

Influence of Lithium Solutes on Double Layer Structure of Ionic Liquids

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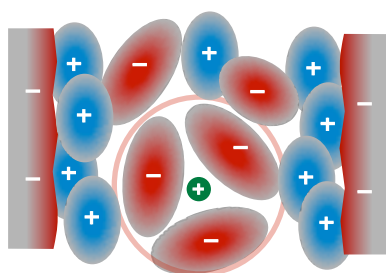
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ABSTRACT

The ionic liquid–electrode interface has attracted much recent interest owing to its importance for development of energy storage devices, however the important step of adding electro-active ions is not yet well understood at the molecular level. Using direct force measurements across confined electrolyte films we study the effect of added lithium-ion solute on the double layer structure of an ionic liquid electrolyte with molecular resolution. We find anionic clusters involving lithium can persist adjacent to the surfaces and, in many cases, this inhibits direct adsorption of lithium ions to the negative surface. Two apparently similar ionic liquid solvents show diverging properties, with one facilitating and the other preventing direct Li-ion adsorption onto the negative surface. The results have implications for the selection of ionic liquids as electrolytes in lithium ion batteries.

TOC GRAPHICS



KEYWORDS Surface forces, SFA, confined liquids, electrical double layer, solvation

Due to their remarkable properties, including non-volatility, non-flammability, high thermal stability and wide electrochemical window, ionic liquids have generated increasing interest in recent years as electrolytes for energy storage¹⁻⁴. One potential use is as electrolytes for lithium-ion batteries⁵.

Conventional battery electrolytes are often composed of a lithium salt such as LiPF_6 dissolved in a carbonate solvent. Organic solvents decompose on electrodes during initial charging, generating a solid electrolyte interphase (SEI) at the surface. This layer is electrically insulating but an ion conductor for lithium ions⁶, and if stable prevents further electrolyte decomposition upon subsequent charges. However short circuits can lead to overheating and ignition of the organic solvent, which has been problematic in the past and motivates the search for alternative electrolytes. Exchanging the organic solvent for an ionic liquid is a promising approach to limit flammability and volatility of the electrolyte. With new generation batteries employing higher voltage cathodes exceeding the safe limit of current organic electrolytes, ionic liquids – with their wide voltage window – may hold the key to extending the possibilities in electrical energy storage^{4, 7-8}.

Despite current interest in the use of ionic liquids as electrolytes in lithium-ion batteries, the nano-scale structure of lithium/ionic liquid mixtures at charged interfaces is not yet well understood and is the focus of the present work. Of particular interest is how the solvation of lithium ions changes as it approaches an electrode. Here, we show that the double layer structure of the ionic liquid is significantly perturbed by the presence of a lithium solute, due to the presence of anionic clusters involving Li^+ ions coordinated to multiple ionic liquid anions. We find that two apparently similar ionic liquids show diverging behavior, with one preventing and the other allowing direct Li^+ adsorption at the negative surfaces.

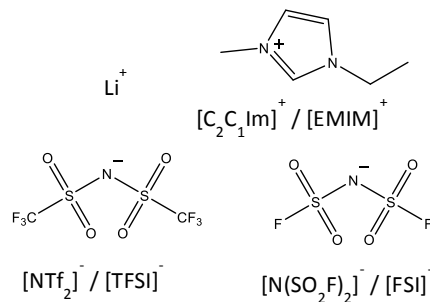


Figure 1. Structures of the ions investigated and commonly encountered abbreviations for each.

We present measurements of the interaction force between atomically smooth and negatively charged mica surfaces in crossed-cylinder configuration across an ionic liquid-based lithium electrolyte, with sub-molecular resolution in liquid film thickness achieved using a surface force balance (SFB)⁹. As we have demonstrated in previous work, force measurements such as these can reveal details of the interfacial structure, such as ion layering, of confined liquids and the relation between molecular (or ionic) structure and near-surface arrangements¹⁰⁻¹¹. Importantly, our geometry is such that the Derjaguin Approximation¹² holds and the measured *force* between crossed cylindrical surfaces normalised by radius of curvature, F_N/R , is proportional to the interaction *energy* between parallel plates at the same separation, $U(D)$: $F_N(D)/R = 2\pi.U(D)$. Thus our measurements of interaction force reveal the energy profile of liquids confined to films between charged surfaces; this, in turn, can be interpreted to give information about the ion arrangements¹³⁻¹⁴.

In this work, we compare pure ionic liquid ‘solvents’ to solutions containing lithium-ion solutes at different concentrations. The ionic liquids 1-ethyl-3-methylimidazolium *bis*[(trifluoromethane)sulfonyl]imide, $[\text{C}_2\text{C}_1\text{Im}][\text{NTf}_2]$ (Iolitec, 99.5%), and 1-ethyl-3-methylimidazolium *bis*(fluorosulfonyl)imide, $[\text{C}_2\text{C}_1\text{Im}][\text{N}(\text{SO}_2\text{F})_2]$ (Solvionic, 99.5%) are studied both pure and with the solute lithium *bis*[(trifluoromethane)sulfonyl]imide, LiNTf_2

(Sigma-Aldrich, 99.95%). The ion structures and abbreviations are shown in Figure 1. The liquids were dried *in vacuo* (10^{-2} mbar, 70 °C) prior to injection between the surfaces.

The measured force profiles are shown in Figure 2. Pronounced oscillations in force as a function of distance between the two confining mica plates are observed in each case. The oscillations indicate layered structures in the liquid film for all concentrations: repulsive forces are observed at film thicknesses corresponding to stable ion configurations, and attractive forces are observed at intermediate film thicknesses corresponding to unstable films. As such, each maximum in normalised force, F_N/R , corresponds to squeezing out a layer of ions as the film thickness, D , is decreased. The measured attractive minima in the oscillatory profiles correspond to the adhesive force required to separate the surfaces from each stable film thickness. In order to ensure overall electroneutrality, each ‘squeeze-out’ of liquid must expel equal numbers of cations and anions from the confined film to the surrounding bulk liquid. The likely structure of these layered ionic liquid films has been the subject of intense investigation, and it is now well established that alternating cation- and anion-enriched layers exist near charged surfaces as has been consistently inferred from a whole suite of methods including x-ray reflectivity¹⁵⁻¹⁶, atomic force microscopy (AFM)¹⁷⁻¹⁹, surface force measurements^{10-11, 20} and computer simulations²¹⁻²⁵. It is also known that, for ionic liquids, the structure exists at each surface independently of the other^{15, 26-27}. We note however that this extended layering structure is not the only possible arrangement of ions in the double layer, and that ‘monolayer’ and ‘crowded’ regimes may emerge at even higher surface charge densities²⁸⁻³¹.

The negative charge on the mica surfaces arises due to dissociation of K^+ from the mica lattice into the liquid. Although we cannot measure directly the resulting negative surface charge on the mica during experiments, the value is likely to be close to the maximal charge

density of one charge per 0.48 nm^2 (or $\sim 33 \text{ } \mu\text{C cm}^{-2}$)^{13, 32}. In our experiments the surfaces are surrounded by a reservoir of bulk ionic liquid, so that the concentration of K^+ resulting from this dissociation is negligible. The potential difference between the surface and bulk electrolyte is not clear in this case of an insulating substrate, however the estimated surface charge density is within the useful range to compare with electrochemical experiments with ionic liquids³³.

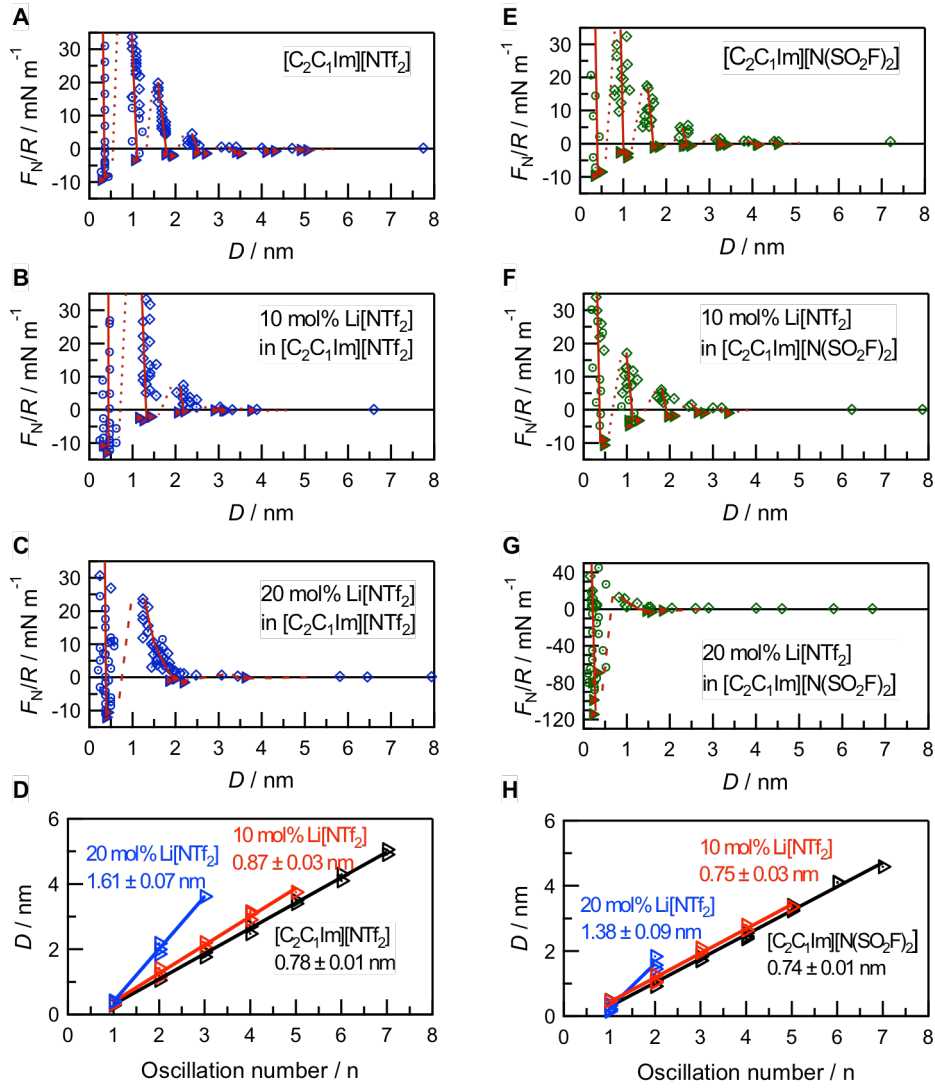


Figure 2. (A-C, E-G) The measured force, F_N , between two mica surfaces (normalised by radius of curvature, R) as a function of electrolyte film thickness, D , for the ionic liquids and their mixtures with Li[NTf₂]. Diamonds indicate points measured on approach of the surfaces while circles indicate points measured on retraction of the surfaces. Filled triangles represent adhesive minima from which the surfaces jump apart to larger separations upon retraction. The lines guide the eye to the oscillatory nature of the forces, with solid lines through measured forces and dashed lines through regions inaccessible to measurement due to instabilities in the force measuring spring. (D, H) Film thickness, D , as a function of oscillation number for each solution. The gradient gives the average periodicity for the layered structure at each concentration.

Liquids and solutions involving [NTf₂]⁻ anions (Figure 2A-D): The pure ionic liquid [C₂C₁Im][NTf₂] between mica surfaces, as shown in Figure 2A, exhibits seven oscillations in force in the range ~0.3 nm (corresponding to a single confined cation layer between the negatively charged surfaces) to ~5.0 nm (corresponding to 13 confined ion layers). Although a weak longer range repulsion between the surfaces exists³⁴, we focus here on the short range

ion ordering. Each squeezed-out layer is found to be close to 0.8 nm for this ionic liquid, corresponding to the dimensions of an ion pair.

Adding a small amount of LiNTf₂ solute to afford a 10 mol% mixture results in a qualitatively similar oscillatory profile to the pure ionic liquid, as shown in Figure 1B. However the presence of the solute results in a reduced range of oscillations, reduced force magnitudes for corresponding distances, and a slight dilation of the layers compared to the pure ionic liquid (see Figure 2D).

Increasing the concentration of lithium ions to 20% of all cations leads to a dramatic change in the interaction profile as shown in Figure 2C. The structuring is considerably reduced to only three oscillations, and the layers are significantly thicker (Figure 2D). The prominent repulsion around 1.2 – 2.1 nm is also decidedly ‘soft’; increase in the applied force leads to compression of the layer, with its thickness decreasing continuously by a full 1.0 nm until an eventual discontinuous ‘squeeze out’ occurs.

The dilation of the layer dimensions with added lithium solute may perhaps come as a surprise given that the Li⁺ ions are considerably smaller than [C₂C₁Im]⁺ ions. To explain the thicker layers for the mixtures, it is important to note that stable anionic clusters involving Li⁺ cations have been well documented, particularly with [NTf₂]⁻ anions³⁵⁻⁴⁰. From simulations, Li[[NTf₂]₂]⁻ and [Li[NTf₂]₃]²⁻ appear the most likely clusters for Li_{0.1}[C₂C₁Im]_{0.9}[NTf₂] and Li_{0.2}[C₂C₁Im]_{0.8}[NTf₂] respectively³⁷. In our experiments the term ‘cluster’ indicates a sufficiently stabilized structure that it is detected as a single unit in the repulsive force between the surfaces, and squeezed out collectively upon decreasing the film thickness. The approximate dimensions of such clusters in fact agree very well with the measured film thicknesses, although we cannot exclude the possibility of a mixture of anions and anionic clusters of different sizes. The inclusion of tri-valent Li-ion clusters in the near-surface layers

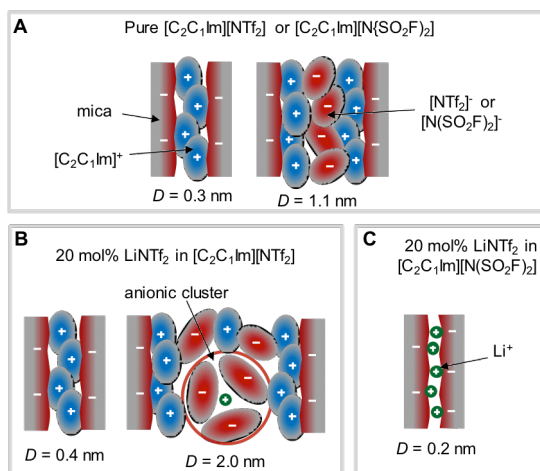


Figure 3. Schematics showing the likely ion arrangements for the different lithium/ionic liquid mixtures at selected surface separations (values of D shown for each).

is shown schematically in Figure 3B, in a manner quantitatively consistent with the observed oscillatory forces. It is also likely that due to their non-spherical shape, the $[\text{NTf}_2]^-$ anions might adopt a different orientation in order to interact with lithium, increasing the dimensions of the layers. These inferred ion arrangements are remarkably similar to those recently proposed from voltammetric and AC impedance measurements⁴¹.

Interestingly, the measured adhesion for the thinnest film thickness (i.e. the minimum in force for each of the 0.2-0.4 nm layers) is closely similar for pure $[\text{C}_2\text{C}_1\text{Im}][\text{NTf}_2]$ and for both of its mixtures (Figure 2A-C). Since these thinnest films are expected to consist of a confined layer of cations, and the nature of the cations determines the adhesion, this appears to suggest that $[\text{C}_2\text{C}_1\text{Im}]^+$ ions alone preferentially adsorb to the surface, even in the mixtures, since significant co-adsorption of the much smaller Li^+ ions would be expected to alter the adhesion. This inference is further supported by very similar friction forces measured between the mica surfaces across this cation monolayer for all three liquids (unpublished results). The preference for $[\text{C}_2\text{C}_1\text{Im}]^+$ over Li^+ at the negative surfaces results from a balance of terms: the energy of forming clusters of $[\text{NTf}_2]^-$ anions around Li^+ ; the difference in adsorption energy of Li^+ compared to $[\text{C}_2\text{C}_1\text{Im}]^+$ on mica; and the entropy changes

accompanying desolvation and adsorption. The net result – in this case of $[\text{NTf}_2]^-$ anions – appears to be that Li^+ ions maintain their solvated configuration in the electrical double layer, preventing closest approach of lithium to the negatively charged surfaces. This balance is apparently rather delicate, as we show in the following section: the exchange of ionic liquid anion from $[\text{NTf}_2]^-$ to $[\text{N}(\text{SO}_2\text{F})_2]^-$ results in an entirely different conclusion.

Liquids and solutions involving $[\text{N}(\text{SO}_2\text{F})_2]^-$ anions (Fig. 2E-H): The results for pure $[\text{C}_2\text{C}_1\text{Im}][\text{N}(\text{SO}_2\text{F})_2]$ are shown in Figure 2E and are similar in range and magnitude to those for pure $[\text{C}_2\text{C}_1\text{Im}][\text{NTf}_2]$. The forces for the 10 mol% LiNTf_2 mixture (Figure 2F) have reduced range and magnitude, but possible dilation in the layers is not apparent at this concentration. This suggests that lithium somewhat disrupts the ion packing without necessarily forming anionic clusters with the $[\text{N}(\text{SO}_2\text{F})_2]^-$ anions.

The mixture containing Li^+ ions at 20 mol% reveals a dramatically different structure (note the different scale in Figure 2G), with the measured adhesion for the thinnest layer of cations increasing by an order of magnitude compared to the lower concentration or compared to any of the mixtures with $[\text{NTf}_2]^-$ anions. The most likely explanation is preferential adsorption of lithium to the surface, leading to a very stable and commensurate arrangement between the two mica lattices at their closest separation, as in Figure 3C. The second oscillation at ~ 1.6 nm shows considerable dilation compared to the pure $[\text{C}_2\text{C}_1\text{Im}][\text{N}(\text{SO}_2\text{F})_2]$; in this case clusters involving multiple anions around central Li^+ ions are again likely, but due to the mixture of $[\text{NTf}_2]^-$ and $[\text{N}(\text{SO}_2\text{F})_2]^-$ anions present here precise interpretation is difficult.

These results invite comparison to molecular dynamics simulations of mixtures of $[\text{C}_4\text{C}_1\text{Im}][\text{BF}_4]$ with LiBF_4 and KBF_4 at charged graphene surfaces⁴² which also show preferential adsorption of imidazolium cations, and with Li^+ and K^+ ions approaching the negatively charged electrodes only when added to the ionic liquid in larger amounts. Weaker

ionic liquid interfacial layering for different surface potentials has also previously been observed with LiCl solutes in ionic liquids based on the $[\text{FAP}]^-$ anion using AFM at gold surfaces⁴³⁻⁴⁴. However there was no clear evidence for clustering even at higher solute concentrations⁴³, possibly due to a differing interaction of Li^+ with $[\text{FAP}]^-$ relative to $[\text{NTf}_2]^-$ or $[\text{N}(\text{SO}_2\text{F})_2]^-$. Another reason may be the differing geometry in that experiment, as follows. For two extended surfaces confining a liquid film, as in the present experiments, the nano-confined films are up to several micrometres in lateral (in-plane) diameter and may contain a mixture of cations, anions, and anionic clusters of different size in the layers (as shown in Figure 3). The measured film thicknesses therefore represent average values with a lateral resolution of $\sim 1 \text{ }\mu\text{m}$. In contrast a sharp AFM tip would probe a very local lateral area consisting of one or several ions, and could also potentially push clusters to the side during approach.

The persistence of anion clusters around Li-ions, as demonstrated here for Li^+ dissolved in $[\text{C}_2\text{C}_1\text{Im}][\text{NTf}_2]$ up to 20 mol% of Li^+ would result in a loss of differential capacitance compared to solutions allowing direct Li-ion adsorption on the electrode (as we observe for $[\text{C}_2\text{C}_1\text{Im}][\text{N}(\text{SO}_2\text{F})_2]$ with 20 mol% of Li^+). This has been shown by Yamagata et al.⁴¹ using glassy carbon electrodes and is likely to account for the differences in cathodic stability for lithium solutes in different ionic liquids where lithium may be directly adsorbed to the electrode surfaces. This direct and preferential adsorption of Li^+ to negative electrodes has been proposed to provide an alternative protective mechanism to SEI formation, where oxidation of $[\text{C}_2\text{C}_1\text{Im}]^+$ ions is prevented.

In summary, we find using direct force measurements that the presence of lithium solute can significantly perturb the prevalent multi-layered structure of ionic liquids in the electrical double layer. In particular, the anionic clusters that lithium forms with ionic liquid anions are

not found to be disrupted adjacent to negatively charged surfaces in the case of NTf₂-based ionic liquids. In contrast, Li⁺ solutions in N(SO₂F)₂-based ionic liquids can lead to much stronger Li⁺ adsorption. Hence careful selection of ionic liquid ions is required to optimise Li⁺ ion adsorption and concentration gradients in the vicinity of electrodes.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work was supported by The Leverhulme Trust, The John Fell Fund (Oxford University) and an EPSRC Doctoral Prize (AMS).

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