Long-range electrostatic screening in ionic liquids

Matthew A. Gebbie^a, Howard A. Dobbs^b, Markus Valtiner^c, and Jacob N. Israelachvili^{a,b,1}

^aMaterials Department, University of California, Santa Barbara, CA 93106; ^bDepartment of Chemical Engineering, University of California, Santa Barbara, CA 93106; and ^cInterface Chemistry and Surface Engineering, Max Planck Institut für Eisenforschung GmbH, 40237 Düsseldorf, Germany

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Electrolyte solutions with high concentrations of ions are prevalent in biological systems and energy storage technologies. Nevertheless, the high interaction free energy and long-range nature of electrostatic interactions makes the development of a general conceptual picture of concentrated electrolytes a significant challenge. In this work, we study ionic liquids, single-component liquids composed solely of ions, in an attempt to provide a novel perspective on electrostatic screening in very high concentration (nonideal) electrolytes. We use temperature-dependent surface force measurements to demonstrate that the long-range, exponentially decaying diffuse double-layer forces observed across ionic liquids exhibit a pronounced temperature dependence: Increasing the temperature decreases the measured exponential (Debye) decay length, implying an increase in the thermally driven effective free-ion concentration in the bulk ionic liquids. We use our quantitative results to propose a general model of long-range electrostatic screening in ionic liquids, where thermally activated charge fluctuations, either free ions or correlated domains (quasiparticles), take on the role of ions in traditional dilute electrolyte solutions. This picture represents a crucial step toward resolving several inconsistencies surrounding electrostatic screening and charge transport in ionic liquids that have impeded progress within the interdisciplinary ionic liquids community. More broadly, our work provides a previously unidentified way of envisioning highly concentrated electrolytes, with implications for diverse areas of inquiry, ranging from designing electrochemical devices to rationalizing electrostatic interactions in biological systems.

electrostatic interactions | intermolecular interactions |
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Electrolyte solutions are multicomponent liquids that are composed of ions (solutes) dissolved in a liquid phase (solvent), a classic example being salt water. Like any ideal mixture, the driving force for the dissolution of ions in electrolyte solutions is entropic. Unlike ideal mixtures, the long-range nature and high interaction free energy of the electrostatic interactions between ions ensures that the physical properties of all but the most dilute electrolyte solutions exhibit pronounced deviations from ideal behavior. These deviations primarily arise from the steric “crowding” of ions and the electrostatic correlation of ions, for example the formation of neutral ion pairs, both of which increase the range of electrostatic interactions, compared with ideal solutions (1). As a result, the development of a general conceptual picture of concentrated electrolyte solutions remains challenging. Nevertheless, electrolytes with high ionic concentrations are prevalent in biological systems (2) and technological applications, such as energy storage devices (3–5), so overcoming this challenge remains an important task.

In this work, we study room-temperature ionic liquids (RTILs), single-component liquids composed solely of ions, in an attempt to provide a starting point for a new conceptual understanding of electrostatic screening in concentrated electrolytes. Although RTILs do not have neutral solvent molecules separating the constituent ions, the high degrees of ion crowding and electrostatic correlations present in RTILs are expected to be fundamentally related to ion crowding and electrostatic correlations in highly concentrated electrolyte solutions (5). To date, thousands of RTILs have been identified with diverse physical properties that can be tuned via careful design of cation–anion

pairs (6). Although these properties are largely governed by the same strong coulombic interactions that underlie the 801 °C melting point of crystalline sodium chloride at atmospheric pressure, the large sizes and asymmetric charge distributions of RTIL ions suppress the formation of ordered crystals. Notably, the high thermal and electrochemical stabilities, negligible volatilities, and variable intrinsic ionic conductivities of many RTILs make them promising materials for numerous applications, including electric double-layer capacitors, batteries, and self-assembly media (3–10). Many of these applications depend critically on interfaces between charged surfaces and RTILs. Nevertheless, the fundamental characteristics of RTIL electric double layers remain an active area of research and discussion (5, 11).

A generally accepted picture is that the electric double layers formed by RTILs consist of ordered layers of cations and anions, with these perturbed ionic concentrations quickly approaching bulk distributions on the order of several ionic diameters (5). Much of this understanding was developed through nanoscale computational studies of coarse-grained ionic systems (5, 11–16) that are reminiscent of high-temperature molten salts. These studies predict that the electric double layers formed by RTILs should be short-range and exhibit pronounced charge density oscillations, similar to the screening behavior identified in pioneering work on molten KCl (15). Recent theoretical studies emphasize that complex ion ordering in RTILs can intimately depend on the electrochemical potentials of the charged surfaces (5, 17–19), but these studies have left intact the picture that the electric double layers formed by RTILs should be very short-ranged.

Experimentally, the short-range, surface-induced ordering of ions in RTILs has been confirmed with X-ray scattering experiments, atomic force microscopy (AFM) force measurements, and surface forces apparatus (SFA) measurements (17, 20–23), with these studies highlighting that the ordering of RTIL ions at surfaces exhibits many subtleties. For example, Atkin et al. (22) used AFM to demonstrate that gold electrode surfaces immersed

Significance

Liquid solutions with high concentrations of electrically charged ions are key elements of many energy storage technologies and are prevalent in biology. Nevertheless, they remain poorly understood. We study ionic liquids—liquids composed solely of ions—with the goal of providing a general picture of concentrated ionic solutions. Using molecular-scale experiments, we show that, surprisingly, less than 0.1% of the ions in ionic liquids are “free” to contribute to electrostatic screening, with the remainder “stuck” as neutral aggregates. Our temperature-dependent results provide fundamental guidance for designing high-performance ionic liquids for numerous applications. More broadly, we provide a novel way of envisioning concentrated ionic solutions with wide-ranging implications, such as elucidating the nanoscale properties of underwater bioadhesives and other self-assembled biomolecules.

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¹To whom correspondence should be addressed. Email: jacob@engineering.ucsb.edu.

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to access the entire range of “oscillatory” forces that were the focus of previous studies (21–23).

To ensure consistency with previous studies and to rule out large surface radii as the origin of the monotonic forces we report, we also prepared 1-cm-radius surfaces for a subset of experiments. These experiments exhibited quantitative agreement with the larger radius surfaces in the intermediate ranges of the force–distance profiles ($D > 5$ nm) and enabled us to measure pronounced nonmonotonic forces at surface separations of $D < 5$ nm. Representative results highlighting the short range nonmonotonic forces are presented in [Figs. S2](#) and [S3](#).

Analysis of Force–Distance Profiles. The lines plotted in Fig. 3 correspond to fits of a constant potential solution to the linearized Poisson–Boltzmann equation, Eq. 1, to the asymptotic long-range distance regime of each force profile, $D > 1.5 (\kappa^*)^{-1}$, where the equation is well approximated by a simple exponential decay (28, 29):

$$\frac{F}{R} = 2\pi E = \frac{8\pi e^2 n^*}{k_B T \kappa^*} \frac{\psi^2 (1 - \exp(-\kappa^* D))}{\exp(\kappa^* D) - \exp(-\kappa^* D)} \approx \frac{8\pi e^2 n^*}{k_B T \kappa^*} \psi^2 \exp(-\kappa^* D) \quad [1]$$

$$(\kappa^*)^{-1} \equiv \sqrt{\frac{\varepsilon \varepsilon_0 k_B T}{2n^*(q^*)^2}}, \quad [2]$$

where $(\kappa^*)^{-1}$ (meters) is the effective Debye length, n^* (meters⁻³) is the number density of effective charge carriers (free ions or coordinated aggregates of ions that behave as electrostatic monopoles, that is, “quasiparticles”), $q^* = ze$ (coulombs) is the effective carrier charge, $z = 1$ is the carrier valence, ψ (volts) is the diffuse double-layer potential of the mica surfaces, $\epsilon = 12.3$ for [C₂mim][NTf₂] and $\epsilon = 11.6$ for [C₃mim][NTf₂] is the (measured) low-frequency bulk dielectric permittivity (30), ϵ_0 (farads per meter) is the vacuum permittivity, T (kelvin) is the temperature, and k_B (joules per kelvin) is the Boltzmann constant. At distances of $D \leq (\kappa^*)^{-1}$, the $F(D)$ profiles deviate from the predictions of mean-field theory and exhibit nonmonotonic “oscillatory” features. The ranges and magnitudes of these

repulsive forces are consistent with previous work that attributed these oscillatory forces to the ordering of the RTIL ions next to charged mica surfaces, with the instabilities corresponding to the abrupt ejection of mixed layers of ions into the reservoir (21–25). Additional discussion of these short-range “oscillatory” forces is presented in [Supporting Information](#).

The average values of the fitting parameters obtained from analyzing force–distance profiles measured over multiple independent experiments are presented in Tables 1 and 2. The quoted uncertainties are based on statistical analysis of at least 15 different force profiles for each temperature, with a 95% confidence interval. Forces were also measured at intermediate and higher temperatures than those shown in Fig. 3. The average surface potentials, ψ , and interaction decay lengths, $(\kappa^*)^{-1}$, for all of the experiments are listed Tables 1 and 2, and the raw data used to calculate averages can be found in [Table S1](#) and [S2](#).

Based on the current literature, a mean-field theory describing the distributions of point charges would seem to be incapable of capturing the asymptotic decay behavior of the electric double layers formed by RTILs. Indeed, if every ion is assumed to independently contribute to electrostatic screening (i.e., full “dissociation”) then the room-temperature Debye lengths of the [C₂mim][NTf₂] and [C₃mim][NTf₂] RTILs used in this study should be on the order of 0.1 Å (calculated with $\epsilon = 1\text{--}10$), which is orders of magnitude smaller than the ionic sizes. However, we propose that the much larger interaction decay lengths that we measure across [C₂mim][NTf₂] and [C₃mim][NTf₂], $(\kappa^*)^{-1} = 6.6\text{ nm}$ and 7.5 nm (room temperature), respectively, are effective Debye lengths, where the effective ionic strength (activity) of the RTILs, n^* (meters⁻³), substantially differs from the total ionic concentration determined from the RTIL density and molar mass.

The effective Debye lengths that we report always exceed the accepted theoretical Bjerrum length, l_B (5), for $[C_2\text{mim}][\text{NTf}_2]$ and $[C_3\text{mim}][\text{NTf}_2]$ (4.6 and 4.9 nm at room temperature), Eq. 3,

$$l_B = \frac{e^2}{4\pi\epsilon\epsilon_0 k_B T}, \quad [3]$$

where e (coulombs) is the elementary charge, ϵ_0 is the vacuum permittivity, ϵ is the relative permittivity of each RTIL, k_B

Table 1. [C₂mim][NTf₂] average electrostatic parameters (Eqs. 1 and 2) and calculated activation energies (Eq. 4)

Temperature, K	Effective Debye length (κ^*) ⁻¹ , nm	Diffuse double-layer potential Ψ , mV	Activation energy E_a , k _B T
22	6.7 ± 0.1	90 ± 25	9.4
40	5.7 ± 0.1	100 ± 20	9.6
50	4.3 ± 0.5	90 ± 25	9.3
60	3.4 ± 0.2	100 ± 25	9.1

(joules per kelvin) is the Boltzmann constant, and T (kelvin) is the temperature. l_B is the distance beyond which electrostatic interactions between the free ions or quasiparticle domains are disrupted by thermal energy. Thus, our rescaled mean-field approach fulfills the fundamental requirement that $(\kappa^*)^{-1} > l_B$. For particles and/or length scales that are smaller than l_B , RTILs cannot be modeled using this approach.

As an extension of our recent “dilute electrolyte” analogy (24), we rationalize these measured effective ionic strengths by considering RTILs to behave as thermally dissociable dielectric fluids that are in equilibrium with a Boltzmann-distributed population of either free ions or quasiparticle “ions” (electrostatic monopoles) that exceed an RTIL specific activation energy, E_a . We are not suggesting that the RTIL ions form exclusive ion pairs where each ion coordinates with only one specific counterion; rather, we propose that the strong coulombic interactions between RTIL ions that drive local charge neutrality by causing each cation to be preferentially surrounded by anions (and vice versa) result in the bulk fluid behaving, for large ensembles, as a dipolar network. This picture is consistent with X-ray and neutron reflectivity measurements that independently establish that the strong electrostatic interactions between RTIL ions drive the ions to order into nanoscale bicontinuous cation–anion networks (31, 32). In our model, we use the measured bulk low-frequency dielectric permittivities of the RTILs, ϵ (30), to account for the dielectric behavior of this network. Thermally activated charge fluctuations, either free ions or correlated charge domains, then behave as (mathematical) point charges (Fig. 4), taking on the role of ions in the traditional Poisson–Boltzmann model for dilute electrolyte solutions.

As an example of the underlying physics, even a simple ion, such as K^+ , is, in reality, composed of highly correlated charged particles (protons and electrons), with the formal positive charge coming from one missing electron. Nevertheless, K^+ ions can be modeled as point charges for length scales (Gaussian surfaces) that are much larger than the angstrom-scale size of K^+ ions. For RTILs, the length scales (Gaussian surfaces) over which electrostatic screening in RTILs can be envisioned in terms of point charges need to exceed l_B (Fig. 4). This picture shares conceptual similarities with the “dressed ion” theory of electrolyte solutions (29), an exact statistical mechanical theory that uses charged quasiparticles to model the electrostatic interaction forces between surfaces that are immersed in (nonideal) primitive model electrolyte solutions. However, RTILs have yet to be fully analyzed within this framework.

The physical relevance of viewing bulk RTILs as thermally dissociable dielectric fluids is substantially strengthened by our observation that the measured effective Debye lengths, $(\kappa^*)^{-1}$, decrease as the temperature increases. In the absence of thermally

driven ion dissociation, double-layer interactions would increase in range at higher temperatures. Furthermore, several recent theoretical studies proposing that RTILs already behave as highly dissociated (uncorrelated) “electrolytes” at room temperature also appear to predict that the electric double layers formed by RTILs should increase in range with increasing temperature (5, 11). In contrast, our weakly dissociated “dilute electrolyte” model (24) predicts that the double layers formed by RTILs should decrease in range with increasing temperature, as we observe in the current study. Thus, these temperature-dependent measurements provide an unambiguous way to distinguish between the various models.

Calculation of Charge Carrier Activation Energies. Charge carrier activation energies of $E_a = 9.4 \pm 0.3$ k_BT for [C₂mim][NTf₂] and $E_a = 9.7 \pm 0.2$ k_BT for [C₃mim][NTf₂] were calculated from the Boltzmann distribution, Eq. 4:

$$n^* = n_{\text{tot}} \exp\left(\frac{-E_a}{k_B T}\right), \quad [4]$$

where n^* (meters⁻³) is the (measured) number density of effective charge carriers, n_{tot} (meters⁻³) is the total ionic concentration, as determined from the RTIL density and molar mass, and E_a is the charge carrier activation energy. E_a values are reported in units of k_BT with $T = 295$ K. The calculated values of E_a were found to be constant over the 22–75 °C temperature range studied, consistent with an electrostatic screening mechanism that is dominated by thermally excited charge carriers. This temperature independence is not expected to hold for substantially elevated temperatures. For extremely high temperatures ($T \geq 1,500$ K), the Bjerrum length would become smaller than the size of the RTIL ions, and n^* will approach the actual molar density of the RTILs. If this temperature limit could be reached without decomposing the RTIL ions, then RTILs should behave as fully “dissociated” ionic melts, as has been observed for high-temperature molten salts (5, 15).

These activation energies of $E_a = 9.4 \pm 0.3$ k_BT for [C₂mim][NTf₂] and $E_a = 9.7 \pm 0.2$ k_BT for [C₃mim][NTf₂] compare well with the activation energy of $E_a = 11$ k_BT that we determined for [C₄mim][NTf₂] (24) and follow the same trend as the dielectric permittivity for this [C₂mim][NTf₂], [C₃mim][NTf₂], [C₄mim][NTf₂] series of RTILs. Using our previous approach of estimating the charge carrier activation energy as the energy required to separate a reference RTIL ion pair within a bulk dielectric fluid also works well for these two RTILs (Eq. 5):

Table 2. [C₃mim][NTf₂] average electrostatic parameters (Eqs. 1 and 2) and calculated activation energies (Eq. 4)

Temperature, K	Effective Debye length (κ^*) ⁻¹ , nm	Diffuse double-layer potential Ψ , mV	Activation energy E_a , k _B T
22	7.4 ± 0.1	72 ± 9	9.6
32	6.6 ± 0.2	75 ± 7	9.7
45	5.5 ± 0.5	66 ± 4	9.8
74	3.5 ± 0.2	50 ± 11	9.5

explanation and provides a quantitative framework for estimating the activation energy of ion dissociation in aprotic RTILs, yielding additional insight into the electrochemical performance of RTIL-based capacitors. More broadly, we provide a molecular-scale framework that can be used to design RTILs with carefully tuned degrees of ionic association by judiciously balancing ion pair interaction energies with bulk dielectric properties.

Beyond RTILs, the general physical insight we offer is that the simple picture of dissociation equilibria between neutral ion pairs and dissociated ions that is often invoked to explain moderately concentrated electrolytes (1) needs to be refined for very highly concentrated electrolytes, where distinguishing between specific pairs of ions loses meaning. We instead propose that local excess charge densities fundamentally determine the length scales of electrostatic screening and show that a “dissociation reaction” between effectively neutral ionic networks and either free ions or higher-order correlated charge domains can provide a useful framework for understanding such systems. For example, recent SFA measurements across concentrated aqueous electrolyte solutions (38, 39) establish that the range of electric double-layer interactions increases as the aqueous electrolyte concentrations are increased from 1 to 3 M, but only as long as the electrolyte cation differs from the K^+ ion that is native to mica surfaces. Our results suggest that this trend may be due to the progressive formation of effectively neutral ionic networks involving large numbers of strongly interacting ions. Over the longer term, our results may also prove useful for deciphering how electrostatic interactions maintain such a dominant role near the active sites of proteins, ion channels, and similar self-assembling biological systems (2), where local effective salt concentrations can exceed 10 M.

Materials and Methods

The $[C_2mim][NTf_2]$ and $[C_3mim][NTf_2]$ samples were clear and colorless, and NMR, UV-visible spectroscopy, and electrochemical analysis were used to establish that the RTILs were of electrochemical-grade purity. After synthesis and drying, Karl Fischer titration was used to ensure that the (trace) water content of the $[C_2mim][NTf_2]$ and $[C_3mim][NTf_2]$ RTILs was under 15 ppm, and the samples were stored under vacuum at all times.

Before each SFA experiment, the $[C_2mim][NTf_2]$ and $[C_3mim][NTf_2]$ samples were dried under vacuum at 373 K for at least 72 h. After drying, a droplet of RTIL (50–100 μ L) was immediately injected between mica surfaces in a gas-tight SFA under dry nitrogen purge conditions, and the SFA was resealed. All experiments were performed in the presence of a reservoir of the desiccant phosphorous pentoxide (P_2O_5). Each experiment lasted between 24 and 72 h, and the P_2O_5 reservoirs were found to be unsaturated at the conclusion of each experiment.

The temperature was monitored during each experiment via a thermistor with a 0.2 °C tolerance. The thermal expansion of mica was accounted for by calibrating the mica thermal expansion in the absence of RTIL samples. The mica thermal expansion coefficient was found to be $1.5 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$, in agreement with literature values.

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