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Influence of Temperature and Molecular Structure on Ionic Liquid Solvation Layers.

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Abstract

Atomic force microscopy (AFM) force profiling is used to investigate the structure of adsorbed and solvation layers formed on a mica surface by various room temperature ionic liquids (ILs) ethylammonium nitrate (EAN), ethanolammonium nitrate (EtAN), ethylammonium formate (EAF), propylammonium formate (PAF), ethylmethyammonium formate (EMAF) and dimethylethylammonium formate (DMEAF). At least seven layers are observed for EAN at 14°C (melting point 13°C), decreasing as the temperature is increased to 30°C due to thermal energy disrupting solvophobic forces that lead to segregation of cation alkyl tails from the charged ammonium and nitrate moieties. The number and properties of the solvation layers can also be controlled by introducing an alcohol moiety to the cation's alkyl tail (EtAN), or by replacing the nitrate anion with formate (EAF and PAF), even leading to the detection of distinct cation and anion sub-layers. Substitution of primary by secondary or tertiary ammonium cations reduces the number of solvation layers formed, and also weakens the cation layer adsorbed onto mica. The observed solvation and adsorbed layer structures are discussed in terms of the intermolecular cohesive forces within the ILs.

1. Introduction

Ionic liquids (ILs) are organic salts consisting entirely of ions, and having melting points less than 100°C. Key physical properties may be controlled by selection of appropriate cations and anions in the first instance, with fine tuning facilitated by subtle variations in molecular structure. The ability to carefully and predictably control physical properties has led to a vast number of papers concerning the use of ILs as solvents for surfactant¹⁻⁵ and polymer⁶ self assembly, in microemulsions,⁷ for extractions,⁸ as organic solvent replacements for synthesis,⁹ as catalytic media,¹⁰ and in electrochemical¹¹ and solar cells.¹² ILs can be broadly classified into two groups, protic and aprotic ILs.^{13,14} Protic ILs are synthesised by proton transfer from a Brønsted acid to a Brønsted base which creates proton donor and acceptor sites and can lead to the formation of hydrogen bonds.¹⁵ Research concerning protic ILs has generally focused on surfactant self assembly^{3,4,16-20} and physical properties.^{13,14,21-24} In previous work we examined the structure of ethylammonium nitrate (EAN) and propylammonium nitrate (PAN) confined between an AFM tip and silica, mica and graphite.²² In this paper we examine the effect of variation in cation and anion structure and temperature on solvation layers.

Molecular ordering at the liquid/solid interface was first demonstrated using the surface force apparatus (SFA) for two mica surfaces immersed in octamethylcyclotetrasiloxane (OMCTS).²⁵ Oscillating forces due to molecules arranging into discrete layers near the solid surfaces were measured with the oscillation period equal to the size of OMCTS molecules, and the magnitude of the force decayed with separation as order decayed into the bulk. Subsequent experiments revealed similar solvation forces in a range of non-polar liquids²⁶ although fewer layers were found for molecularly flexible solvents that are able to space fill more effectively.²⁷ Solid surfaces in polar solvents produced oscillations superimposed on a double layer repulsion, but the period of the oscillations was still determined only by molecular size.^{28,29}

Atomic force microscopy (AFM) is an alternative method for measuring near surface forces. However, compared to SFA, AFM has lower signal to noise ratios, a smaller contact area, and unknown absolute separation. Sensitivity can be improved via the use of lock-in amplifiers, which allows the tip-sample interaction stiffness and deflection to be monitored simultaneously, and by conducting experiments in tapping mode.³⁰⁻³⁵ The sharp tips used in AFM experiments also reduce the influence of hydrodynamic forces.³⁰ AFM has been used to study force profiles in OMCTS,³⁰⁻³² n-dodecanol,^{30,31} squalane,³³ hexadecane,³⁴ water,³⁵ and mixtures of OMCTS with squalane and hexadecane³⁴ on various substrates. The results obtained generally agree with the interfacial structure suggested by molecular dynamics simulations. Models using both unstructured^{36,37} and structured³⁸ tips and surfaces have found that the magnitude of oscillations depends on the radius of the AFM tip, but the period and number of oscillations does not.

Solvation layers in conventional molecular solvents form due to the solid surface inducing order in an otherwise unstructured liquid. However, recent small angle neutron scattering (SANS)³⁹ and X-Ray diffraction (XRD)⁴⁰ experiments have shown ILs are often nanostructured in the bulk. Partially deuterated EAN and PAN were investigated using SANS, and Bragg spacings equal to approximately twice the IL molecular dimension were determined from the position of the scattering peak. SANS spectra were fit using alternating polar-apolar layers and could not be fit using spheriodal aggregates of any type with various structure factors. XRD studies of alkylimidazolium ILs with various anions also revealed nanostructure. For both the SANS investigation of protic ILs and the XRD study of aprotic ILs, increasing alkyl chain length led to larger, more regular domains; Nanostructure is therefore a consequence of alkyl tail aggregation, driven by solvophobic forces inducing alkyl chains to segregate from the charged cation group and the anion, which form ionic domains.

The effect of cation and anion variation on the bulk structure of pure ILs has also been investigated using electrospray ionisation mass spectrometry (ESI-MS).⁴¹ For primary amines with nitrate anions the formation of $C_8A_7^+$ aggregates was favoured, but when the anion was changed to

formate or lactate, there was no evidence of aggregation, attributed to decreased levels of cation – anion hydrogen bonding. For secondary and tertiary cations increased steric hindrance and reduced hydrogen bond capacity also lead to a reduction in aggregate size. It was concluded that the extent of hydrogen bonding plays an important role in determining the degree of IL structure.⁴²

Structure at solid-IL interfaces was first investigated for the EAN-mica system using the SFA.²⁴ Four to five oscillations were measured, however it was suggested on the basis of absolute surface separations that up to eight or nine surface layers could be present. The oscillation period was approximately 0.5nm, equal to the molecular diameter of EAN. Our previous AFM study of this and other ILs²² (exhibiting step-like rather than oscillating force profiles obtained due to differences in instrument operating mechanisms) also yielded a step size of 0.5nm, in good agreement with SFA data. The ease with which IL solvation layers can be measured using a standard AFM is attributed to the fact that EAN is structured in the bulk; rather than the surface *inducing* liquid layering it acts to *orient* the existing bulk structure. In light of this, it is somewhat surprising that fewer and more compressible surface layers were measured for propylammonium nitrate (PAN) than EAN, given that PAN is more strongly structured in the bulk. This apparent contradiction is a consequence of PAN's increased cation alkyl chain length imparting greater molecular flexibility, which allows it space fill more effectively.²⁷ The relationship between bulk and interfacial structure of ILs has recently been reviewed.⁴³

Molecular simulations of ILs confined between surfaces have been used to predict layer structures. The predicted density profile of 1,3-dimethylimidazolium chloride perpendicular to the walls suggested an interfacial layer rich in the cation due to favourable surface interactions.⁴⁴ The orientation of interfacial cations was tilted relative to surface normal, but the model suggested no preferred orientation after this first layer. Subsequent layering was primarily due to the distribution of the anions. Order decayed towards the centre of the cell and the number of layers present depended on wall separation distance.

The effect of temperature on IL interfacial structure has been examined using high-energy x-ray reflectivity (HEXRR)⁴⁵ and XRD.⁴⁰ Fluorinated ILs were studied with HEXRR at various temperatures above and below their melting points. At low temperature the results indicate the presence of five to six interfacial layers, decreased to 4 as temperature was increased. XRD results also showed structure was temperature dependant for a variety of imidazolium ILs, and multiscale coarse grain modelling simulations of similar ILs also suggest structure is temperature dependant.⁴⁶ Model fitting of XRD data showed the shift in peak position as the temperature was increased did not correlate with density changes for temperatures above T_g , but below T_g a density model produced good fits. The general conclusion from these investigations is that at higher temperatures the thermal motion disrupts attractive interactions between alkyl chains, decreasing structure. Simulations of solvation forces based on an Ornstein-Zernicke-type integral equation found temperature change does not affect the periodicity of the oscillations,³⁷ while other models have suggested that the magnitude of the oscillations decreases as the temperature is increased.⁴⁷ The experiments conducted here allow these conclusions to be tested using protic ILs.

In this study the effect we compare the solvation structure formed as the molecular structure of the cations and anions is varied. Comparison between EAN and EtAN, and EAF with PAF, EMAF and DMEAF, allows the effect of the cation structure to be elucidated, while substitution of formate for nitrate allows the effect of the anion to be ascertained. The effect of temperature on solvation layers formed by EAN is also examined.

Table 1: Structure, molecular weight (MW), density (ρ), molecular volume (M_v), ion pair diameter (D) and melting point (MP) of the ionic liquids examined. M_v is determined from ρ and MW while D is found by taking the cube root of M_v as described by Horn et al., which assumes a cubic packing geometry.²⁴

IL	Abbrev	Structure	MW (g)	ρ (g.cm ⁻³)	M_v (nm ³)	D (nm)	MP (°C)
Ethylammonium nitrate	EAN		108.1	1.21	0.15	0.53	13
Ethanolammonium nitrate	EtAN		124.0	1.26	0.16	0.54	-25.2
Ethylammonium formate	EAF		91.1	0.99	0.15	0.53	-15
Propylammonium formate	PAF		105.1	0.90	0.19	0.57	-55.4
Ethylmethyammonium formate	EMAF		106.1	1.03	0.17	0.56	
Dimethylethylammonium formate	DMEAF		119.2	1.03	0.19	0.57	

2. Materials and Methods

Nitrate ILs were prepared by slow addition of nitric acid (Merck) to ethylamine or ethanolamine (Aldrich or Fluka). Equimolar amounts were mixed in an aqueous solution below 10°C. Excess water was removed by rotary evaporation followed by nitrogen purging and heating at 105-110°C overnight. This lead to water contents undetectable by Karl-Fischer titration. Formate ILs were prepared by slow addition of equimolar formic acid (Fluka) to the appropriate amine (ethylamine, propylamine, ethylmethylaniline and dimethylethylaniline, Aldrich or Fluka). Excess water was removed by rotary evaporation at temperatures below 30°C. The formate ILs were not heated to avoid the formation of amides.⁴⁸ Water contents of formate ILs were determined by Karl-Fischer titration to be less than 0.5 wt%.

Force curves were measured using a Digital Instruments Nanoscope III Multimode AFM in contact mode. A scan rate of 0.1Hz and scan size of 20nm was used. Si₃N₄ standard cantilevers with sharpened tips were irradiated with ultraviolet light for 20 minutes before use. All cantilevers used were from the same batch and had an average spring constant of 0.07 N/m $\pm$ 0.005. A fluid cell with a silicone O-ring was used to house the IL. These were cleaned by ultrasonication for 20 minutes, rinsed with ethanol and Milli-Q water, then dried with nitrogen before use. Mica was the solid substrate used for all experiments. The mica surface was prepared by cleaving along the basal plane using adhesive tape. A fresh mica surface was used for all experiments except were otherwise stated. All force curves were collected at 21°C, except where otherwise stated. Temperature was maintained using an incubator. All experiments were repeated at least three times.

3. Results and Discussion

Force versus distance curves for the EAN/mica system at various temperatures (Figure 1) show a series of steps, corresponding to the displacement of EAN layers by the AFM tip as it approaches the mica surface. While the AFM cannot in itself determine the orientation of the molecule in layers, analysis of the force curve data in light of our SANS investigation allows inferences to be made. The SANS data revealed that alkyl chains aggregate together, segregated from charged regions in a lamellar-like structure. The step size of 0.5 nm determined using AFM correlates to the calculated EAN ion pair dimension (Table 1), and is half of the SANS Bragg peak spacing as expected. This suggests each step corresponds to alternating layers of cation and anion pairs, with the alkyl tails orientated towards each other in every second layer. As mica is negatively charged, it is assumed the layer closest to the substrate is cation rich with the NH_3^+ group orientated towards the mica and ethyl groups facing the bulk liquid. The second step is then be a cation/anion pair with the alkyl chains orientated towards the tails of the first layer, with the NO_3^- anion facing towards the anion of the third layer, and so on. Under this model, the first layer closest to the substrate should be narrower than 0.5 nm, but a distance of 0.5 nm is observed, indicating a cation/anion pair. This is due to the AFM tip being unable to penetrate the electrostatically adsorbed layer of EA^+ as reported previously.²² Mica has a lattice area of 0.48nm^2 while EA^+ occupies a surface area of 0.55 nm^2 ,²⁴ thus each EA^+ ion is adsorbed to 1.15 charged mica sites, which accounts for adsorption strength. It can be concluded that when the AFM tip is at zero distance from the substrate it effectively has reached an impenetrable layer of EA^+ ions. Therefore, the first layer in the force profile probably consists of a cation and an anion with the NO_3^- orientated towards the bulk. The retraction data (Figure 1e) also highlights the attraction between the EA^+ ions and the mica. EA^+ ions will also be adsorbed to the surface of the AFM tip with alkyl groups facing the bulk.²² Significant force (12 nN.) is required to withdraw the tip from the mica surface due to solvophobic attractions between alkyl chains adsorbed to the surface and tip. Zero force

is reached at a distance of 3.5 nm, which is equivalent to seven cation/anion pairs. Similar retractions occurred at all temperatures (not shown).

Figure 1: Force versus distance profiles for an AFM tip approaching a mica surface in EAN at varying temperatures. Each force curve was measured with the same AFM tip, same mica surface and EAN sample and therefore direct comparisons

can be made between each temperature. The retraction of the AFM tip data is included for 30°C

As the temperature is increased the number of layers present decreases from 7 layers at 14°C to 4 layers at 30°C and the force required for the AFM tip to penetrate the innermost solvation layer decreases from 22 nN at 14°C to 10 nN at 30°C. Both effects are due to increased thermal motion of ions disrupting solvophobic attractions between cation alkyl groups which decreases structure, in line with previous reports.⁴⁶ The size of the steps remains constant at approximately 0.5nm at all temperatures (Figure 1) consistent with the fact that EAN's density hardly varies over this temperature range.⁴⁹

Addition of an alcohol moiety to the alkyl chain (EtAN) decreases the number of detectable layers and gives rise to non-vertical (compressible) steps in the force profile at room temperature (Figure 2). The compressibility of the EtAN layers is similar to our previous observations on propylammonium nitrate (PAN),²² and can be attributed to the greater flexibility of the longer cation chain (propyl- or ethanol-, see Table 1). EtAN also exhibits fewer surface layers than either EAN or PAN. This might reasonably be expected, as the melting point of EtAN is 38°C below that of EAN (Table 1), and the results for EAN demonstrate that layering decreases the further the temperature is increased above melting point.

On a molecular level, the OH group will also lower cohesive forces within the layers by disrupting solvophobic attractions. Our hypothesis is that for EAN strong solvophobic forces combined with molecular inflexibility results in many rigid layers, but for EtAN reduced solvophobic attractions, increased molecular flexibility and lower melting combine to produce fewer, less well-defined, compressible layers.

Figure 2: Force versus distance profile for an AFM tip approaching a mica surface in EtAN at 21°C

Effect of Anion. Figure 3 shows that the most obvious effect of replacing the nitrate anion with formate (EAF and PAF) is that fewer layers are detected by AFM. As with EtAN, this might be expected from the melting points of EAF and PAF, which are 28°C and 64°C lower than those of EAN and PAN, respectively. Like the corresponding nitrates, the retraction curves for EAF and PAF show a strong adhesion between the cation layers adsorbed to the AFM tip and the mica substrate, requiring a force in excess of 10 nN to withdraw the tip, which jumps to zero force beyond 3 nm separation. The interactions between ethylammonium ions and both the AFM tip and mica substrate seem to be unaffected by changing anion.

Figure 3: a) Force versus distance profile for an AFM tip approaching a mica surface including retraction data at 21°C in a) EAF, and b) PAF

EAF exhibits two (possibly three), equally-spaced solvation layers on mica (Figure 3a). Like EAN, the regular 0.5nm spacing is consistent with molecular dimensions, as substitution of nitrate by

formate does not alter the molecular volume (Table 1). However, not only does EAF have fewer layers than EAN at the same temperature, the force required to rupture each layer is reduced, and the EAF layers are markedly more compressible than EAN.

We attribute the reduced layering to the lower hydrogen bond capacity of formate, which has one less proton acceptor site than nitrate, and in which hydrogen bonding is expected to be weaker. Simple molecular mechanics simulations of small clusters EAN and EAF confirm this expectation in that they uniformly yield 0.25-0.35 Å longer H-O hydrogen bond distances in EAF than EAN. Lower hydrogen bond capacity in the anion limits the ability of the IL to form an extended H-bonding network between ammonium moieties and anions, and hence reduces the strength of solvophobic forces driving segregation of the cations' alkyl groups. Solvophobic segregation is further diminished if the H-bonds are themselves weaker, and this is overall consistent with fewer and weaker solvation layers.

The observed compressibility of the EAF layers cannot be due to cation flexibility. We therefore attribute it to the same reduced attractions between the cation and anion, and to the limited H-bonding network. Together these permit greater freedom of motion within the layers, somewhat analogous to Helfrich undulations in confined lamellar phases.⁵⁰ More flexibility equates to more compressible layers, and to a decrease the extent of layering.

Changing from propylammonium nitrate to formate results in considerably different data to that observed for PAN.²² Significantly thinner than expected steps are observed at 0.28 and 0.60 nm in the force-separation curve, with the outermost layer clearly more compressible. There is also evidence of further layers at 0.83 and 1.17 nm, determined by jumps on approach between barely-detectable repulsive walls (Figure 3b). These small steps are attributed to cation and anion sublayers. As the apparent zero separation actually corresponds to a layer of PA⁺ ions electrostatically adsorbed to the mica substrate with the propyl chain oriented towards the bulk liquid, we infer from the experimental bulk structure of PAN³⁹ that the closest measurable layer at 0.28 nm corresponds to PA⁺ with the alkyl tails orientated towards the mica surface. The layer between 0.28 and 0.60 nm must then be a

neutralising layer of HCOO^- anions. Therefore, the thickness of the cation sub-layer is 0.28 nm and the anion sub-layer of 0.32 nm, giving a total thickness of 0.6 nm, close to the molecular dimension of PAF (Table 1) and the observed layer spacing in PAN.³⁹ The next two layers have similar thicknesses within the accuracy of the measurement of jump distances. This result provides strong evidence of alternating sublayers of cations and anions in ILs which was first suggested by Horn et al.²⁴ Modelling of molten KCl ⁵¹ has also suggested that ionic sublayers may form when the surface charge density is high, like that of mica.

As with the ethylammonium systems, substitution of nitrate by formate in propylammonium systems reduces the number of complete (ion-pair) layers observed.²² The observation of separate cation and anion sublayers in PAF but not PAN is a further consequence of the weaker hydrogen bonds and limited H-bond network in formate salts. As the ions are less strongly bound together, the AFM tip is able to disrupt one ion layer but leave the other in place. It should be noted cation and anion separation was sometimes observed for EAF, but not consistently enough to be commented upon in detail.

When the primary ammonium cation is replaced by a secondary or tertiary ammonium, only single layers are observed as steps in the force curves (Figure 4). EMAF (Figure 4a) exhibits a single solvation layer at a separation of 0.57 nm, in good agreement with the calculated ion pair diameter (Table 1), but requiring very little force (2 nN) to disrupt it. DMEAF also exhibits a single layer 0.45 nm thick, but requires a larger force of 8 nN to disrupt it (Figure 4b). This layer is thinner than either EAF or EMAF, or the ion pair diameter of 0.57 nm (Table 1), suggesting that it may be the surface-adsorbed cations, which the AFM tip displaces, and that no subsequent solvation layers can be detected. The retraction data supports this conclusion. Unlike primary and secondary ammonium cations, no strong adhesion is observed. Instead, once the force is reduced just below that required to penetrate the layer, the tip is repelled from the surface as DMEA^+ cations re-adsorb.

This shows how the strength of cation adsorption and IL layering can be tuned by changing the cation and anion molecular structure. Increasing the substitution of the ammonium cation sterically hinders packing into layers, but also limits hydrogen bonding network formation by reducing available hydrogens. Both effects favour decreased solvophobic segregation and nanostructure within the IL, and hence less layering at the surface. In the surface-adsorbed cation layer, substitution at the charged nitrogen centre moves it further from the negative sites on the mica, becoming more weakly bound and permitting the AFM tip to displace it.

This suggests an approach to selecting ILs to control solute adsorption onto hydrophilic (charged) substrates. Sterically hindered ions that interact with the substrate relatively weakly should be used for applications where adsorption or transfer of species to a substrate is required, such as in heterogeneous catalysis, electrodeposition and dye-sensitised solar cells.

Figure 4: Force versus separation profile for an AFM tip approaching and retracting from a mica surface at 21°C in a) EMAF and b) DMEAF.

4. Conclusions

AFM force curves have shown how changing interactions between the cation and anion constituents of ILs affects the formation of solvation layers on solid substrates, and bulk solvophobic segregation within the IL.

The number and strength of solvation layers on mica decreases with increasing temperature, and suggests that the bulk nanostructure should also decrease. This will be investigated in the near future.

Intermolecular forces and through them the number, strength, and compressibility of solvation layers can be tuned by modifying the cation and anion molecular structure to control geometrical packing and H-bonding capacity. Compressibility is a consequence of flexible layers, which may be achieved by increasing the flexibility of the alkyl moiety of the cation (longer chain, including adding a terminal hydroxyl) or by weakening the H-bond network that creates solvophobic segregation. This is achieved by reducing the number of hydrogen bond donor/acceptor sites on each cation or anion, or by weakening individual H-bonds. Layering is disrupted by weakening the H-bond network structure that favours bulk solvophobic segregation, or by increasing the bulkiness of the cations, which hinders packing into layers. Tuning these forces, as exemplified by PAF, even allows the observation of distinct cation and anion sublayers.

Increasing substitution around the ammonium cation also reduces its electrostatic attraction to the mica surface, allowing the strength of adsorption of the cation layer to be modulated, and even displaced by an AFM tip.

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