



Neutron reflectometry of anionic surfactants on sapphire: A strong maximum in the adsorption near the critical micelle concentration

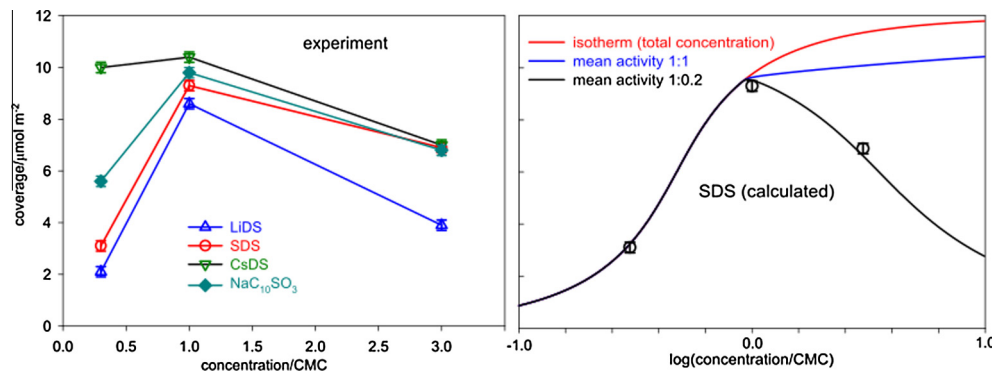


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GRAPHICAL ABSTRACT



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ABSTRACT

The adsorption of the anionic surfactants, lithium, sodium and cesium dodecylsulfates, and sodium decylsulfonate, on the positively charged C-plane (0001) of sapphire (alumina) has been measured using neutron reflection. For each of the four surfactants there is a strong maximum in the adsorption at about the critical micelle concentration. The maximum becomes more marked from lithium to cesium. The measurements were reproduced over a range of different physical conditions and could not be accounted for in terms of impurities. The maximum is explained quantitatively by using the combination of a mass action model to calculate the mean activity of the surfactant, and a cooperative model of the adsorption (Frumkin), in which saturation of the layer is not attained until well above the critical micelle concentration.

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1. Introduction

Many authors have observed adsorption maxima in the adsorption of surfactants at the hydrophilic solid–aqueous interface in the

concentration range around the critical micelle concentration (CMC) and several alternative explanations have been proposed. A thorough summary of the earlier work has been given by Vold and Sivaramakrishnan [1] and there are three moderately recent reviews of experimental observations [2–4]. In particular, an outline of explanations of adsorption maxima is given in one of these by Paria and Khilar, in which the authors state “the adsorption

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mechanism . . . is not well understood". Until relatively recently, the method of studying adsorption on solids has been to analyse depletion from the bulk solution in conjunction with a high surface area and/or partly organic material, which brings problems of heterogeneity and contamination from the solid surface in addition to the usual risks of impurities in the surfactant sample (see e.g. Vold and Sivaramakrishnan [1]). The general suspicion is then that the maximum can often be attributed either to impurities or to polydispersity in the surfactant. Thus Paria and Khilar explain some of their own data in terms of a mixture of surfactants along similar lines to those earlier used by Trogus et al. [5]. The use of a flat surface would greatly reduce the chance of such interference from the surface. Thus, Arnebrant et al. studied adsorption at a flat surface, using ellipsometry [6] and concluded that there was no maximum for hexadecyltrimethylammonium bromide (C_{16} TAB) or sodium dodecylsulfate (SDS) at either the hydrophobically modified or the hydrophilic chromia–aqueous interface, although they had earlier observed a sharp maximum for SDS at the hydrophobically modified chromia surface. Just like the air–aqueous interface, a hydrophobic surface is highly vulnerable to the main impurity of SDS, i.e. dodecanol, and Arnebrant et al. showed that the maximum was completely removed by purification of the surfactant.

Apart from impurities, the main explanation for a maximum has been in terms of the decreasing activity or monomer concentration of the surfactant ion above the CMC. Although this decrease was first described by Murray and Hartley in 1935 [7], it seems to have been first suggested as the possible cause of a maximum by Corrin et al. [8], but not fully expounded until Sexsmith and White [9] (see also Wennerström and Evans [10] for an account integrated into a more modern context). The micelles of ionic surfactants carry a charge because they partially dissociate. The law of mass action then requires the concentration of counterions to exceed the concentration of monomer surfactant ions and this gap increases with concentration as more micelles are formed, i.e. increasing overall concentration above the CMC causes the surfactant monomer concentration to decrease steadily from its value at the CMC while the counterion concentration steadily increases. The simple argument is then that since the adsorption is dominated by the surfactant ion, it will also decrease. This was criticized by Trogus et al. on the grounds that this would cause a similar effect at the air–water interface and no such effect has ever been observed [5]. However, the argument of Trogus et al. is not correct in practice because adsorption at an interface is usually, though not necessarily, determined by the mean activity of the surfactant and its counterion. Although adsorption at the air–aqueous interface can lead to charge separation and a potential across the interface, thermodynamics requires that a neutral ion pair is adsorbed. In most cases the neutralizing ion is the surfactant counterion and adsorption is then determined by the mean activity, a_{\pm} , or, approximately, by the mean concentration, where

$$a_{\pm} = \sqrt{a_+ a_-} \approx \sqrt{m_+ m_-} = m_{\pm} = m \quad (1)$$

Adsorption of ions other than the surfactant counterion will change the apparent activity in a different way. This was first suggested by Pethica [11] and examples of the consequences are discussed in detail by Xu et al. [12], although none has so far been so extreme as to produce a maximum at the air–aqueous interface. For pure systems direct determination of a_{\pm} by Cutler et al. [13] and model calculations using the law of mass action [14] show that the mean activity increases gradually above the CMC so that adsorption at the air–aqueous interface should also increase or stay the same if saturation has been reached. However, at a charged solid–aqueous interface the species adsorbed will not generally be symmetrically charged, i.e. $m'_+ \neq m'_-$ and $m'_{\pm} \neq m_{\pm}$, where the prime indicates the species adsorbed. If the adsorption of counterion is less than

of surfactant ion, m'_{\pm} will start to decrease below m above the CMC and adsorption should then peak in the vicinity of the CMC. The obvious condition for unsymmetrical adsorption of this type is either in a mixture of surfactants, as considered by Trogus et al. and Paria and Khilar, or when the surface carries a charge opposite to that of the surfactant ion. In both cases the nature of the isotherm may also be an important factor. Systems that might exhibit the charge effect are alkyltrimethylammonium surfactants (C_n TAB) on negatively charged silica or mica, and SDS on positively charged sapphire. Tulpar and Ducker have shown that the nature of the charge at a solid surface is also important [15]. They have argued that fixed charges on a solid surface are the driver for the low level adsorption of charged surfactants that is commonly observed at a solid–aqueous interface whereas laterally mobile ions are important for the more extensive adsorption of surface micelles and related structures. Speranza et al. have used X-ray reflectometry to study the series of C_n TABs with even n from 10 to 16 adsorbed on mica and found no maximum in the adsorption, although there was a pronounced maximum in the thickness [16]. The assumption above that a maximum in the adsorption will follow a maximum in the mean activity, which must occur for the C_n TABs, depends on the assumption that the mechanism of adsorption does not change. The marked change in structure of the layer suggests that the mechanism of adsorption does change for the C_n TABs on mica, adding a further layer of complication to the problem.

In this paper we examine the adsorption of SDS and related surfactants on a flat sapphire surface using neutron reflectometry (NR). The experiments have been done on the C-plane, the basal or (0001) plane, of sapphire (alumina). In a previous paper, which we refer to as paper I [17], we found that adsorption decreased steadily with increasing pH for the C-plane, in contrast with the R-plane (1 $\bar{1}$ 02), which is consistent with the higher isoelectric point of pH = 6 estimated for the C-plane by Kershner et al. [18]. We also found that adsorption was in the form of a double molecular layer but with an unusually low total thickness of 24 Å for two chains. As discussed in paper I, the contrast in the NR experiment with sapphire as substrate, D₂O as solvent and normal protonated surfactant gives an unusually strong reflected signal, which makes the accuracy of both coverage and thickness measurements higher than obtainable by any other technique. Here we extend the previous measurements to the region above the CMC and focus on the occurrence of a marked maximum around the CMC.

2. Experimental details

Most of the experimental details have already been given in paper I, in particular the purification and its assessment, and we give only minimum detail here. Protonated lithium dodecylsulphate (LiDS), sodium dodecylsulphate (SDS) and sodium 1-decanesulfonate ($C_{10}SO_3Na$) were all purchased from Fluka. Caesium dodecylsulphate (CsDS) was prepared by neutralizing dodecylhydrogensulphate with caesium hydroxide (Aldrich, 99%). Purification of the sulfates followed Weil [19] and of the sulfonate followed Read and Tartar [20]. The surface purity was assessed by surface tension measurements and there was no sign of a minimum in the final products except where noted below (the surface tension data is in the Supporting Information of paper I).

Reflectivity experiments were done on three different reflectometers, SURF at ISIS [21], and D17 and ADAM at ILL [22]. Some of the measurements were simple repeats and some varied the conditions of adsorption. The reasons for repeating the experiments were partly that the results were unexpected and partly that, at higher concentrations, the background scattering becomes significant and care has to be taken in the subtraction. This background scattering arises from multiple small angle scattering

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