

Spotlight on ionic liquids

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Spotlight on ionic liquids

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Ionic liquids are an emerging class of materials with a diverse and extraordinary set of properties. Understanding the origins of these properties and how they can be controlled by design to serve valuable practical applications presents a wide array of challenges and opportunities to the chemical physics and physical chemistry community. We highlight here some of the significant progress already made and future research directions in this exciting area. © 2010 American Institute of Physics. [doi:10.1063/1.3373178]

INTRODUCTION

The explosion of interest in ionic liquids (ILs) continues apace, both because they lead to fascinating chemical physics problems and because of the multiplicity of their uses. The realization that task-specific ILs can be created via simple and systematic chemical modifications of the constituent ions takes these systems beyond the promise of designer solvents to highly useful systems for diverse applications including drug delivery and as active pharmaceutical ingredients,^{1–3} solvents for green processing of otherwise insoluble biomolecules such as cellulose,^{4,5} highly energetic materials,¹ and novel electrolytes for energy applications such as batteries, fuel cells, and solar photoelectrochemical cells.^{6–9}

Plechkova and Seddon¹⁰ estimated that there may be in excess of 10^6 possible ILs if all currently known IL cations and anions were to be paired, and as many as 10^{18} if all ternary systems were to be investigated. The history of ILs predates even the early report of the room temperature IL ethylammonium nitrate by Walden¹¹ in 1914. Since that time, a great deal of work has been done on high temperature molten salts, especially alkali and alkaline earth halides. Current usage is to call salts with melting temperatures below 100 °C ILs. Indeed, a large number of ILs melt well below ambient temperatures, with typical glass transition temperatures in the range from 180 to 220 K. While high-temperature molten salts are usually metal halides, popular ILs often comprise organic cations paired with organic or inorganic anions. Cations and anions that are commonly used in recent generations of ILs are shown in Fig. 1.

Excellent reviews on molten salts are available.^{12–14} Research on high-temperature molten salts continues, motivated both by advances in chemical physics methods and by cross fertilization between the IL and molten salt communities. Molten salts may play important roles in nuclear energy, possibly as liquid fuel systems or as media for electrorefining of spent nuclear fuel. Structures of molten salts have been

widely investigated both experimentally using scattering methods,^{12–14} as well as using classical^{15–19} and quantum methods molecular dynamics (MD) simulations.^{20,21}

The popularity of ILs as a research topic is reflected in the numerous reviews,^{1,10,22} monographs,⁶ and conference proceedings^{23–25} that have been published recently. The reviews by Hamaguchi and Ozawa²⁶ and Kobrak,²⁷ as well as several journal special issues^{28–30} have focused primarily on the physical chemistry and chemical physics of ILs.

IL STRUCTURE

The structure of ILs plays a key role in so many of the interesting and useful ways that their properties depart from those of conventional solvents. Their binary, Coulombic nature imposes a degree of order on the short-range scale and their amphiphilic combination of polar and nonpolar components leads to different types of correlations on longer scales. Some important recent revelations about IL structure are described below, but the area remains a fertile ground for new discoveries with important applications.

It is well known that high-temperature molten salts display charge ordering in the liquid pair distribution functions. Specifically, the structure of cation-cation and anion-anion peaks and valleys in the pair distribution are diametrically out of phase with the cation-anion pair distribution.^{12–14} MD

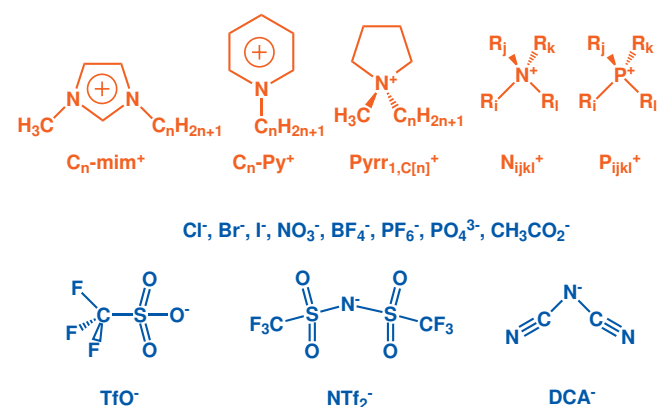


FIG. 1. Chemical structures for common IL cations (red) and anions (blue).

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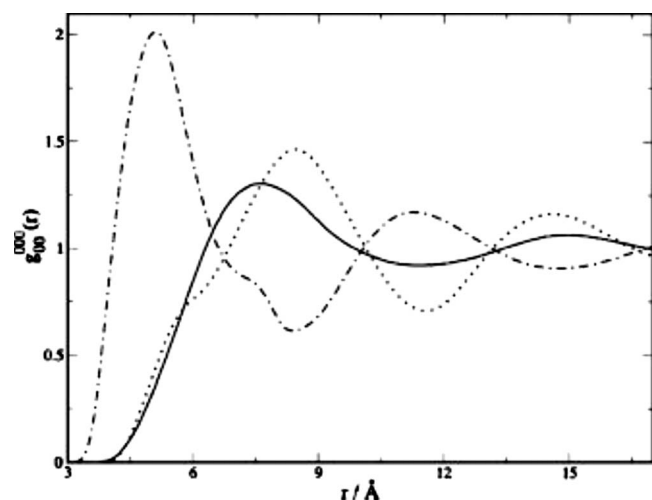


FIG. 2. Charge-ordered ion structure in liquid $[\text{bmim}]^+ / [\text{CF}_3\text{SO}_3]^-$. Pair distribution functions $g_{00}^{00}(r)$ are plotted for cation-cation (solid line), anion-anion (dotted line), and cation-anion (dash-dotted line). Reprinted from Schröder *et al.*, J. Chem. Phys. **127**, 044505 (2007). Copyright 2007, American Institute of Physics.

simulations of ILs also display similar charge-ordering, though the anticoincidence between the cation-anion and self-ion peaks in the pair distribution function are usually not as cleanly defined in systems with larger, flexible cations and anions compared with alkali halides. The charge ordering characteristics of ILs are illustrated in Fig. 2 for the pair distribution function of 1-butyl-3-methylimidazolium triflate $[\text{bmim}]^+ / [\text{CF}_3\text{SO}_3]^-$ from the simulations by Schröder *et al.*³¹

Neutron and x-ray scattering and diffraction have provided great insights into the structure of ILs. Neutron diffraction experiments coupled with empirical potential structure refinement methods were applied to 1,3-dimethylimidazolium chloride ($[\text{mmim}]^+ / \text{Cl}^-$) by Hardacre *et al.*³² Figure 3 shows the spatial density function for a Cl^- anion near the $[\text{mmim}]^+$ cation. A comparable density distribution obtained from MD simulations for $[\text{bmim}]^+ / \text{Cl}^-$ (Fig. 4) shows the effect of the volume swept out by the butyl group (compared to methyl, Fig. 3) and demonstrates the sensitivity of IL interactions to alkyl group substitution.^{33–35} Such intricate details of IL structure have been picked apart by careful analysis and examination of

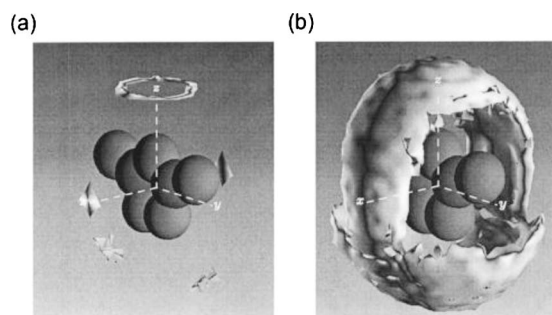


FIG. 3. Neutron diffraction structure of liquid $[\text{mmim}]^+ / \text{Cl}^-$. Graph from Hardacre *et al.*, J. Chem. Phys. **118**, 273 (2003). Copyright 2003, American Institute of Physics.

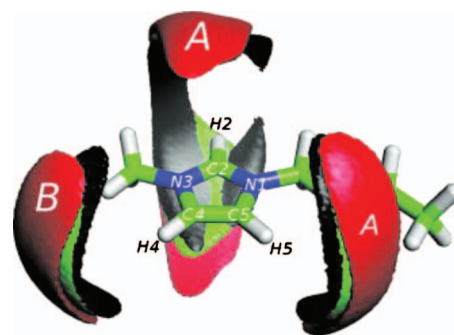


FIG. 4. Simulation of the liquid structure of $[\text{bmim}]^+ / \text{Cl}^-$. Graph from Schröder *et al.*, J. Chem. Phys. **125**, 244506 (2006). Copyright 2006, American Institute of Physics.

structure factors and higher-order correlation functions obtained from molecular dynamics simulations.^{31,33–37}

Structural heterogeneity in ILs

One of the most striking findings about ILs has been that they can display remarkable structural heterogeneity. Self-aggregation effects between alkyl tails can lead to strongly ordered local environments, even for alkyl chains as short as butyl. MD simulations by Wang *et al.*³⁸ and by Canongia Lopes and Pádua^{39,40} presented convincing evidence of this nanostructural organization, which was corroborated by x-ray experiments from Triolo and coworkers.^{41,42} In the intermediate range x-ray scattering, so-called “prepeaks” occur in the scattering vector range of 2–5 nm^{-1} for ILs having 1-alkyl-3-methylimidazolium cation paired with several anions, ranging from small spherical Cl^- anions to pseudo-spherical $[\text{BF}_4]^-$ and $[\text{PF}_6]^-$.⁴¹ These prepeaks correlate with domain sizes ranging from 14 Å for $[\text{bmim}]^+ / [\text{PF}_6]^-$ to 26 Å for 1-decyl-3-methylimidazolium $[\text{BF}_4]^-$,⁴¹ with similar bilayerlike aggregation behavior observed for ILs in which the imidazolium cations are paired with other anions.^{41,42}

Triolo *et al.*⁴³ subsequently showed that other modes of self-interaction between alkyl substituents on the ions also occur. The nature of this self-aggregation is critically dependent on the precise chemical nature of the component ions. Results from the x-ray scattering on N-alkyl-N-methylpiperidinium ILs are shown in Fig. 5, demonstrating a smaller domain size consistent with interdigitated alkyl chains rather than bilayerlike domains. Results for a number of ILs having the $[\text{NTf}_2]^-$ anion paired with nonaromatic ammonium cations show that while evidence for aggregation occurs, bilayerlike structures are not observed for these liquids.^{44–46} In particular, the x-ray scattering prepeak structures in methyl-trialkylammonium $[\text{NTf}_2]^-$ ILs are interpreted as arising from short-range hydrophobic interactions of the trialkyl groups in structures that look more interdigitated than bilayerlike.⁴⁶ Nanostructural organization has been observed in ILs having relatively small ions, such as propylammonium nitrate.⁴⁷

Structural heterogeneity underlies all the aspects of the chemical physics of ILs, including solvation, dynamics, and transport. It remains a very vibrant area of theoretical and experimental study. For example, understanding the role of the anion-cation interactions in modulating side-chain aggre-

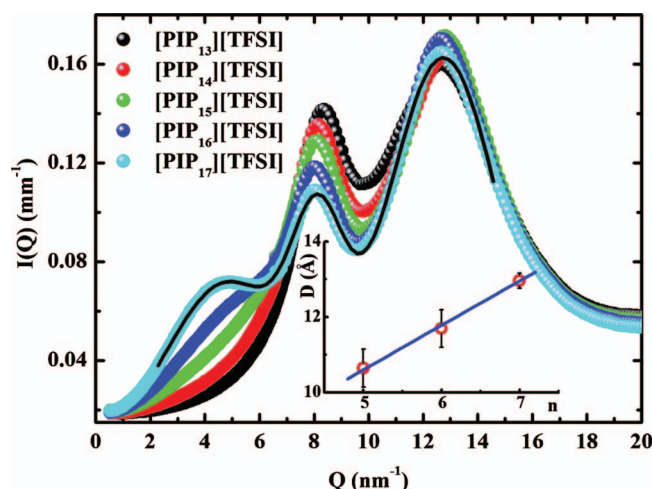


FIG. 5. X-ray scattering for a series of N-alkyl-N-methylpiperidinium ILs; note that the [TFSI] anion is also called [NTf₂][−] by other authors. Graph from Triolo *et al.*, J. Chem. Phys. **130**, 164521 (2009). Copyright 2009, American Institute of Physics.

gation and controlling the nature of the nonpolar domains has important applications in industrial separations chemistry including gas separation and carbon capture, and in IL-based catalytic systems.

THERMAL PROPERTIES OF ILs

By design, ILs have unusual thermal properties and phase behavior because their anions, cations, and side chains have been selected to make their crystalline forms weakly bound and hence low melting. Molecular asymmetry, size mismatch between ions, charge delocalization, side-chain elaboration, and fluorine substitution are among the most popular methods used to invent new ILs. The result is often an interesting combination of nonspecific interactions and ensembles of specific interactions of roughly equal strength, leading to glassy systems that frequently persist as deeply supercooled liquids instead of crystallizing. It is common to find experimental data on the fluid properties of ILs below their melting points. Some ILs do not crystallize unless they are warmed from very low temperatures (“cold crystallization”) and others have no apparent melting point at all, remaining fluid down to their glass transition temperature.

The phase behaviors of ILs that do crystallize are often complex, as differential scanning calorimetry (DSC) and x-ray diffraction (XRD) data have revealed several intermediate solid-solid phase transitions as the crystals are warmed from low temperatures, with each successive phase showing more side-chain disorder as revealed by XRD.⁴⁸ In some cases, most notably [Pyr₁₄]⁺/[NTf₂][−], crystals formed far from equilibrium are metastable with respect to annealed ones and they melt at lower temperatures.⁴⁹ Elegant work by Endo and coworkers^{50,51} using very sensitive and slow DSC scanning, coupled with Raman spectroscopy, have shown that the dynamics of cooperative change between side chain conformers complicate the crystallizing and melting processes, contributing to the complex thermal behaviors of ILs. MD simulations by Jayaraman and Maginn⁵² on crystalline

isomorphs of [bmim]⁺/[PF₆][−] provide support for the role of alkyl chain conformational exchange in the crystallization transition.

The field of IL thermal phase behavior is still largely in the discovery period, but it has already provided some important lessons about how dynamical processes such as conformational interchange affect phase transitions. The unusual properties of ILs, and the ability to design them to answer specific research questions, allows them to serve as a testbed for further investigations into phase transition dynamics.

VISCOSITY AND TRANSPORT IN ILs

Viscosities and conductivities for glass-formers depend strongly on the values of the glass transition temperature T_g . For a homologous series of 1-alkyl-3-methylimidazolium [BF₄][−] ILs, the T_g values increase as the alkyl chain length increases from butyl to decyl, while the corresponding fragility parameters decrease over the same range.⁵³ It is clear that IL fragilities depend strongly on the nature of the anion.⁵⁴ Li *et al.*⁵⁵ have sought to connect the observed viscosities to the ion structure, in particular by characterizing the *charge lever moment* of the ions.

IL viscosities are most often fit to the empirical Vogel–Fulcher–Tammann equation, which is equivalent to Arrhenius temperature dependence only in the high-temperature limit. Roland *et al.*⁵⁶ have shown that like other glass-forming materials, IL viscosities scale with molecular volume as $\eta \propto 1/(TV^\gamma)$ where the scaling exponent γ spans the range from 2.25 to 2.9.

As mentioned above, when ILs are cooled they display thermal and transport properties that are similar to other glass-forming materials. Thus, a number of ILs show transport properties that are inconsistent with hydrodynamic scaling. Instead of observing self-diffusion coefficients that are linearly proportional to the temperature-to-viscosity ratio, a fractional power law behavior is observed, where $D \propto (T/\eta)^\alpha$, where $\alpha < 1$.⁵⁷ This trend has been observed for a series of ILs that were also reported to be very fragile glass-formers.⁵⁸ Self-diffusion coefficients of photochemically generated CO were reported in both molecular solvents, including alkanes and alcohols, as well as in typical ILs including [bmim]⁺ cations paired with [NTf₂][−], [BF₄][−] and [PF₆][−].⁵⁹ Figure 6 plots the self-diffusion of CO following photodissociation. Fractional Stokes–Einstein behavior is observed with the exponent $\alpha = 0.68$.⁵⁷

A primary means to measure self-diffusion in fluids is the pulse-gradient spin-echo (PG-SE) NMR method. In most cases, the ¹H or ¹⁹F NMR signals for IL species can be used to uniquely measure the self-diffusion of both the cation and anion species in ILs as a function of temperature.^{60–64} By comparing the single-particle self-diffusion coefficients measured using PG-SE. NMR experiments with the bulk conductivity, Watanabe’s group estimated the effective fraction of ions that undergo diffusive transport as single ions relative to those ions that diffuse as aggregates. It now seems generally accepted that the cations and anions in ILs may aggregate into clusters that are at least metastable. Mechanistically, this might be a consequence of the polar/nonpolar domain

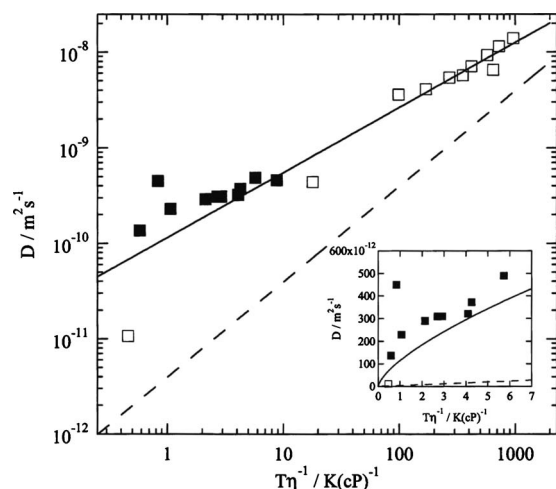


FIG. 6. Self-diffusion of CO in molecular solvents (open symbols) and ILs (filled symbols). The dashed line is the prediction from the Stokes–Einstein hydrodynamic law. Graph from Nishiyama *et al.*, J. Chem. Phys. **128**, 164514 (2008). Copyright 2008, American Institute of Physics.

heterogeneity of ILs. A specific test comparing self-diffusion from NMR measurements compared with electrical mobilities from dielectric spectroscopy and conductivity measurements claims that there is no evidence for any mode arising from reorientation of stable ion pairs, indicating that lifetimes for ion clusters must be shorter than reorientational time scales.⁶⁵

Molecular dynamics simulations have provided a wealth of information regarding transport in ILs, yet there does not seem to be a general rule for understanding ion transport in these systems. Certainly, Stokes–Einstein hydrodynamic scaling is frequently not observed. Because of specific interactions, larger [bmim]⁺ cations can have faster self-diffusion than smaller Cl[−] anions.⁶⁶ A more detailed study of series 1-alkyl-3-methylimidazolium cation ILs considered a range of anion sizes from F[−] to I[−] and [PF₆][−]; these larger cations showed faster self-diffusion than the anions.⁶⁷ Ongoing research will help to unravel whether the amphiphilicity of the cation facilitates its diffusion relative to compact, charge-dense anions.

SOLVATION AND SOLVATION DYNAMICS IN ILs

The cationic and anionic components of ILs offer a wide range of chemical and physical properties that can be independently tuned to provide a wide variety of molecular environments. The cationic charge can be localized as in ammonium or phosphonium cations, or delocalized as is the case for imidazolium and pyridinium cations. In addition to the contribution of the charges to the total electrostatic energy, the effective dipole moments play a substantial role.³⁷ Typical ions that form ILs are often highly polarizable. Functional groups can range from alcohols that provide strong H-bond interactions to strongly dipolar alkylcyano groups. Another alternative is to add alkyl or perfluoroalkyl groups to IL cations or anions to thereby minimize charge- and higher-order electrostatic interactions in favor of van der Waals interactions. These effects have been addressed in a number of articles describing MD simulations of

ILs.^{31,33,68–77} Madden and Kobrak have each addressed charge interaction effects in ILs quite specifically, taking care to define the appropriate coordinate system in which to calculate the electrostatic energies of the ions.^{27,37,55,68,78–80} Shim *et al.*^{69–74} reported several studies of both equilibrium and nonequilibrium solvation, orientational dynamics, vibrational relaxation, and electron-transfer reactions in [emim]⁺/[PF₆][−]. Song⁷⁷ has presented a method to extend dielectric continuum models for solvation to include precise molecular shapes and an extension beyond the Debye–Hückel model for high concentrations of charges, up to neat ILs. Because of the greater number of possibilities in the binary IL systems, it will be necessary to develop a battery of methods ranging from course-grained MD simulations to full quantum methods.

Heterogeneous solvation dynamics

Time-resolved fluorescence experiments are frequently used to characterize both the reorientational dynamics and the solvation dynamics that result after photoexcitation of a strongly dipolar, solvatochromic probe molecule such as 4-aminophthalimide, prodan or coumarin 153.⁸¹ The review by Samanta provides an excellent entry point into this literature,⁸² which is also addressed in other reviews.^{27,83} Early experimental results did not always agree, in part because the solvent relaxation dynamics are strongly heterogeneous. For typical ILs, solvation dynamics at room temperature occur on time scales ranging from less than 100 fs to more than 10 ns.^{84,85} As sample temperatures approach T_g , solvation dynamics in ILs extend to time scales of seconds.⁸⁶ When the experimental time window used in the spectroscopic measurement does not include either end of this time scale, fits to various nonexponential relaxation models will not agree. The ultrafast part of the solvent relaxation at hundreds of fs is more challenging to resolve for ILs than for neutral organic solvents because the former have viscosities that are typically 2–3 orders of magnitude larger. Thus, only a few research groups have reported the sub-ps solvation dynamics in ILs.^{84,87,88} One significant reason to fully characterize the solvation dynamics in ILs is to determine whether chemical reactions such as photoinduced electron-transfer reactions are influenced by solvent reorganization on time scales extending to nanoseconds, as is often the case for neutral dipolar solvents on faster time scales.

For lower temperatures and higher viscosities, the broad distributions of rates for solvation dynamics in ILs cause the average solvation time scale to become longer than the excited-state lifetime of the solvatochromic probe. This leads to red-edge excitation effects. For example, Samanta⁸² found that the maximum emission frequency for fluorescence of 2-amino-7-nitrofluorene (ANF) depends strongly on the excitation wavelength. Hu and Margulis⁸⁹ simulated the spectroscopy of ANF in [bmim]⁺/[PF₆][−] and reproduced the observed red-edge excitation effect.

Such dynamic heterogeneity for photochemical and photophysical systems in ILs is not surprising given that dynamic heterogeneity has been widely observed in MD simulation of pure ILs. Del Pópolo and Voth⁹⁰ noted this effect,

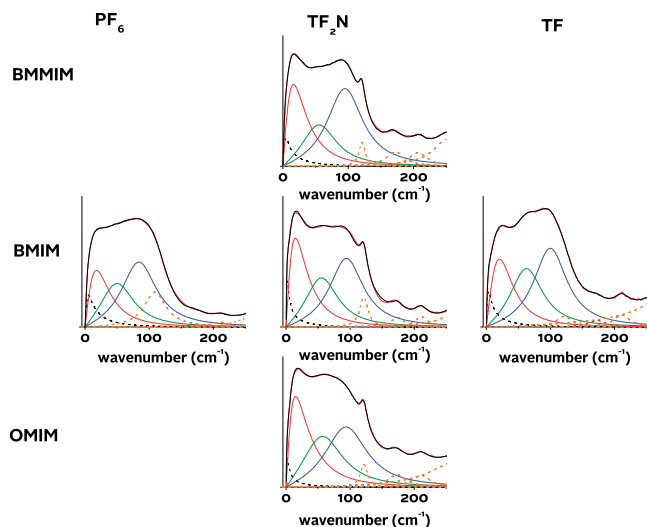


FIG. 7. Low-frequency Raman spectra of two series of ILs: The $[\text{NTf}_2]^-$ anion paired with $[\text{bmmim}]^+$, $[\text{bmim}]^+$ and $[\text{omim}]^+$; and the $[\text{bmim}]^+$ cation paired with $[\text{PF}_6]^-$, $[\text{NTf}_2]^-$ and $[\text{CF}_3\text{SO}_3]^-$. The sharper features correspond to intramolecular modes of the anions and cations. Graph from Giraud *et al.*, J. Chem. Phys. **119**, 464 (2003). Copyright 2003, American Institute of Physics.

and Hu and Margulis⁹¹ reported non-Gaussian mean-square displacements of the ions as a hallmark of the dynamic heterogeneity. Furthermore, when Habasaki and Ngai⁹² quantified heterogeneous dynamics in their MD trajectories for $[\text{emim}]^+/\text{NO}_3^-$, the ions were found to be both dynamically localized and capable of rapid diffusive jumps.

The observation of heterogeneous dynamics in excited state photophysical processes, including the time-resolved emission shift observed for solvatochromic fluorescence probe molecules, means that great care must be exercised in designing, executing, and analyzing any experiment that can be sensitive to such effects. In particular, the observation of the “red-edge effect” requires that multiple excitation and emission energies be measured over the shortest to the longest time scales in any time-resolved photophysics or photochemistry experiment to ensure that the reported dynamics are truly global and not representative of only a small subsection of the molecular ensemble.

INTERMOLECULAR INTERACTIONS AND SPECTROSCOPY IN ILs

Because of the binary and heterogeneous natures of ILs, intermolecular vibrational and reorientational dynamics are of particular interest. These have been studied by several spectroscopic techniques, including low-frequency Raman spectroscopy,⁹³ femtosecond optical heterodyne-detected Raman-induced Kerr-effect spectroscopy (OHD-RIKES),^{42,83,94–100} and terahertz spectroscopy.^{101,102}

The OHD-RIKES low-frequency spectra depicted in Fig. 7 are typical for ILs.⁹⁶ As with polar solvents, strong electrostatic caging effects lead to molecular librations of the ions with peak frequencies near 50 cm^{-1} . Spectral features with maxima near 15 cm^{-1} are often attributed to translational dynamics for both molecular solvents and ILs.^{94,96–98}

If the cation in a series of ILs is held constant, changes in the low-frequency spectrum upon anion substitution illustrate the differences in the strength and specificity of anion-cation interactions, as shown in Fig. 7. Another illustration of the effect of the nature of the anion on intermolecular vibrational dynamics was reported by Shirota *et al.*⁹⁸ among the series of ethoxyethyl-methyl-pyrrolidinium $[\text{N}(\text{CN})_2]^-$, Br^- , and $[\text{NTf}_2]^-$ ILs, where the interionic interactions of the $[\text{NTf}_2]^-$ anion were clearly weaker than the other two, consistent with the observed viscosities and orientational relaxation.

Several researchers have examined heterogeneous inter-MD in ILs. Such dynamics arise because higher-viscosity ILs do not average their environments as rapidly as for typical organic solvents and water, and also because the ILs themselves present a greater multiplicity of persistent polar and nonpolar environments. Both the cations and anions in ILs are shown to present multiple conformations in solution,²⁶ in addition to the longer-range nanostructural organization that is present in these fluids. The slower parts of the intermolecular relaxation spectrum have been meticulously characterized by the Fayer group. They observed multiple power-law relaxations that occur prior to the onset of the α -relaxation, in accordance with predictions from mode coupling theory.^{95,99} How the nanostructural organization affects the dynamical environment in ILs has been probed by Xiao *et al.*¹⁰⁰ They used the CS_2 probe at low concentrations to probe the intermolecular line shapes in ILs. The fs OHD-RIKES results of Xiao *et al.*¹⁰⁰ for solutions of CS_2 in the IL 1-pentyl-3-methylimidazolium $[\text{NTf}_2]^-$ provide convincing evidence that the non-dipolar CS_2 localizes in the nanostructured domains of the self-aggregated pentyl chains.

Intermolecular spectroscopy will continue to be a useful method to investigate the heterogeneous dynamics in ILs. A fundamental question is whether there must always be a connection between structural heterogeneity and heterogeneous dynamics, or whether the binary nature of ILs and their propensity to behave as supercooled liquids is a sufficient reason for the existence of such dynamics. Application of recent multidimensional optical spectroscopy methods that probe the response of the solvent to a photoinitiated dynamical event^{103–106} will likely provide useful insights to such questions.

IL INTERFACES

Many of the important chemical applications of ILs will occur at interfaces, including electrochemical processes at the IL-electrode interface and at the interface between polymer and electrolyte in fuel cell membranes. A wide variety of experimental, theoretical, and simulation methods have been applied to the study of ILs at interfaces.^{107–122}

Santos and Baldelli¹¹² have used interfacial sum-frequency generation (SFG) to show that at IL interfaces with gases or vacuum, alkyl chains on either the cations or the anions extend from the surface into the gas or vacuum. Rutherford backscattering spectra for the $[\text{bmim}]^+/\text{PF}_6^-$ -vacuum interface also show the cation butyl group protruding from the bulk liquid into vacuum.¹¹³ SFG measurements at the air-IL interface¹¹⁸ showed that for

longer alkyl chains, the number of gauche defects on this cation substituent decreased relative to short chains. This is in contrast to the substantial fraction of gauche defects on bulk alkyylimidazolium cations in ILs deduced from Raman spectroscopy.²⁶ Similar gauche defect reduction was seen in SFG studies of short-to long-chain 1-alkyl-3-methylimidazolium salts at the SiO₂ interface.^{116,117}

The structure of the IL-vacuum interface for [emim]⁺/NO₃⁻ was reported by Yan *et al.*¹¹⁹ Surface tension and thickness of IL-vapor interfaces have been reported from both simulations¹²⁰ and experiment.¹²¹ By accounting for both capillary waves and zero-point motions, the underlying structure of the IL surface has been determined by comparing MD simulations with x-ray reflectivity experiments.¹²²

The ordering of ILs at solid surfaces is also a subject of intense research activity. Atkin and co-workers^{107,108} applied atomic force microscopy (AFM) to ILs on mica surfaces; they found that 3–6 solvation layers of IL form between the AFM tip and the mica surface depending on the nature of the IL. X-ray reflectivity experiments on [bmim]⁺/[BF₄]⁻ and [bmim]⁺/[PF₆]⁻ provide details of the IL layering behavior at charged sapphire surfaces.¹¹⁴ MD simulations of [bmim]⁺/[PF₆]⁻ at a planar graphite surface showed that the preferred orientation of the aromatic cation is flat on the surface.¹¹⁵ Rivera-Rubero and Baldelli¹¹¹ used SFG to detect the reorientation of [bmim]⁺ cations at a Pt electrode as the potential was varied, and the effects are different depending on whether the anion is [BF₄]⁻ or [PF₆]⁻. The cation-metal surface interaction is extremely important in electrodeposition processes such as occur in batteries or electroplating. Abedin and Endres¹⁰⁹ have shown how the choice of cation causes profound differences in the morphology of electrodeposited metals. Recently, *ab initio* calculations have been applied to understand the interactions of [emim]⁺/[BF₄]⁻ with a Li(100) surface as a model for a lithium-ion battery electrode.¹¹⁰ Lithium batteries are a very important potential application of ILs; however due to the general utility of ILs for electroplating, a great deal is to be gained if comparable calculations are also carried out on a variety of metal surfaces with a wide range of cation types.

REACTIVITY IN ILs

ILs have received a lot of attention as reaction media and as electrolytes for devices that transport charge to collect solar or mechanical energy, to store energy in batteries or supercapacitors, or to efficiently utilize energy in actuators or displays.²² Much has been published on the different ways that ILs influence organic reaction pathways, the reactivities of metal catalysts, and the resulting product yields and distributions that potentially have far-reaching economic impact.^{123,124}

Underlying the largely empirical survey studies of products and yields, there are rich territories of specific solvation and dynamical effects controlling these reactions in ILs that have been largely unexplored by chemical physicists. Because of the diverse environments available in ILs, the range and tunability of these effects is much larger than in conventional solvents, and the value of being able to understand,

predict, and control them is very high. Pioneering work in this area was reported by Arantes and Ribeiro¹²⁵ in 2008. They used hybrid quantum-mechanical/molecular-mechanical simulations to model nucleophilic substitution reactions of halides toward the aliphatic carbon of methyl *p*-nitrobenzenesulfonate in [bmim]⁺/[PF₆]⁻. In this system, their calculations showed that the reaction is slower in the IL due to stabilization of the halide anion reactant relative to the delocalized charge of the transition state. Conversely, it is reasonable to expect that reactions with transition states that create or localize charge might become faster in ILs. The magnitude of the effects will depend on the specific ions involved.

Electron and hole transport in ILs

The high conductivity, low volatility, and large liquidus range typical of ILs make them useful in devices that depend on the transport of electrons for energy capture and storage. It is therefore important for improving our energy future to understand the effects of the IL environment on charge transport reactions. The problems are extremely complex due to many factors discussed in the preceding sections—structural and dynamical heterogeneity, time scales for solvent reorganization dynamics that overlap and extend beyond the electron transfer timescale in question, dramatic differences in equilibrium solvation environments depending on redox state, polaron-ion interactions in molecular wires, etc. Regardless, the challenge must be undertaken in order to reap the maximum benefit from this new technology. The advances in our knowledge of IL structure, solvation of redox species,¹²⁶ and solvation dynamics enumerated above are important foundations for understanding charge transfer reactions and charge transport in ILs.⁷⁴

Electron transfer reactions, in solution and at electrode surfaces, are useful tools for exploring the complex and charge-dependent diffusional behavior of solutes in ILs. As mentioned above, electrochemical studies have demonstrated that identical solutes with different charge types (e.g., O₂ and O₂⁻) have widely different diffusion coefficients depending on the IL and size of the solute.^{127,128} Several research groups have observed bimolecular rates for electron-transfer reactions that are faster than would be predicted by standard diffusion-limited rates calculated from shear viscosity, molecular sizes and temperatures using the Smoluchowski equation. Using neutral electron-donors such as dimethylaniline, both Paul and Samanta¹²⁹ and Vieira and Falvey¹³⁰ observed fluorescence quenching rates that were 2–4 times the diffusion-limited reaction rates predicted on the basis of viscosity. In 2002, McLean *et al.*¹³¹ reported the energy transfer reaction between triplet benzophenone and naphthalene to be ten times faster than predicted. Skrzypczak and Neta¹³² demonstrated that the anomalously fast electron transfer reactions of pyridinyl radicals in mixtures of ILs were due to faster-than-predicted diffusion of the neutral radicals instead of the mechanism of electron hopping between cations originally proposed after the first experimental observations.

These apparently anomalous diffusion rates for neutral solutes can be rationalized on the basis that the viscosity

depends on the diffusion of the ionic constituents of the IL, whose movements are electrostatically coupled to their neighbors. On the other hand, neutral solutes are not as strongly coupled to their neighbors and may sample less polar, lower friction nanoenvironments, resulting in faster diffusion. The effects can also occur in the opposite direction—Quinn *et al.*¹³³ predicted viscosities 3.4 times higher than were observed for two ILs based on electrochemically obtained diffusion coefficients for the divalent $\text{Ru}(\text{bpy})_2^{2+}$ cation. Pulse radiolysis studies have shown that the diffusion-limited reactions of (anionic) solvated electrons with aromatic molecules in ILs are slower than those of neutral hydrogen atoms with the same substrates, reversing the trend observed in regular solvents.^{134,135}

Elucidation of the principles controlling transport and reactivity of charged and neutral species in ILs can lead the way to directing reactivity along desired paths, exploiting the phenomena for energy collection and storage, and in highly selective IL membrane-based separations processes.

Heterogeneity of reaction dynamics in ILs

The broad distributions of relaxation rates and dynamic heterogeneity (including red edge effects) that are frequently observed in ILs also lead to heterogeneous rates for chemical reactions in ILs. Jin *et al.*¹³⁶ showed that rates for both photoinduced intramolecular electron-transfer of crystal violet lactone (CVL) and photoisomerization of malonitriles were dependent on the excitation wavelength in dimethyl-isopropyl-propyl-ammonium/[NTf₂][−]. Annapureddy and Margulis¹³⁷ performed computational studies on CVL in a related IL, revealing that the kinetics of intramolecular electron transfer between the locally excited and charge transfer states of CVL in the IL is local solvent-environment-dependent due to slow solvent relaxation. The experimental and theoretical results suggest that ILs could be used to control the products of photoinduced reactions by tuning the excitation wavelength. This selectivity could be exploited to design chemical systems that adapt to their environment, mimicking to a small extent the abilities of living organisms. On a more practical level, these results serve as a reminder that even relatively simple reactions such as intramolecular electron transfer will show heterogeneous kinetics in ILs, at least on nanosecond and shorter timescales, which will influence device performance.

SOME AREAS OF SPECIFIC INTEREST

ILs will continue to enjoy a growth in uses for energy applications, bio-friendly solubilization of biomolecules, as active pharmaceutical ingredients, and more. In addition to the questions and conjectures mentioned above, we detail below some of the provocative issues that remain to be addressed in the chemical physics of ILs.

Water in ILs

The presence of water has profound effects on the physical properties of ILs. ILs are hygroscopic; even those that are hydrophobic enough to phase separate from water can absorb up to 20%–30% water by mole fraction at saturation. Many

uses of ILs, such as liquid/liquid extractions relevant to industrial separations processes or spent nuclear fuel processing, will depend on an understanding of the physical and solvating properties of water/IL mixtures and transport phenomena across the water/IL interface. On the other hand, many electrochemical and interfacial applications of ILs require a high degree of dryness. In such cases, analyte volumes are often too small for accurate Karl Fischer titration and *in situ* water detection is highly desirable. Development of non-invasive spectroscopic means for determining water content to levels of 1 ppm by mass would be very useful.

Predictive capabilities for physical and chemical properties of ILs

Given the large number of possible ILs, it would be most helpful if we can develop methods to accurately predict their properties before synthesizing them. For example, it is most helpful to know: The glass transition and melting temperatures; whether or not persistent deeply supercooled states of the liquid will be present; what the usable voltage range will be between reduction and oxidation of the ions; and what will be the viscosity and conductivity as a function of temperature. While empirical linear free energy approaches have been quite successful in predicting IL properties for analytical chemistry applications,¹³⁸ it will also be important to develop approaches that make accurate predictions from a molecular perspective. The underlying difficulty in making such predictions is that a unique set of synergistic physical and spatial interactions exist for each specific combination of ions, on top of which is frequently imposed a heterogeneous nanostructure dependent on that combination.

IL nanostructure and its implications for transport and reactivity

When even modest-length alkyl substituents are present on the cations or anions comprising ILs, a certain degree of nanostructural organization has been demonstrated to exist but it is not well characterized as yet. For a number of ILs having nonaromatic cations, the effective sizes for the self-organized domains seem consistent with interdigitated structures in the liquids, while for ILs with 1-alkyl-3-methylimidazolium cations, a bilayerlike ordering results. Will the observed trend for ILs with aromatic cations having larger nanostructured domains than for non-aromatic cations be general? Another significant question is whether these nanostructured features will persist at elevated temperatures. As described above, the local nanoenvironments in ILs exhibit different solvation, transport, and dynamic profiles depending on the probe solute used, with significant consequences for reactivity and transport processes.

CONCLUSION

Our goal in writing this relatively brief overview has been to spotlight selected topics that we believe will engage the imagination of chemical physics and physical chemistry researchers, and to stimulate them to tackle important scientific questions about ILs that have far-reaching practical applications. We regret that space limitations did not permit us

to mention all of the exciting and valuable work done to date and we apologize to those whose work we were unable to include. If recent trends are any indication, the pace of discoveries in the wide ranging field of ILs will continue to accelerate for some time to come. This bodes well for the prospect of development of a coherent picture of ILs with full predictive capabilities.

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