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## THE STRUCTURE OF SURFACES OF SURFACTANT SOLUTIONS ABOVE THE CRITICAL MICELLE CONCENTRATION

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**Abstract** Specular reflection of neutrons from surfactant solutions above their critical micelle concentrations indicates that layer structures are formed in the vicinity of the surface. The mean spacing of the structures varies with chainlength in a way that suggests the presence of surfactant bilayers. The number of layers is estimated to be between about 5 and 15. Near the surface the structure seems to be similar to either a nematic phase or a lamellar phase. The presence of a layered structure would require there to be a large surface excess of surfactant.

## 1 - INTRODUCTION

The specular reflection of neutrons is very sensitive to structure at planar surfaces /1/. We have demonstrated its versatility by experiments on surfactants and polymers adsorbed at the air/solution interface /2-4/ and at the quartz/water interface /5,6/. The special feature of neutron reflection in comparison with X-rays is the possibility of using isotopic substitution either to highlight different parts of the surface layer or to eliminate the contribution of one of the components altogether. Thus in a surfactant solution it is possible to study the air/solution interface under circumstances where either surfactant or solvent refractive index is matched to that of air. Apart from some background scattering, which is easily eliminated, the reflectivity profile (reflectivity plotted against momentum transfer) is then determined respectively only by the surfactant or solvent structure at the interface.

Adsorption at the air surface of a surfactant solution is manifested by a fall in the surface tension,  $\gamma$ . The decrease in the surface tension is related to the amount adsorbed by the Gibbs equation

$$d\gamma/d\ln a = -RT \quad (1)$$

where  $a$  is the activity of the surfactant in the solution. Measurement of surface tension in conjunction with the Gibbs equation is commonly used to follow the adsorption of a surfactant up to the critical micelle concentration (c.m.c.). As with the other main method for determining adsorption at the air/solution interface, radiotracer measurement, the surface tension method gives no structural information about the adsorbed layer. At the c.m.c. there is a sharp change in the variation of  $\gamma$  with  $\ln a$  and above the c.m.c. both  $\gamma$  and  $\ln a$  change much more slowly with concentration. When both  $d\gamma$  and  $d\ln a$  are close to zero it becomes very difficult to apply the Gibbs equation to determine the surface excess of surfactant. Cutler et al. /7/ have attempted to apply the Gibbs equation to data for sodium dodecyl sulphate (SDS) and found that the surface excess of surfactant continued to increase with concentration above the c.m.c.

In recent work using neutron reflection to study the structure of decyl trimethylammonium bromide (C<sub>10</sub>TAB) adsorbed at the air solution interface we found that in D<sub>2</sub>O solutions the

reflectivity was unexpectedly enhanced above the c.m.c. /2/, unexpected because protonated  $C_{10}TAB$  has a scattering length density (related to neutron refractive index) approximately the same as air. It is easy to show that for any simple structure of the adsorbed layer the reflectivity ought then to be lower than that of the pure solvent. We deduced that there must either be a layer of water of abnormally high density next to the surfactant layer at the surface or a multilayer structure, which we were not able to identify.

We have now done further experiments on a range of surfactants at different concentrations and find that the enhancement of reflectivity of  $D_2O$  occurs for many of the solutions above the c.m.c. We present the new results in this paper.

## 2 - EXPERIMENTAL DETAILS

The experiments were all done on the reflectometer CRISP at ISIS which has been fully described elsewhere /8/. The reflectivity was measured over a limited range of momentum transfer  $\kappa$  ( $= 4\pi \sin\theta/\lambda$  where  $2\theta$  is the scattering angle and  $\lambda$  the wavelength of the neutrons), from  $0.05 - 0.4 \text{ \AA}^{-1}$ , and calibrated by reference to  $D_2O$ . However, because some of the features observed in the present work were unusual we also measured a number of complete profiles down to values of the momentum transfer below the critical angle, which for  $D_2O$  is at about  $0.017 \text{ \AA}^{-1}$ .

The samples were contained in Teflon troughs which had been cleaned by prolonged soaking in heptane to remove organic materials, followed by soaking in concentrated  $HNO_3$  containing 4% HF. The troughs were rinsed in clean water (Elga Elgastat) before use. The surface of the liquid was  $70 \times 250 \text{ mm}$ , sufficiently large that only about a third of the liquid was illuminated by the beam and there were no edge effects. The troughs were enclosed in airtight containers to eliminate evaporation effects. The windows of the containers were quartz (Suprasil) which is transparent to neutrons. All the surfactants were purified immediately before the experiment, either by recrystallization in the case of the CTABs /2/ or by Soxhlet extraction with heptane in the case of SDS and LiDS.

## 3 - THE CALCULATION OF REFLECTIVITY PROFILES

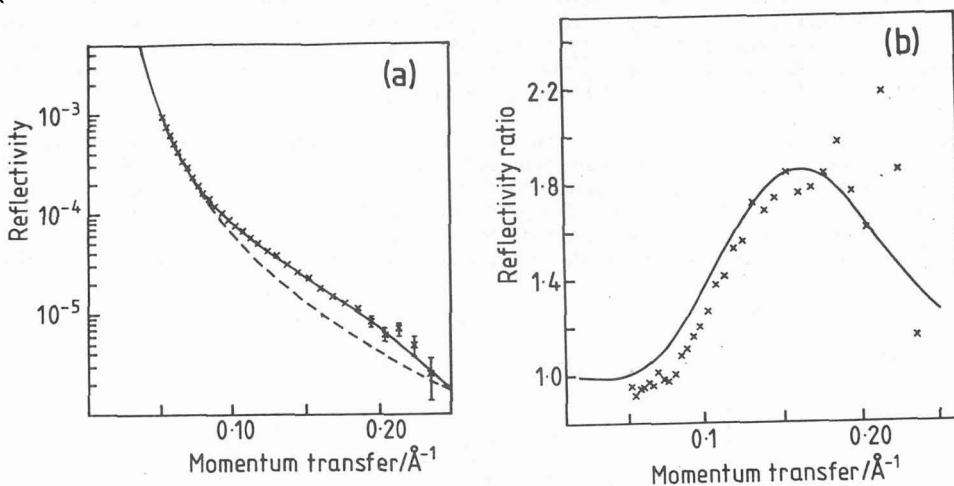
The basis of the specular reflection technique is that the variation of the specular reflectivity with momentum transfer normal to the interface,  $\kappa$ , can be related to any inhomogeneity at the interface /1/. The calculation of specular reflectivity profiles can be done exactly for any model scattering length density profile using the optical matrix method for light polarised perpendicular to the plane of reflection /9/. Since the scattering length density is directly determined by the composition profile the match between experimental and observed profiles provides an accurate means of assessing the validity of any structural model of the interface. Throughout this paper we use the optical matrix method. Fuller details are given in references /2/ and /9/.

## 4 - SPECULAR REFLECTION FROM SURFACTANT SOLUTIONS ABOVE THE C.M.C

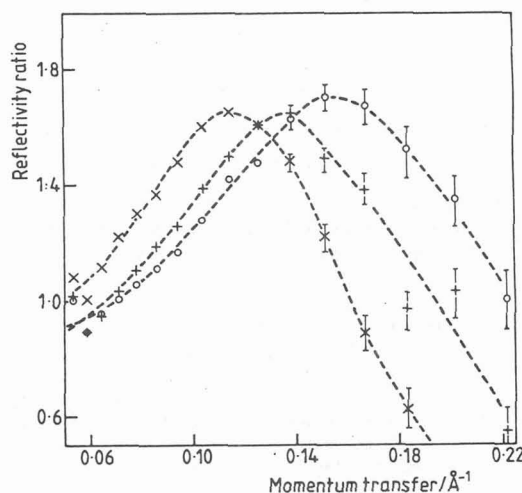
Figure 1 compares the reflectivity profile for a solution of protonated  $C_{10}TAB$  in  $D_2O$  at a concentration of  $0.1 \text{ M}$  with the reflectivity profile for pure  $D_2O$ . The c.m.c. of  $C_{10}TAB$  is at  $0.065 \text{ M}$  /10/ so that the amount of surfactant present as micelles is  $0.035 \text{ M}$ . The enhancement of the reflectivity is clearly seen in Figure 1(a) but, since the ordinate in the figure is a logarithmic scale, the magnitude of the effect is not particularly striking. In Figure 1(b) we plot the ratio of the reflectivity of the surfactant solution to the profile calculated for the  $D_2O$  surface with no surface roughness (the reflectivity of  $D_2O$  is somewhat lower than the ideal surface which would make the enhancement even greater). The ratio plot shows that at a momentum transfer of about  $0.16 \text{ \AA}^{-1}$  the reflectivity is almost doubled. Since the scattering length of the  $D_2O$  has been lowered by the addition of surfactant, by about 3%, the reflectivity should also have been lowered. Indeed, at concentrations just below the c.m.c. the reflectivity of the surfactant solution was found to be lower than that of  $D_2O$ . Something unusual must therefore be happening at the surface to cause the enhancement.

Similar measurements on CTABs of different chain lengths showed that enhancement of the reflectivity is related more to the fraction of surfactant present as micelles than to the c.m.c. itself. For example, the c.m.c. of  $C_{14}TAB$  is  $3.5 \times 10^{-3} \text{ M}$  in comparison with  $0.065 \text{ M}$  for  $C_{10}TAB$  /10/. At a concentration of double its c.m.c.  $C_{14}TAB$  only enhances the

reflectivity of  $D_2O$  by a small amount. However, at a micellar concentration the same as used for Figure 1, i.e. at the c.m.c. + 0.035 M, there is a large enhancement. The enhancement is shown in Figure 2 for  $C_{10}$ ,  $C_{12}$ , and  $C_{14}$ TAB. The extent of the enhancement is the same in the three cases but the value of  $\kappa$  at which the maximum occurs is different, being 0.16, 0.135, and 0.115  $\text{\AA}^{-1}$  respectively. Curiously, we observed no effect for  $C_8$ TAB and only a small enhancement for  $C_{16}$ TAB.  $C_{16}$ TAB is more difficult because its Krafft temperature is above room temperature but we have no explanation for the difference of  $C_8$ TAB. As for  $C_{10}$ TAB the reflectivity of solutions below the c.m.c was lower than that of  $D_2O$ .



**Figure 1** (a) Observed and calculated specular reflectivity profiles of a 0.1 M solution of fully protonated  $C_{10}$ TAB in  $D_2O$ . The model for the calculated profile is discussed in the text. (b) Ratio of the observed reflectivity in (a) to the calculated reflectivity for perfectly smooth  $D_2O$ . The continuous line is calculated for the same model as in (a).

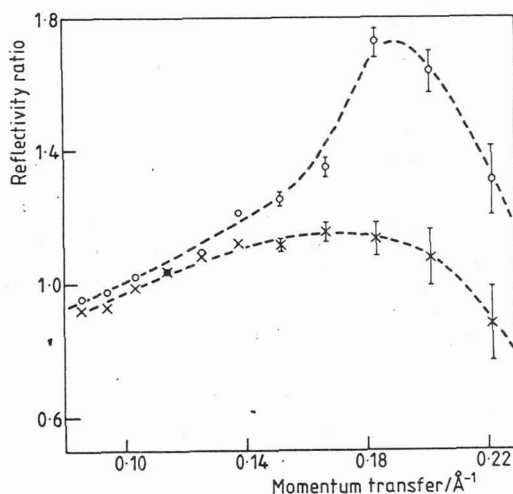


**Figure 2** The observed ratios of the reflectivities of solutions of CTABs to the calculated reflectivity of perfectly smooth  $D_2O$ . The concentrations were 0.1 M for  $C_{10}$ TAB (o), 0.051 M for  $C_{12}$ TAB (+) and 0.0385 for  $C_{14}$ TAB (x). The dashed lines are to guide the eye.

We have also observed enhancements of reflectivity for other types of surfactant. In the case of SDS the effect is always present at a concentration double the c.m.c (the c.m.c is

0.008 M) but its magnitude is not accurately reproducible. This may have two possible origins. Firstly it is extremely difficult to be sure that no dodecanol is present as an impurity. Even when the SDS has been rigorously purified there is still the possibility that a small amount of dodecanol is produced by hydrolysis in the  $D_2O$  solution. Separate experiments where dodecanol was deliberately introduced as an impurity indicate that its presence reduces the reflectivity enhancement. Secondly, we found that the reflectivity enhancement was sensitive to the nature of the counterion in the system. Thus pH affected the enhancement and the equivalent concentration of LiDS showed only a small enhancement of the reflectivity. However, in both cases and in all circumstances the reflectivity from solutions of SDS and LiDS at concentrations just above the c.m.c. showed an enhanced reflectivity over that for  $D_2O$ . Indications that the effect may be very sensitive to impurities are that SDS is the only surfactant where we have sometimes also observed an enhancement of the reflectivity of  $D_2O$  below the c.m.c.

Figure 3 shows the reflectivity ratio for two further surfactants, sodium decyl sulphate and sodium octyl sulphonate. Both solutions were 50% above their c.m.c., at 0.06 M and 0.22 M respectively. The effect is quite pronounced for the octyl sulphonate and the maximum occurs at a larger value of  $q$  than observed for  $C_{10}TAB$  in line with the trend with decreasing chainlength shown by the series in Figure 2. The effect for sodium decyl sulphate is smaller. Once again, both surfactants depress the reflectivity of  $D_2O$  at concentrations below the c.m.c.



**Figure 3** The observed ratios of the reflectivities of fully protonated sodium octyl sulphonate (o) and sodium decyl sulphate(x) to the calculated profile for perfectly smooth  $D_2O$ . The dashed lines are to guide the eye.

Certain protonated surfactants at concentrations above the c.m.c. undoubtedly enhance the reflectivity of  $D_2O$ . The effect is not confined to one particular chain length of surfactant nor to a particular type of head group. Its magnitude may be sensitive to impurities but even were it entirely attributable to impurities, which is unlikely, the impurities themselves will also be protonated and the effect would be no less interesting. It seems to be most closely related to the volume fraction of micelles. Thus it is not observed, or is only very weak, when the c.m.c. is low and the concentration is only a little above the c.m.c.

## 5 - DISCUSSION

The reflectivity ratio shown in Figures 1 to 3 is closely related to the form factor of the inhomogeneity at the interface /11/. It was shown in reference /2/ that for simple structures involving no more than three layers a reflectivity enhancement can be brought about only if one of the layers has a scattering length density greater than that of  $D_2O$ . Indeed a surface structure consisting of a monolayer of surfactant, a layer of  $D_2O$  and

counterions with scattering length density about 10% greater than  $D_2O$ , and a layer of micelles, was found to reproduce the  $C_{10}TAB$  data shown in Figure 1 with great accuracy. The continuous line in Figure 1 is the result of just such a fit. However, there are two problems with this interpretation. Firstly, it is difficult to understand how the density of such an incompressible fluid as water could increase by such a large factor. Only in the most strongly hydrated salts, for example involving  $Li^+$  or  $F^-$  ions, is the molar volume of water reduced on this scale. Secondly, the variation of the maximum in the reflectivity enhancement shown in Figure 2 shows that the position of the maximum depends strongly on the chainlength. Unless the thickness of the abnormal water layer correlates perfectly with the chain length of the surfactant, and there seems little reason for it to do so, the model used to fit the data of Figure 1 cannot be extended to fit the profiles of  $C_{12}TAB$  and  $C_{14}TAB$  in Figure 2.

A clue to the type of layered structure needed to cause the observed range of enhanced reflectivities comes from the structures used to produce highly reflecting mirrors for neutrons /12/. To maintain the reflectivity close to unity at glancing angles above the critical angle for total reflection such mirrors consist of alternating layers of a metal of large scattering cross section ( $^{58}Ni$ ) and one of almost zero cross section (Ti). The layer spacing is varied in a systematic way so as to give an ill defined and therefore broad diffraction peak. It is this ill defined Bragg peak which can maintain the reflectivity close to unity out to an angle about double the critical angle. The mean spacing of the layers in the mirror defines the position of the Bragg angle. The effect of alternating a large scattering length element with a zero scatterer is to reduce the mean scattering length of the multilayer. This would have the unwanted effect of moving the critical angle for total reflection to lower glancing angles. To prevent this side effect the first layer at the surface consists of  $^{58}Ni$  at a sufficient thickness (of the order of 200 Å) to fix the critical angle at the large value characteristic of pure  $^{58}Ni$ . Thereafter the layers alternate with a steadily decreasing thickness to produce the desired reflectivity profile. A good mirror may consist of several tens of layers.

The formula used to generate the mirror spacings suggests some possibilities for explaining the data for the surfactant solutions.

(i) The maximum in the reflectivity ratio is probably an ill defined and very weak diffraction peak. The values of the maxima for  $C_{10}TAB$ ,  $C_{12}TAB$ , and  $C_{14}TAB$  then give mean spacings for a layered structure of 40, 46, and  $55 \pm 2$  Å respectively, while that for sodium octyl sulphate gives one of about 33 Å. The fully extended chainlengths for  $C_8$ ,  $C_{10}$ ,  $C_{12}$ , and  $C_{14}$  are 11.5, 14.1, 16.7, and 19.3 Å /13/, an increase of 2.6 Å per  $C_2H_4$  unit. Since the observed increases are 7, 6, and 9 Å from  $C_8$  to  $C_{10}$ ,  $C_{10}$  to  $C_{12}$ , and  $C_{12}$  to  $C_{14}$  respectively, the mean spacing appears to be associated with a bilayer structure.

(ii) To maintain the same critical angle as that of the layer with higher scattering length density it is necessary that the first layer of a mirror consists of this material at a thickness greater than about 150 Å. However, the critical angle for the surfactant solutions is always that of the average composition of the solution. Thus, if there is a spread of water spacings in the layered structure up to values in the region of 150 Å then the thinner layers must be those closest to the surface.

(iii) To produce a sufficiently strong Bragg peak it is necessary that the contrast between the two component layers be large. The only way that this can be achieved in the surfactant solutions is if one set of layers is close to pure water in its composition and the other is close to pure surfactant. This again is consistent with the presence of surfactant bilayers.

We have made some preliminary attempts to find a model that will fit all the data. The most probable structure consistent with the three features outlined above is one where the layers nearest the surface are alternating water (plus counterions) and surfactant bilayers with a total spacing less than the mean value. As the distance from the surface increases the thickness of the water layers increases until the composition of the system has reached its bulk value. When the water layer thickness is large it is probable that the surfactant bilayers will start to break up, possibly into disc like micelles, as they approach the bulk spherical micellar structure. Thus, as well as the variation in water layer spacing, the scattering length density of the surfactant layers will gradually increase from the surface into the solution. A further feature to be expected if the surfactant layers break up into smaller units is that these layers will be characterized by a large "roughness" factor.

Whilst the qualitative model necessary to reproduce the data is quite easy to describe there

is a great variety of quantitative models to choose from. In Figure 4 we show the calculated reflectivity ratio for a structure with the following parameters:

- (i) The surfactant bilayer has a constant thickness of 30 Å,
- (ii) The scattering length density of the surfactant layer varies with distance into the solution between an arbitrary starting point and the average value for the solution as a whole, the variation being described by a Gaussian distribution,
- (iii) The scattering length density of the water layers is constant but their thickness increases from an arbitrary starting value up to a value consistent with the composition of the solution, the variation being described by a Gaussian distribution.
- (iv) The effect of the numerous "rough" interfaces is incorporated by artificially broadening the resolution function of the instrument.

The calculation in Figure 4 is only intended to show that a disordered, layered structure can account for the experimental observations. Undue significance should not be given to the parameters used, which were 20 Å for the initial water layer thickness,  $4.5 \times 10^{-6} \text{ Å}^{-2}$  for the initial surfactant scattering length density (this would correspond to an already highly disordered initial layer), and a total of ten double layers.

Whilst we have not been able to fit the reflectivities of surfactant solutions above the c.m.c. quantitatively, a number of qualitative conclusions can be drawn. Layering almost certainly does occur. A multilayer structure of the kind described requires there to be a large surface excess of surfactant. As discussed in the introduction the surface excess is difficult to measure via the Gibbs equation, although the activity measurements of Cutler et al. /7/ did indicate continuing adsorption of SDS above the c.m.c. The structure of the surfactant near the surface bears some resemblance to the lyotropic lamellar phase. For the surfactants used here the lamellar phase is not formed until the surfactant volume fraction is about 50%, an order of magnitude greater than the bulk concentrations used for these experiments.

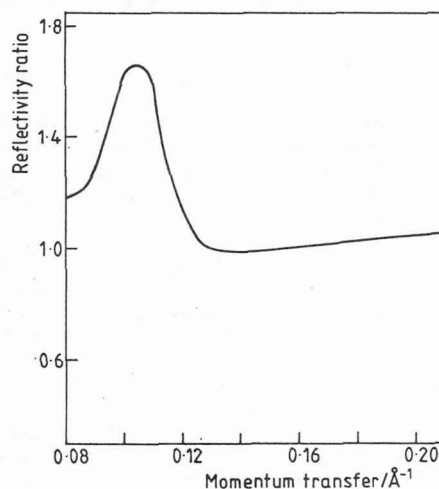


Figure 4 The calculated reflectivity ratio for a disordered multilayer structure at the surface of a surfactant solution. The calculation is described in the text.

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