



A comparison of didodecyldimethylammonium bromide adsorbed at mica/water and silica/water interfaces using neutron reflection

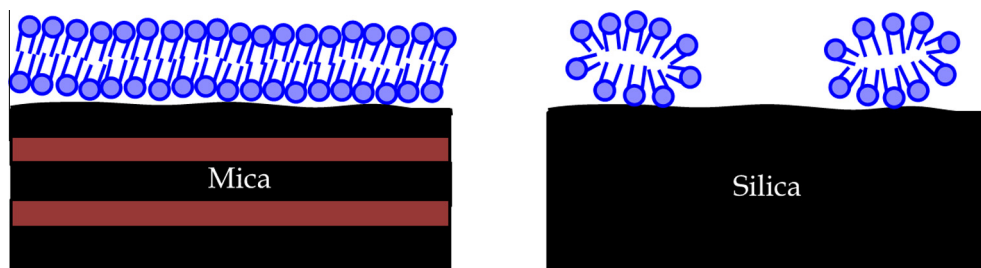


Lucy R. Griffin^a, Kathryn L. Browning^a, Chris L. Truscott^a, Luke A. Clifton^b, John Webster^b, Stuart M. Clarke^{a,*}

^aBP Institute and Department of Chemistry, University of Cambridge, Madingley Road, Cambridge, Cambs CB3 0EZ, UK

^bISIS, Rutherford Appleton Laboratory, Didcot, Oxfordshire, UK

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 8 March 2016

Revised 1 June 2016

Accepted 3 June 2016

Available online 4 June 2016

Keywords:

Mica
Silica
Neutron reflection
DDAB
Didodecyldimethylammonium bromide
Surfactant
Adsorption

ABSTRACT

The layer structure of the dichain alkyl ammonium surfactant, didodecyldimethylammonium bromide (DDAB), adsorbed from water on to silica and mica surfaces has been determined using neutron reflection. Although sometimes considered interchangeable surfaces for study, we present evidence of significant differences in the adsorbed layer structure below the critical micelle concentration.

A complete DDAB bilayer was assembled at the water/mica interface at concentrations below the critical micelle concentration (CMC). In contrast it is not until the CMC was reached that the complete bilayer structure formed on the oxidised silicon crystal. Removal of the complete bilayer on both surfaces was attempted by both washing and ion exchange yet the adsorbed structure proved tenacious.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

The neutron reflection (NR) technique is a powerful tool for structure determination at interfaces. Its capability for “contrast variation” by isotopic H/D substitution of both the adsorbate and solvent allows extra information to be obtained from systems which are essentially chemically identical but scatter neutrons differently. Each component of the system has a scattering length density from

the sum of all the isotopes within the material. This helps to remove the somewhat ambiguous nature of structure determination. However, the technique is not without its difficulties; for optimised experiments samples should be extremely flat with low roughness over a large area, allowing a sufficient reflected signal to be collected in a reasonable time. These restrictions can limit the number of different mineral surfaces it is possible to study. Silicon/silica, quartz and sapphire crystals have all been extensively studied due the availability of large defectless single crystals and their low attenuation cross sections [1–9].

* Corresponding author.

E-mail address: stuart@bpi.cam.ac.uk (S.M. Clarke).

Information from NR studies often supplements that from other surface specific techniques such as surface force apparatus (SFA) and atomic force microscopy (AFM). For these techniques, muscovite mica is often the substrate of choice due to the exceptional flatness achieved by cleaving the mica layers, negating the need for extensive polishing (as with silicon/sapphire/quartz). These techniques require the introduction of a second surface or probe onto the adsorbate during data collection. It has been shown that this can introduce deformation in delicate surface structures and induce crystallisation in specific systems [10,11]. In contrast, neutron reflection is a non-invasive probe of interfacial structures.

In order to perform complementary measurements using all these methods, it would be convenient to experimentally study adsorption to mica using NR. However, single crystals of mica large enough for reflectivity studies (greater than 25×25 mm) are very uncommon. Crystals of this size tend to include defects which cause additional scattering of the beam which, coupled with a large attenuation cross section, mean penetration through bulk mica is problematic.

Attempts have been made previously by Cosgrove et al. but experienced a number of experimental difficulties [12]. As a result of these difficulties, comparison is often drawn between adsorbate structures imaged using AFM/SFA on mica and those determined using neutron reflection technique on other surfaces [13–15]. These comparisons rely on the assumption that adsorbate structures are not significantly affected by the differences between mica and other substrates. It is likely that there will be rather different behaviour in the adsorption on mica from other silicates. The silica surface consists of OH groups that can be protonated/deprotonated leading to a strongly pH dependent surface charge in direct contrast to the pH independent structural charge of mica, resulting from isomorphous substitution [16].

Recently it has been shown that the difficulties accompanying neutron reflection from bulk mica can be circumvented by supporting a thin layer of mica on a silicon substrate [17,18]. As a result, we can directly compare adsorbate structures at the mica/water and silicon/water interfaces using neutron reflection, and here present evidence indicating adsorption on silica and mica is not the same.

This present study complements other recent synchrotron X-ray reflection work which has successfully been used to study adsorbed layers adsorbed on mica from the liquid [19–21]. This work uses a novel bent mica approach to provide a suitable surface for study.

Here we present a detailed study of the adsorption and desorption behaviour of DDAB at both the mica/water and silica/water interfaces. The surfactant adsorption isotherm up to the CMC was determined for each surface, highlighting interesting differences in the adsorption behaviour of the surfactant on the two surfaces. Reversibility of the adsorption through both washing and ion exchange with monovalent and divalent salt species was also investigated.

1.1. The silica surface

Crystalline silica is composed of a combination of Si–O bonds which include Si–O–Si bridging oxygens and hydrated Si–OH groups. Each oxygen atom may have one or two associated protons as shown by Iler [22]. In solution the charge of the silica surface is governed by the protonation and deprotonation of these Si–OH and Si–OH₂ groups. These equilibria are pH sensitive and, as such, the surface charge is also a function of pH. The isoelectric point of silica is rather low at approximately pH 2 [22]. Hence on raising the pH, deprotonation of Si–OH groups at the surfaces results in a negative charge. This negative surface increases most strongly up to approximately pH 6 where after it increases much more

slowly. The negative charge at the silica surface must be compensated by counterions which can be protons or other ions in solution including inorganic cations or cationic surfactants.

1.2. The mica surface

Muscovite mica is a dioctahedral phyllosilicate mineral with unit formula $KAl_2(AlSi_3O_{10})(F,OH)_2$. The bulk structure is comprised of repeating layers with each layer containing an octahedral (Al_2O_3) sheet sandwiched between two tetrahedral (SiO_4) sheets. In muscovite mica, approximately a quarter of the silicon atoms in the tetrahedral sheet are isomorphically substituted for aluminium resulting in a single negative charge for each 47 \AA^2 of the surface [23,24]. This high degree of substitution in mica means that the surface has a high charge density compared to other clay minerals and leads to a zeta potential of up to -150 mV in distilled water [25,26]. The surface charge remains constant with varying pH owing to the structural nature of the charge. In the naturally occurring mineral, potassium ions compensate the layer charge and sit on the basal plane between the layers. These bound cations act to pin adjacent layers to one another, this strong interaction makes mica a non-swelling clay (unlike montmorillonite for instance).

Muscovite mica is easily cleaved uniformly over large areas between the covalently bonded layers, exposing the basal plane which consists of a hexagonal array of oxygen atoms/potassium ions. During the cleavage process half the potassium ions remain associated with each layer; these surface ions may be exchanged with other ions including surfactants when exposed to an aqueous solution. Hence, we expect the mica will behave differently from silica reflection substrates where the surface charge originates from protonation or deprotonation of surface and is a strong function of pH.

1.3. Didodecyldimethylammonium bromide (DDAB) surfactant

The surfactant of interest in this work is didodecyldimethylammonium bromide (DDAB) illustrated in Fig. 1. This is a dichain cationic surfactant with molecular parameters given in Table 1. A first estimate of the shape/geometry of a given surfactant aggregate can be given from the packing parameter (P):

$$P = \frac{V_c}{A_0 l_c} \quad (1)$$

where V_c is surfactant chain volume, A_0 the head group area and l_c the alkyl chain length [27]. DDAB has a packing parameter of 0.620 and so is expected to form flat (either lamellae or vesicle) structures at concentrations above the CMC. This has been shown by small angle X-ray scattering [28]. Similarly one would expect the formation of flat, bilayer structures above the CMC at the solid/liquid interfaces.

The adsorption behaviour of this surfactant, DDAB, on mica has been reported using AFM [13]. Uniform and featureless images were interpreted to indicate a flat bilayer formed at the surface at 0.30 mM (above the CMC). In a recent publication by our group,

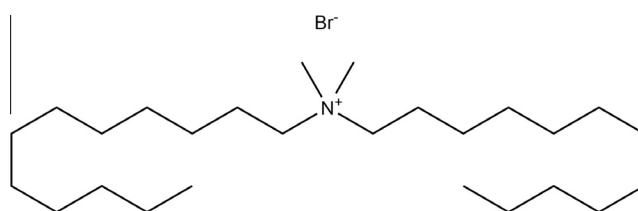


Fig. 1. Illustration of the molecular structure of didodecyldimethylammonium bromide (DDAB).

Download English Version:

<https://daneshyari.com/en/article/606225>

Download Persian Version:

<https://daneshyari.com/article/606225>

[Daneshyari.com](https://daneshyari.com)