



BNL-81574-2008-CP

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Dynamics and Reactivity Patterns***

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*Submitted to the 5th DOE Condensed Phase and Interfacial Molecular Science
(CPIMS) Meeting
to be held in Warrenton, VA
October 19-22, 2008*

September 2008

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Managed by
Brookhaven Science Associates, LLC
for the United States Department of Energy under
Contract No. DE-AC02-98CH10886

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Ionic Liquids: Radiation Chemistry, Solvation Dynamics and Reactivity Patterns

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Program Definition

Ionic liquids (ILs) are a rapidly expanding family of condensed-phase media with important applications in energy production, nuclear fuel and waste processing, improving the efficiency and safety of industrial chemical processes, and pollution prevention. ILs are generally nonvolatile, noncombustible, highly conductive, recyclable and capable of dissolving a wide variety of materials. They are finding new uses in chemical synthesis, catalysis, separations chemistry, electrochemistry 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 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 chemical reactions and product distributions.

Successful use of ionic liquids in radiation-filled environments, where their safety advantages could be significant, requires an understanding of ionic liquid radiation chemistry. For example, characterizing the primary steps of IL radiolysis will reveal radiolytic degradation pathways and suggest ways to prevent them or mitigate their effects on the properties of the material. An understanding of ionic liquid radiation chemistry will also facilitate pulse radiolysis studies of general chemical reactivity in ILs, which will aid in the development of applications listed above. Very early in our radiolysis studies it became evident that slow solvation dynamics of the excess electron in ILs (which vary over a wide viscosity range) increases the importance of pre-solvated electron reactivity and consequently alters product distributions. Parallel studies of IL solvation phenomena using coumarin-153 dynamic Stokes shifts and polarization anisotropy decay rates are done to compare with electron solvation studies and to evaluate the influence of ILs on charge transport processes.

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. We and our collaborators (R. Engel (Queens College, CUNY) and S. Lall-Ramnarin, (Queensborough CC, CUNY)) develop and characterize new ionic liquids specifically designed for our radiolysis and solvation dynamics studies. IL solvation and rotational dynamics are measured by TCSPC and fluorescence upconversion measurements in the laboratory of E. W. Castner at Rutgers Univ. Investigations of radical species in irradiated ILs are carried out at ANL by I. Shkrob and S. Chemerisov using EPR spectroscopy. Diffusion rates are obtained by PGSE NMR in S. Greenbaum's lab at Hunter College, CUNY and S. Chung's lab at William Patterson U. Professor Mark Kobrak of CUNY Brooklyn College performs molecular dynamics simulations of solvation processes. A collaboration with M. Dietz at U. Wisc. Milwaukee is centered around the properties and radiolytic behavior of ionic liquids for nuclear separations. Collaborations with C. Reed (UC Riverside), D. Gabel (U. Bremen) and J. Davis (U. South Alabama) are aimed at characterizing the radiolytic and other properties of borated ionic liquids, which could be used to make fissile material separations processes inherently safe from criticality accidents.

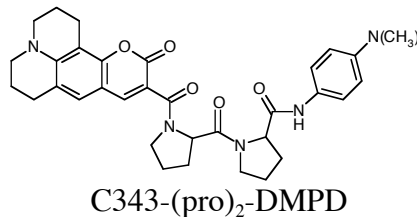
Recent Progress

EPR studies of radical species in ILs. Since our standard technique of transient optical detection cannot detect many important intermediates that lack strong absorption features, particularly hole-derived species, we have begun to use EPR to identify ionization products in ILs [11]. Radical intermediates were generated by radiolysis or photoionization of low-temperature ionic liquid glasses composed of ammonium, phosphonium, pyrrolidinium, and imidazolium cations and bis(triflyl)amide, dicyanamide, and bis(oxalato)borate anions. Large yields of terminal and penultimate C-centered radicals are observed in the aliphatic chains of the phosphonium, ammonium and pyrrolidinium cations, but not for imidazolium cation (where the ring is the predominant site of oxidation). This pattern is indicative of efficient deprotonation of a hole trapped on the parent cation (the radical dication) that competes with rapid electron transfer from a nearby anion. This charge transfer leads to the formation of stable N- or

O-centered radicals; the dissociation of parent anions is a minor pathway. Production of $\bullet\text{CF}_3$ from $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ evidently proceeds primarily through an excited state of the anion rather than via ionization.

Radiolysis of simulated IL-based nuclear extraction systems. Addition of 10-40 wt% of trialkylphosphate (a common agent for nuclear separations) has relatively little effect on the fragmentation of the ILs. The yield of the alkyl radical fragment generated by dissociative electron attachment to the trialkylphosphate is $< 4\%$ of the yield of the radical fragments derived from the IL solvent. The currently used hydrocarbon/tributylphosphate extraction systems involve a highly resistant, structurally simple solvent (like kerosene) that efficiently transfers charge and energy to the functional solute (tributylphosphate), resulting in the fragmentation of the latter and degradation of extraction efficiency. The results suggest a different paradigm for radiation protection: a solvent in which the damage transfer is reversed. Such a solvent actively protects the functional solute in a sacrificial way, but overall radiolytic damage is still kept to a low level by the radiolytic properties of the solvent [11] (in collaboration with I. Shkrob and S. Chemerisov, ANL).

Charge transfer in ionic liquids - effects on driving force/thermodynamics, reorganization energy and reorganizational dynamics. Charge transfer processes in ionic liquid (IL) media are important to understand because of their applications in solar photoelectrochemical cells, electrochromic displays, fuel cells, batteries and other advanced devices where the properties of ILs provide advantages. Our program to investigate the effects of ionic liquids on intramolecular charge transfer reactions continued with the development of a new peptide-bridged donor acceptor complex incorporating coumarin 343 and the excited-state electron acceptor and dimethylphenylenediamine as the donor (C343-(pro)_n-DMPD). This complex was chosen over the previously studied system using a tetramethylrhodamine acceptor because of the latter chromophore's conformational lability and resultant complicated photodynamics. The C343 chromophore has several advantages, the first being that it is conformationally rigid. The photophysics of the structurally similar coumarin 153 have been well characterized, and it has been used previously to measure solvation dynamics in many ionic liquids, as well as molecular solvents, by means of the emission Stokes shift. Solvation dynamics in ionic liquids are known to be slower than in molecular solvents and to have components that are spread across picosecond to nanosecond time scales. To the extent that the solvation process extends into the time scale for electron transfer (ET), it affects the thermodynamics and reorganization energy of the ET process, resulting in complicated kinetics that need to be understood in order to exploit the advantages of ILs in the above-mentioned applications. The emission Stokes shift of the C343 chromophore provides an internal gauge of the solvation process while at the same time participating in the electron transfer reaction. In preliminary work, the subject compounds have been prepared and studies in methanol (where solvation is much faster than ET) have indicated an electron transfer process with straightforward kinetics ($\tau \sim 470$ ps at 21 °C for C343-(pro)₁-DMPD). (in collaboration with H. Y. Lee, E. W. Castner, S. S. Isied, and Y. Issa, Rutgers Univ.)



Ultrafast Single-Shot radiolysis of ionic liquids. UFSS experiments were done on the ionic liquids C₄mpyr NTf₂ and MeBu₃N NTf₂ in neat form and with various concentrations of several electron scavengers. Data collected at 900 nm with increasing benzophenone concentrations shows the disappearance of the spectral shift associated with the electron solvation process, indicating highly effective scavenging of pre-solvated electrons. Additional results will be presented.

Future Plans

Electron solvation and reactivity. The competition between the electron solvation and electron capture processes in ionic liquids will be explored to test the validity of pre-solvated electron scavenging mechanisms advanced in the literature. Electron solvation dynamics in several families of ILs will be measured by pulse-probe radiolysis and ultrafast single-slot spectroscopy (UFSS) developed at BNL by Andrew Cook. Solvation phenomena in ionic liquids will also be measured by observing the time-resolved absorption spectral shift of highly solvatochromic benzophenone anion and time-resolved fluorescence Stokes shifts of solvatochromic dyes such as coumarin 153. Our experimental work will be supported by molecular dynamics simulations performed by Prof.

Mark Kobrak of Brooklyn College, CUNY. Subsequently, scavengers will be added to measure the kinetics of pre-solvated electron capture. It is well known from work in molecular solvents that many scavengers, for example SeO_4^{2-} , have widely different reactivity profiles towards pre-solvated and solvated electrons. We have begun quantitative measurement of the scavenging profiles of benzophenone, SeO_4^{2-} , NO_3^- , and Cd^{2+} using the UFSS detection system. By quantitative measurement of the scavenging profiles of many reactants, we seek to provide a mechanistic basis for understanding scavenging profiles that can be applied to real-world applications such as predicting radiolytic product distributions during the processing of radioactive materials.

The influence of ionic liquid on charge transfer reactions. Pulse radiolysis and flash photolysis will be used to study how ionic liquids affect electron-transport reactions related to solar energy photoconversion systems, where their characteristics may prove valuable. IL-based photoelectrochemical cells have already been reported. Focus areas will be the combined effects of ionic solvation and slow solvent relaxation on the energy landscape of charge transport, including specific counterion effects depending on the ionic liquid, and the influence of the lattice-like structure of ionic liquids on the distance dependence of electron transport reactions.

The studies of ionic liquid environment effects on photoinduced electron transfer in the C343-(pro)_n-DMPD system will be continued with extensive measurements on the $n = 1, 2, 3$ systems in several ionic liquids and representative molecular solvents (methanol, water, acetonitrile, dichloromethane). Electrochemistry will be used to estimate the reaction driving forces and kinetic measurements will be used to obtain activation parameters (including pressure dependence) for the ET systems in the various ionic and molecular liquids. The ionic liquids will be selected so as to vary the solvation time scales across the electron transfer regime, but the early work will focus on low-viscosity, quick-relaxing ionic liquids that most resemble molecular solvents. Conformational and electronic structure calculations will be performed on the donor-acceptor systems to aid interpretation of the experimental results. This detailed information will allow elucidation of ionic liquid effects and quantitative comparison of the differences between ionic and molecular liquids. In the second year, electron transfer studies on the C343-(pro)_n-DMPD system will be carried forward into ionic liquids that are more viscous and have solvation dynamics on longer timescales than electron transfer in order to examine the influence of dynamics on the electron transfer process, a long-sought but difficult to achieve goal when working with molecular solvents. The results with the C343 chromophore will be supplemented by studies using the system we studied previously in molecular solvents (*J. Phys. Chem. B.* **2007**, *111*, 6878) with pyrenesulfonate in place of C343. The dipole change in the pyrene excited state is much smaller than for C343, making the Stokes shift negligible and providing another vantage point from which to examine the ET process. (in collaboration with H. Y. Lee and E. W. Castner, Rutgers Univ.)

EXAFS studies of structure and reaction dynamics in ionic liquids. In collaboration with R. Crowell and D. Polyanskiy, we are using Br EXAFS to study IL structure and Br^- ion solvation environment in neat and diluted bromide ionic liquids and the effect of solutes. We will use photoionization coupled with time-resolved EXAFS to probe the solvation dynamics of Br^0 atoms in ILs and the effect of the ionic liquid environment on the $\text{Br}^- + \text{Br}^0 \rightarrow \text{Br}_2^-$ reaction. The results can be applied to understanding related iodide systems of interest in solar photoconversion.

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