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Adsorption of non-ionic surfactants to the sapphire/solution interface – Effects of temperature and pH

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ABSTRACT

The adsorption of the non-ionic surfactants tetraoxyethylene glycol monododecyl ether ($C_{12}EO_4$), pentaoxyethylene glycol monododecyl ether ($C_{12}EO_5$), and hexaoxyethylene glycol monododecyl ether ($C_{12}EO_6$) to single crystal sapphire substrates has been studied using specular neutron reflection for solutions at the critical micelle concentration. The effects of temperature and pH of the solutions were studied as well as the differences between two different crystal faces, the C and the R planes. At neutral pH, significant adsorption was only observed when the temperature was raised above the cloud temperature. This adsorption was reversible and surfactant was displaced on cooling. Reducing the pH to 3 results in significantly increased adsorption of $C_{12}EO_5$ at 25 °C with a central layer consisting mainly of surfactant (about 90%) on the C-plane substrate. A slightly smaller surface excess was observed for the R-plane. This contrasts with the significantly lower density observed even at high temperatures at neutral pH on both substrates. The results suggest that for neutral solutions surfactant association above the cloud point is the primary driving force for adsorption. At low pH, specific interactions with protonated surfaces are important. The structures of the highly hydrated layers are similar to those found for the surfactants at hydrophilic silica surfaces.

1. Introduction and background

Surface-active molecules, surfactants, are major components in a wide range of industrial products as well as in domestic cleaning materials, pharmaceutical delivery systems and personal care products. These applications usually depend on the capacity of the materials to bind to interfaces and to associate as micelles or other structures in concentrated solutions. Understanding the behavior of different surfactants in solution, and how they interact at interfaces is thus a key to improving formulations and to providing better products. Many general aspects of surfactant adsorption to solid/liquid interfaces have been described in review articles [1,2]. Although many applications exploit mixtures of surfactants, it is useful first to understand the role of single components. Tiberg et al. have highlighted the importance and role of structural studies of adsorbed layers in providing an understanding of the mechanisms that control interaction between surfactant molecules and a substrate. This study addresses the adsorption from dilute aqueous solution of linear alkyl ethoxy surfactants to alumina surfaces. These materials are widely used commercially and there is an extensive literature describing various fundamental studies. Two books provide an extensive review of the literature about these classes of surfactants [3,4] and there is a recent review of the phase behavior [5]. The ethylene glycol groups are water-soluble but this decreases with temperature and a well-defined cloud point is observed for dilute solutions as the temperature is increased. Addition of salts to solutions also reduces the solubility.

This paper is concerned specifically with three surfactants tetraoxyethylene glycol monododecyl ether ($C_{12}EO_4$), pentaoxyethylene glycol monododecyl ether ($C_{12}EO_5$), and hexaoxyethylene glycol monododecyl ether ($C_{12}EO_6$) that come from a homologous series with an increasing critical micelle concentration and increasing cloud temperature. Some properties of these surfactants taken from literature [5,6] are listed in Table 1. For $C_{12}EO_4$ there is some variation in the reported critical micelle concentration (CMC) but the experimental determination is difficult for values below 1×10^{-4} mol dm^{-3}, particularly when the cloud point is low. The micelles of these surfactants are the subject of extensive studies using light scattering [7] and small-angle neutron scattering [8–11]. These papers provide a consistent picture of micelles with significant hydration of the ethylene oxide (EO) groups that is in agreement with nuclear magnetic resonance experiments [12] that suggested about two water molecules are associated with each EO moiety. The micelles tend to elongate and depart from a spherical structure at high concentrations although near a critical point (cloud temperature), the scattering may change because of large

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Table 1
Surfactants and their solution properties.

Surfactant	Critical micelle concentration (mol dm^{-3}) (at 25 °C)	Cloud point (°C)
$C_{12}EO_4$	6.4×10^{-5}	6
$C_{12}EO_5$	5.7×10^{-5}	30
$C_{12}EO_6$	8.7×10^{-5}	48

Table 2
Molecular parameters used to model surfactants.

Material	Volume, V (Å^3)	Extended length[a], l (Å)	Scattering length[a], b (fm)	Scattering length density, $\rho \times 10^{-6}$ (Å^{-2})
$C_{12}H_{25}$	350	16.7	−13.7	−0.39
$C_{12}D_{25}$	350	16.7	245.5	7.01
$(OC_2H_4)_4OH$	270	15.9	22.4	0.83
$(OC_2H_4)_5OH$	330	19.3	22.8	0.69
$(OC_2H_4)_6OH$	395	22.8	26.9	0.68

[a] Extended molecular lengths are taken from Ref. [34] and scattering lengths are taken from Ref. [31].

Table 3
Neutron scattering lengths of solvents and substrate.

Material	Volume, V (Å^3)	Scattering length[a], b (fm)	Scattering length density, $\rho \times 10^{-6}$ (Å^{-2})
H_2O	30	−1.68	−0.56
D_2O	30	19.15	6.35
50%D_2O	30	8.73	2.89
90%D_2O	30	17.07	5.66
α-Al_2O_3	42.5	24.31	5.71

[a] Scattering lengths are taken from Ref. [31].

concentration fluctuations and the evidence for different shape at these compositions is less clear.

The association of the surfactants in solution is related to their behavior at interfaces. Apart from studies using surface tension measurements, the structure at air-solution interfaces has been reported for an extensive range of alkyl ethoxy surfactants using neutron reflection measurements [13–19]. The two experimental methods are generally in good agreement for these materials provided that the purity is adequate. The area per molecule at the interface is seen to increase with increasing EO length and the density of the alkyl chain region decreases [20]. At solid–liquid interfaces, such as those between silica and solutions, there have also been a number of studies that have used fluorescence microscopy [21–23] and neutron reflection. The latter technique has shown adsorption of $C_{12}EO_6$ to silica gives rise to broken or disordered bilayers [24,25] and can be readily removed by increasing the pH of the solution. At hydrophobic surfaces such as those formed from grafted alkyl chains, the surfactants form monolayers [26]. The chemistry of the surface is clearly very important and different cleaning processes are thought to alter the adsorption to silica as they can change the proportion of siloxane and silanol groups. Adsorption to grafted monolayers that are hydrophilic such as those with an organic alcohol termination are found to change the structure and in place of a bilayer on silica, a thin monolayer was observed [27]. The sensitivity of the adsorption of these surfactants to surface chemistry makes it interesting to explore the behavior of solutions with other substrates. At neutral pH, silica is negatively charged and so investigation of adsorption to other oxides with different tendencies to dissociate is useful – the present study is of two specific crystal faces of sapphire (α-Al_2O_3).

Colloidal alumina usually has an amorphous surface but the macroscopic single crystals with well-defined crystal faces can be investigated and the properties of the different surfaces may be significantly different. Sapphire has a trigonal structure with space group $\bar{3}2/m$ and it is conventional to use four indices to describe crystal planes. The basal plane (0001) is known as the C-plane in technological applications. Some other faces are also known by particular designations and one that is widely used in the electronics industry because of the facility for epitaxial growth is the $(1\bar{1}02)$ or R-plane. The chemical composition of these faces is significantly different with a higher density of oxygen atoms accessible on the C-plane surface. The point of zero charge for the R-plane occurs at around pH 4.5 and shifts to pH 6 for the C-plane [28]. Above these values for pH, the surfaces have a net negative charge in aqueous solutions.

2. Neutron reflection – experimental principles and interpretation of data

Specular reflection of neutrons is a valuable tool to investigate both the structure and the chemical composition of layers at interfaces [20,29,30]. The technique involves determination of the reflectivity of an interface as a function of wavelength or angle and this depends on the profile of the refractive index, n, in the direction perpendicular to the surface. The refractive index for neutrons is related directly to the atomic composition of a material via the scattering lengths, b of the component atoms. It is useful to consider the scattering length density, ρ that is given by:

$$\rho = \sum N_i b_i \tag{1}$$

where N_i is the number density of the element, and b_i is the coherent neutron scattering length of the element i. A particular advantage of neutron reflection is that b can vary between isotopes of an element and there is a particularly large difference [31] for normal hydrogen (^1H) and deuterium (^2H or D). Tables 2 and 3 show the scattering length densities of materials used in the present study. The refractive index for neutrons of wavelength λ is related to ρ by:

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

The reflectivity for an interface can be calculated using conventional methods of optics [32] with a recursive matrix algorithm that divides the structure into layers of defined refractive index and thickness, t. It is also straightforward to include a small amount of roughness or mixing of components between adjacent layers using an approximation for a Gaussian roughness profile [33]. For surfactant molecules at an interface, this structure is shown schematically in Fig. 1. The scattering length density, and hence the refractive index, is related to the volume fraction of each component in a layer by:

$$\rho = \varphi_s \rho_s + \varphi_w \rho_w \tag{3}$$

where φ_s and φ_w are the volume fractions of surfactant and water, and ρ_s and ρ_w their scattering length densities. The constraint $\varphi_s + \varphi_w = 1$ is used. These equations can be extended readily to layers that consist of different parts of the molecules, such as heads and tails of surfactants. If an adsorbed surfactant is modeled as a single layer and the molecule has a total scattering length b_s (from the sum of b for all component atoms), the area per molecule, A in an interfacial layer of thickness, t is

$$A = b_s/(t\phi_s\rho_s) \tag{4}$$

The surface excess is related to A, by

$$\Gamma = M/AN_A \tag{5}$$

where M is the molecular mass of the surfactant and N_A is Avogadro's constant. If surfactants pack as bilayers at an interface with