



BNL-98448-2012-CP

***Ionic Liquids: Radiation Chemistry, Solvation
Dynamics and Reactivity Patterns***

James F. Wishart

Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973-5000

Presented at the 8th DOE Condensed Phase and Interfacial Molecular Science Meeting

*Potomac, MD
October 21-24, 2012*

January 2012

Chemistry Department

Brookhaven National Laboratory

**U.S. Department of Energy
DOE - OFFICE OF SCIENCE**

Notice: This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE-AC02-98CH10886 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

This preprint is intended for publication in a journal or proceedings. Since changes may be made before publication, it may not be cited or reproduced without the author's permission.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Ionic Liquids: Radiation Chemistry, Solvation Dynamics and Reactivity Patterns

James F. Wishart

Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973-5000

wishart@bnl.gov

Program Definition

Ionic liquids (ILs) are a rapidly expanding family of condensed-phase media with important applications in energy production, storage and consumption, including advanced devices and processes and nuclear fuel and waste processing. ILs generally have low volatilities and are combustion-resistant, highly conductive, recyclable and capable of dissolving a wide variety of materials. They are finding new uses in dye-sensitized solar cells, chemical synthesis, catalysis, separations chemistry, batteries, supercapacitors and other areas. Ionic liquids have dramatically different properties compared to conventional molecular solvents, and they provide a new and unusual environment to test our theoretical understanding of primary radiation chemistry, charge transfer and other reactions. We are interested in how IL properties influence physical and dynamical processes that determine the stability and lifetimes of reactive intermediates and thereby affect the courses of reactions and product distributions. We study these issues by characterization of primary radiolysis products and measurements of their yields and reactivity, quantification of electron solvation dynamics and scavenging of electrons in different states of solvation. From this knowledge we wish to learn how to predict radiolytic mechanisms and control them or mitigate their effects on the properties of materials used in nuclear fuel processing, for example, and to apply IL radiation chemistry to answer questions about general chemical reactivity in ionic liquids that will aid in the development of applications listed above.

Soon after our radiolysis studies began it became evident that the slow solvation dynamics of the excess electron in ILs (which vary over a wide viscosity range) increase the importance of pre-solvated electron reactivity and consequently alter product distributions and subsequent chemistry. This difference from conventional solvents has profound effects on predicting and controlling radiolytic yields, which need to be quantified for the successful use under radiolytic conditions. Electron solvation dynamics in ILs are measured directly when possible and estimated using proxies (e.g. coumarin-153 dynamic emission Stokes shifts or benzophenone anion solvation) in other cases. Electron reactivity is measured using ultrafast kinetics techniques for comparison with the solvation process.

A second important aspect of our interest in ionic liquids is how their unusual sets of properties affect charge transfer and charge transport processes. This is important because of the many applications of ionic liquids in devices that operate on the basis of charge transport. While interest in understanding these processes in ionic liquids is growing, the field is still in an early stage of development. We are using donor-bridge-acceptor systems to study electron transfer reactions across variable distances in a series of ionic liquids with a range of structural motifs and whose dynamical time scales vary from moderately fast to extremely slow, and to compare them with conventional solvents.

Methods. Picosecond pulse radiolysis studies at BNL's Laser-Electron Accelerator Facility (LEAF) are used to identify reactive species in ionic liquids and measure their solvation and reaction rates. This work is aided greatly by the recent development of Optical Fiber Single-Shot (OFSS) detection at LEAF by A. Cook (DOI: 10.1063/1.3156048) and its forthcoming extension into the NIR regime. IL solvation and rotational dynamics, and electron transfer reactions are measured by TCSPC in the laboratory of E. W. Castner at Rutgers Univ. Picosecond transient absorption measurements of excited state dynamics and electron transfer reactions are done in the laboratory of R. Crowell (BNL). Diffusion rates of anions, cations and solutes are obtained by PGSE NMR in S. Greenbaum's lab at Hunter College, CUNY and by Castner's group at Rutgers. We have extensive collaborations with other major groups in ionic liquid synthesis, physical chemistry, simulations and radiation chemistry.

Ionic liquid synthesis and characterization. Our work often involves novel ILs that we design to the requirements of our radiolysis and solvation dynamics studies and are not commercially available. We have developed in-house capabilities and a network of collaborations (particularly with S. Lall-Ramnarine of Queensborough CC and R. Engel of Queens College) to design, prepare and characterize ILs in support of our research objectives. Cation synthesis is done with a CEM microwave reactor, resulting in higher yields of purer products in much shorter time than traditional methods. We have assembled an instrumentation cluster including DSC, TGA, viscometry, AC conductivity, Karl Fischer moisture determination and ESI-mass spec (for purity analysis and radiolytic product identification). The cluster serves as a resource for our collaborators in the New York Regional Alliance for Ionic Liquid Studies and other institutions (Penn State, ANL). Our efforts are substantially augmented by student internships from the BNL Office of Educational Programs, particularly the VFP (formerly FaST) program, which brings collaborative faculty members and their students into the lab for ten weeks each summer. Since 2003, a total of 34 undergrads, two graduate students, one pre-service teacher, one high school student and four junior faculty have worked on IL projects in our lab, many of them for more than one summer.

Recent Progress

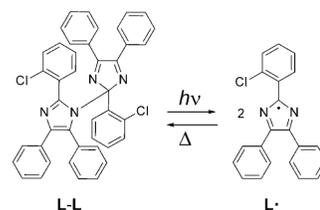
Electron solvation and pre-solvated reactivity in ionic liquids.⁵ On time scales of a nanosecond or less, radiolytically-generated excess electrons in ionic liquids undergo solvation processes and reactions that determine all subsequent chemistry and the accumulation of radiolytic damage. Using picosecond pulse-probe and OFSS detection methods, we observed and quantified the solvation response of the electron in 1-methyl-1-butyl-pyrrolidinium bis(trifluoromethylsulfonyl)amide and used it to understand electron scavenging by duroquinone in terms of the competition between electron solvation and pre-solvated electron capture. (with A. Cook, BNL)

Electron transfer (ET) in ionic liquids.⁶ Photoinduced charge-separation reactions in a system comprised of an N,N-dimethyl-1,4-phenylenediamine donor, proline bridge and coumarin 343 acceptor (DMPD-pro-C343) were studied as a function of temperature and viscosity and analyzed using a distribution of exponential lifetimes. The ET kinetics were distributed broadly in the ILs and narrowly in CH₃CN and CH₃OH. The results showed the complexity of simple reactions in IL systems and in the case of the most viscous IL, the effects of overlapping dynamical and ET time scales. (with H. Y. Lee and E. W. Castner, Rutgers)

Tuning ionic liquid properties independent of structural changes.² In the interest of developing sets of isostructural ionic liquids with different viscosities and therefore different dynamical properties for studies of chemical reactivity, we prepared ammonium and phosphonium NTf₂ salts with the same alkyl side chains and compared their properties and OKE spectra. Viscosities of the phosphonium ILs were roughly half those of the ammonium salts, which the OKE analysis attributed to a weaker interionic interaction arising from the larger ionic volume. (with H. Shirota, Chiba U.)

Future Plans

Cage escape and recombination in ILs. The early steps of photoinduced reactions often involve a competition between recombination and escape of the photoproducts, whether they are radicals or charge-separated states, which largely determines the quantum efficiency of energy capture and in some cases, photodegradation yields in catalytic systems. Compared to molecular solvents, ionic liquids may show unusual dynamical effects in cage relaxation, in addition to slower cage escape due to higher viscosity. In previous work, we observed such effects in the photolysis of *ortho*-chloro-hexaarylbisimidazole (*o*-Cl-HABI, L-L in the adjacent scheme) where quantum yields of the lophyl radical (L•) were much lower in three ILs than in DMSO. Work by others showed that recombination of



lophyl radical pairs that are covalently constrained in a near-optimal configuration is quite slow ($t_{1/2} = 33$ ms, $\Delta G^\ddagger = 65.5$ kJ/mol) due to the large structural rearrangement required. We would like to know if ILs promote recombination through slower cage structural relaxation, holding the radical pair close to the transition state configuration for a longer time, and whether the viscosity-lengthened cage escape time promotes recombination of the relaxed pair through interactions with the IL environment. The OFSS system is critical to this effort because the diffusive recombination of lophyl radicals takes many seconds in ILs and in ordinary solvents, making typical repetitive pump-probe experiments completely impractical. In contrast, OFSS provides picosecond-resolution, 5-nanosecond-range transient absorption data using relatively small numbers of shots that can be collected at arbitrarily long delays in-between. With this advantage, we will examine the kinetics of cage escape and recombination in ILs of different viscosities, and the effects of slow IL relaxation dynamics on the planarization of the lophyl radical, which provides the very large reorganization barrier for radical dimerization. (Collaboration with Prof. V. Strehmel (U. of Applied Sci., Krefeld, Germany) and A. Cook and D. Polyanskiy (BNL))

Effects of ionic liquids on intramolecular ET processes. Over the years, we have successfully used oligopropylene-bridged electron donor-bridge-acceptor (D-B-A) systems to probe various aspects of the energetics and distance dependence of ET processes. As noted above,⁶ we are using these D-B-A systems to study how ET processes are affected by ionic liquids and showed how slow IL dynamics leads to distributed ET kinetics as predicted by theory. The question of local environment effects (dynamical and energetic) is very important in ILs because of their molecular-scale polar/non-polar heterogeneity. To explore these aspects, we will use D-B-A systems of different charge types, which we expect to occupy different regions within the IL. The neutral DMPD-pro-C343 system undergoes photoinduced charge separation to form a zwitterion, followed by charge recombination during the back electron transfer. Building on the previous emission work,⁶ we are using picosecond transient absorption techniques to observe the back ET process and any forward ET processes too fast for TCSPC, and we are extending the bridge length to look for effects of IL structural heterogeneity on both processes. For comparison, we will use the charged [(bpy)₂Ru^{II}MCbpy-(pro)_n-ampyRu^{III}(NH₃)₅]⁵⁺ (n = 1,2) system we have studied extensively in water, which should preferably be located in the polar region of the IL. The (bpy)₂Ru^{II}MCbpy center is an excited state electron donor, so the forward and back ET reactions are charge-shift (2+,3+/3+,2+). (J. Wishart, with R. Crowell (BNL, psec TA), E. W. Castner (Rutgers, TCSPC) and R. Rachid (Fordham, synthesis))

Scavenging and solvation processes of pre-solvated electrons in ionic liquids. Our early work in the reactivity of excess electrons in ionic liquids demonstrated the importance of pre-solvated electron scavenging in trying to understand and predict the distributions of early radiolysis products and radiolytic damage accumulation. It was also clear that the slower relaxation dynamics of ILs made them excellent media for the general study of fundamental radiolysis processes without the need to use cryogenic techniques, in combination with the advanced instrumentation of the LEAF Facility. As noted above,⁵ we have recently connected our observed electron solvation dynamics to the kinetics of electron scavenging. In other preliminary work we have observed that selected scavengers (e.g., nitrate, benzophenone) in ILs show different reaction profiles towards the various precursor states to the solvated electron. Different scavenger reactivities towards pre-solvated and solvated electrons have been known empirically for many years and cryogenic kinetic work by Jonah and Lewis showed specific mechanistic differences between scavengers similar to what we have seen in ILs. However, the combination of extended IL dynamical time scales and the time resolution of the LEAF OFSS detection system, coupled with the fact that it uses only small amounts of samples that do not have to be flowed, as well as the ability of ILs to dissolve polar and nonpolar scavengers, provides a unique opportunity to characterize the fundamental reactivity of pre-solvated electron species and understand how the properties of scavengers control their reaction profiles. This knowledge will permit the design of better systems to control radiation-induced reactivity, for example in the processing of radioactive materials (whether in ionic liquids or not), in systems for radiation processing and sterilization, and during long-term exposure to space, for example.

Studies of structure and reaction dynamics in ionic liquids using EXAFS and femtosecond spectroscopy. In collaboration with R. Crowell, R. Musat and D. Polyanskiy, photoionization of Br⁻ anion in neat and diluted bromide ionic liquids is being used to probe the dynamics of excess electrons and excited states. Static and time-resolved Br EXAFS is employed to study the structure of the ionic liquid and the dynamics and reactivity of the Br atom formed by the photoionization. The results can be applied to understanding analogous iodide systems of interest in dye-sensitized solar cells.

Publications on ionic liquids

1. *Radiation Chemistry and Photochemistry of Ionic Liquids*, K. Takahashi and J. F. Wishart in "Charged Particle and Photon Interactions with Matter" Y. Hatano, Y. Katsumura and A. Mozumder, Eds. Taylor & Francis, (2010) Ch. 11, pp 265-287.
2. *Heavy Atom Substitution Effects in Non-Aromatic Ionic Liquids: Ultrafast Dynamics and Physical Properties* H. Shirota, H. Fukazawa, T. Fujisawa, and J. F. Wishart, *J. Phys. Chem. B*, **114**, 9400-9412 (2010)
3. *Ionic Liquids and Solids with Paramagnetic Anions*, B. M. Krieger, H. Y. Lee, T. J. Emge, J. F. Wishart, E. W. Castner, Jr., *Phys. Chem. Chem. Phys.*, **12**, 8919-8925 (2010)
4. *Exploring the Effect of Structural Modification on the Physical Properties of Various Ionic Liquids*, S. I. Lall-Ramnarine, J. L. Hatcher, A. Castano, M. F. Thomas, and James F. Wishart in "ECS Transactions - Las Vegas, NV, Vol. 33, Molten Salts and Ionic Liquids 17" Fox, D., *et al.*, Eds.; The Electrochemical Society, Pennington, NJ, (2010) pp. 659 - 665.
5. *Electron solvation dynamics and reactivity in ionic liquids observed by picosecond radiolysis techniques* J. F. Wishart, A. M. Funston, T. Szreder, A. R. Cook and M. Gohdo, *Faraday Discuss.* **154**, 353-363 (2012).
6. *A Comparison of Electron-Transfer Dynamics in Ionic Liquids and Neutral Solvents* H. Y. Lee, J. B. Issa, S. S. Isied, E. W. Castner, Jr., Y. Pan, C. L. Hussey, K. S. Lee and J. F. Wishart, *J. Phys. Chem. C*, **116**, 5197-5208 (2012).

Publications on other subjects

7. Book: "Recent Trends in Radiation Chemistry," J. F. Wishart and B. S. M. Rao, Eds.; World Scientific, Singapore, (2010). (ISBN 978-981-4282-07-9)
8. *Ultra-fast pulse radiolysis methods*, J. Belloni, R. A. Crowell, Y. Katsumura, M. Lin, J.-L. Marignier, M. Mostafavi, Y. Muroya, A. Saeki, S. Tagawa, Y. Yoshida, V. De Waele, and J. F. Wishart in "Recent Trends in Radiation Chemistry," J. F. Wishart and B. S. M. Rao, Eds. Ch. 5, pp 121-160, World Scientific, Singapore, (2010).
9. *Application of External-Cavity Quantum Cascade IR Lasers to Nanosecond Time-Resolved Infrared Spectroscopy of Condensed-Phase Samples Following Pulse Radiolysis*, D. C. Grills, A. R. Cook, E. Fujita, M. W. George, J. M. Preses, and J. F. Wishart, *Appl. Spect.* **64**, 563-570 (2010), cover publication.