Water adsorption on a liquid surface†

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Monolayer adsorption of water onto an ionic liquid in ultrahigh vacuum has been demonstrated, revealing a heat of adsorption which exceeds the heat of absorption into the bulk liquid by ≈ 40 kJ mol^{-1}.

Understanding the gas–ionic liquid (IL) interface in general, and the water–IL interface in particular, is of crucial importance to understanding a wide range of industrial processes; see ref. 1 for a recent review. Of particular relevance here is the use of ILs to remove CO_2 from flue stacks, where water and CO_2 (both products of hydrocarbon combustion) are in direct competition for adsorption at the IL surface and subsequent absorption into the bulk. It is commonly accepted that ILs are hygroscopic, even those which are hydrophobic,[2] and indeed there have been a number of previous studies of water on/in ILs using a variety of techniques.[1,3] In one case sum frequency generation at room temperature[3] showed that even for an H_2O partial pressure of 24 Torr over [C4MIm]BF$_4$[4] (corresponding to a mole fraction of $x_{IL} = 0.7$) water could not be detected at the surface of the IL. In this work we describe an X-ray photoelectron spectroscopy (XPS) study of D_2O adsorption on the surface of 1-octyl-3-methylimidazolium tetrafluoroborate, [C8MIm]BF$_4$,[4] in ultra-high vacuum (UHV). Using temperature programmed desorption (175–300 K) monitored by XPS, we determine the heat of adsorption to be 74 kJ mol^{-1}. As far as we are aware, this is the first work to isolate and directly study an adsorbate on an IL liquid surface, opening up a new field of exploration into the liquid–gas interface using surface science techniques developed over the past four decades for solid/gas studies. Using these methods we can be assured that the substrate is pure, the surface clean and uncontaminated, and the adsorbate identifiable.

Adsorption and desorption were monitored by XPS using a Kratos Axis Ultra spectrometer comprising a focused, mono-chromated, Al Kα (1486.6 eV) X-ray source with a hybrid magnetic/electrostatic input lens and a concentric hemispherical analyser.[5] The [C8MIm]BF$_4$ substrate, which with an enthalpy of vaporisation of 162 kJ mol^{-1} [6] is UHV compatible to ≈ 400 K, took the form of a horizontal thin liquid film (≈ 5 mm diam. $x \approx 1$ mm thick ≈ 0.02 ml) within a shallow cylindrical depression in a gold plated stainless steel sample stub. The sample was degassed to $< 5 \times 10^{-7}$ mbar prior to being transferred to the XPS analysis

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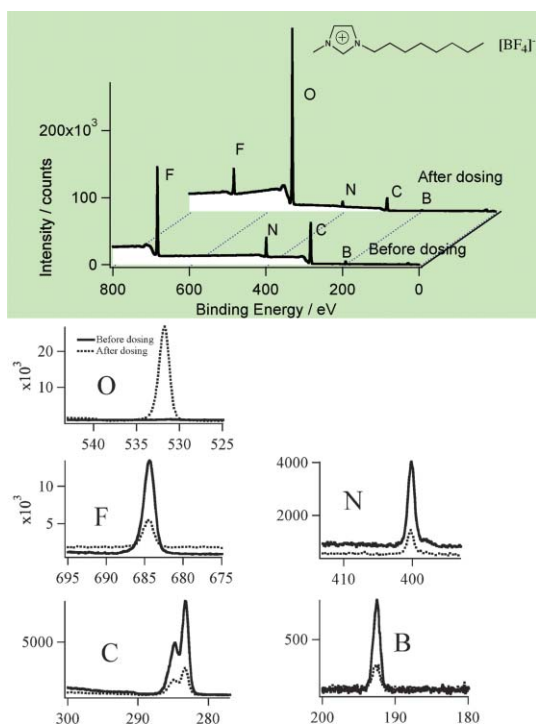
chamber ($\approx 3 \times 10^{-9}$ mbar) where accurate temperature measurements (± 2 K) were obtained by pressing a spring loaded type K thermocouple onto the side of the sample stub. D_2O vapour, used in preference to H_2O for consistency with later mass spectrometric experiments, was delivered to within ≈ 50 mm of the sample surface by a capillary doser, thus minimising the pressure rise experienced by the rest of the vacuum chamber.

The freshly inserted IL surface was contaminated with a silicone material exhibiting silicon 2s and 2p and oxygen 1s photoelectron peaks, which could be removed after brief argon ion bombardment (4 keV, ≈ 600 s, ≈ 1 μA cm^{-2}) to give a clean liquid surface exhibiting only photoelectron and Auger electron peaks due to the elements in [C8MIm]BF$_4$. B, F and N exhibited single 1s photoelectron peaks, as expected, as there is only one chemically distinct type of each element (the nitrogens in the imidazolium cation are indistinguishable by XPS). The C 1s photoelectron peak showed two peaks which can be decomposed into components corresponding to the various carbons in the [C8MIm] cation (see ref. 5 for further details). Quantitative measurements showed that the IL selvedge analysed by XPS had the same composition as the bulk material, and angular dependent measurements showed no change in composition for grazing emission, indicating that the surface composition is close to, or the same as, the bulk.

Initial adsorption experiments were carried out on the IL at room temperature. After exposure to an indicated 10×10^{-6} mbar s of D_2O (equal to many monolayer equivalents impinging on the surface, see below), no detectable changes were observed in the XP spectra of the IL, indicating a complete absence of D_2O on the surface.

The sample was then cooled for adsorption at low temperature. The glass–liquid transition was determined by an abrupt shift in the XP spectra as the IL switched from electrically conducting (ionic conduction as a liquid) to insulating (solid) and was found to occur at 216–223 K. This transition is somewhat higher than the 192 K reported for [C8MIm]BF$_4$[7] which may be due to our sample having a lower level of dissolved volatiles due to the UHV conditions, and hence a higher transition temperature. The transition could also be observed visually when small cracks in the solid disappeared during melting. When taking XPS data from the IL glass a charge neutraliser was used to supply the surface with low energy electrons, to neutralise the build up of positive charge due to photoemission of electrons, and hence keep the IL surface at approximately earth potential.

Fig. 1 shows the clean XP spectrum of the IL glass at 175 K, which is identical to the liquid spectrum except for a slight shift in binding energy (< 2 eV) due to the charge neutraliser. Dosing the clean IL glass at 175 K with an indicated $\approx 4 \times 10^{-6}$ mbar s of D_2O, caused multilayer adsorption, due to the higher local

Fig. 1 Wide scan XP spectra taken at 175 K before and after adsorbing multilayers of D_2O. Insets show details of the O, F, C, N and B 1s photoelectron peaks, and the structure of [C8MIm]BF_4.

pressure at the sample position, Fig. 1. A large O 1s peak is visible, together with the substrate IL peaks, which are attenuated in intensity due to the D_2O multilayer, but otherwise unchanged in shape or position, Fig. 1. XPS measurements were then taken as the sample was slowly heated at an average rate of 0.01 K s^{-1}. Fig. 2 shows the D_2O coverage (measured as the area under the O 1s peak), as a function temperature. Desorption of multilayer D_2O occurred at ≈ 185 K, leaving a monolayer, which then disappeared at ≈ 245 K (thus explaining the lack of adsorption at room temperature). Even with the charge neutraliser on, melting (216–223 K) could still be detected by a slight shift in peak positions due to the IL returning to a conducting state. Beyond the melting point, a second peak at lower binding energy was seen to grow in the N 1s spectra, Fig. 2 inset, while the original N 1s imidazolium peak decreased in intensity. Simultaneous with these changes, the C 1s peak also changed shape, and the B and F 1s peaks decreased in size. Fig. 2 shows how the intensities of the N 1s imidazolium and the new N 1s peaks changed with increasing temperature; both changed linearly during desorption of the D_2O monolayer, and then continued to change in the same manner after the monolayer had disappeared. A series of XPS scans taken across the area which had been exposed to the focused X-ray beam showed that outside of the irradiated area, the XP spectra were the same as for the clean IL surface (with a single nitrogen peak), but within the irradiated area, two distinct N 1s peaks were observed with the same separation (≈ 2.6 eV) as shown in Fig. 2 inset. We attribute these changes in the substrate peaks to the products of beam damage diffusing to the surface as the IL glass melts. The chemical shift of the nitrogen damage peak corresponds to nitrogen in an uncharged species.
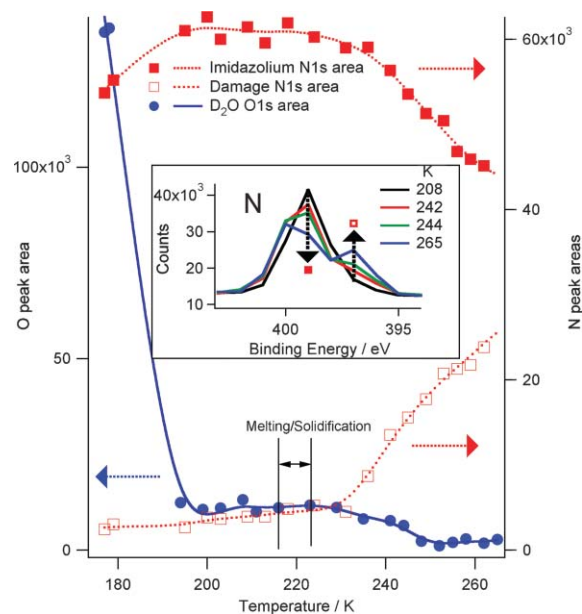

Fig. 2 Peak areas of O 1s, N 1s imidazolium and N 1s damage peaks as a function of temperature with smooth curves to guide the eye. Inset shows N 1s peak illustrating the decrease/increase of the imidazolium/damage components with temperature.

D_2O ice condensed from vapour at 175 K is expected to be normal, or hexagonal ice. Multilayers of such ice, comprising ≈ 10–30 layers, and having an enthalpy of sublimation of ≈ 62 kJ mol^{-1} [8] are expected to desorb at about 190 K, as observed. The monolayer of ice is clearly strongly bound to the IL surface as it only disappears at ≈ 245 K. To obtain the activation energy for this process, the O 1s peak area *versus* temperature data were smoothed using cubic splines to produce a D_2O coverage *versus* temperature plot, Fig. 3A. This smooth curve was then differentiated with respect to temperature to produce a rate of desorption *versus* temperature plot, Fig. 3B, corresponding to a temperature programmed desorption curve[9] in which the heating
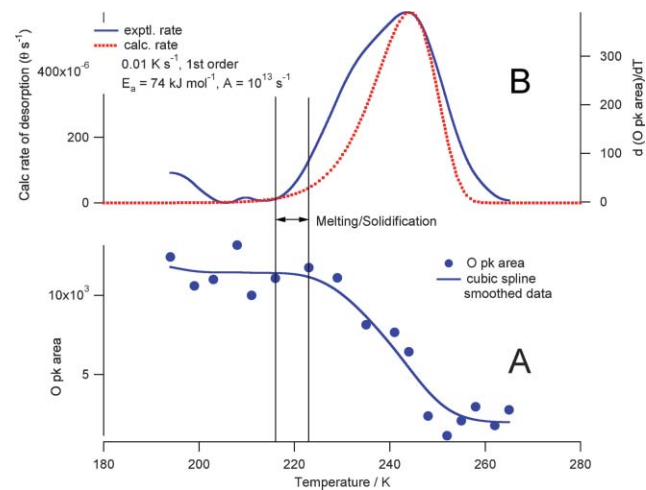

Fig. 3 A, oxygen 1s peak area *versus* temperature with fitted smooth curve. B, derivative of smooth curve in A with respect to temperature and the rate of desorption calculated for a first order process with an assumed pre-exponential of 10^{13} s^{-1} and a best fit activation energy of 74 kJ mol^{-1}.

rate was, on average, ≈ 0.01 K s^{-1}. Fig. 3B also shows a simulation of the temperature programmed desorption curve using first order desorption kinetics, an assumed pre-exponential of $A = 10^{13 \pm 1}$ s^{-1} and a best fit activation energy of $E_a = 74 \pm 4$ kJ mol^{-1} (error in E_a depends on choice of A). As the experiment was carried out in UHV, the activation energy equals the heat of adsorption ($= -U$, the internal energy change) and the enthalpy (H) can be found using a correction of RT at the desorption temperature, giving an $H = -76 \pm 4$ kJ mol^{-1}.

The behaviour of the damage material with temperature, as monitored with the N 1s spectra, requires further explanation. The attenuation length (distance for the incident intensity to drop to 1/e of its initial value) for Al Kα radiation through our ionic liquid is calculated to be 8.69 µm (86900 Å).[10] This attenuation length is far larger than the inelastic mean free path (distance for photoelectron intensity to drop to 1/e of its initial value) of the detected photoelectrons, <20 Å. So for the solid IL, the only damage observable by XPS is that within the top ≈ 100 Å of the surface, which was too small to be detectable. However, during the several hours that the solid IL was irradiated by the focused X-ray beam, damage material (generated by photoelectrons, Auger electrons and secondary electrons, as well as directly by photoabsorption), accrued and was held frozen in position throughout the X-ray path through the IL to a depth of $\approx 4.3 \times 10^5$ Å. When the IL melted, the damage products from this very extended region were able to diffuse towards the IL surface, where they preferentially accumulated. Such behaviour is unique to liquid surfaces and hence is not encountered in XPS studies of solids in UHV. At the melting point the viscosity is high and very little diffusion occurs, but as the temperature rises, the viscosity of the IL falls and so the rate of diffusion increases, until multilayer equivalents of damage products are present in the ≈ 100 Å depth detected by XPS at room temperature. That peaks from the IL species are still strong at room temperature implies a mixing of the IL and damage species. As the distance the damage products are likely to diffuse is much smaller than the lateral dimensions of the liquid sample (mm), the damage remains localised in its lateral position on the IL surface.

The thin film of IL in this study was ≈ 1 mm thick, corresponding to $\approx 2 \times 10^6$ ionic layers. If the full monolayer of D$_2$O had dissolved into this thin film it would produce a mole fraction of $x_{H_2O} \approx 10^{-6}$. The solubility of water in [C$_8$MIm]BF$_4$, in the form of Henry's constant (K, in bar), has been evaluated over the range 10–35 °C.[11] Extrapolating this data to 245 K, the temperature at which water was lost from the surface (using log$_e$ K vs. 1/T), we find that $K \approx 2 \times 10^{-3}$ bar. For a background water partial pressure of $\approx 10^{-9}$ mbar in the vacuum chamber, this corresponds to an equilibrium mole fraction of water in the IL of $x_{H_2O} \approx 5 \times 10^{-10}$, $\approx 2000 \times$ smaller than expected by complete dissolution of the water monolayer into the IL. It follows that the monolayer of D$_2$O must have desorbed into the gas phase.

The enthalpy of absorption of H$_2$O into [C8MIm]BF$_4$ is 34 ± 5 kJ mol^{-1},[11] which should be compared with the enthalpy of adsorption into the chemisorbed state, 76 kJ mol^{-1}. Clearly water is stabilised to a significant degree at the surface of the IL. Simulations using the analogue [C4MIm]BF$_4$[12] show that the

liquid vacuum interface consists of alkyl, imidazolium and BF$_4$$^-$ groups exposed in approximately equal proportions at the surface. Assuming the same behaviour for [C8MIm]BF$_4$, D$_2$O is most likely to interact with the charged imidazolium and BF$_4$$^-$ species, and unlikely to interact with the alkyl chains. A theoretical investigation[13] of water interacting with BF$_4$$^-$ and [C2MIm]$^+$ ions in the gas phase indicates that the BF$_4$$^-$–H$_2$O complex has an optimised energy of $-42 > H > -52$ kJ mol^{-1}, while the [C2MIm]$^+$–H$_2$O complex has an energy of $-30 > H > -40$ kJ mol^{-1}, the exact values being geometry dependent. From this we might expect D$_2$O to be more strongly associated with the BF$_4$$^-$ species than with the imidazolium species, due to a larger hydrogen bonding component between fluorine and hydrogen. Our experimental value of $H = -76$ kJ mol^{-1} is significantly higher than either of these values; this may possibly be due to the water being attached to two ions, though calculations for water bonded to an [C2MIm]Cl ion pair[13] indicate that the bonding is weaker than when it is associated with the separate ions individually.

For such a strong interaction between a water and an ion(s) one should really consider the water–ion(s) combination as a single entity ($RT = 1.83$ kJ at 220 K). Hence, when the IL melts at ≈ 220 K, the D$_2$O will remain fixed to the ion(s) it was originally bonded to, but the water–ion(s) complex would now be capable of diffusion. As the damage products move by diffusion to the surface, the water–ion(s) complex finds itself in an altered environment comprising ionic liquid and damage products. However, the water–ion(s) complex bond strength might be expected to be only marginally affected by this change and as the temperature is raised, the complex eventually ruptures, and the D$_2$O desorbs.

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