Anionic Surfactants on Anionic Substrate: Monovalent Cation Binding

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**Abstract**

Neutron reflectometry has been used to study the adsorption of the anionic surfactant bis(2-ethylhexyl) sulfosuccinate cesium salt (CsAOT) on the anionic surface of mica. Evidence of significant adsorption is reported. The adsorption is reversible and changes little with pH. This unexpected adsorption behaviour of an anionic molecule on an anionic surface is discussed in terms of recent models for surfactant adsorption such as cation bridging, where adsorption has been reported with the divalent ion calcium but not previously observed with monovalent ions.

**Introduction**

There is continuing interest in the interaction of molecules adsorbed from solutions to solid substrates for a wide range of applications, such as detergency, oil recovery and wetting. The surfaces of minerals are particularly important for several reasons, not least that clays like mica are important components of oil reservoirs but also because they have been used for many years as the substrate of preferences for a number of elegant surface measurements, such as the surface force apparatus/balance (SFA/SFB) and as a substrate for Atomic Force Microscopy (AFM) [1–4 and many others]. This extensive use of mica is because the natural layered crystal structure is readily cleaved to reveal atomically flat surfaces over very large areas5,6.

In recent years there has been interest in expanding the study of mica surfaces from the approaches outlined above which require two surfaces in intimate contact. It is not clear what the effects of this and other ‘frontal confinement’ might be relative to a single surface, with some evidence that these techniques may not give quite the same structures as single surface studies.7–10

Mica is a layered structure that may be considered as two layers of silica tetrahedra sandwiching a layer of alumina octahedra. There is significant isomorphic substitution of Al3+ ions for Si4+ ions in the silica tetrahedra, leading to a high structural negative charge6. This negative charge is compensated in the natural mineral by potassium ions. The layers are generally held tightly together in water/ionic solutions. Related layered minerals, such as smectites, can swell dramatically, depending upon the nature of the cation. When mica crystals are cleaved and put in water, the surfaces are considered to be strongly negatively charged. This structural charge is not expected to be significantly pH dependent11.

Recently there has been some pioneering work by Briscoe *et al.* who developed a synchrotron X-ray scattering method to investigate adsorption from solution onto mica using a novel bent crystal approach7,8,12. This was followed by the development of a neutron reflection approach to study mica/liquid interfaces9,11,13. It is this neutron reflection approach that is used here.

There are a large number of studies of different species adsorbed onto mica from aqueous solution. As might be expected, the adsorption of cationic surfactant molecules on the negative mica surface is very strong and can be irreversible to further washing/removal by water or ionic solutions of mono or divalent ions13. A bilayer of cetyl trimethylammonium bromide (C16TAB) has been shown to form (essentially immediately) perfect bilayers7–9 by the reflectivity approaches, while there are some AFM reports that suggest some initial micelle formation prior to the bilayer formation. Recently the behaviour of an ionic liquid at the mica surface has been reported, where the ionic liquid is reported to exhibit layering on the mica very similar to that observed with SFA5.

More interesting is the observation that anionic surfactants can adsorb to mica with adsorption mediated by divalent cations (such as Ca2+) but not by monovalent ions (such as Na+). Similar behaviour has been observed on silica14 (which is a negatively charged surface at pH above the isoelectric point of approximately 2 15).

In this work the cesium salt of the anionic surfactant bis(2-ethylhexyl) sulfosuccinate (CsAOT) was used. The principle question we will address is whether this negatively charged surfactant adsorbs on the negatively charged mica in the presence of the cesium monovalent cation.



**Figure 1.** Schematic illustration of the molecular structure of the CsAOT. One may consider that there are two ‘tails’ each with formula of C8H17, or a combined composition of C16H34 for both tails. ‘Heads’ may be considered to be the C4H3O7SCs unit.

The adsorption of AOT salts at both the air/liquid and solid/liquid interface using neutron reflection both above and below the CMC16–21 have been reported, with some studies of Ca(AOT)2 at solid/liquid interfaces14,20.

The bulk solution behaviour of these different salts is also a significant factor. For example, the critical micelle concentration (CMC) of Ca(AOT)2 is approximately 0.5 mM, significantly lower than for NaAOT (2.5 mM)22, a large reduction that is typical for calcium surfactants14,18. The cesium salt has been observed to form disc-like micelles at 1 wt %, compared to oblate micelles for the sodium salt.23 We are not aware of any neutron reflection adsorption studies using the cesium salt.

**Experimental Section**

The mica substrate was prepared using the route previously described9,13, where a thin mica crystal is stuck to a very highly polished silicon wafer (100mm by 50mm by 10mm from Siltronix, France) using a UV cured glue (Loctite 3301). The surface was freshly cleaved prior to use, where it was sealed against a PTFE trough (which had been cleaned in nitric acid and washed copiously with ultra-pure water) to make a solid/liquid interface. The neutron beam was incident through the silicon crystal, through the layer of native oxide on the silicon wafer, through the glue and mica to the mica/water interface of interest. The mica was a natural mineral from Attwater and Sons. As described below, the mica was either used as freshly cleaved or after cleaving and UV/ozone treatment.

The Cs exchanged AOT was prepared from sodium AOT according to the method of Eastoe *et al.*24 and dried in a vacuum oven. Elemental analysis indicates greater than 99% ion exchange. Surface tension measurements were performed to confirm there was no evidence of a minimum, which would have suggested a surface-active impurity, as given in Figure S1 in the Supplementary Information. This measurement also confirms no inorganic salts remain in the sample.

The experiments were performed on the OFFSPEC instrument at the ISIS neutron facility, UK25 and the D17 Instrument at the Institut Laue Langevin, Grenoble, France26. Both instruments were used as time of flight reflectometers, where the wavelengths of the neutrons produced by the spallation process or a pulse produced by a chopper have their wavelength determined by the time of flight to the detector. The collimated incident beam was inclined at several angles () to the sample surface where the key parameter is the momentum transfer, Q, given by:

$$Q=\frac{4π sinθ}{λ}$$

With several incident angles, , a wide range of Q could be accessed. The high Q range is usually limited by the background scattering level.

The method used to analyse the data has been given previously9,13 and is based on the usual approach considering the reflection from every interface in the system and the coherent addition of the reflected amplitudes. However, because the mica and glue layers are thicker than the neutron coherence length, there is no coherent addition for waves reflected from interfaces that bound these thick layers (no interference), though their significant thickness means a correction is required for the attenuation of the neutron beam through them. In this work the correction is based on separate experimental measurements of the sample attenuation11 which varies with wavelength. The calculations were performed using the program I-CALC13. The data can be normalized using the scattering below the critical edge, which should be unity (here we use the lowest Q region where there is no significant attenuation).

Table 1 below gives the scattering length densities (SLD) of the different components of the system used to fit the reflection data. The calculation of the SLDs of the surfactant components is now briefly described.

A range of values for the bulk density of NaAOT is reported between 1.14 − 1.16 g cm−3 17,19,27,28. The molecular weight of NaAOT (444 g mol−1) and the density gives the molecular volume of 636 − 648 Å3. Assuming a density of 1.15 g/cm3, we obtain a molecular volume of the NaAOT as 641 Å3. The volume of the Na and Cs ions are a very small fraction of the volumes of these species and hence to a reasonable approximation the molecular volume of the CsAOT is also 641 Å3. We expect that the total molecular volume calculated in this way is reasonably well defined and thus the SLD of the whole CsAOT group is +0.677 x 10-6 Å-2.

We can also attribute volumes to the head and tails separately, but the apportionment between the head and the tail is a matter of opinion. Based on simple hydrocarbons, the molecular volumes of CH3, CH2 and CH are 56.2 Å3, 26.5 Å3 and zero respectively.29 The AOT hydrocarbon tails consist of 10 CH2, 4 CH3 and 2 CH groups giving a total volume of 490 Å3 and hence an SLD of -0.42 x 10-6 Å-2.

The head group can therefore be attributed a volume of (641 Å3 less 490 Å3) 151 Å3 yielding an SLD of 4.25 x 10-6 Å-2. Others have made similar but slightly different apportionments.27 Different fitting models were applied to the experimental data, with both a single layer of uniform SLD and a three layer model of heads and tail regions being used.

|  |  |  |  |
| --- | --- | --- | --- |
| Material | Formula | Density / Vol | SLD/10-6 Å-2 |
| Silicon | Si | 2.33 g/cm3 | 2.07 |
| Silicon oxide | SiO2 | 2.21 g/cm3 | 3.49 |
| Glue | C41H65NO15 | 1.16 g/cm3 | 1.08  |
| Muscovite Mica | [K](https://en.wikipedia.org/wiki/Potassium)[Al](https://en.wikipedia.org/wiki/Aluminum)2(Al[Si](https://en.wikipedia.org/wiki/Silicon)3[O](https://en.wikipedia.org/wiki/Oxygen)10)(O[H](https://en.wikipedia.org/wiki/Hydrogen))2 | 2.83 g/cm3 | 3.79 |
| Heavy Water | D2O | 30 Å3 | 6.35 |
| Water | H2O | 30 Å3 | -0.57 |
| Water contrasted matched to Silicon (CMWSi) | D2O/ H2O | 30 Å3 | 2.07 |
| CsAOT | C20H37CsO7S | 641 Å3 | 0.678 |
| CsAOT head | C4H3CsO7S | 151 Å3 | 4.25 |
| CsAOT tails | C16H34 | 490 Å3 | -0.42 |

Table 1. Scattering length densities used in this work

**Results**

Figure 2 presents the D17 neutron reflection data from the bare mica surface (‘MICA01’) in three contrasts of water- H2O, D2O and a mix of H2O and D2O with the same scattering length density as silicon (‘CMWSi’). The structural parameters required to simultaneously fit these data sets are given in Table 2 and are in good agreement with similar studies.16,17 Similar neutron reflection data and fitting for the bare mica samples studied on OFFSPEC data from ISIS are given in the Supplementary Information (Figure S2 and Table S1).

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**Figure 2.** Experimental reflection data from the bare mica substrate ‘MICA01’ in three water contrasts D2O (top), contrast matched to silicon, CMWSi (middle), and H2O (bottom). The data are offset for clarity. The fitted scattering length density is illustrated below, with axes breaks.

**Table 2**. Structural parameters used to fit the bare mica MICA01 data.

|  |  |  |  |
| --- | --- | --- | --- |
|  | Thickness  | Roughness / Å | SLD / x10-6 Å-2 |
| silicon substrate |  | 4 | 2.07 |
| silicon oxide | 19 Å | 4 | 3.49 |
| glue | 12 m | 11 | 1.08 |
| mica | 20 m | 3 | 3.79 |

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**Figure 3.** Experimental neutron reflection data from the MICA01 substrate in both D2O and D2O with 1 CMC CsAOT (top two data sets), and water contrast matched to Si with and without 1 CMC CsAOT (the lower two data sets). The data for each contrast are superimposed to clearly illustrate the significant change in reflection of adsorption and the contrasts are offset for clarity. The fitted scattering length density is illustrated below the reflectivity profiles.

Figure 3 presents neutron reflection data from the MICA01 substrate exposed to 1 CMC of CsAOT in two different contrasts. It is evident from this figure that there are significant changes in reflection and hence we conclude there is significant adsorption of CsAOT at 1 CMC. This adsorption is surprising given that both the mica and the AOT molecule will be significantly negatively charged at this pH. This contrasts with previous neutron reflectometry measurements, carried out in the same way, of AOT in the presence of the monovalent ion sodium, where no adsorption was observed.30

Table 3 gives the structural parameters used to fit the experimental data in Figure 3. In this table all contrasts of both the bare mica and adsorbed AOT are simultaneously fitted to the most simple one block AOT model, as discussed in more detail below.

 **Table 3**. CsAOT layer structural parameters for the layer formed on MICA01 and MICA02.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Data | Thickness / Å | Roughness / Å | SLD / x10-6 Å-2 | Hydration | Area/pair of molecules / Å 2 |
| D17 | 22 ± 2 | 4 | 0.678 ± 0.1 | 0.03 ± 0.02 | 60 ± 5 |
| OFFSPEC | 16 ± 2 | 2 | 0.678 ± 0.1 | 0.03 ± 0.02 | 82 ± 9 |

*Concentration dependence:* Similar data collected at the higher concentration of 2 CMC gave essentially the same reflectivity profile (not shown).

*Reversibility:* Neutron reflection data taken after washing the surface with copious amounts of water (not shown) indicate that the AOT layer is lost and the scattering returns to that of the bare mica. On re-exposure to the 1 CMC CsAOT the layer reforms essentially the same layer as the first exposure. This reversibility is in marked contrast to the cationic surfactant reported previously13.

*Substrate preparation:* There are several methods in the literature for preparing the mica surface from a simple freshly cleaved mica to other chemical treatments. In this work we considered a freshly cleaved substrate and the same substrate after it was dismantled, the crystal UV/ozone cleaned for a period of 20 minutes, and returned to the cell. The reflectivity profile of the subsequently adsorbed CsAOT layer was the same on the cleaned substrate as for the layer adsorbed to the freshly cleaved mica.

Similar reflection data collected on the OFFSPEC instrument at ISIS for another completely separate mica sample (prepared by UV/ozone) exposed to 1 CMC of CsAOT is given in the supplementary information (Figure S2). The data also show adsorption of a well-defined CsAOT layer that adsorbs reversibly.

*pH dependence:* The reflectivity profile of the mica surface exposed to 1 CMC CsAOT was recorded at pH 4, pH 7 and pH 9. The same reflectivity profile was observed in each of these cases, as illustrated in the supplementary information (S4). Hence we conclude that the adsorbed layer structure is independent of pH over this pH range. This is in good agreement with the structural charge of mica where isomorphic substitution leads to the negative surface charge and pH dependence is not expected, in contrast to silanol groups on silica where protonation and deprotonation lead to surface charge.

The structural parameters of the CsAOT layers on D17 and OFFSPEC are given in Table 3 below. In this model, the AOT is represented by a single layer with uniform scattering length density, as the most simple model consistent with the experimental data. The extended chain length of a monolayer of the AOT is reported to be ∼18 Å 16,17. The single block model for the D17 data indicates a layer somewhat thicker than this (22 Å). Hence, we conclude there is a bilayer of AOT. A bilayer is to be expected as the mica surface is highly charged and hydrophilic and so we might expect the AOT to adsorb ‘head down’. This would leave a surface covered by hydrophobic tails which is unfavourable. Hence a second layer of AOT adsorbs to make the external surface hydrophilic however the overall layer thickness is significantly less than the 36 Å expected for two AOT molecules end to end. The AOT molecules must therefore be significantly interdigitated and/or tilted at the surface. The scattering length density indicates that there is little solvent in the layer and hence the bilayer is essentially all CsAOT. The adsorbed layer structure is schematically illustrated in Figure 4 below.

More complex models such as a three-layer model, where the head and hydrocarbon tail regions are treated separately, have also been considered but when the SLD’s of the layers are fixed at the values calculated in Table 1 for the heads and tail layers (without mixing) no reasonable fit of the data can be achieved. This is true over the parameter space spanned by physically reasonable layer thickness, roughness, and hydration values and an example of such a calculation is shown in the supplementary information (Figure S3). We attribute this to the enhanced contrast that arises when the heads and tails are separated. When the SLD of the head layer region is allowed to decrease with some alkane penetration into this region, then the fits improve. We conclude that there is significant mixing of head and tail components in the head group region, either from interdigitation or undulation in the adsorbed layer.

The bilayer thickness calculated from the single block model has a thickness of 22 Å. The reported AOT chain length is 18 Å; hence there is significant interdigitation of the tails. The head group layer has been estimated as approximately 7.1 Å 31. We therefore conclude that some of the tails may overlap the opposite head group regions. An illustration is given below.

Interestingly the data collected on OFFSPEC indicate a rather thinner layer (16 Å), than observed on D17 (22 Å), with the bilayer thickness approximately the same as the extended chain length. We still expect the external surface to prefer to be covered in hydrophilic head groups. Hence we conclude that this bilayer is almost completely interdigitated and/or tilted. There is again rather little solvent in the layer.



**Figure 4**. Schematic illustration of the highly interdigitated AOT surfactant on the mica surface.

The difference in layer thickness between these two layers (measured on OFFSPEC and D17) is significant. As reported above, we have considered the surface preparation method which we find makes no difference to the adsorbed layer structure, so we conclude that the differences are not due to the preparation method. The adsorption is completely and rapidly reversible in both cases and so we do not consider that attaining equilibrium is an origin of the differences between the two samples.

However, the samples of mica are natural materials and so there may well be slight sample to sample variations. This may well include variations in charge density which may significantly affect the amount of adsorption, as discussed further below. It is perhaps worth noting that the measurement geometry is vertical for the D17 instrument, but horizontal for OFFSPEC though we do not expect this to alter the layer structure.

*Relevance of mica charge density:* The experimentally determined area per pair of AOT molecules in the adsorbed layer, or equivalently the area per molecule in the inner leaflet of the bilayer, is found to be approx. 60 - 82 Å2/molecule (for MICA01 and MICA02 respectively). The mica charge density is reported to be 0.33 C/m2 32 or 48 Å2 per charge group. This suggests that the AOT layer is reasonably well packed, tail to tail, but there may be some charged mica sites that are not compensated by the AOT groups (approximately 0.17 – 0.4 of the sites). We conclude that additional Cs+ ions compensate the remainder of the mica surface charge.

Similar estimates of the AOT tail size can be made. A fully close packed alkyl chain has an area of approximately 19 Å2 33. Hence the two alkyl chains should take up at least 38 Å2. These are branched alkyl chains so an even larger area, approximately double, might be expected. Hence 60 – 82 Å2 is not unreasonable, for the two molecules in the bilayer. This is also consistent with values found by others for AOT salts; Stocker *et al.* found an area of 86 ± 14 for NaAOT at the calcite/water interface20, Wang *et al.* found an area of 70 ± 5 for NaAOT at the water/silica interface14.

At present, we do not consider that many water molecules will be in the head group region and this is supported by the low hydration determined experimentally by the fit to our data, of order of one per head group. This is attributed to the low energies of hydration of the Cs+ and the RSO3- head groups, meaning they can more easily lose water molecules and prefer to bind directly without intervening water, forming an inner sphere complex. We expect similar behaviour for the Cs+ ion on the mica. The loss of water upon this kind of coordination is supported by the absence of solid crystalline hydrates of Cs+ and sulfate. Similarly, the hydration of Cs+ is reported to be much lower than the other group IA elements, particularly Li+ and Na+.34 Our results are also consistent with those of Li *et al.* who found that cesium dodecyl sulfate adsorbed to the (positively charged) sapphire/solution interface with essentially no hydration. 35

**Discussion**

In this work, we have presented evidence for the adsorption of an anionic surfactant on an anionic surface in the presence of the monovalent Cs+ cation, a somewhat unexpected result. This cannot arise from the usual explanation of divalent (or multivalent) ion ‘bridging’ where the divalent ions form a bridge between the two negatively charged species, a concept found in several related areas from DNA binding36–39 to oil recovery.40,41

Previous work indicted that the monovalent sodium salt of AOT did not show any adsorption at all on mica or silica.14,30 This is in contrast to the divalent calcium ion, which showed adsorption on both mica and silica.30 Hence one might previously have imagined that a divalent cation might be able to ‘bridge’ between these two anions (mica and the AOT) holding them together, whereas a monovalent ion cannot. The interesting behaviour of the monovalent cesium ion reported here shows that it is not simply the valency of the ion that is significant.

We consider that the charge density of these ions is part of the explanation and this also characterises several aspects of solution behaviour, such as the Hoffmeister series and the swelling or non-swelling nature of smectite clays. In outline, the interaction of these ions with water is strongly dependent on the charge density. If the ions are small and highly charged, water molecules are strongly bound and the ion is reluctant to bind to the mineral surface or the surfactant head group.

However, if the ion has a lower charge density (such as Cs+ compared to Na+) then the interaction strength with water is much reduced. Hence the loss of water is relatively easy and the bare ion can bind more effectively to the mineral surface and to the AOT anionic groups. In some senses, Cs+ is a rather ‘hydrophobic’ cation. As discussed previously the divalent Ca2+ ion, which is strongly hydrated, was also found to mediate adsorption of AOT to mica.30 The hydration effect might not fully explain which cations will cause bridging but may be a consideration when comparing cations of the same valency. In the case of montmorillonite, a less highly charged clay than mica, Ca2+ montmorillonite swells significantly less than Na+ montmorillonite42 although both clays swell. This suggests a stronger interaction between the clay and Ca2+ ion tan with Na+, which is consistent with our results. We plan additional studies to identify where the ‘break point’ (adsorption/non-adsorption) occurs for the Group 1 elements. In addition, the binding of the cations also will depend upon the hydration of the clay surface charge with the expectation that isomorphic substitution in the tetrahedral layer will be more hydrated than substitution in the octahedral layers. Finally, the hydration of the organic anion will also be expected to have a key role in completing the binding.

In addition, other recent work has been able to report Cs+ adsorption to the mica surface using X-ray diffraction43, with some evidence of a chloride counter ion being co-adsorbed at the surface, indicating that there is strong Cs+ adsorption on mica.

*Other related studies of Cs*+ *ions and Mica:*

There are a variety of studies of Cs+ binding to mineral surfaces and related systems due to the significant interest in the capture of radioactive Cs+ ions. There are some reports in the literature of a particular ion behaviour on mica arising from the fit of the ions with the mica surface structure.44 Cs+ ions (with K+ and Rb+) exchange on mica rapidly, unlike Li+ and Na+ where less than quantitative adsorption was observed. The affinity of the alkali metal ions to the mica decreased in the order K+, Rb+, Cs+ > Na+ >Li+.45 Similar behaviour is reported by DFT studies, which also support the relatively strong interaction of the Cs+ ion to the mica surface relative to the sodium ion, with the ion-selectivity order of the mica interlayer site of K+ > Cs+ > Na+ .46 There are reports that the mica has a high selectivity for divalent ions but also that high charge density micas can essentially fix K+, Rb+, Cs+ and ammonium ions irreversibly such that re-exchange is difficult.47

There have been recent molecular dynamics simulation studies of ion binding on related clay surfaces (smectites/montmorillonite).48 The ions bind in the sequence of binding strength: K+ > Na+ > Ca2+ > Cs+ > Ba2+. This work discusses the favoured position of the ions on the clay basal surfaces and the inner or outer sphere nature of the coordination. Mica is subtly different to montmorillonite because the isomorphic substitution is in the tetrahedral layers (where Al3+ is substituting for Si4+), while in montmorillonite the substitution is mainly from the substitution of Mg2+ for Al3+ in the octahedral layer. In the tetrahedral layer the charge is close to the surface, which is expected to lead to strong hydration and ion binding relative to charge in the octahedral layer, which is somewhat further from the clay surface.

We have also investigated this divalent/monovalent adsorption on silica using neutron reflection and attenuated total internal reflection IR spectroscopy.14 This system shows more complex behaviour than the mica. There is a marked change in adsorption between the calcium and sodium ions where the divalent ion adsorbs AOT and the sodium salt does not. However, the adsorption with the calcium salt also seems to be pH dependent with significantly more adsorption at higher pH. We attribute this to the variation in surface charge density with pH. However, we do not expect such a pronounced pH dependence with mica as there is a structural surface charge that should not be pH dependent. This leads to a difference in behaviour between mica and silica.11

**Conclusions**

In this work we have made the surprising observation that negative AOT binds to the negative mica surface in the presence of Cs+ monovalent ions. Clearly the conventional explanation of divalent cation bridging cannot be invoked. We have proposed that this bridging effect is rather due to the different hydrations of cations.

**Associated Content**

Supporting Information. Interfacial tension measurements, neutron reflection data from CsAOT on mica collected at OFFSPEC, three-layer reflectivity model fitting, tables of parameters for fitted models, neutron reflectivity profiles for different pH values.

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