

Measurement of Forces across Room Temperature Ionic Liquids between Mica Surfaces

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Ionic liquids (ILs) are liquids that consist only of cations and anions. In spite of a plethora of emerging processes involving ionic liquids, there is no experimental measurement of the structure and dynamics of ILs at the solid–liquid interface comparable to the double layers of electrolyte solutions. Here, we report the direct measurements of the interactions (force–distance functions) between two atomically smooth mica surfaces across three different types of room temperature ILs. The forces are repulsive at all measured distances in all three cases, decaying exponentially with distance. Effective Debye screening lengths are found to be around 1–4 nm, much longer than expected from traditional theories, and strongly dependent on the size and molecular structure of the anion/cation. At small separations, in addition to the exponential repulsions, oscillatory forces are observed, while any monotonically attractive van der Waals forces, if present, are overwhelmed by the repulsive electrostatic and oscillatory forces.

Introduction

Ionic liquids (ILs), also which combine tunable solubility properties with a negligible vapor pressure, have recently received much attention as solvents in the development of *green chemistry* to reduce environmental impact.^{1,2} Use of ILs has been demonstrated in organic synthesis,³ chemical separation,⁴ hazardous chemical storage and transportation,⁵ and many electrochemical applications,^{6–8} and their applications continue to expand.^{9,10} Understanding the molecular interactions of ILs is important to better control and understand their assembly, liquid structure, and solvation processes.

Aside from their technological importance, ILs are also scientifically significant: The Debye screening length is the scale over which mobile anions and cations screen out electric fields in solutions or plasmas. In the case of electrolyte solutions, an increase in electrolyte concentration causes a reduction in the Debye length, better screening of electric fields, and a reduction in the double-layer forces. Some questions about ILs come naturally to mind: What is the Debye length of these apparently very concentrated electrolyte solutions, and are the traditional formulas, based on the Poisson–Boltzmann equation and assuming point charges, to calculate the Debye lengths still valid for such systems? Measuring experimental Debye lengths of ILs has not previously been feasible because of the need for extreme temperatures to melt the more common types of ILs. With the advent of room temperature ionic liquids (RTILs), this problem has been overcome. Here, we have tried to answer some of these questions by directly measuring the forces between two mica surfaces across three different types of RTILs using a surface forces apparatus (SFA).

Structure at solid–ionic liquid interfaces was first investigated for the ethylammonium nitrate–mica system by Horn et al.¹¹ They measured four to five oscillations, and the oscillation period was approximately 0.5 nm, equal to the molecular diameter of ethylammonium nitrate. In their force profile, there was no monotonic force that is stronger than ~ 1 mN/m. Recently, Mezger et al.¹² have utilized high-energy X-rays to investigate interfacial layering properties of ILs (ionic liquids with the tris(pentafluoroethyl)trifluorophosphate) on a charged sapphire substrate and they found that RTILs show strong interfacial layering, starting with a cation layer at the substrate and decaying exponentially into the bulk liquid, and the observed decay length and layering period point to an interfacial ordering mechanism, akin to the charge inversion effect, which is suggested to originate from strong correlations between the unscreened ions. Compared to the previous studies, we have utilized both aromatic and nonaromatic and much larger ionic liquids to understand the effect of molecular size and localization on the IL structuring on solid interfaces in this study. In addition, we have focused on the long-range forces to investigate the electrostatic screening behavior of ILs rather than layering properties at short separations.

Experimental Section

Materials. Highest grade 1-butyl-3-methyl-imidazolium-trifluoromethane sulfonate (BMIM-OTF), 1-butyl-3-methyl-imidazolium-tetrafluoro borate (BMIM-TFB), and trihexyl-tetradecyl-phosphonium bromide (THTDP-Br) were purchased from Sigma-Aldrich.

Methods. Dielectric measurements were carried out using a Novocontrol high resolution alpha dielectric analyzer (0.1 Hz–10 MHz) and an HP impedance analyzer (1 MHz–1.8 GHz) in the temperature range -100 to 100 °C, stabilized to better than 0.2 °C by Quatro temperature controllers. Forces were measured using an SFA 2000 (see the Supporting Information for further details).

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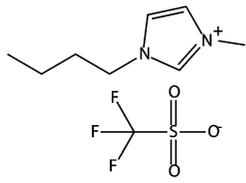
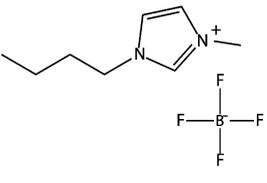
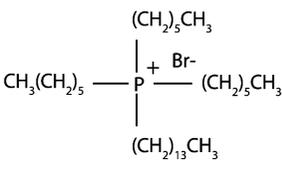
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TABLE 1: Molecular Structures and Physical Properties of the Three Ionic Liquids Studied^a

Property	BMIM-OTF [†]	BMIM-TFB [‡]	THTDP-Br [§]
			
Molecular weight, M_w (Da)	288.3	226.02	563.8
Molecular diameter (nm)	$0.9 \oplus, 0.4 \ominus$	$0.9 \oplus, 0.3 \ominus$	$2.4 \oplus, 0.2 \ominus$
Density, ρ (kg/m ³)	1292	1210	960
Refractive index, n	1.4358	1.4251	1.4879
Static dielectric permittivity, ϵ_s , at $f/f_c=0.1$ ($f_c=10^4$ - 10^5)	12.1	13.5	5.5
Melting point, T_m (°C)	17	Not applicable	-20.5
Glass transition temperature, T_g (°C)	Not applicable	-80	-66.4
Fully dissociated concentration, $C=\rho/M_w$ (M)	4.48	5.26	1.70
Effective free ion concentration at 25 °C, C_{eff} (M)	2.61	4.32	1.22

^a Refractive indices n were measured using an Abbé refractometer (ATAGO 3T, ATAGO U.S.A., Inc.) with an accuracy of ± 0.0002 . Dielectric constants ϵ were measured using a high resolution alpha dielectric analyzer (Figure 1). Melting points and glass transition temperatures were measured using a modulated differential scanning calorimeter (MDSC Q2000, TA Instruments). The effective concentrations of mobile ions, C_{eff} , were determined from the measured conductivity σ_0 and diffusion coefficients D using the Einstein–Smoluchowski equation,^{14,17} which revealed that 58–82% of the ILs are dissociated.[†] BMIM-OTF, 1-butyl-3-methyl-imidazolium-trifluoromethane sulfonate;[‡] BMIM-TFB, 1-butyl-3-methyl-imidazolium-tetrafluoro borate;[§] THTDP-Br, trihexyl-tetradecyl-phosphonium bromide.

Results and Discussion

Table 1 gives the three RTILs used in our studies and lists their physical properties relevant to this study. Some of the properties are taken from the literature,^{13–15} and others were specially measured for these experiments.

Before showing our force measurements, we would like to highlight our results on the complex dielectric function $\epsilon^* = \epsilon' - i\epsilon''$ and the complex conductivity function $\sigma^* = \sigma' + i\sigma''$, as measured in a broad frequency (0.01 Hz–1.6 GHz) and temperature (–100 to 100 °C) range.^{16,17} $\sigma^* = i\epsilon_0\omega\epsilon^*$, where ω is the radial frequency and ϵ_0 the permittivity of vacuum. Both σ^* and ϵ^* comprise, besides the free ion concentration, the main parameters determining the screening length and the strength of the double-layer forces.

The conductivity σ' is characterized on the low frequency side by the plateau in the DC limit (σ_0); at the characteristic frequency f_c , the dispersion sets in and turns into a power law. We have shown in recent publications that, by employing

Einstein and Einstein–Smoluchowski equations and taking f_c as the diffusion rate, the diffusion coefficient is obtained in quantitative agreement with pulsed field gradient nuclear magnetic resonance measurements. This enables separation of mobility from the measured σ_0 and provides a direct estimate of the effective free ion concentration in the ionic liquid, an essential parameter in the computation of the double layer forces. On the other hand, the real part of the dielectric function ϵ' at f_c turns from the high frequency limit to the static value ϵ_s , as shown in Figure 1. The static dielectric permittivity/constant ϵ_s , a measure of electrostatic interaction, can be accurately obtained if ϵ' is measured in a broad frequency range, as discussed in our earlier article.¹⁸ This makes it possible to avoid errors associated with the influence of secondary dynamic processes in high frequencies and interfacial effects in the low frequency limit. Rescaled with respect to f_c , both σ' and ϵ' , as measured over widely varying temperatures, collapse into one chart (see Figure 1), thus proving the uniqueness of the

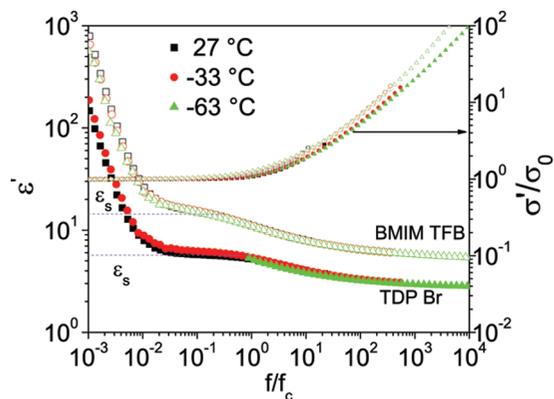


Figure 1. The real part of the complex dielectric function, ϵ' , and complex conductivity, σ' , of BMIM-TFB (open symbols) and TDP-Br (filled symbols) versus the scaled frequency f/f_c at different temperatures. Dielectric measurements were carried out using a Novocontrol high resolution alpha dielectric analyzer (0.1 Hz–10 MHz) and an HP impedance analyzer (1 MHz–1.8 GHz) in the temperature range -100 to 100 °C, stabilized to better than 0.2 °C by Quatro temperature controllers.

mechanism of charge transport. It also underscores the finding that, for the ionic liquids studied, the dielectric permittivity/constant is practically independent of temperature. For $f/f_c \leq 10^{-2}$, a steep increase is observed due to electrode polarization. We recently proved that f_c in ionic liquids is experimentally identical to the structural α -relaxation rate as measured by dynamic mechanical spectroscopy, thereby providing its molecular interpretation.¹⁹

Figure 2 shows force–distance profiles measured between two mica surfaces across three different types of ILs. The force is monotonically repulsive, decaying roughly exponentially with distance for all ILs, as can be better seen from a semilog plot (Figure 2b) where λ is the exponential decay length and B the pre-exponential factor in eq 1 for each liquid.

The exponentially decaying repulsive forces with decay lengths λ from 1 to 4 nm and extending from 2.5 to 20 nm suggest that they are “of electrostatic origin”. (The attractive van der Waals forces between the two mica surfaces across the ionic liquids, given by $F/R = -A/6D^2$, where A is the Hamaker constant, calculated to be $A \approx (1-7) \times 10^{-22}$ J, are estimated to be very much smaller than the measured repulsive forces at all of the distances measured.) The measured force profiles $F(D)/R$ were fitted to the standard approximate expression for the double-layer force:²⁰

$$\frac{F}{R} = \kappa Z e^{-\kappa D} = 64\pi\epsilon\epsilon_0 \left(\frac{k_B T}{e}\right)^2 \tanh^2\left(\frac{e\psi_0}{4k_B T}\right) \kappa e^{-\kappa D} = B e^{-D/\lambda} \quad (1)$$

where k_B is the Boltzmann constant, T the temperature, ψ_0 the surface electrostatic potential, e the electronic charge, and κ^{-1} the Debye screening length, given by

$$\kappa^{-1} = \left(\frac{\epsilon\epsilon_0 k_B T}{e^2 \sum_i n_i z_i^2} \right)^{1/2} \quad (2a)$$

$$\kappa^{-1} = \frac{0.0343\sqrt{\epsilon}}{\sqrt{C}} \text{ nm} \quad (2b)$$

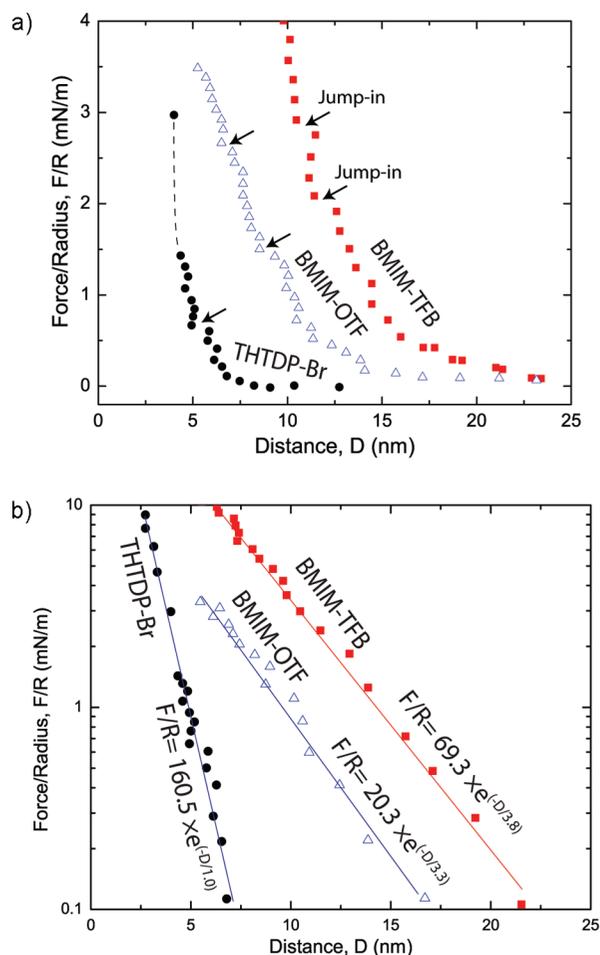


Figure 2. (a) Measured normalized repulsive force F/R between two cylindrically curved mica surfaces of radii $R \sim 2$ cm as a function of distance D across BMIM-OTF (open blue triangles), BMIM-TFB (solid red squares), and THTDP-Br (solid black circles) at 25 °C. Arrows indicate where jumps in occur, and errors in the distance measurements are very small (± 0.2 nm). (b) Measured repulsive force profiles of the three ionic liquids studied at 23 °C on a semilog plot.

where z_i is the valency of the different dissociated ions (for our ionic liquids, $z_i = \pm 1$), n is the number density in units of $\#/m^3$, and C is the concentration in units of mol/liter (M). In addition, the Grahame equation

$$\zeta^2 = 8\epsilon\epsilon_0 k_B T \sinh^2[e\psi_0/2k_B T] \times n \quad (3a)$$

$$\zeta = 0.0132\sqrt{\epsilon} \sinh(\psi_0/51.4) \times C^{0.5} \quad (3b)$$

relates the surface potential, ψ_0 in (mV) in eq 3b to the surface charge density ζ (C/m^2).

Table 2 shows the values for the measured and theoretically estimated decay lengths, λ and κ^{-1} , using eq 2a and the measured values of ϵ and C_{eff} . Also shown are the measured surface potentials and surface charge densities calculated using eqs 1 and 3a. As can be readily seen, the measured decay lengths λ are much larger than the theoretically expected values κ^{-1} . The surface potentials ranged from 6 to 15 mV, and the surface charge densities from 0.06 to 0.15 e/nm^2 are below the maximum possible surface density of ~ 2 e/nm^2 for a fully ionized mica surface.²¹

Although the general features of the measured forces were very reproducible, some fine details were difficult to obtain in

TABLE 2: Experimental (Effective) and Theoretical Double-Layer Parameters for the Three Ionic Liquids Studied

IL	Debye length using eq 2a with $C=C_{\text{eff}}, \kappa^{-1}$ (nm)	measured Debye length, λ (nm)	measured surface potential using eq 1, ψ_0 (mV)	charge density using eq 3a, ζ (e/nm^2)
BMIM-TFB	0.07	3.8 ± 0.2	-12.2 ± 1.1	0.15 ± 0.02
BMIM-OTF	0.06	3.3 ± 0.2	-6.5 ± 0.6	0.06 ± 0.01
THTDP-Br	0.07	1.0 ± 0.2	-14.9 ± 1.4	0.06 ± 0.01

a systematic manner: During some experiments, we observed a few abrupt instability “jump-ins” of 1–2 nm on approach, and similar jump-outs on separation. These weak jumps occurred at separations below less than five to six molecular diameters (Figure 2a). Such jumps are characteristic of the oscillatory structural forces of confined finite-size liquid molecules, where the jump distances are close to the sizes of the molecules.²² Since the oscillations were superimposed on a strong and fairly steep exponential repulsion, it was difficult to accurately measure the oscillatory force–distance functions, as also previously noted by Christenson and Horn in their measurements of the structural forces of polar liquids.²³ Small oscillations might also indicate only a partial solidification of the (thick) films.

One of the most widely used analytical methods to describe electrolyte solutions is based on the Poisson–Boltzmann (PB) equation. However, as can be seen from Table 2, the PB equation does not appear to successfully describe the double-layer forces in ILs. As pointed out by others,²⁴ the unexpectedly large screening lengths of ILs may be attributed to one or more of the following:

(i) Steric effects due to the finite counterion, co-ion, and solvent size will tend to enhance the repulsion between two surfaces, analogous to the increased pressure of a van der Waals gas or the osmotic pressure of a solution due to the finite size (excluded volume) of the gas or solute molecules. Strictly, steric effects and molecular interactions should be considered together because, as the molecules get larger, the relative importance of the attraction decreases and eventually the force always becomes purely repulsive.²⁵ Our observation that ILs showed larger decay lengths than simple (point-charge) electrolytes might presumably be attributed to such finite size effects. Statistical mechanics calculations and molecular dynamics simulations have shown that the effective thickness of the electrical double layer increases with increasing counterion size.^{26–30} This is attributed to “lattice saturation”: since the counterions cannot pack too densely on the surface to screen a high surface charge density, they instead occupy several layers.³⁰ Thus, the effective thickness of the double layer grows with the potential. However, for mica exposed to aqueous electrolyte solutions, the fraction of dissociated surface charges is less than a few percent.²¹ When exposed to liquids such as ILs of even lower dielectric constant than water, the surface potentials and charge densities are expected to be even lower. Indeed, our results and analysis indicated that the surface charge density deduced from the force measurements was much lower than the maximum charge expected for mica, suggesting that the lattice saturation effects should be negligible in our system. However, the finite size effect might also influence the electrostatic screening behavior of ILs by other means. For example, ILs are both solute and solvent in our system, and an increase in the IL size increases the average charge separation between dissociated ions. That can, in turn, influence the effective Debye (screening) length, λ .

(ii) The relative screening contribution of ions might be reduced for benzene-like structures because aromatic ions are more mobile.³¹ With increasing charge delocalization, electrons are less strongly spatially located in the vicinity of the charge

center. This could explain why the two BMIM-X, containing delocalized charge, exhibited much longer decay lengths than the THTDP-Br IL containing no delocalized charge (this is in spite of BMIM-X being smaller than THTDP-BR).

(iii) Recent computer simulations and statistical mechanics models have indicated that one should find oscillatory decay behavior when the Debye length is comparable to the average ion size.^{28,31,32} Two types of oscillations can occur in such systems: one is in the charge density (electrostatic-dominated oscillatory decay) where the counterion and co-ion densities oscillate out of phase; the other is in the number density (core-dominated oscillatory decay) where the counterion and co-ion densities oscillate in phase.²⁴ The origin of the latter force can be understood in terms of the overlapping of the density distribution profiles of the liquid molecules from each surface. The density distribution of the liquid molecules from the liquid molecules from one surface has a decaying oscillatory profile, with a periodicity close to some characteristic dimension of the molecules. On the other hand, theory suggests that the periodicity is much larger in the electrostatic regime.²⁴ The charge oscillations correspond to alternating shells of positive and negative charge, and hence, the period in this case is at least twice the characteristic dimension of the molecules.²⁴ ILs also showed oscillatory trends as seen from the “jump-ins” in Figure 2a, which are one of the main characteristics of oscillatory forces. Although we observed some indications of oscillatory behavior (layering) in the forces, we were unable to distinguish these two types of oscillations due to experimental limitations of resolution when a strong exponential repulsion is superimposed on the oscillations. Horn et al.¹¹ measured forces between a much smaller ionic liquid, ethylammonium nitrate (EAN), at small separations and found out that oscillatory forces can be observed at smaller separations up to 2–4 molecular diameters. Likewise, Wakeham et al.³³ have recently used AFM to investigate the influence of temperature and molecular structure on various derivatives of ethylammonium nitrate (EAN) solvation layers. They found that the force measurements on dimethylethylammonium formate (DMEAF) showed only one oscillation, whereas EAN showed four to five oscillations. They suggested that layering is disrupted by increasing the bulkiness of the cations, which hinders packing into layers. Such steric effects related to molecular structuring can explain why we could only observe a few oscillations for BMIM-X and THTDP-BR, making forces mostly monotonic.

(iv) The surface charge that gives rise to the electric double layer when a surface is exposed to an electrolyte arises either from dissociation of ionizable groups on the surface or from preferential adsorption of ions from the electrolyte. In both cases, the charges are discrete, although for utilitarian reasons the double layer is almost always modeled with a uniform (smeared out) surface charge. The discreteness effects decay exponentially at a rate that is inversely proportional to their separation. For a periodic array of surface charges, the discrete contribution to the mean electrostatic potential decays as $\exp[-(G^2 + \kappa^2)^{1/2}z]$, where the smallest reciprocal lattice vector is related to the mean spacing between the surface charges, a , by $G = 2\pi/a$.²⁰ For the case of fixed charges, discreteness effects become negligible at

distances (surface separations) larger than the distances between the discrete changes on the surfaces.

(v) Fumino et al. have recently shown that strong and directional H bonds formed between cations and anions destroy the charge symmetry.³⁴ H bonds introduce defects into the Coulomb network of ILs and increase the dynamics of the cations and anions, resulting in decreased melting points and reduced viscosities. Such effects should also play a role in the forces observed in our experiments.

Comprehensive recent molecular dynamic simulations taking into account finite size, delocalization, and discreteness of charges on molten ionic fluids have shown that Debye-Hückel (DH) theory overestimates the ionic screening behavior of RTILs by about 2 orders of magnitude because of the aforementioned reasons.^{28,31,32} Specifically, Shim et al.³¹ estimated that the effective screening length is of the order of 1 nm for RTILs. Our findings are in good agreement with these recent simulations.

Conclusions

To sum up, we found that the forces between two atomically smooth mica surfaces across three different types of ILs are repulsive at all measured distances in all three cases, decaying exponentially with distance. Effective Debye (screening) lengths, λ , are found to be around 1–4 nm, in the order of molecular size, and strongly dependent on the size and molecular structure of the anion/cation. When the Debye length is comparable to the average ion size, in addition to the exponential repulsions, oscillatory forces are observed. However, any monotonically attractive van der Waals forces, if present, are overwhelmed by the repulsive electrostatic and oscillatory forces. All of these observations are in good agreement with recent comprehensive computer simulations taking into account size, strong coupling, and delocalizations.

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Supporting Information Available: Detailed explanation of SFA 2000 and experimental procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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