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Neutron Reflection Study of the Adsorption of the Phosphate Surfactant NaDEHP onto Alumina from Water

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Ⓢ Supporting Information

ABSTRACT: The adsorption of a phosphorus analogue of the surfactant AOT, sodium bis(2-ethylhexyl) phosphate (NaDEHP), at the water/alumina interface is described. The material is found to adsorb as an essentially water-free bilayer from neutron reflection measurements. This is similar to the behavior of AOT under comparable conditions, although AOT forms a thicker, more hydrated layer. The NaDEHP shows rather little variation with added salt, but a small thickening of the layer on increasing the pH, in contrast to the behavior of AOT.
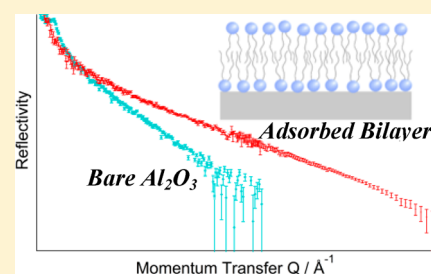
■ INTRODUCTION

Aluminum oxide (alumina) is an important material both in its own right as an engineering solid and as a model for other important materials, such as the aluminosilicate clay surfaces. Because of its amphoteric nature, the alumina surface can be the more surface active toward adsorption than the silicate under some pH conditions. Similarly, an aluminum metal surface is rapidly covered with an oxide layer under most conditions due to its high reactivity. Therefore, in most engineering situations it is the alumina surface that forms the interfacial surface, rather than the metal itself. Alumina can provide a good approximation to this native oxide surface and hence a model for the adsorption of lubrication additives or corrosion inhibitors to this metal surface.

In general, surfactants have widespread use as dispersants, lubricants, detergents, wetting agents, or emulsifiers due to their inherent surface activity. A number of surfactants have been used to modify the properties of aluminum/alumina surfaces in numerous industrial applications. The studies of these surfaces on a molecular length scale are also of interest academically.[1−3] In this work we consider the interactions of the alumina surface with a particular phosphate surfactant (NaDEHP), the phosphate equivalent of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) (Figure 1).

AOT is a reasonably well-studied surfactant in surface studies.[4,5] As Figure 1 illustrates, it is a branched dichain molecule—a feature that can be important in enhancing oil solubility of the molecule[4]—with a sulfate−ester headgroup. The solution chemistry of AOT has been reported based on surface tension and SANS measurements, with the aqueous critical micelle concentration (CMC) reported to be 2.5 mM at
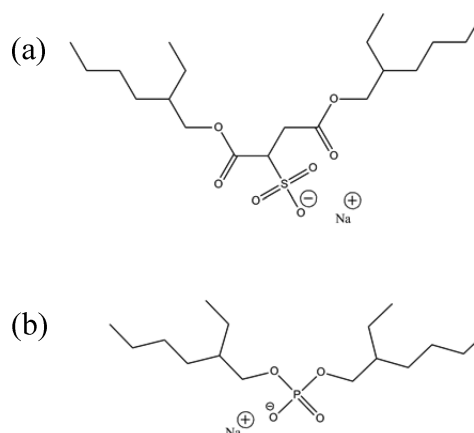

Figure 1. Molecular structure of (a) AOT for comparison and (b) NaDEHP, of interest in this work.

25 °C and pH 7. At higher concentrations than the CMC a lamella phase is reported to form in water.[5−8]

Hellsing et al.[9] have observed the adsorption of AOT from water onto the alumina (sapphire) surface by neutron reflectometry. This reference reports that AOT forms a bilayer at this interface, which becomes slightly thinner under addition of salt or on changes in pH. At higher concentrations a stack of bilayers (lamella type) are reported.[10] These changes in adsorption structure on the alumina surface reflect the bulk

phase transformations. The adsorption of AOT has also been observed from aprotic solvents and onto a range of other surfaces, including silica,[5,11] air,[7,12] and graphite.[13] In agreement with the alumina work, these studies with hydrophilic fluids generally show bilayers at the hydrophilic surface with multilayers at higher concentrations and monolayers at hydrophobic surfaces.

In this work our focus is on the role of the hydrophilic headgroup in the binding of the surfactant to the solid/liquid interface. The headgroup is expected to affect the solubility of the surfactant in the water as well as the binding constant between the surfactant and the surface groups of the solid. It has been reported[2] that fatty acids bind to alumina through a ligand-exchange mechanism, which is strongly dependent on this binding constant. For alumina these surface groups are generally considered to be surface hydroxyls such as $\rangle Al-OH$, $\rangle Al-O^-$, and $\rangle Al-(OH)_2^-$, where "$\rangle Al$" represents a surface bound aluminum. In this work the adsorption sodium bis(2-ethylhexyl) phosphate (NaDEHP) is determined and compared to the related surfactant AOT. These surfactants have identical tail groups and differ only in the headgroup: sulfosuccinate vs phosphate (Figure 1), enabling a comparison of these binding groups on adsorption. The phosphate group is important for a number of reasons, particularly corrosion inhibition for alumina (and aluminum). It has been shown that the phosphate group can prevent the corrosion of alumina in amine solution, whereas the sulfate equivalent only slowed the corrosion process when monochain surfactants were used.[14]

It has also been reported that the surface species on alumina are dependent on the crystal plane, giving rise to different zeta potentials for different crystal faces.[15,16] Hence, a powder consisting of a range of different exposed surfaces will have a number of different simultaneous zeta potentials, which average to a single measured value. A comparison of the adsorption of NaDEHP onto powder and single crystal samples is included in this work. The single crystal work was carried out on the (0001) plane of alumina, which shows the closest IEP to the powdered sample.[15,16]

The nonaqueous solution behavior of NaDEHP (and its conjugate acid, di-2-ethylhexylphosphoric acid (HDEHP)) has been extensively reported due to use in heavy metal extraction.[17−22] However, rather little work has been carried out into the activity of NaDEHP in water. There has been some comparison of NaDEHP behavior to AOT in the presence of polymers,[23−25] or other surfactants,[26,27] which report the CMC in water in the range 15.6−22 mM. Also, there is an indication of pronounced decrease in the aqueous solubility of NaDEHP around the pK_a (3.24[22] or 3.95[28]) due to the immiscibility of HDEHP with water at room temperature.

In this work we present an initial study of the bulk solution behavior of the NaDEHP surfactant in water, before considering the adsorption behavior of NaDEHP onto powdered alumina and NaDEHP adsorbed on the (0001) face of alumina single crystals using neutron reflection. To the best of our knowledge, this is the first study into the adsorption of this surfactant at the solid−liquid interface using these approaches.

■ EXPERIMENTAL SECTION

Bis(2-ethylhexyl) phosphate sodium salt was synthesized from the acid equivalent by reaction with NaH in THF using the method of Harvey[29] by Chris Sporikou, Department of Chemistry, Cambridge. The purity was checked by elemental composition analysis (55.85% C,

10.02% H, and 8.84% P). H and P NMR showed a single phosphorus environment and appropriate H peaks. The synthesized surfactant used in this work was characterized in bulk solution by pendant drop tensiometry.

The phosphate acid starting material and all other chemicals were purchased from Sigma-Aldrich and used as supplied. All water was prepared from a Millipore system with a conductivity of 18.2 MΩ·cm. The D_2O was also obtained from Sigma-Aldrich, with a quoted purity of 99.9% D. The pH was altered using NaOH/NaOD and HCl/DCl as appropriate and measured after addition of these agents by narrow range pH paper. The alumina single crystals (sapphire (0001)) for the neutron studies were purchased from Pi-Kem, UK and were polished by SurfaceNet GmbH, Germany to ≤5 Å roughness (RMS) (2 in. diameter × 5 mm). These were cleaned with a mild-piranha solution (5:4:1 H_2O:H_2SO_4:H_2O_2) for 15 min at approximately 80 °C. To minimize Si contamination,[30] all labware used in the preparation of solutions was made of PTFE and cleaned with concentrated nitric acid, followed by copious rinsing in ultrapure water before use. The α-alumina powder was purchased from Absco Materials: CR30, purity >99.99%, surface area 20.91 ± 0.15 m^2/g determined by BET analysis at the University of Cambridge, using a TriStar micromeritrics system. This was smaller than that quoted by the supplier of 26 m^2/g.

Neutron Reflectometry. Neutron reflectometry (NR) is a powerful technique for probing buried interfaces[5,11,31,32] and has been successfully used at the alumina/water interface for a range of additives, such as phospholipids,[33] saliva,[34] and surfactants.[9,10,35,36] In this study, the adsorption behavior of NaDEHP has been characterized using this NR technique.

In brief, the intensity of a beam of neutrons reflected from an interface is a sensitive probe of the structure and composition perpendicular to that interface.[37−40] Importantly here, the technique can be used to measure the adsorption of an organic layer at the buried solid−liquid interface. The theory of this technique is given in detail by Penfold[38] and essentially indicates that the reflected signal is determined by the neutron refractive index profile at the interface, similar to optics.

The neutron refractive index is dependent on the scattering length density (SLD) of the material, which varies apparently randomly across the periodic table, and even with isotope. In particular, there is a large difference in scattering length with ^{1}H and ^{2}H (D) so that deuterated materials provide a large difference in scattering behavior (contrast) to hydrogenated materials. This feature can be used to highlight particular species of interest by simplifying the scattering from complex multicomponent mixtures, particularly using a contrast matched sample (H/D ratios controlled so that certain layers (or the bulk substrate) experience the same SLD as the liquid phase and thus do not lead to any neutron reflection due to the absence of contrast).

In NR experiments from a solid/liquid interface, a collimated beam of neutrons is passed through the solid and reflected off the highly polished interface. Interference of the scattered beam by surface layers produces features in the reflectivity profile, which can be used to characterize these layers. The data are obtained as the reflected intensity vs the momentum transfer vector (q, which combines the scattering/reflection angle and neutron wavelength).

In this work the experimental data were fitted using the program RasCAL (version Beta 1, A. Hughes, ISIS Neutron Source, Rutherford Appleton Laboratory), where each layer at the interface is para-metrized by a thickness, a roughness, and the SLD. The SLDs of the substrate and solution phase were given by the bulk material compositions (see Table 1). The scattering length density of the adsorbate layer is considered as a mixture of the surfactant and water (hydration) constrained to conserve volume. For NaDEHP, a density of 1.039 g cm^{-3} was used as measured by Lovera[41] using the hydrostatic method. The fitted SLD can then be used to determine the adsorbate layer composition.

The neutron reflectometry experiments were carried out at the reactor source: Institute Laue-Langevin (ILL), France, on D17[42] and at the spallation source: ISIS, UK, on the SURF[43] instrument. Both instruments use time-of-flight (TOF) to separate the different wavelengths. On D17 the sample is held vertically (the normal to

Table 1. Relevant Neutron Scattering Length Densities Used in This Work

species	SLD $(\times 10^{-6})/Å^{-2}$
Al_2O_3	5.75
D_2O (100%)	6.35
H_2O	−0.57
NaDEHP	0.20

the solid/liquid interface is horizontal), and all measurements here were taken at room temperature and pressure. To provide the full range of q including the critical edge to background, data were taken at two reflection angles of 0.6° and 3.2°, with a wavelength range of 2−27 Å. The solid/liquid interface was made by clamping a PTFE trough against the alumina crystal (see Supporting Information).

On the SURF reflectometer the sample is held horizontally (surface normal is approximately vertical). In order to obtain the widest q-range possible on the SURF instrument four reflection angles of 0.15°, 0.25°, 0.65°, and 1.2° were required due to the smaller wavelength range. All other experimental details are the same as for D17.

■ RESULTS AND DISCUSSION

Initial Characterization. Pendant drop surface tension measurements were used to determine the critical micelle concentration (CMC) of the NaDEHP sample used in this work. This work used a Kruss drop shape tensiometer at the BP Institute, University of Cambridge, with a 1.830 mm syringe. The experimentally determined drop shape was analyzed by the KRUSS software. Because the solution concentrations are very small and vary over a small range, a constant solution density of pure water was used in the calculations. Given that the break in the surface tension dependence was of most importance any small variation in density would not significantly change the experimentally measured CMC.

Figure 2 shows a representative data set of the variation of the surface tension with concentration of surfactant. It was
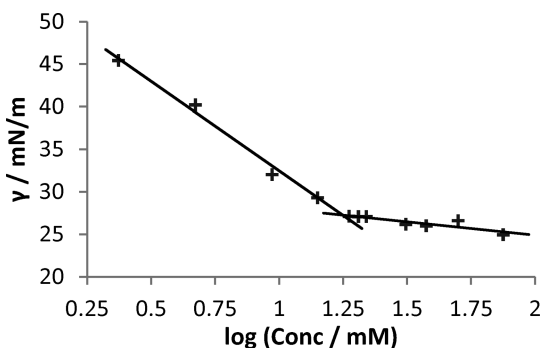

Figure 2. Concentration dependence of surface tension of NaDEHP in H_2O at pH 7 measured by the pendant drop method. The change in gradient represents the experimentally determine CMC.

found that at pH 7 and pH 9 as well as in low (3 mM) NaCl solution the CMC is 18 ± 2 mM. On addition of further NaCl (to a concentration of 30 mM), the CMC decreases to 11 ± 2 mM. This salt dependence is typical of ionic surfactants where salt screening of the charged surfactant head groups favors micellization and hence a fall in the CMC.

At pH 5, which is closer to the pK_a of NaDEHP (3.24−3.95), the CMC decreases dramatically to 1.6 mM. This behavior can be rationalized by a reduction of inter headgroup repulsion and hence a favoring of aggregation, with a resultant reduction of the CMC. The corresponding protonated phosphate acid,

HDEHP, is insoluble in aqueous solution. Hence, care must be taken to ensure the pH does not fall sufficiently to avoid phase separation.

Neutron Reflectometry. Figure 3a presents the experimental neutron reflection data from a clean alumina surface in pure water, fully characterized in three different water contrasts (H_2O, D_2O, and a 50% mix "HDO"). The solid lines indicate the fit to the data expected for clean alumina surface with the expected bulk water phase scattering length densities and with a roughness of 3 Å. The close fits to experiment in Figure 3a demonstrate that the crystals are clean, flat, and suitable for subsequent adsorption. Each crystal used in this study was characterized in this way.

Increasing concentrations of the surfactant NaDEHP were introduced into the sample cell. Figure 3b shows the reflectivity curves with NaDEHP concentrations of 2, 10, 20, and 40 mM, corresponding to approximately 0.1, 0.5, 1, and 2 times the CMC. All of these curves were fitted using the parameters for the bare alumina and water given above for the clean substrate, along with a single block model for the surfactant layer, with the structural parameters given in Table 2. Uncertainty in the model parameters was determined by a bootstrap analysis within the RasCAL program, with systematic errors estimated from repeat measurements. Equilibrium scattering was reached rapidly in each case (no further change was observed after 1 h). The reflectivity measurement of each surfactant concentration was carried out in D_2O to maximize the contrast between the surfactant layer and the relatively high SLD of the alumina/water, highlighting the contribution of the surfactant layer. The changes seen on addition of surfactant are large, clearly indicating the presence of an adsorbed layer. The 20 mM measurement was repeated in H_2O and HDO to provide a full characterization of the complete bilayer, allowing greater constraint and accuracy in the fitting model (see Supporting Information).

The fitted layer thickness is found to be 13.5 ± 0.4 Å at all the concentrations measured above 2 mM. Using the molecular conformational information from Luan et al.[24] and assuming an all-trans conformation, the projected length of the surfactant chain from P atom to the end is 7.76 Å. Hence, an adsorbed mono- or bilayer is expected to be approximately 8 or 16 Å thick, respectively. On the basis of the experimentally determined layer thickness (13.5 Å), we conclude that the adsorbed material is not a monolayer. A bilayer is much closer to the experimental value, with either a tilted (ordered or random) or an interdigitated bilayer believed to have formed here. A bilayer is also expected on hydrophilic/hydrophobic grounds as the alumina surface is hydrophilic. An adsorbed monolayer would thus have an exposed hydrophobic tail/water interaction, which would be unfavorable. On the other hand, an adsorbed bilayer can have hydrophilic regions against both alumina and water—a much more favorable arrangement.

The SLD of the surfactant layer can be used to determine the surface excess and the effective area per molecule. Figure 4 shows the adsorption isotherm determined from this data, which shows a rise in adsorbed amount with increasing concentration. The adsorbed amount quickly reaches a plateau by a concentration of 10 mM (well below the CMC). The plateau in adsorption is at 0.0041 mmol m^{-2} (1.4 mg m^{-2}), corresponding to an area of 82 Å^2/dimer in the bilayer (assuming complete dimerization). This is in reasonable agreement with an area of 90 Å^2/ion for the ionic orthophosphate ion on α-alumina.[44] The similarity between
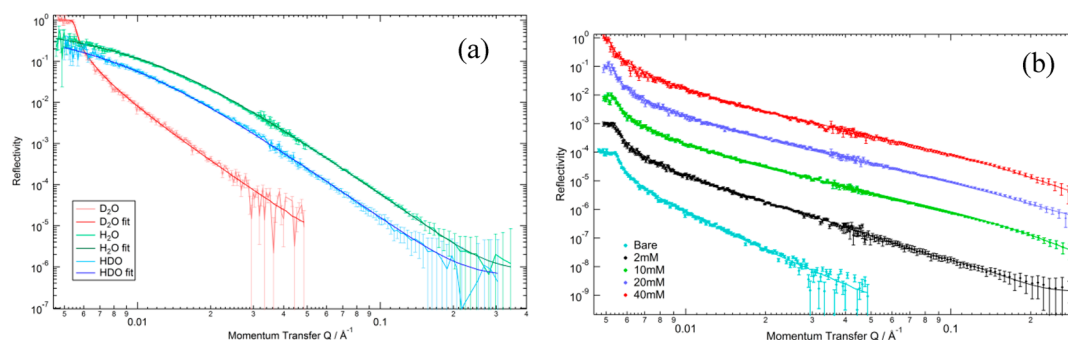
Figure 3. (a) Neutron reflectivity curves of a clean alumina crystal in D_2O (red), H_2O (green), and HDO (blue), showing experimental data alongside model fits. (b) Neutron reflectivity curves of alumina in D_2O with increasing NaDEHP concentration: bare (blue), 2 mM (black, two block model), 10 mM (green), 20 mM (dark blue), and 40 mM (red). The curves in (b) have been offset by factors of 10 in the y-direction for clarity. Solid lines show model fits.

Table 2. Summary of Model Fits of Neutron Reflection Data of NaDEHP Adsorption onto Alumina[a]

NaDEHP (mM)	layer thickness (Å)	layer roughness (Å)	surface excess (mg m^{-2})
10	13.6 ± 0.4	3.6 ± 0.7	1.40 ± 0.05
20	13.2 ± 0.3	0.5 ± 0.3	1.37 ± 0.04
40	13.5 ± 0.4	0.5 ± 0.4	1.40 ± 0.05

[a]2 mM data are not included due to several possible fits (see text and Supporting Information).

the adsorbed surfactant and orthophosphate ion is interesting given that one has the alkyl chains attached and the other is a bare ion. However, if the two species bind on particular surface sites rather than simply close pack, then the similarity is not unreasonable.

A series of points are shown in Figure 4 for the 2 mM NaDEHP surfactant concentration as a variety of structural models were considered. Unlike the other higher concentrations, a single block model for the surfactant was insufficient to provide a good fit to the experimental data. To successfully fit these data, a two block model was required, consisting of an 18 Å (approximately) 50% hydrated layer and a thicker (40 Å) very hydrated (89%) layer on top. These two blocks when combined correspond to the same surface excess as the higher concentrations of the isotherm, within experimental error. Splitting the surfactant layer into further blocks, such as treating head and tail portions separately, did not improve the fit. Further structural parametrizations were also considered for

this lowest concentration layer with more details provided within the Supporting Information. The best fit was found using a thin single uniform layer at the surface combined with an exponential decay model for the surfactant concentration away into the bulk water.

Therefore, several parametrizations provide a good agreement with the experimental data and a unique structural solution cannot be given for this lowest concentration layer, with the different models representing different adsorbed amounts, as illustrated in Figure 4. However, the three higher concentration data sets are all in reasonable agreement and give rise to a final adsorbed plateau amount of 4.1 μmol/m^2 (1.4 mg m^{-2}), which is of most significance here. The solid lines show Langmuir-type model fits to the data, with full details in the Supporting Information.

Influence of pH and Salt. Data were also collected at pH values of 5 and 9. At pH 9, the CMC is essentially the same as pH 7, and a concentration of 10 mM NaDEHP was used. The surface excess was found to be 1.56 mg m^{-2}, corresponding to a layer approximately 15.2 Å thick. The excess is slightly higher than that found at pH 7 due to the thicker layer (approximately 15% increase), but no significant change in hydration was found, suggesting a reduction in interdigitation or a more "upright" orientation on the surface.

At pH 5, a large amount of surfactant NaDEHP is found at the surface, even at very low solution concentrations (1.6 mM). Significant off-specular scattering was observed, indicative of aggregation and possible phase separation. Therefore, the
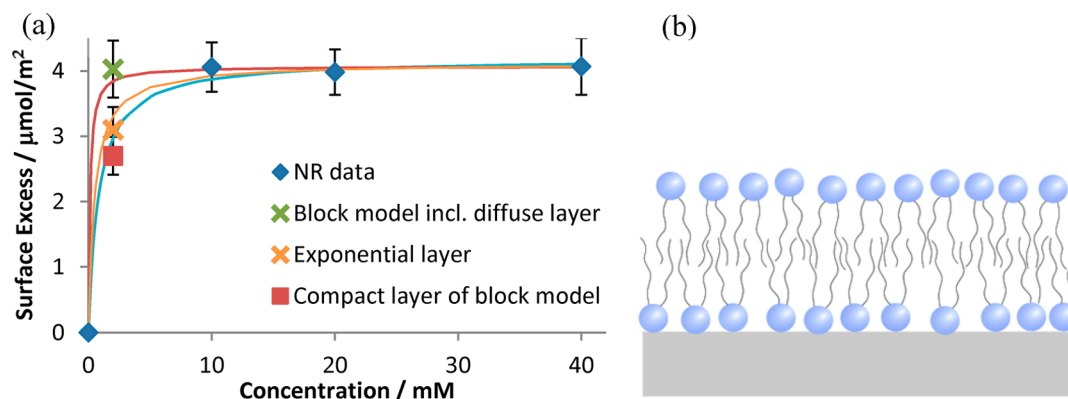

Figure 4. Adsorption isotherm of NaDEHP onto alumina in D_2O determined from neutron reflectivity data and schematic of the possible interdigitated bilayer profile (side chains have been left off for clarity but lead to a more homogeneous density).

reflectivity data cannot be modeled with confidence. There are several origins for this behavior: the CMC undergoes a large change due to the proximity in pH to the pK_a, alongside a large change in solubility due to formation of the insoluble, protonated form of NaDEHP. Hence, the behavior at this pH is interpreted as surfactant sorption and related to the onset of bulk phase separation.

Preliminary investigations into the effect of salt on adsorption were made by measuring the reflectivity with 0, 3, and 30 mM NaCl, at a fixed surfactant concentration of 10 mM and pH 7. This initial data suggest that adding up to 30 mM NaCl does not affect the amount of NaDEHP adsorbed within the plateau region of the isotherm. Higher salt content (e.g., 300 mM) leads to a change in bulk surfactant phase and is not studied here. However, it is important to note that the initial characterization of the substrate used here suggested an amorphous "gel" layer of alumina may be present on the surface. It is believed that this originated from residual H$_2$O left on the surface before UV/ozone cleaning. A similar layer has previously been observed on quartz crystals.[45] When this layer was taken into account in the fitting, the adsorbed NaDEHP bilayer was found to be essentially the same as on the other alumina substrate presented here. Thus, we conclude that adding up to 30 mM NaCl does not significantly change the structure of the NaDEHP bilayer. Further discussion of this behavior is given in the Supporting Information.

Comparison of NaDEHP and AOT. The NaDEHP binding is similar to the sulfosuccinate headgroup analogue, AOT, which also forms a bilayer on alumina at pH 7. In the absence of salt, the AOT (33.0 Å thick) bilayer is thicker than the NaDEHP layer (13.5 Å), and the surface excess of NaDEHP (1.4 mg m^{-2}) is approximately half the value for AOT (2.9 mg m^{-2}). In this case, the area per AOT molecule is calculated[9] at 57 Å^2, compared to 82 Å^2/pair for NaDEHP. A comparison is shown in Table 3. These differences are partially due to the

Table 3. Summary of Neutron Reflection Fits at the CMC Concentration for NaDEHP and AOT (NaDEHP Data from This Work and AOT from Hellsing[9])

	thickness (Å)	roughness (Å)	no. waters per head	surface excess (mg/m^2)	area per pair of molecules (Å^2)
NaDEHP	13.2 ± 0.3	0.5 ± 0.3	1[b]	1.4	82
AOT	33 ± 2[a]		12	2.9	57

[a]Value for AOT thickness was produced by fitting the head and tail portions separately. [b]Upper bound for NaDEHP is 4 waters per head, but the fit is accompanied by an equivalent increase in thickness to 16.2 Å (see Supporting Information).

"ester spacer" region in the AOT which is absent in NaDEHP. This succinate linkage creates a longer headgroup and hence a thicker layer. In addition, the linkage provides greater orientational freedom of the tails, allowing a smaller angle between the two tails, and a more "upright", thicker layer on the surface, with a correspondingly lower area per molecule.

From the surface excess and thickness of each surfactant from the NR model fit the surface density of each can be calculated. These are found to be 1.04 and 0.879 g/cm^3 for NaDEHP and AOT, respectively, from the reflection experiments here and of Hellsing.[9] The bulk solid-state densities for these surfactants are 1.039[41] and 1.16[9] g/cm^3, respectively. The phosphate−surfactant layer has a very similar density to the

bulk solid, attributed to virtually no water present in the layer. In contrast, the AOT has a somewhat lower surface density than the bulk material, suggesting more hydration for the sulfosuccinate equivalent (as seen in the models for the NR fits).

Figure 5 shows a comparison of the NaDEHP and AOT adsorption isotherms from NR, with concentration plotted as a
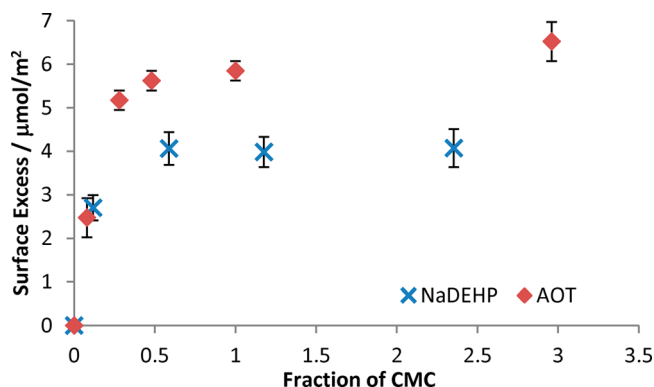

Figure 5. Adsorption isotherms at pH 7 from neutron reflectivity data of NaDEHP (blue; this study) and AOT (red; adapted from Hellsing[9]). Concentration is plotted relative to the CMC of each surfactant.

fraction of each CMC. As mentioned, AOT has a higher plateau surface excess, but both surfactants are similar in showing complete bilayer coverage below the CMC. This suggests that any solubility (aggregation) driving affects to adsorption are similar for the two surfactants.

The affinity of the surface Al groups to bind with the surfactant head groups is important in determining the surface binding. The relative ligand exchange binding constants (pK_L) of PO$_4^{3-}$ and SO$_4^{2-}$ with the AlOH surface groups are −13.57 and 0.48, respectively.[46] This implies that phosphate anions can readily ligand-exchange and bind on the alumina surface, but the sulfate anion may require an alternative/additional driving force. In fact, phosphates have previously been reported to ligand exchange on alumina,[47] with sulfonates not.[48]

The ligand-exchange model[2,49] involves the exchange of an OH$^-$ anion from the Al atom coordination shell, with a ligand anion (DEHP$^-$) to form a stronger chemical bond than occurs even in inner-sphere complexation.[50] Therefore, on varying the pH the ligand will not respond in the same way as a species held purely by electrostatics. Ligand exchange is often particularly dependent on the pH around the ligand pK_a, where the ligand is deprotonated. However, any pH dependence here is obscured by the insolubility of HDEHP. At higher pH there is a competition between the phosphate surfactant and OH$^-$ for the surface. The lack of a significant change here may suggest that the binding of the phosphate is stronger than hydroxide over the pH range studied. We do not want to propose a definitive binding mechanism, but ligand exchange appears to provide one reasonable explanation for the observed results.

Based on the Hofmeister series[51] for anions and relative polarizability, phosphate and sulfate may be expected to show relatively similar adsorption. However, within this series, the sulfate group shows a slightly more hydrophilic interaction and may be preferentially adsorbed over the phosphate. This may

help to explain the greater surface excess and hydration of the AOT layer in comparison to NaDEHP.

Hellsing[9] found that the AOT bilayer becomes thinner on addition of salt or changes in pH, which was not observed here for NaDEHP. Previous work[24] has shown a similar lesser effect of NaCl on the surface tension of NaDEHP compared to AOT. This difference may be due to the variation in hydration of the two bilayers: AOT is more hydrated, with space to contract on increased salt screening, whereas NaDEHP is highly packed with little space to contract further.

In addition to the NR studies, the depletion isotherm of NaDEHP onto powdered alumina was studied. The concentration of the surfactant was determined through the P composition using both chemical elemental analysis (colorimetric molybdate method by Alan Dickerson in the Department of Chemistry, University of Cambridge) and ICP-AES (Varian Inc. Liberty AX Sequential, Department of Materials, University of Cambridge). In each case a series of known NaDEHP solutions were used as a calibration.

Figure 6 shows this isotherm data alongside the NR single crystal data. The powdered sample surface excess is found to be
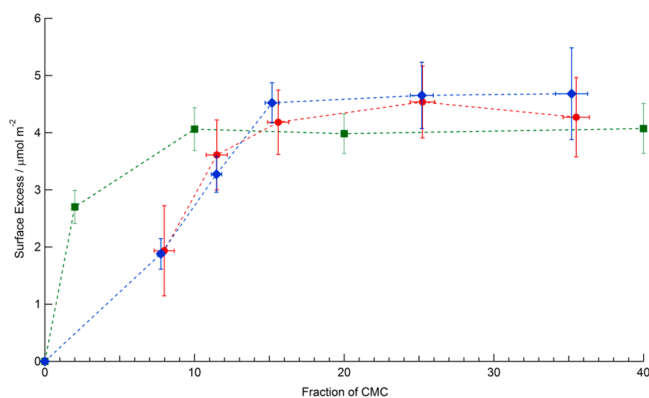

Figure 6. Depletion powder isotherm results by chemical elemental analysis of the P concentration (blue diamonds) and ICP-AES analysis (red circles), with a comparison to the single crystal NR data (green squares). The dashed lines are simply a guide to the eye.

approximately 4.5 μmol m^{-2} by both depletion methods: slightly higher than that observed for the single crystal NR studies. There also appears to be a slower rise to the bilayer composition within the depletion studies. As outlined above, the balance of surface groups present on alumina powder compared to the (0001) crystal face is different, which may help to explain this variation. Several of the other alumina faces (which will be present in the powder) have a greater density of "OH" groups than the (0001) face,[15] which could lead to a more "upright" orientation of NaDEHP within the bilayer. In addition, at pH 7 the powder is positively charged, whereas the (0001) is approximately neutral.[52] Lim[3] has also reported differences in the adsorption mechanism of stearic acid onto powder vs single crystal. The ICP detected a small amount of dissolved aluminum in solution (approximately 3 mM). This amount represents approximately 0.2% of the solid and therefore should not significantly reduce the specific surface area.

CONCLUSION

The adsorption of NaDEHP on alumina from water has been investigated using solution depletion isotherms and neutron

reflection. We find that the surfactant is adsorbed as a bilayer, in a similar fashion to the sulfosuccinate analogue, AOT, although the bilayer here is somewhat thinner and denser. These differences are partially explained by the succinate linkage in AOT, which is absent in NaDEHP, and creates a larger head group. In addition, the sulfosuccinate group has a larger hydration shell and thus can hold more water within the bilayer than the phosphate, in line with the Hofmeister series. This means that changing the pH or adding electrolyte has differing effects on these two surfactant bilayers. NaDEHP shows no significant change on addition of NaCl since there is a lack of water within the layer to enable charge-screening effects.

ASSOCIATED CONTENT

Supporting Information

Information on experimental setup, preplateau adsorption, the Langmuir-type model, additional neutron reflection contrasts, alternative model fits, and the pH/salt behavior. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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