Effects of functional group substitution on electron spectra and solvation dynamics in a family of ionic liquids

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Abstract

Ionic liquids containing ether-, alcohol- and alkyl-functionalized quaternary ammonium dications were studied by pulse radiolysis. Spectra on nanosecond timescales revealed that solvation of the excess electron is particularly slow in the case of the alcohol-derivativized ionic liquids. The blue shift of the electron spectrum to the customary 650 nm peak takes 25-40 ns at 21 °C. Comparison with the relaxation dynamics observed in viscous 1,2,6-trihydroxyhexane reveals the hindering effect of the ionic liquid lattice on hydroxypropyl side chain reorientation.

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1. Introduction

Ionic liquids (salts that melt below 100 °C) have unusual properties that give them certain advantages over conventional molecular solvents in widespread use today (Wasserscheid and Welton, 2003; Rogers and Seddon, 2003; Davis and Fox, 2003). For example, the negligible vapor pressure of ionic liquids means that they do not evaporate and cannot support combustion, making them attractive alternatives to volatile, flammable organic solvents. In addition, the constituent cations and anions can be mixed and matched to control liquid properties such as melting point and viscosity, and to modulate solubilities for phase transfer applications.

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The potential safety, environmental and economic benefits of ionic liquids have attracted a great deal of interest in their potential applications as solvents for chemical reactions (Welton, 1999; Wasserscheid and Keim, 2000; Shelddon, 2001), as processing media for the nuclear fuel cycle (Fields et al., 1999; Harmon et al., 2001; Allen et al., 2002), and many other purposes. Accordingly, it is important to study the radiation chemistry of ionic liquids, in order to: (1) understand the factors that control their stability under ionizing radiation for fuel processing applications; and (2) employ pulse radiolysis as a method to study chemical kinetics in ionic liquids. The first step toward both of the goals is the identification and quantification of initial radiolysis products (electrons, holes and diverse radical species) and measurement of their reactivities.

In the last couple of years, several ionic liquid radiolysis studies have been published. The earliest
reports (Behar et al., 2001; Marcinek et al., 2001; Allen et al., 2002) centered on imidazolium salts, by far the most-commonly used class of ionic liquids. In imidazolium liquids and those consisting of pyridinium salts (Behar et al., 2002; Skrzypczak and Netu, 2003) radiolytically produced electrons are rapidly scavenged by the solvent cations to form neutral radicals that can subsequently be used to study redox reactions. Ionic liquids containing fully saturated alky lammonium cations, have been used to examine reactions of several radical species (CF$_3$H, Br$_2$, R$^+$ and H$^+$) as well as redox reactions (Behar et al., 2002; Grodkowski and Netu, 2002a-c; Wishart and Netu, 2003; Grodkowski et al., 2007).

Direct observation of the solvated electron in an ionic liquid was first reported for methyltributylammonium bis(trifluoromethylsulfonyl)imide (MB$_3$N$^+$NTf$_2$) where $c_{solv}$ has a lifetime of $\sim$300 ns and a broad absorption spectrum that peaks at 1400 nm (Wishart and Netu, 2003). In the course of measuring solvated electron reaction rates it was observed that scavenging of presolvated electrons is a significant factor, perhaps due to weaker competition from a slower solvation process, as observed spectroscopically. Time-resolved Stokes shift measurements of coumarin-153 in MB$_3$N$^+$NTf$_2$ (viscosity 520 mPa s) showed an average solvation time of 4.5 ns at 25°C (Archanzhev et al., 2003). Pre-solvated electron scavenging in ionic liquids enormously complicates the interpretation of kinetic competition studies (Grodkowski et al., 2003) and the prediction of radiolysis product yields in complex mixtures as might be found in nuclear fuel cycle applications. Clearly, an understanding of ionic liquid solvation processes is an important component of comprehending general reactivity trends in ionic liquids.

Preliminary studies on related ionic liquids indicate a correlation between electron solvation timescales and viscosity (Manston et al., 2003). Evidence for such a relationship in the case of molecular alcohol solvents had previously been sought by a group of coworkers including M. Ferradini (Jay-Gerin et al., 1995). They measured the solvated electron spectrum in 1,2, 6-trihydroxyhexane (viscosity 2490 mPa s at 20°C, 1 mPa s = 1 cP), but were unable to detect evidence for a slow solvation process longer than the time resolution of their instrumentation (pulse width 4 ns FWHM). In the present paper, we report the observation of a slow electron solvation process in a series of alcohol-functionalized ionic liquids (viscosities 4570–6860 mPa s at 25°C) and compare the time-resolved spectra with those of the solvated electron in alkyl- and ether-terminated ionic liquids of the same basic structure.

Until this juncture there have been no reported radiolysis studies of functionalized ionic liquids, although many “task-specific” liquids have been designed to control solubility or to provide a specific prosthetic group as a reagent or catalyst. For this report, we used dicationic liquids of the type (CH$_3$)$_2$(R$^+$)$^+$N$^+$((CH$_2$)$_n$OH, (CH$_2$)$_2$OCH$_2$CH$_2$) or (CH$_2$)$_n$CH$_3$ and $n = 3–8$. The structural motif of the cation was originally selected to be the simplest member of a large family of oligomeric and polymeric polycations with many applications, including antibacterial agents (Kohen et al., 1998; Lull et al., 2002; Fabian et al., 1997). A detailed account of the synthesis and properties of the ionic liquids used in this study will be reported elsewhere (Jell-Rammarine et al., 2004). The structures of the cations are shown in Fig. 1. The cations in which the R substituent is a 3-hydroxypropyl group will be designated “SHn”, where n represents the number of CH$_2$ units linking the two ammonium sites and the “H” stands for hydroxyl. Similarly, “SAN” will be used to describe compounds where the R substituent is a butyl group (“A” for alkyl) and “SEN” to describe compounds where the R substituent is a 2-ethoxyethyl group (“E” for ether).

2. Experimental

The halide salts of the alcohol-functionalized dications were prepared by reaction of 1,3-dibromopropane or the corresponding $\alpha$, $\omega$-dichloroalkane (~0.161 mol) with two equivalents of 3-dimethylamino-1-propanol (0.322 mol) in about 80 mL acetonitrile. The reactions were stirred under reflux at 60–70°C for 48 h. Ether- and alkyl-functionalized dications were prepared similarly by the reaction of $\alpha$, $\omega$-diaminoalkanes with 2-chlorodiethylether or 1-chlorobutane. The resultant white precipitates were collected by rotary evaporation and dried on a high vacuum pump. The structures of these salts were confirmed by $^1$H and $^{13}$C NMR.

The bis(trifluoromethylsulfonyl)imide (NTf$_2$) ionic liquids containing SHn and SEN cations were prepared as described by Boulié et al. (1996) by dissolving the halide salt in water and adding 2 equivalents of LiNTf$_2$. The reaction was stirred for two days under reflux at
60–70 °C. The resultant liquid was isolated from the mixture containing two immiscible layers by extraction with ether (3 × 30 mL). The liquid was then tested for residual halide with AgNO₃ and washed with water if halide was present. The resultant liquid was dried on the high vacuum pump with heat (60–70 °C), for 5–7 days or until the water content was reduced to less than 0.5%. ¹H and ¹³C NMR in DMSO-d₆ indicated the product to be that of the same cation as the halide salt. An additional quartet in the ¹³C spectrum centered at 19.45 ppm confirmed the presence of the NTf₂ anion. Alkyl-terminated SA and NTf₂ salts precipitated as solids from the aqueous anion metathesis reaction.

Fast transient absorption pulse radiolysis experiments were carried out at the Brookhaven National Laboratory Laser-Electron Accelerator Facility (LEAF) (Wishart, 2001). The LEAF RF photocathode electron accelerator was used to generate 8.7 MeV electron pulses of <120 ps duration. A pulsed xenon arc lamp was used as the detection source. Bandpass filters (40 nm) were used to select the analyzing light wavelength. Transient absorption signals for the liquid studies were collected with FND-100 silicon (<1050 nm) or GAP-500 InGaAs (>900 nm) photodiodes and digitized with a Tektronix TDS-680B oscilloscope. A Hamamatsu R1338U-03 biplanar phototube and a Tektronix TDS-694C oscilloscope were used for the 1,2,6-trihydroxyhexane measurements. Other details of these experiments were as described before (Wishart and Neta, 2001). The ionic liquids were placed in septum-capped, 1 cm Suprasil spectrophotometer cuvettes and purged by bubbling with argon gas under gentle heat (50 °C, higher for high-melting liquids) for at least twenty minutes. 1,2,6-trihydroxyhexane was air-saturated and used as supplied from Aldrich. Unless stated otherwise, the measurements were performed at room temperature, (21 ± 1) °C. The dose per pulse was determined by thiosulfate dosimetry and ranged between 19 and 32 Gy, corrected for electron density.

3. Results and discussion

Fig. 2 shows the transient absorption spectra observed in alcohol-functionalized SH₈ (NTf₂)₂ at various times after the electron pulse. The spectrum observed at 2 ns has a peak at 800 nm and a significant shoulder around 1200 nm. At successive time intervals the shoulder disappears and the peak shifts to the 650 nm value typical of the solvated electron in terminal alcohols (Gay-Gern and Herrmann, 1999). The relaxation process is nearly complete after 50 ns. Slow relaxation behavior on a similar time scale can also be seen in Figs. 3 and 4, respectively, for the shorter-chain alcohol-functionalized liquids SH₆ (NTf₂)₂ and SH₄ (NTf₂)₂. The viscosities of SH₈ (NTf₂)₂ and SH₆ (NTf₂)₂ are 4570 and 6860 mPa s, respectively at 20 °C, and that of SH₄ (NTf₂)₂ is unmeasured but similar in magnitude. The solvated electron lifetimes are 990, 740 and 720 ns, going from SH₈ to SH₄.

The solvated electron spectra in the ether- and alkyl-terminated liquids behave differently from the alcohols. In ether-terminated SE₆ (NTf₂)₂ (viscosity 1120 mPa s), only a slight spectral shift is observed between 3 and 10 ns, after which the solvated electron absorbance peaks at 1100 nm with a lifetime of 160 ns (Fig. 5). SE₃ (NTf₂)₂ also has a solvated electron absorbance maximum at 1100 nm (not shown). The time-resolved spectra of alkyl-terminated SA₄ (NTf₂)₂ in Fig. 6 were recorded at 80 °C, just above the melting point. At the elevated temperature, no spectral shift is observed within
the time resolution of the experiment and the peak occurs at 1000 nm. The same $\lambda_{\text{max}}$ is observed for high-melting SA5 (NTf$_2$)$_2$ and SA6 (NTf$_2$)$_2$ (not shown). The solvated electron absorption maxima for these liquids occur at higher energy than in MB$_3$N$^+$ NTf$_2$ (1400 nm), however, the $\lambda_{\text{max}}$ values observed in N-methyl-N-(alkyl or ether)-pyrrolidinium NTf$_2$ liquids are similar [~1100 nm (Funston et al., 2003)].

Comparison of the temporal response of the absorption spectra of the alcohol-terminated ionic liquids with those observed in the ethers and alkyls implies that at least some of the excess electrons in the alcohols pass through a state of partial relaxation that is similar in character to the resting state of the solvated electron in the related ethers and alkyls. The results recall the observations of Shida et al. (1972) on the spectra of excess electrons in $\gamma$-irradiated alcohols at 77 K.

In addition to the regular visible absorption band, longer-chain primary alcohols (butanol and pentanol) showed absorption features in the near IR (ca. 1300-1600 nm) that were similar in energy to solvated electron absorption bands in ethers and alkanes. The lower energy band was attributed to electrons localized in paraffinic regions, which increase in domain as the chain length increases. In the ionic liquid alcohols, aliphatic and hydroxyl domains are likely to exist within a distribution of configurations. Some excess electrons will become localized within the hydroxyl domains while others may localize within aliphatic regions and give rise to the near IR absorption feature on the nanosecond time scale, although incompletely solvated electrons in the hydroxyl domain may also contribute to the near IR absorption. Kevan (1989) used a glassy mixed-solvent system of 2-methyltetrahydrofuran and methanol to address the issue of whether an electron in an aliphatic environment relaxes by tunneling into a hydroxyl domain or by a stepwise change in solvation shell. Spectroscopic evidence of an absorption band corresponding to a mixed solvation shell was cited as evidence for a stepwise mechanism.

The question remains as to the relationship of the relaxation processes in the ionic liquid alcohols and those in ordinary alcohols. The most striking difference is the relaxation time scale at room temperature. Average solvation time constants for methanol, ethanol and ethylene glycol are about 2-9 ps (Silva et al., 1998), while in the ionic liquid alcohols the observed time constants for absorbance decay in the region 1000-1200 nm are 25 ns (SH4, SH5) to 40 ns (SH6). The final step of the solvation process involves the reorientation of the hydroxyl groups to an equilibrium geometry around the solvated electron. In methanol at room temperature, reorientation occurs on a timescale of 5 ps, comparable to the average solvation time.
The population of hydroxyl groups is relatively sparse in the ionic liquids. Hydrogen bonding to the oxygen and nitrogen atoms of the NTf₂ anions may occur as well as between hydroxyl groups. In order to fully solvate the excess electron, pre-existing hydrogen bonds must be broken and the cation-tethered hydroxypropyl groups have to be re-oriented into the solvation sphere of the electron. In addition, the ionic lattice of the liquid must reorganize to accommodate the excess negative charge. The relaxation process is thereby linked to extremely hindered hydroxypropyl side chain reorientation and the translation of ions in the viscous, glassy medium.

The relative contributions of side chain hindrance and bulk viscosity to the slow solvation dynamics in the ionic liquid alcohols were evaluated by reinvestigation of the radiolysis of 1,2,6-trihydroxyhexane as envisaged by Jay-Gerin et al. (1995). Fig. 7 shows kinetic traces taken in aerated 1,2,6-tri hydroxyhexane with a detection setup having a rise time of ~200 ps. The 550 nm trace shows the time-resolved absorbance at the peak of the equilibrated solvated electron spectrum. The trace at 800 nm (the red limit of the detector) clearly shows a decay process with a time constant of 1.0 ns. This is plausible evidence for a slow solvation process just beyond the reach of the previous experiment. The viscosity of 1,2,6-tri hydroxyhexane at room temperature is 2490 mPAs (Jay-Gerin et al., 1995), about half that of the ionic liquid alcohols with electron solvation processes 25 times slower. Bulk viscosity is therefore not a direct determinant of the observed solvation rates, but it may correlate with other factors that make solvation processes slow. In the case of the ionic liquid alcohols, dynamic hindrance of hydroxypropyl side chain reorientation imposed by the electrostatic constraints of the ionic lattice plays the largest role in slowing the electron solvation process.

Differences in reactivity among various solvation states of the electron have been the subject of intense study for the information they may provide concerning the energetics and mobility of intermediate solvation states, and by extension the dynamics of the solvation process (Lewis and Johnson, 1986). The existence of a slow final solvation step in the ionic liquid alcohols presents an opportunity to probe this process with unprecedented detail. In the continuation of this work we will combine electron scavenging studies with measurements of solvation dynamics using solvatochromic probes and molecular dynamics simulations to develop a more detailed picture of the electron solvation process.

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