

Research Paper

Anionic surfactant induced desorption of a cationic surfactant from mica

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ABSTRACT

The adsorption and desorption of a cationic surfactant, didodecylmethylammonium bromide, from water onto a mica surface have been investigated using neutron reflectivity. The surfactant was observed to adsorb strongly as a bilayer that was tenacious to a sustained water wash, but on the addition of an anionic surfactant, sodium dodecyl sulfate, at its critical micelle concentration complete desorption was observed.

1. Introduction

The interaction between clays and surfactants is of relevance to numerous fields, from surfactant based enhanced oil recovery (EOR) (Sheng, 2015), to organoclays, which are frequently synthesised from quaternary alkylammonium compounds (de Paiva et al., 2008). The behaviour of these surfactants at the clay surfaces is challenging to experimentally determine. Muscovite mica is often used as a model clay surface due to the perfect basal cleavage the crystal undergoes, which allows flat and clean surfaces to be easily generated. Muscovite is a phyllosilicate mineral with isomorphous substitution of one Si^{4+} by Al^{3+} per unit cell. This structural charge is compensated for by interlayer K^+ ions, giving an idealised formula of $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ and an area of 47 \AA^2 per charge site (Schlegel et al., 2006). As this charge is structural, little pH dependence of the mica surface charge is expected or observed. The use of ‘bulk’ techniques to observe behaviour of mica and other clays requires a powder to be used to give sufficient surface area for analysis. This complicates measurements of the basal surface due to the vastly increased contribution of edge site behaviour and properties which are different in most aspects to the basal plane. The number of techniques which can be used to observe basal plane behaviour is therefore limited.

A variety of techniques are used to investigate the solid/liquid interface though typically these are techniques where a second surface is introduced in order to make the measurement. Examples of these are atomic force microscopy (AFM), and the surface force apparatus (SFA) (Perkin, 2012). There is evidence that the ‘frontal confinement’ caused by the second surface can perturb the system and result in non-equilibrium structures being measured (Speranza et al., 2013; Striolo and

Grady, 2017), though a recent combined AFM and neutron reflectivity study showed good agreement (Griffin et al., 2017).

Neutron reflectometry is a well established, and non-invasive technique that allows behaviour at buried interfaces to be measured. In addition to the use of contrast variation, exchanging hydrogen for deuterium to change the scattering of different components while maintaining the chemistry, can allow simultaneous fitting of multiple datasets for a system (Sivia, 2011). Substrate preparation is challenging as an extremely flat surface is required over a large area (the order of cm^2) and, as the beam passes through the solid to reach the solid-liquid interface, substrate attenuation of the beam must be minimised. Both of these factors present particular issues for the mineral mica, which shows crystal waviness if unsupported and attenuates strongly.

In recent work, Browning et al. (2014) showed that by using a silicon wafer to support a thin mica sheet, neutron reflectivity (NR) could be successfully applied to the mica/solution interface. This setup has since been applied successfully to numerous studies (Allen et al., 2017; Griffin et al., 2016) and has previously been used to investigate adsorption of didodecylmethylammonium bromide (DDAB) to the mica basal plane (Browning et al., 2014; Griffin et al., 2016). The layer was observed to adsorb as a bilayer of thickness $24 \pm 2 \text{ \AA}$ and roughness $2 \pm 1 \text{ \AA}$ in one case, and $23 \pm 2 \text{ \AA}$ and roughness $2 \pm 1 \text{ \AA}$ in the other, with effectively no water inclusion in the layer in both cases. These numbers are in good agreement with other measurements of DDAB bilayers on mica (Dubois and Zemb, 1991) and on quartz (Blom et al., 2007), and indicate an interdigitated or tilted bilayer. It was observed that a wash with D_2O caused the bilayer thickness to decrease to $20 \pm 1 \text{ \AA}$. However subsequent washes with 10 mM KCl or CaCl_2 did not alter the layer structure further. A UV/ozone treatment was required to

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remove the surfactant from the mica surface. In this work we probe the behaviour of sequential surfactant solutions at the mica surface rather than a single one-component solution as previously studied.

The interaction of cationic and anionic surfactants in solution has been the subject of much research, and mixed micelles termed catanionic micelles are known to form in solution (Sohrabi et al., 2008). Due to the favourable interactions the critical micelle concentration (CMC) of a cationic-anionic mixture would be expected to show a minimum at some concentration ratio with a surface tension below that of the CMC surface tension of either pure surfactant, and this has been observed experimentally (Holland and Rubingh, 1983).

There have been studies of the didodecyltrimethylammonium bromide - sodium dodecyl sulfate (SDS) mixed system specifically; Marques et al. (1993) showed the pseudo-ternary phase diagram to be complex, containing regions of lamellar liquid crystalline phases, and regions of vesicles rich in the cationic or anionic surfactant depending on the molar ratio. The anionic rich region of the phase diagram has been studied further and for SDS solutions at the CMC of 0.24 wt. %, which is the concentration used in this work, it was observed that the solution was stable on addition of DDAB up to a mole fraction of 0.06 (Marques et al., 1999). Above this mole fraction precipitation occurred. This is in agreement with work by (Bai et al. (2002)) who identified this region as consisting of SDS-rich micelles. It is noted that these works were carried out in H₂O, and the use of D₂O, as in this study, has been seen to lead to small shifts in phase boundaries in similar systems (Kaler et al., 1992).

2. Experimental

2.1. Materials

Didodecyltrimethylammonium bromide, DDAB, (Sigma, ≥98%) and sodium dodecyl sulfate, SDS, (Sigma, ≥99%) were used as received. The structures of the two surfactants are shown in Fig. 1. The CMC of DDAB has previously been determined for an identical batch of compound by surface tension measurements as 0.08 mM and no minimum in the surface tension was observed (Browning et al., 2014). The CMC for SDS was taken from the literature to be 8.2 mM (Mukerjee and Mysels, 1971). Solutions of each surfactant at the respective CMC value were made up in D₂O, supplied by the ISIS neutron facility.

High quality clear ruby muscovite mica was supplied by Attwater and Sons, as sheets of 25 μm thickness, 100 mm by 50 mm. The composition of the mica was characterised using energy dispersive X-ray spectroscopy of a gold coated sample. The idealised formula for mica gives a ratio of K:Al:Si of 1:3:3, with two Al atoms in the octahedral sheet per unit cell, and three Si atoms and one Al atom in the tetrahedral sheet. Relative to the atomic percentage of K, the measured K:Al:Si ratio was 1:2.9:3.5, in reasonable agreement with the model formula. Na is a common impurity, replacing some of the exchangeable

K ions, and Fe and Mg are common lattice impurities. Na, Fe, and Mg were all measured at less than 10% of the measured K quantity in the sample. Neglecting impurities, the extent of tetrahedral isomorphous substitution may be estimated from assuming that there are two octahedral Al ions for each K (as mica is dioctahedral), and hence calculating the ratio of Al to Si in the tetrahedral sheet. This calculation gives a value of 21% of the tetrahedral sites filled by an Al substitution. This is again in reasonable agreement with the ideal structure, where 25% substitution is assumed.

2.2. Substrate preparation

Substrates for NR were prepared in the manner of Browning et al. (2014), with the modification of Griffin et al. (2015) to a larger substrate size, and is only briefly described here. A UV-curable glue (Loctite 3301) was spin coated onto a nitric acid cleaned neutron grade polished Si block (Crystran). A mica sheet was carefully cleaved, clamped against the glue layer using a highly polished Pyrex block (OptoSigma), and the glue was cured with a UV lamp (UVP CL-1000, λ = 254 nm). The mica was then cleaved again to yield a fresh surface which was UV/ozone cleaned and clamped against a teflon trough to form the sealed solid-liquid interface cell.

The cell was carefully filled to prevent trapped bubbles. Thereafter solutions were exchanged using an HPLC pump. A volume of 30 ml and flow rate of 2.0 ml/min was used for each solution change and washing step to ensure complete exchange of the solution in the cell. This has previously been determined as a more than sufficient volume, using dye solutions to monitor exchange. The flow lines were flushed before and after each surfactant to avoid contamination.

2.3. Neutron reflectivity measurements

Neutron reflectivity measurements were carried out at the INTER instrument at the ISIS neutron facility, UK (Webster et al., 2006), using time of flight to determine the wavelength of the incident neutron pulse. Three angles of incidence, 0.4°, 0.9°, and 2.3°, were used to give access to the desired range of momentum transfer to the surface, Q_z , as defined in Eq. (1) where λ is the neutron wavelength and θ the angle of incidence.

$$Q_z = \frac{4\pi}{\lambda} \sin(\theta) \quad (1)$$

2.4. Data analysis

NR data are analysed by modelling to a series of layers at the interface. Each layer is characterised by a thickness, roughness and scattering length density (SLD) which gives information about the

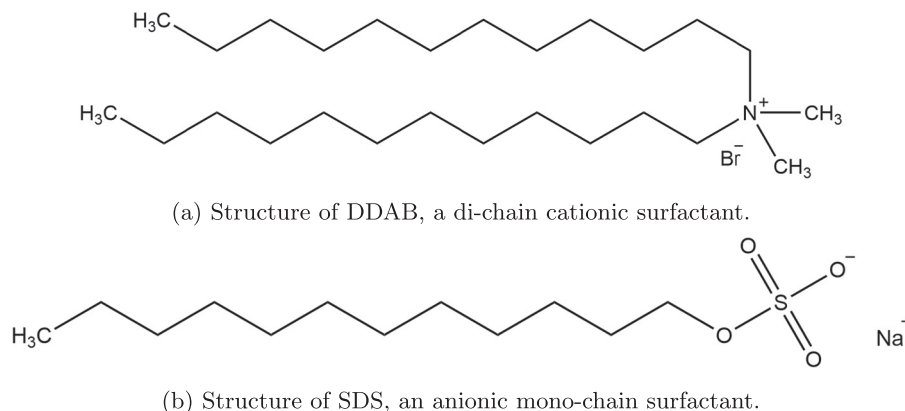


Fig. 1. Structures of the surfactants used in this work.

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