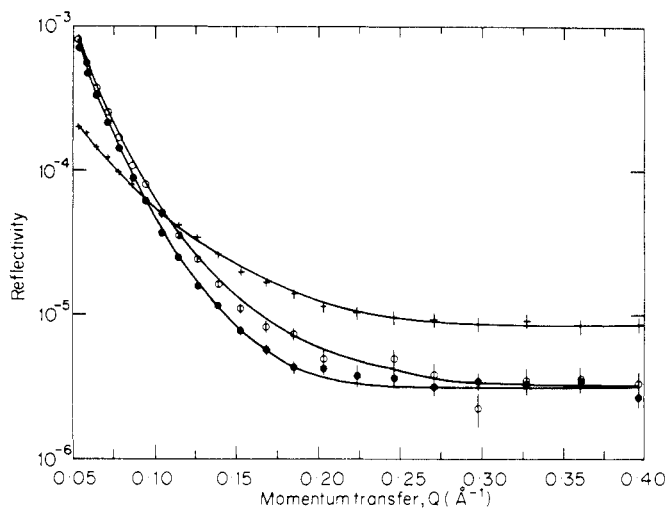
Figure 4. Specular reflection from 0.006 M SDS at $\theta = 1.5°$ for (i) +, deuterated SDS in null reflecting water, (ii) ● deuterated SDS in D_2O and (iii) ○, protonated SDS in D_2O; solid lines are least square model fits (for parameters see text).

Table 1. Structural parameters for SDS.

Surfactant concentration (M)	*ahg*	*fhg*	*fc*
0.0067	43.8	0.20	0.87
0.00338	45.3	0.28	0.71

Table 2. Structural parameters for (*a*) deuterated SDS/protonated dodecanol mixtures and (*b*) protonated SDS/deuterated dodecanol mixtures.

	SDS concentration (M)	Dodecanol concentration (%)	*ahg*	*fhg*	*fc*
(*a*)	0.0067	0.5	45.3	0.35	0.7
(*b*)	0.009	1.25	64.5	0.23	0.6
	0.0067	1.25	39.0	0.10	0.9

concentrations less than the CMC, only 10% of the dodecanol chains are in the headgroup region, and the hydrocarbon chains are fully extended; which is close to the structure of a pure spread dodecanol layer. Above the SDS CMC the configuration of the dodecanol molecules more closely match that of the SDS, associated with the increasing area per molecule of the dodecanol, the fraction of chains in the headgroup region increases, and the chains become less extended (see table 2(*b*)).

References

[1] Penfold J and Thomas R K 1990 *J. Phys.: Condens. Matter* **2** 1369
[2] Crowley T L, Lee E M, Simister E A, Thomas R K, Penfold J and Rennie A R 1990 *Colloids Surf.* at press
[3] Lekner J 1987 *Theory of Reflection* (Dordrecht: Nijhoff)
[4] Born M and Wolf E 1975 *Principles of Optics* 5th edn (Oxford: Pergamon)
[5] Penfold J 1989 *J. Physique Coll.* **50** C7 99
[6] Lee E M, Thomas R K, Penfold J and Ward R C 1989 *J. Phys. Chem.* **93** 381
[7] Penfold J, Lee E M and Thomas R K 1989 *Mol. Phys.* **68** 33
[8] Penfold J, Ward R C and Williams W G 1987 *J. Phys. E: Sci. Instrum.* **20** 1411
[9] Penfold J 1990 *Proc. 'Enrico Fermi' Summer School* at press