PROGRESS REPORT FOR ALNGRA09147

<table>
<thead>
<tr>
<th>PROJECT TITLE</th>
<th>Structure of protic ionic liquids at the air interface</th>
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</thead>
<tbody>
<tr>
<td>INVESTIGATOR(S)</td>
<td>Institution and Department</td>
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<td>Chief Investigator Dr Rob Atkin</td>
<td>Chemistry, The University of Newcastle</td>
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<tr>
<td>Other Investigators</td>
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<td>Students Mrs Deborah Wakeham</td>
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<td>ANSTO Investigators Andrew Nelson</td>
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<td>Specialist Committee N</td>
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</table>

**SCIENTIFIC OBJECTIVES**

The aim of this work is to use x-ray reflectivity to elucidate the structure at the air - liquid interface of propylammonium nitrate (PAN), ethanolammonium nitrate (EtAN), ethylammonium formate (EAF), propylammonium formate (PAF), ethanolammonium formate (EtAF), and dimethylethylammonium formate (DMEAF). These experiments will allow the effect of cation and anion molecular structure on interfacial arrangement to be determined, and will extend on our previous work investigating the ethylammonium nitrate (EAN) - air interface.

**PROGRESS REPORT and RESEARCH OUTCOMES**

**DATA**

X-ray reflectivity was used to elucidate the structure at the air-liquid interface of propylammonium nitrate (PAN), ethanolammonium nitrate (EtAN), ethylammonium formate (EAF), propylammonium formate (PAF), ethanolammonium formate (EtAF), and dimethylethylammonium formate (DMEAF). All experiments were performed at room temperature under a nitrogen atmosphere to minimise water contamination.

The x-ray reflectivity profiles of the air-liquid interface for all the ionic liquids investigated are presented in Figure 1. The reflectivity profiles show a decrease in reflected intensity with increasing $Q$ for all ionic liquids, and which differ from that predicted for a flat surface (Fresnel interface). This indicates diffuse scattering which can be the result of interfacial surface roughness (capillary waves) or interfacial layering.

**Figure 1:** X-ray reflectivity profile for the liquid-air interface at room temperature for EAF, PAF, DMEAF, EtAF, PAN, and EtAN.
To determine if surface roughness causes deviation of the experimental data from that predicted for a Fresnel interface, roughness is applied to the Fresnel reflectivity using

\[ R = R_F \exp^{-2q^2\sigma^2} \]

where \( R \) is the reflected intensity, \( R_F \) is the Fresnel reflectivity, \( q \) is the wave vector transfer normal to the interface, and \( \sigma \) is the roughness contribution. The PAN–air interface Fresnel reflectivity curve, with and without roughness is plotted in Figure 2 along with the experimentally obtained PAN-air interface reflectivity profile. The addition of roughness to the reflectivity profile improves the fit between theoretical and experimental data, however there are still two regions in which the data deviates: \( q = 0.1 \) to 0.25 Å\(^{-1}\) and 0.25 to 0.35 Å\(^{-1}\). This suggests that surface roughness alone is not adequate to account for the differences in the reflectivity curves. Therefore, interfacial layering is likely. This was also observed for the other ionic liquids.

![Figure 2: Fresnel reflectivity from the PAN-air interface with and without roughness, and the experimentally obtained PAN-air interface reflectivity.](image)

The simplest model that adequately describes the PAN-air interface, with physically reasonable parameters, consists of three layers 5.7 ± 0.1 Å thick (Figure 3 and Table 1). The fitted layer thicknesses are consistent with the molecular dimensions for PAN (5.7 Å, calculated by taking the cube root of the molecular volume). The scattering length density (SLD) of each layer, which describes the layer electron density normal to the interface, increases with each layer, before reaching the bulk liquid SLD. This indicates the packing arrangement for the cations and anions in the three interfacial layers differ from that observed for the bulk.
Figure 3: X-ray reflectivity profile for the PAN-air interface at room temperature. The solid line is the fit to the data obtained using the parameters listed in Table 1. The inset shows the scattering length density profile.

Table 1: Best fit parameters to x-ray reflectivity results for the pure PAN-air interface.

<table>
<thead>
<tr>
<th>LAYER</th>
<th>THICKNESS (Å)</th>
<th>SLD (x10⁻⁶ Å⁻²)</th>
<th>ROUGHNESS (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (Uppermost)</td>
<td>5.7</td>
<td>5.5</td>
<td>1.5</td>
</tr>
<tr>
<td>2</td>
<td>5.7</td>
<td>7.5</td>
<td>0.5</td>
</tr>
<tr>
<td>3</td>
<td>5.7</td>
<td>9.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Similar results have also been achieved for EAF (Figure 4 and Table 2). The EAF-air interface model consists of two layers, each 5.3 Å thick with increasing SLD before reaching the bulk EAF properties. As for PAN, the layer thicknesses are consistent with the molecular dimensions of EAF, and the SLD profile suggests a different interfacial structure to the bulk.

Figure 4: X-ray reflectivity profile for the EAF-air interface at room temperature. The solid line is the fit to the data obtained using the parameters listed in Table 1. The inset shows the scattering length density profile.
Table 2: Best fit parameters to x-ray reflectivity results for the pure EAF-air interface.

<table>
<thead>
<tr>
<th>LAYER</th>
<th>THICKNESS (Å)</th>
<th>SLD (x10⁻⁸ Å⁻²)</th>
<th>ROUGHNESS (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (Uppermost)</td>
<td>5.3</td>
<td>3</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>5.3</td>
<td>6.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Data fitting of the other ionic liquids is still being conducted, hence no clear conclusions regarding the effect of cation and anion molecular structure on interfacial arrangement can be made at this stage. However, Figure 1 shows the reflectivity curves differ for each ionic liquid, and previous atomic force microscopy investigations of these ionic liquids (which revealed the periodic layering observed at the liquid-air interface also exists at the solid–liquid surface) have shown the layer morphology can be controlled by modifying the cation and anion molecular structure. Therefore it is expected differences will be observed here.

PUBLICATIONS / REPORTS arising as a result of your work.

N/A

PhD STUDENTS

Deborah Wakeham, anticipated date of PhD award is October 2011, thesis title is Surfactant Adsorption and Structure at Ionic Liquid Interfaces