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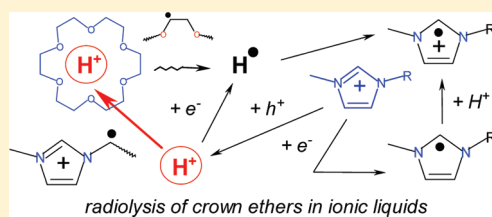
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On the Radiation Stability of Crown Ethers in Ionic Liquids

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S Supporting Information

ABSTRACT: Crown ethers (CEs) are macrocyclic ionophores used for the separation of strontium-90 from acidic nuclear waste streams. Room temperature ionic liquids (ILs) are presently being considered as replacements for traditional molecular solvents employed in such separations. It is desirable that the extraction efficacy obtained with such solvents should not deteriorate in the strong radiation fields generated by decaying radionuclides. This deterioration will depend on the extent of radiation damage to both the IL solvent and the CE solute. While radiation damage to ILs has been extensively studied, the issue of the radiation stability of crown ethers, particularly in an IL matrix, has not been adequately addressed. With this in mind, we have employed electron paramagnetic resonance (EPR) spectroscopy to study the formation of CE-related radicals in the radiolysis of selected CEs in ILs incorporating aromatic (imidazolium and pyridinium) cations. The crown ethers have been found to yield primarily hydrogen loss radicals, H atoms, and the formyl radical. In the low-dose regime, the relative yield of these radicals increases linearly with the mole fraction of the solute, suggesting negligible transfer of the excitation energy from the solvent to the solute; that is, the solvent has a “radioprotective” effect. The damage to the CE in the loading region of practical interest is relatively low. Under such conditions, the main chemical pathway leading to decreased extraction performance is protonation of the macrocycle. At high radiation doses, sufficient to increase the acidity of the IL solvent significantly, such proton complexes compete with the solvent cations as electron traps. In this regime, the CEs will rapidly degrade as the result of H abstraction from the CE ring by the released H atoms. Thus, the radiation dose to which a CE/IL system is exposed must be maintained at a level sufficiently low to avoid this regime.



1. INTRODUCTION

Room temperature ionic liquids (ILs) represent a relatively new class of organic solvents typically consisting of an irregularly shaped organic cation such as 1-methyl-3-alkyl imidazolium or 1-alkyl-4-methylpyridinium ($C_n\text{mim}^+$ and $C_n\text{MePy}^+$, respectively, in Scheme 1) in combination with any of a wide variety of organic or inorganic anions (e.g., triflate, TfO^- , and bistriflimide, NTf_2^-). Because the structure of the ions comprising the IL can be readily varied, the physicochemical properties of such solvents, including their hydrophobicity, polarity, conductivity, and viscosity, are highly tunable.^{1,2} Ionic liquids typically also exhibit low volatility and high chemical stability. In addition, they have been found to solubilize a variety of organic molecules and polymers (e.g., cellulose) and in the presence of an appropriate extractant, metal ions.^{4–14} For these and other reasons, ILs have attracted considerable attention as possible replacements for the molecular solvents (e.g., saturated or aromatic hydrocarbons, long-chain aliphatic alcohols) normally employed in the liquid–liquid extraction of various radionuclides in nuclear fuel cycle separations.^{4–14} By exploiting the properties of ILs, it may be possible to avoid the need for cosolvents to improve ion transport across the interface, to suppress third phase and

micellar aggregate formation, and to improve the solubilization of extracted metal complexes.⁴

A typical extraction system consists of an organic solvent (and often, a cosolvent), together with an extracting agent capable of forming a hydrophobic (and therefore, extractable) complex with the metal ion of interest. The separations generally proceed in a countercurrent fashion and involve forward extraction of the metal ion into the organic phase followed by back extraction of the separated ion into an appropriate aqueous phase (i.e., a solution of different proticity).^{4,5} Because ILs are good electrical conductors, electrochemical deposition of the extracted ions from the solvent directly onto a metal electrode can serve as an alternative approach to metal recovery.^{15,16}

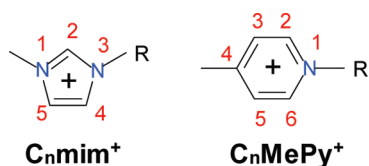
In nuclear applications, an extraction system will be exposed to ionizing radiation generated by decaying radionuclides. As a result, an understanding of the radiation stability of both the solvent and the extracting agent is of considerable importance. While a number of studies have addressed the radiation stability of neat ILs,^{17–22} the stability of extracting agents in an IL matrix

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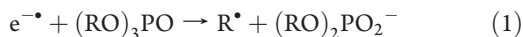
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Scheme 1. Structures of Derivatized Imidazolium and Pyridinium Cations



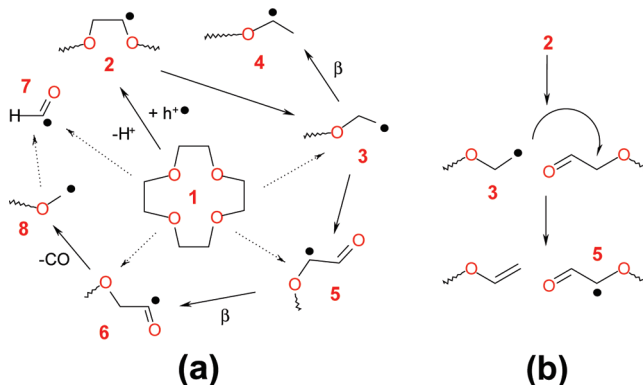
has not been systematically examined. In conventional extraction systems, the radiation stability of extractants has often been found to be both critically important to the design of a practical extraction process and intimately related to the radiation chemistry of the solvent employed. For example, in the PUREX (plutonium–uranium extraction) process, plutonium and uranium are extracted into *n*-dodecane containing 30% tributylphosphate (TBP), which serves both as the extraction agent and the solvent modifier. Radiolytic dealkylation of tributylphosphate (here e^- is the (pre)solvated electron generated in the organic diluent)^{23–25}



results in the formation of mono- and dibutyl phosphate anions that extract the lanthanide products of uranium fission.^{23,25} The formation of these ions necessitates continuous processing of the extraction solvent to remove them, complicating the separations. The ultimate cause of this problem is the high ionization potential and negative electron affinity of the alkane solvent. As a result, a large fraction of the energy released through the ionization and excitation of the alkane solvent by the ionizing radiation is channeled to the solute (here, TBP), resulting in the scission of the C–O bonds.^{23,24} While the radiation damage to the alkane solvent can be considerable,^{23,25} it generally does not result in the formation of degradation products that interfere with the separations. On the other hand, even limited damage to the extractant can have significant deleterious effects on the extraction efficacy and specificity. A highly undesirable situation is thus one in which the greater radiation stability of the solvent results in the exclusive channeling of radiation damage to the extracting agent.

In an earlier report,^{20,26} we suggested that ILs should behave in a manner opposite to alkane solvents. Indeed, the ionization potentials of the constituent ions of the ILs considered are generally lower than that of extracting agents. In addition, the energies of the corresponding excited states are lower, so the excitation energy in the solute is accepted by the solvent. Furthermore, the constituent ions readily trap the excess electrons and holes (electron deficiencies) generated in the ionization,^{19–22} so dissociative charge transfer reactions (such as reaction 1 above) are suppressed. To demonstrate this, we used electron paramagnetic resonance (EPR) spectroscopy to observe methyl radicals produced in the radiolysis of 1-methyl-3-decylimidazolium bistriflimide containing 10–40 wt % trimethylphosphate.²⁰ The yield of the $\cdot\text{CH}_3$ radicals in reaction 1 was minor even at high concentrations of the trimethylphosphate. Most notably, *while damage to the IL solvent was considerable during radiolysis, it was restricted to the solvent.*

In the present study, we address the radiation stability of an important class of extracting agents: crown ether (CE) ionophores.

Scheme 2. Radiation-Induced Radical Formation in CEs: (a) Possible Reaction Pathways to the Known Radical Products; (b) Mechanism for C–O Fragmentation in Radical 2, after Refs 27, 29, 31, 34, and 38^a

^a The hypothesized reactions are indicated with the dashed arrows.

The CEs that are used in radionuclide separations typically have 5–12 ethyleneoxy units derivatized with aliphatic or aromatic side groups (such as cyclohexano or *tert*-butylcyclohexano) to increase hydrophobicity.^{4,5} These macrocyclic polyethers can be used to separate the TcO_4^- , Cs^+ , and Sr^{2+} that are present in the spent nuclear fuel.^{4–16} CE/IL solvents provide a striking example of the potential utility of ILs in solvent extractions:⁵ for the same concentration of the CE in the extracting solvent, the distribution coefficients for TcO_4^- and Sr^{2+} ^{4,5} in the IL can be orders of magnitude greater than in a molecular solvent of comparable polarity. In some systems, this increase is accounted for by ion exchange involving the constituent cations.^{4,5} In other systems, this is a consequence of favorable solvation energetics.¹⁶

Some mechanisms for radiation induced-degradation of ILs containing CEs have been described in the previous studies.¹⁸ In particular, it has been shown that continuous irradiation of $\text{C}_n\text{mim NTf}_2$ results in increased acidity^{18a} and generation of SO_3^{2-} and/or SO_4^{2-} anions.^{18b} The hydronium ions form the $\{\text{H}_3\text{O}^+ \cdot \text{CE}\} \text{NTf}_2^-$ ion pair, which interferes with the formation of $\{\text{Sr}^{2+} \cdot \text{CE}\} (\text{NTf}_2^-)_2$ complexes during the extraction of Sr^{2+} , reducing the extraction efficacy of the solvent.^{18b} Furthermore, radiolytic generation of sulfite/sulfate due the fragmentation of the NTf_2^- ^{18a} leads to the formation of insoluble salts at the interface, further reducing this efficacy. Despite the potential detriment posed by these two processes, neither results in permanent damage to the solute.

Here we employ EPR spectroscopy to demonstrate that the damage to CEs in aromatic ILs is negligible unless the mole fraction χ of the CE is relatively high ($\chi > 0.1$) and the acidity is low. *Our study provides yet another example of the propensity of the IL solvent to channel the radiation damage away from the solute and toward itself, that is, of the “radioprotective” nature of certain ILs.*

1.1. An Overview of the Radiation Chemistry of Crown Ethers. Before examining crown ether-containing IL systems (section 3.2), it is important to first consider briefly the known radiation chemistry of neat CEs.^{27–38} Ionization of unsubstituted CE (1) causes the formation of a radical cation $1^{+\bullet}$ that promptly deprotonates (Scheme 2a).^{27,38} The resulting radical 2 can also be generated via H^+ transfer to an excess electron, homolytic cleavage of the C–H bonds in an electronically excited CE

molecule, or hydrogen abstraction by radiolytically generated H^\bullet atoms. This radical 2 (most likely, in the excited state precursor, see section 3.1) undergoes C–O fragmentation yielding terminal radical 3. The latter undergoes β -shift, yielding the penultimate radical 4 or radical 5,³⁸ which subsequently undergoes β -shift, yielding the acyl radical 6. (Note that the reactions shown in Scheme 2 have been hypothesized rather than observed directly.) There is also an unknown fragmentation channel that yields the formyl radical 7, possibly by secondary radiolysis.³⁴ Exposing radical 3 to 400–600 nm light converts it to radical 6 and causes its fragmentation to radical 8, by elimination of CO .^{31,34} The latter radical been suggested as the possible progenitor of the formyl radical.³¹

The resulting EPR spectra are congested, and the individual spectral signatures for the radicals shown in Scheme 2 are poorly known.^{27,31,34,38} In a Freon matrix (that suppresses electron trapping reactions), the EPR spectrum of 12-crown-4 (12C4) is mainly from radicals 2 and 5,³⁸ while in Xe, there are also resonance lines from radicals 4, 6, and 7.³¹ In terms of this radical chemistry, there is little difference between larger macrocycles and 1,4-dioxane (formally, 6C2).²⁷ The latter, in fact, has frequently been used as a reference for more complex CEs. Generally, an increase in ring size decreases the radiation stability of the CEs.^{28,31} For instance, the observed radical yields in γ -irradiation of neat 6C2, 12C4, 15C5, and 18C6 were 2.3, 3.7, 5.9, and 5.7 radicals per 100 eV absorbed.³¹ ^1H nuclear magnetic resonance (NMR) spectra indicate the formation of $-\text{CHO}$ and $-\text{CH}_3$ groups due to the ring-opening reactions, and the $-\text{C}=\text{O}$ group is also observed in the infrared spectra of irradiated CEs.³¹ Head space analysis indicates radiolytic generation of H_2 (1.4–2.0 molecules per 100 eV), CH_4 (0.01–0.025 molecules per 100 eV), C_2H_4 (0.1–0.36 molecules per 100 eV) and CO .²⁸ The yields of the volatiles from the CEs are comparable to such yields in irradiated poly(ethylene glycol)s, suggesting that cyclization has little effect on the chemistry.²⁸ Dicyclohexano- (DCH) substitution in the CE also has only a minor effect on the decomposition yields.^{30,35} On the other hand, substitution of bridging oxygens to $>\text{S}$ and $>\text{NH}$ bridges considerably improves the radiation stability.³⁷ This stability is also improved for dibenzo-substituted CEs (the radical yields are only 0.5–1.4 per 100 eV and the H_2 yield is only 0.1 molecules per 100 eV).³³ This increase could be accounted for by the formation of phenoxy radicals and generation of phenols that exhibit antioxidative, radio-protective properties.^{33,36} However, the choice of the ionophores for practical applications is mainly determined by their ion-binding properties rather than their radiation stability.

1.2. An Overview of the Radiation Chemistry of Aromatic Ionic Liquids. Ionizing radiation induces redox reactions involving the constituent ions in the ionic liquids.^{19–22,26} Electron detachment from the anions (A^-) yields neutral radicals (A^\bullet), which frequently fragment (for example, oxidized CF_3SO_3^- dissociates to $^\bullet\text{CF}_3$ and SO_3).^{20,21} Dissociative electron attachment to fluorinated anions results in F^- loss (for CF_3SO_3^- , this reaction yields $^\bullet\text{CF}_2\text{SO}_3^-$ radicals).²¹ Electron attachment to aromatic cations (C^+) yields the corresponding C^\bullet radicals. The reduction of imidazolium cations (Scheme 1) yields 2-imidazolyl radicals, whereas the reduction of pyridinium cations yields 4-pyridyl radicals.

The fate of these cation-derived radicals depends on the nature of the IL. For imidazolium cations that are not substituted in their C(2) position (Scheme 1), the radical is either protonated at its

C(2) carbon (forming the $\text{CH}^{+\bullet}$ radical cation)²² or forms a $\text{C}(2)-\text{C}(2) \sigma^2\sigma^{*1}$ bond with the parent cation (forming radical cation $\text{C}_2^{+\bullet}$).³⁹ Such reactions do not occur for 2-substituted imidazolium and 4-substituted pyridinium cations.²² $\text{CH}^{+\bullet}$ can also be generated by the addition of the H^\bullet atoms to the parent cation; the mobile H^\bullet atoms are generated via electron trapping by protons. These protons are present in the ILs either as an impurity (e.g., water impurity) or are generated radiolytically^{21,22} by deprotonation from the aliphatic arms of ionized parent cations (that is, the $\text{C}^{2+\bullet}$ radical dications),^{20,22} leading to formation of the corresponding $\text{R}^\bullet(\text{C}^+)$ alkyl radicals. The electronically excited C^\bullet radicals and C^+ cations can eliminate their long arms as R^\bullet radicals and 1,2-olefins, respectively.^{17,22}

2. EXPERIMENTAL METHODS

If not stated otherwise, the reagents used in this study and room-temperature ionic liquids (such as $\text{C}_4\text{mim TfO}$ and $\text{C}_4\text{MePy BF}_4$) have been obtained from Aldrich. The ionic liquids were dried at 90 °C in a vacuum oven for 12 h prior to use, and the concentration of water in these ILs was less than 2 mol % with exception of the triflate ILs that contained 10 mol % water, as determined using ^1H nuclear magnetic resonance (NMR) spectroscopy. The deuterio-substituted imidazolium ILs in 2,4,5 positions in the aromatic ring were obtained following the procedure discussed in ref 21. The choice of the specific ILs for this study was dictated by two concerns: (i) choosing examples of aromatic ILs representing typical constituent ions in practically used IL-based diluents and (2) choosing ILs that enabled us to observe solute-derived radicals against the background of organic radicals that are derived from the IL solvent itself (section 3). For example, radiolysis of CF_3SO_3^- anions yields $^\bullet\text{CF}_3$ and $^\bullet\text{CF}_3\text{SO}_3^-$ radicals that do not yield resonance lines overlapping with the resonance lines of other organic radicals in the EPR spectra of irradiated solutions.^{20,21} Likewise, irradiation of BF_4^- anions yields reactive fluorine atoms that promptly abstract hydrogen from aliphatic arms of the organic cations, yielding no additional radicals interfering with our measurements.²¹

Spectroscopic, and computational approaches used in this study were similar to those used in prior work.^{20–22} The IL samples were frozen by immersion in liquid nitrogen and irradiated to 3 kGy (1 Gy = 1 J/kg) at 77 K using 3 MeV electrons. The radicals were observed using a 9.44 GHz Bruker ESP300E spectrometer, with the sample placed in a flow He cryostat (Oxford Instruments CF935). The magnetic field and the hyperfine coupling constants (hfcc) are given in the units of gauss (1 G = 10^{-4} T). If not stated otherwise, the first-derivative EPR spectra were obtained at 50 K using 2 mW radiation and 2 G modulation at 100 kHz. Second-derivative EPR spectra were obtained by the numerical differentiation. The radiation-induced EPR signal from a silicon dangling bond center in the Suprasil sample tubes was deleted from the EPR spectra.

To generate radicals 2 without spectral interferences from other radicals, 0.1 M polyethers were added to aqueous solutions of 2 nm diameter anatase nanoparticles, frozen to 77 K, and irradiated using 10 mJ, 6 ns pulses of 355 nm light from a Nd:YAG laser. Hence, the radicals are formed photocatalytically upon photoexcitation of the anatase. The photoirradiated samples exhibit a narrow line at $g \approx 1.97$ from lattice-trapped electrons ($\text{Ti}^{3+\bullet}$ ions), a broad line at $g \approx 1.93$ from surface-trapped electrons. The part of the EPR spectra where the

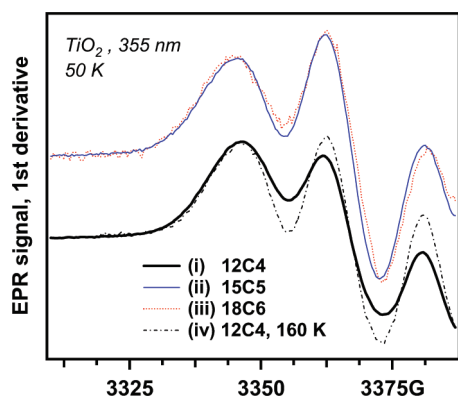


Figure 1. EPR spectra of photoirradiated frozen aqueous solutions containing anatase nanoparticles (pH = 2) and 0.1 M of (i) 12-crown-4, (ii) 15-crown-5, (iii) 18-crown-6 at 50 K, and (iv) 12-crown-4 at 160 K. The solutions were irradiated at 77 K using 355 nm light.

resonance lines of the organic radicals overlap with the lines of the electron centers are not shown in the figures below. (See refs 21 and 22 for more details.)

To conserve space, some figures have been placed in the Supporting Information. Such figures have the designators “S” (e.g., Figure 1S).

3. RESULTS

3.1. Reference Systems. As noted in section 1.1, EPR spectra from irradiated CEs are congested and the spectral signatures of the contributing radicals and the radical products of their transformation (Scheme 2) are poorly known. To establish the spectral signature of radical 2, we generated it photochemically by oxidation of chemisorbed CEs by photoexcited titania nanoparticles.^{21,40} The EPR spectrum of 1,4-dioxane, the simplest representative molecule of its class, exhibited resonance lines that we attribute to the corresponding $\cdot\text{H}$ radical (Figure 1S). This attribution is supported by simulations using the hfcc parameters given in the literature^{27,41} and our own density functional theory (DFT) calculations using B3LYP/6-31+G(d,p) method⁴² from Gaussian 98.⁴³ In addition to radical 2, the low-field line of the formyl radical is observed. For 1,4-dioxane- d_8 , this line was absent, indicating that the proton in the formyl radical is obtained from the 1,4-dioxane.

Since the deuteron is a spin-1 nucleus having $\approx 15\%$ of the magnetic moment of the proton (a spin- $1/2$ nucleus), D/H substitution has the effect of “collapsing” the EPR spectra of the alkyl radicals. In the EPR spectra of the h_8 and d_8 isotopomers of tetrahydrofuran, the formyl radical line was absent, suggesting that the opening/contraction of the CE macrocycle requires the presence of at least two bridging oxygens. Warming of the irradiated 1,4-dioxane to 180 K caused the gradual decay of radicals 2 and 7 without the anticipated fragmentation of radical 2, as shown in Scheme 2b. The ground state radical 2 appears to be very stable.

We expect that radical 2, which is the product of the photocatalytic oxidation of 1,4-dioxane, is the same type of radical produced by the photooxidation of larger polyethers. As shown in Figure 1, photoreactions of 12C4, 15C5, and 18C6 produce similar EPR spectra, specifically, triplets of broad lines that can be attributed to their corresponding 2 radicals. These resonance lines become narrower as the samples are warmed to 160 K

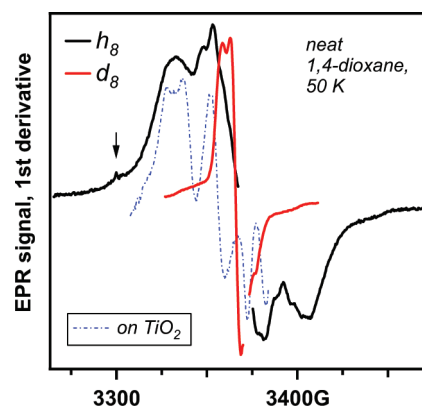


Figure 2. EPR spectra of the neat dioxane- h_8 and - d_8 irradiated with 3 MeV electrons at 77 K. The dash-dot trace is the EPR spectrum of 2- h_8 on TiO_2 from Figure 1S. The low-field line of the formyl is indicated with the arrow.

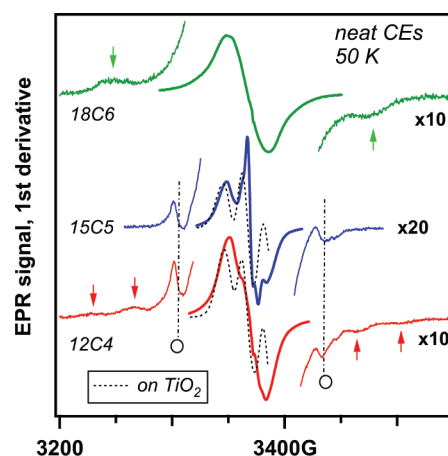


Figure 3. EPR spectra from irradiated frozen neat crown ethers. The lines of the formyl radical are indicated with dash-dot lines and open circles. The lines attributed to 4 are indicated with arrows. The EPR spectra of the corresponding radicals 2 are indicated with dashed lines.

(Figures 1 and 2S). (That is, the reactions shown in Scheme 2b were not observed upon the thermal activation.) Similar EPR spectra were obtained for acyclic polyethers (shown in Figure 3S). The 12-, 15-, and 18-atom macrocycles are too large to exhibit conformational effects (including the nonequivalence of β -hydrogens) that are apparent in the smaller 1,4-dioxane radical. Furthermore, in all of these systems, radical 2 does not appear to undergo C–O fragmentation, so the reactions shown in Scheme 2b cannot involve the ground state of this radical.

When neat 1,4-dioxane is irradiated using 3 MeV electrons, the resulting EPR spectrum is congested (Figure 2), but the presence of radical 2 is apparent from the comparison to the EPR spectrum on TiO_2 . The low-field line of the formyl radical is also discernible against the broader EPR signal. That more than one radical center contributes to this broad EPR line transpires from the changes observed upon d_8 substitution. While the spectrum of the d_8 isotopomer of radical 2 in Figure 1S is a narrow singlet, the EPR spectrum for irradiated 1,4-dioxane- d_8 shown in Figure 2 reveals another radical with a narrower resonance line superimposed on the line of radical 2. This is consistent with the alkyl radical coupled to fewer protons, such as

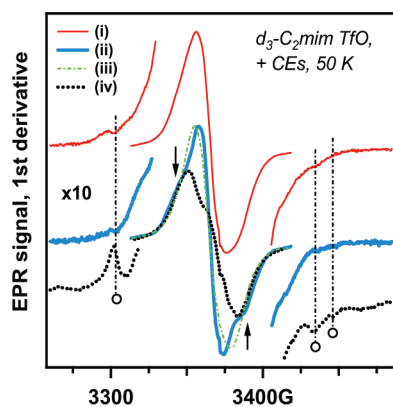


Figure 4. EPR spectra of irradiated frozen (i) 9 mol % 18-crown-6 and (ii) 12-crown-4 in 2,4,5- $C_2\text{mim-}d_3$ TfO (that is, C₂mim TfO that was deuterio trisubstituted in 2, 4, and 5 positions of the imidazolium ring). The spectra of (iii) neat 12-crown-4 and (iv) $C_2\text{mim-}d_3$ TfO are shown for comparison. The vertical lines and open circles indicate the resonance lines from the formyl radical. The arrows indicate the shoulders due to radical 2.

radicals 5 or 6. On the other hand, the wide, structureless wings indicate the presence of a radical with a greater number of coupled protons than radical 2, which suggests either radical 3 or 4. In the EPR spectra of irradiated 12C4 and 15C5 (Figure 3), there are two resonance lines from the formyl radical. For 12C4, the EPR signal at $g \approx 2$ is similar to the one observed for this compound in a Freon matrix.³⁸ This spectrum was interpreted as superposition of the triplet of radical 2 and the doublet of radical 5.^{31,34,38} In addition to these features there are weak, widely spread resonance lines that can only be from radical 4.³¹ The same (broadened and collapsed) lines are present in the EPR spectrum of 18C6. For 15C5, there is a narrow line superimposed on the line of radical 2, which is likely to be from the acyl radical 6. When 8 mol % 15C5 is dissolved in 2-propanol- d_8 and cyclohexane- d_6 (Figure 4S), the features of radicals 2 and 7 are still recognizable.

3.2. Radiolysis of CE in Aromatic Ionic Liquids. Because the radicals generated by radiolysis of the IL yield a strong background signal, observing the lines of the CE-derived radicals against this background is challenging. Nevertheless, such radicals can be observed at concentrations of the solute much higher than those typically employed in extraction processes (i.e., 5–50 mol % vs less than 2 mol %). (Figure 4, traces i and ii). To minimize the spectral overlap, we used the d_3 (2,4,5- D_3) isotopomer of $C_2\text{mim TfO}$ synthesized as described in ref 21. The EPR spectrum for the neat IL at $g \approx 2$ exhibits the narrow line of the d_3 -isotopomer of radical cation $C_2^{+\bullet}$ (trace iii) in Figure 4). When 35 mol % 12C4 is added to this IL, the EPR spectrum of the mixture reveals two new features that are also apparent for neat 12C4 (trace iv in Figure 4). One of these features is the presence of the narrow lines of the formyl radical, which is also observed for 9 mol % 18C6. The second observed feature is the presence of two shoulders superimposed on the $C_2^{+\bullet}$ - d_3 line (indicated with the arrows in Figure 4) from radical 2. No lines from radical 4 (that are apparent in Figure 3) were observed. The formyl radical, due to its readily recognized spectral signature, can also be observed in other CE/IL systems. As an example, Figure 5S exhibits this feature for $C_4\text{mim PF}_6$ and for $C_2\text{mim TfO}$ containing 14 mol % DCH18C6.

Unfortunately, spectral congestion in the CE/IL mixtures makes it difficult to recognize radicals. To overcome this

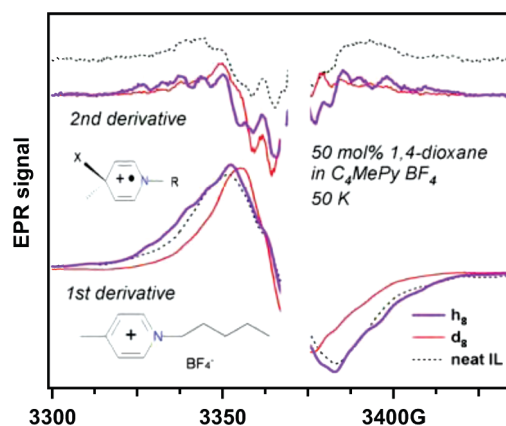


Figure 5. First- and second-derivative EPR spectra of irradiated frozen $C_4\text{MePy BF}_4$ containing 50 mol % 1,4-dioxane- h_8 or d_8 . The dashed line indicates the EPR spectrum of neat ionic liquid. The pattern of the resonance lines separated by 5–6 G is from the corresponding $\text{CH}^{+\bullet}$ and $\text{CD}^{+\bullet}$ radicals.

limitation, we studied the simplest of the CE systems: 1,4-dioxane. The convenience of this solute is that it can be obtained as a d_8 isotopomer, with the corresponding radicals having narrow resonance lines that can be distinguished against the background of other radicals. This is illustrated in Figure 6S(a) for $C_2\text{mim TfO}$ containing 25 wt % and 48 wt % 1,4-dioxane- d_8 . The narrow line of radical 2- d_7 (as it appears in Figure 1) is superimposed on a broader line from $C_2^{+\bullet}$. These EPR spectra indicate that radiation damage to the solute becomes significant in concentrated solution. Concomitant spectral transformations can be observed in the spectral wings (Figure 6S(b)), where the resonance lines from $\cdot\text{CF}_3$ and $\cdot\text{CF}_2\text{SO}_3^-$ radicals^{20,21} (indicated with arrows in the plot) become progressively weaker as the mole fraction of 1,4-dioxane increases.

Yet another important change becomes apparent when the irradiated sample is warmed to 175 K (Figure 7S). At this temperature, the $C_2^{+\bullet}$ and radical 2- d_7 both decay, and an underlying doublet (shown at the top of Figure 7S) can be observed. This EPR spectrum reveals a 7 G pattern and spectral envelope consistent with radical cation $\text{CD}^{+\bullet}$.²² In our previous study,²² we showed that irradiation of neat $C_2\text{mim TfO}$ does not generate this type of radical cation, whereas radical cation $\text{CH}^{+\bullet}$ is generated in the IL containing water. This was rationalized by the observation that radical cation $\text{CH}^{+\bullet}$ can be produced by either protonation of the C^\bullet radical or by addition of the H^\bullet atom to the parent cation. In $C_n\text{mim TfO}$, the C^\bullet radical adds to C^+ , and the resulting $C_2^{+\bullet}$ radicals cannot be protonated, as the accepting C(2) carbon in this C(2)–C(2) bound structure is substituted. Thus, the only pathway to the $\text{CD}^{+\bullet}$ in this ionic liquid is via the generation of the D^\bullet atoms that add to the C^+ . Our observation of the $\text{CD}^{+\bullet}$ implies that mobile, reactive D^\bullet atoms are generated in fragmentation of 1,4-dioxane- d_8 .

The same point can be demonstrated using $C_4\text{MePy BF}_4$. In prior work,²² it was shown that radiolysis of this IL does not result in the formation of radical cation $\text{CH}^{+\bullet}$ at 77 K (see Figure 5). When 50 mol % 1,4-dioxane- h_8 or $-d_8$ was added to this IL; however, the multiplets of the $\text{CH}^{+\bullet}$ and $\text{CD}^{+\bullet}$ (respectively) appeared in the EPR spectra. Since the width of the EPR spectrum is determined by the coupling of the unpaired electron to the H(4) proton (which has h_{fcc} of ~ 60 G), the substitution of H(4) for D(4) narrows the spectrum without destroying the

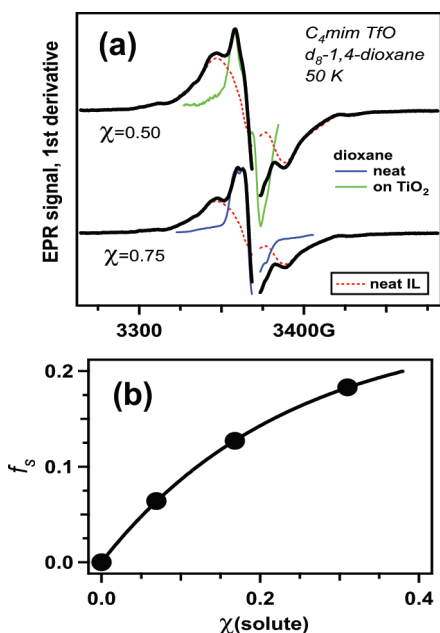


Figure 6. (a) EPR spectra from irradiated frozen $C_4\text{mim TfO}$ containing 50 and 70 mol % 1,4-dioxane- d_8 . The dashed line is the EPR spectrum from neat ionic liquid. For comparison, EPR spectra from irradiated neat 1,4-dioxane- d_8 and photoirradiated 1,4-dioxane- d_8 in the aqueous TiO_2 are shown in the same plot. (b) Relative fraction f_s of solute radical 2 on the mole fraction χ of the solute, for the same system.

modulation pattern from the proton hfcc's in the aromatic ring.²² The low-temperature generation of the $\text{CD}^{+\bullet}$ indicates the formation of D^\bullet atoms from the solute, suggesting either the direct fragmentation to ($\text{H}^\bullet + 2$) or the deprotonation of the ionized solute with concomitant electron trapping by the released proton.

To obtain an estimate of the radical yield, we varied the mole fraction χ of d_8 -1,4-dioxane in $C_4\text{mim TfO}$ (Figures 6a and 8S). This IL was chosen because it yields a rather broad line from the imidazolium radicals, which makes it easier to observe the narrow resonance line from radical 2- d_7 . Figure 6a shows the EPR spectra obtained for $C_4\text{mim TfO}$ containing 50 mol % and 75 mol % 1,4-dioxane- d_8 . The EPR spectra from the electron-irradiated IL and 1,4-dioxane- d_8 (separately) and photoirradiated 1,4-dioxane- d_8 on TiO_2 are superimposed onto these spectra. These EPR spectra decompose into the EPR signals from the solvent and the solute (Figure 8S). Figure 6b exhibits the relative fraction f_s of the 2- d_7 radical to the total radical yield, as estimated by double integration of the first-derivative EPR spectra. As seen from this plot, in the low-loading regime, $f_s \approx 0.5 \chi$. Given that for every radical 2 there is the H^\bullet atom that adds to the IL cation (as suggested by the results obtained in the high-loading regime) while the yield of the formyl is low as compared to these radicals, we conclude that the relative radical yield is approximately equal to the mole fraction of the 1,4-dioxane. Extrapolating from this plot to the region of practical interest (<2 mol % CE in IL), we conclude that less than 2% of the radicals in the IL solutions are derived from the solute.

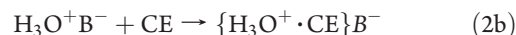
4. DISCUSSION AND CONCLUDING REMARKS

To summarize our results, unless $\chi > 0.1$, very few radicals derived from the solute are observed in the EPR spectra of frozen

CE/IL mixtures. These species include H^\bullet atoms, the formyl radical, and H atom loss radical 2. The relative yield of $\text{H}^\bullet + 2$ (to the total radical yield at 77 K) approximately equals the mole fraction of the solute. The latter quantity approximately equals the fraction of the electron density in the solute, which in turn determines the stopping power for the high-energy electrons and γ rays and the fraction of the electrons stopped by each component. Since all of these fractions are $\sim \chi$, the radiolytic yield of radicals per energy absorbed by each two component is approximately the same. This result implies that no significant transfer of charge and/or excitation energy from the aromatic IL to the CE solute occurs; there are no reactions converting the excess electrons, solvent holes, and the solvent excited states to radical ions or the excited states of the solute. (This is unlike the case of the trialkylphosphates in saturated hydrocarbons, as depicted in reaction 1 shown above). The reverse process (radical species derived from the CE reacting with the solvent) certainly occurs (*i.e.*, we demonstrated that the H^\bullet atoms generated by fragmentation of 1 react with the C^+). Since the concentrations of CE employed in extraction systems of practical interest are typically low, the damage to the IL due to such reactions should be negligible. These results indicate that aromatic ILs function as radioprotective solvents, channeling the excitation/ionizations in the solvent away from the solute.

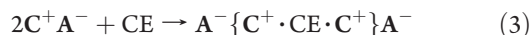
From the results presented in section 3.1, it appears that the ground state of radical 2 does not undergo the fragmentation reactions shown in Scheme 2b. From previous product analysis studies,³² it is known that in most organic solvents such radicals cross recombine, react with molecular O_2 with the subsequent elimination of a monomer unit, or recombine with inorganic radicals generated in the aqueous phase, yielding the corresponding -Cl and - NO_2 derivatives.³² In analogy, it may be expected that in ILs, radical 2 can recombine or disproportionate with the anion fragment radicals (such as CF_3^\bullet) and the $\text{R}^\bullet(\text{C}^+)$. While such secondary radical reactions could be facile, the radiolytic yield of such products cannot exceed the radiolytic yield of the progenitor radical 2.

Since protons (or hydronium ions) are continuously generated in the radiolysis of the IL, the most potentially problematic reaction from a separations standpoint is the formation of an ionophore–proton complex, such as is depicted here:



where B^- is the generic base (that may include the constituent anion, A^-). The protonation of the CEs is well-known from gas phase studies,⁴⁴ and it can be observed in aprotic organic solvents (such as chloroform and 1,2-dichloroethane) using conductivity methods.^{45,46} For crown ethers with $n < 6$, the binding constants (K) for H_3O^+ (reaction 2b) are quite low, but for 18C6, $\log K > 6$,⁴⁵ as the three hydrogens in the hydronium ion form strong bonds with the three equivalent oxygens in the crown ring.^{47,48} Apparently, reaction (2) also occurs in imidazolium ILs, as suggested by the depressed extraction efficacy in the presence of radiolytically generated acid.^{18a} While the degree of the $\text{HB}/\text{H}^+\text{B}^-$ dissociation in the IL is not known,^{49,50} it is known that 5–50% of 4-nitroaniline in $\text{C}_n\text{mim NTf}_2$ is protonated in the presence of 0.01–0.1 M of HNTf_2 ; this fraction rapidly increases

in the presence of water.⁴⁹ ¹H NMR studies also indicate the dissociation of HB in the presence of water in the IL.^{50,51} The occurrence of the reactions in eq 2a may considerably increase the degree of the HA dissociation. Elsewhere, we estimated equilibrium constant *K* for reaction 2a of DCH18C6 + TfOH in C₄mim TfO to be $25 \pm 7 \text{ M}^{-1}$.⁵⁰ This constant is much lower than the corresponding constant in the chloroform, which can be attributed to the strong H-bonds formed by free H₃O⁺ ions with the solvent ions in chloroform,⁵² poor dissociation of TfOH in the IL,⁵⁰ and weak interaction of the constituent cations of the IL with the crown, which is known to result in the formation of a symmetrical 2:1 H-bond complex^{13,53}



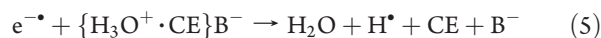
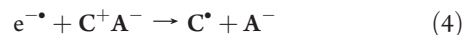
While the stability constant for this complex might be low, the concentration of the constituent cations in neat IL is high, resulting in the decreased protonation of the CE.

For a conventional organic solvent in which the metal ion (M^{n+}) extraction process involves only the free crown ether, the effect of reaction 2b reducing the concentration of free CE would clearly be detrimental. In an ionic liquid, however, the situation is more complicated, making the precise effect of radiolysis more difficult to predict. As has been noted previously,⁴ the extraction of a metal ion (e.g., strontium) by a crown ether into an IL, unlike its extraction into a conventional organic solvent, is a multipath process comprising up to three distinct pathways for partitioning:

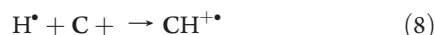
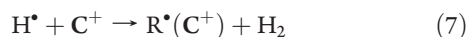
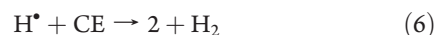
- Extraction of a neutral metal ion–crown ether complex, in which the cationic $\{\text{M}^{n+} \cdot \text{CE}\}$ complex initially formed is paired with an aqueous phase anion (e.g., NO_3^-) to yield a neutral species, which then partitions into the IL phase.
- Formation of a cationic metal ion–crown ether complex $\{\text{M}^{n+} \cdot \text{CE}\}$, followed by its exchange for the cationic component of the IL.
- Formation of an acid–crown ether complex, followed by the exchange of an aqueous phase metal ion for the complexed proton (or hydronium ion).

The parameters governing the balance among these three pathways remain incompletely understood at present, but are known to include such factors as the charge on the metal ion, the hydrophobicity of the IL cation, the aqueous acidity, and the nature of the aqueous phase anion(s) present. For IL systems in which the first of the pathways predominates (e.g., for systems in which the IL cation is relatively hydrophobic), the effect of the “consumption” of the CE by radiolytically generated acid seems likely to be significant for cations such as Sr^{2+} only at high levels of irradiation. This conclusion follows from studies of Sr^{2+} extraction into C₁₀mim NTf₂ containing DCH18C6, for which the efficiency of strontium extraction from aqueous nitric acid is seen to increase with acidity, declining only when high acid concentrations ($\geq 3 \text{ M}$) have been reached.⁴ For less hydrophobic ILs (e.g., C₅mim NTf₂), for which ion exchange represents the predominant mode of metal ion extraction in the presence of a crown ether, protonation of the crown ether would be expected to shift the balance between the two possible types of ion exchange, disfavoring that involving exchange of the cationic metal ion–crown ether complex for the cationic component of the IL. Prior studies of the acid dependency of the efficiency of extraction of representative alkali (Na^+) and alkaline earth (Sr^{2+}) cations by DCH18C6 indicate that the result of this shift could be a significant decline in extraction, particularly at high acid concentrations.⁴

A less obvious detrimental effect of this reaction is that it places the protic site immediately adjacent to the macrocycle, so that the excess electrons generated in the ionization of the IL can now react with the $\{\text{H}_3\text{O}^+ \cdot \text{CE}\}\text{B}^-$ complex instead of the solvent cations C^+ if the macrocycle–proton complex is a deeper electron trap than the constituent aromatic cation. Using the conventional notation e^- for the primary “electron” species released in the ionization events (which may be a presolvated electron or a short-lived solvated electron)

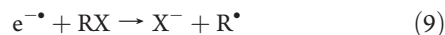


For aliphatic cations in the ILs, reaction 4 does not occur, and reaction 5 preceded by reaction 2b can be important even at low radiation doses. The H^\bullet atom can abstract from either the CE (reaction 6) or the aliphatic arms of the parent cation (reaction 7) or add to the aromatic ring of these cations (reaction 8).^{20–22}



Since the hydrogen atom in reaction 5 is generated at the site of the crown ether, reaction 6 might be preferred to reactions 7 and 8 despite the facility of these two reactions and the great excess of the solvent cations over the CE molecules. Thus, the protonation of the CE (reaction 2a) can lead to radiation-induced deterioration of the extraction efficacy not only through the direct effect on metal binding but also through directing radiolytic damage toward the extractant. Optimally, the radiation exposure should be sufficiently low that reaction 4 is preferred to reaction 5.

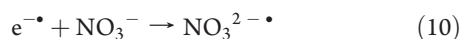
Such behavior has precedence in previously studied molecular solvents. For some of these solvents, the decrease in the distribution coefficient of Sr^{2+} , D_{Sr} (a measure of extraction efficiency defined as the ratio of the Sr^{2+} concentration in the organic and aqueous phases at equilibrium), is pronounced even at low radiation doses. For example, in radiolysis of 50 mM DCH18C6 in CHCl_3 , D_{Sr} decreased from 10^3 before irradiation to 10^2 at 70 kGy;³² a similar decrease was observed for other CEs and halogenated solvents. In the radiolysis of such solvents, the RX molecules release halides via this reaction:^{23,32}



The observed decrease in D_{Sr} values has been attributed to $\{\text{H}_3\text{O}^+ \cdot \text{CE}\}(\text{Cl}^-)_{1,2}$ pairing.³² For solvents in which such acids are not generated during radiolysis, the decrease in the D_{Sr} is much lower. For extraction of Sr^{2+} from 3 M HNO_3 using 0.2 M di(*tert*-butyl)-DCH18C6 in 1-octanol, D_{Sr} falls from 40 before irradiation to 14 at 386 kGy.³² In such solvents, the decrease of D_{Sr} was attributed mainly to slow radiolytic damage to the CE (such as ring-opening reactions) rather than reaction 2b. For this reason, halogenated solvents are avoided in extraction systems based on CEs.

Our EPR results, along with the results of ref 20, suggest that ILs more closely resemble halogenated alkanes in their behavior than other types of organic solvents. That is, although the irreversible radiolytic damage to the CEs is rather small, damage to the IL is considerable^{17–22} and it results in the acidification of the solvent.¹⁸ In the presence of the CEs, the protons form $\{H_3O^+ \cdot CE\}(A^-)_{1,2}$ pairs less able to accept Sr^{2+} ions from the aqueous phase than the free CE (or the CE complexes with the constituent ions, reaction 3). When the acidity increases considerably in such “neat” IL solutions (that occurs in the high dose regime), this may cause excessive damage to the CE solute through the diversion of the electron trapping from the solvent to the solute and the subsequent H^\bullet atom abstraction from the CE. If the radiolytic generation of the protons is relatively low (that is, in the low-dose regime) the IL solvent actively “protects” the CE solute (as explained above) so that the solute deteriorates slowly, as is the case for typical (nonhalogenated) molecular organic solvents.

A subject of some concern is that the extraction of H_3O^+ from the aqueous phase (which, typically, contains 1–4 M HNO_3 added to facilitate neutral extraction of metal ions) can shift equilibrium reaction 2b to the right side, leading to redirection of radiolytic damage toward the CE. Our recent NMR studies⁵⁰ indicated that the typical hydrophobic ILs used for Sr^{2+} separations, such as $C_8mim NTf_2$ and $C_{10}mim NTf_2$, in contact with 3 M HNO_3 (1:1 v/v) extracted both water and nitric acid. The extraction of the nitrate to the IL phase was 0.23 and 0.16 M, respectively, and this concentration further increased in the presence of 0.1 M DCH18C6 (to 0.35 and 0.37 M, respectively). Most of the nitric acid was extracted as the $\{H_3O^+ \cdot CE\}NO_3^-$ complex, although some was extracted as the $CE \cdot (H_2O \cdots HNO_3)$ complex, and the IL solvent also contained ~ 15 mol % water.⁵⁰ The extraction of nitric acid remained considerable even for extremely hydrophobic ILs, such as trihexyltetradecylphosphonium bistriflimide.⁵⁰ These results suggest that radiation damage in the IL solutions could be rather different for the pre-equilibrated IL solutions that contain significant amounts of water and nitric acid. In particular, our NMR results suggest that all CE molecules in such IL solutions are protonated. Nevertheless, the directed damage to the CE via reactions 5 and 6 in such pre-equilibrated ILs may not be as significant as it may appear at first glance, as the NO_3^- anions introduced through such an extraction would compete with the hydronium ions for the electrons, as the nitrate anions are one of the deepest electron traps in the ILs:^{21,50}



The resulting $NO_3^{2-\bullet}$ radicals are promptly protonated to yield $HNO_3^{2-\bullet}$ that in turn reacts with acids and water to yield NO_2^\bullet radicals. In radiolysis of 1:1 mol/mol $C_2mim NO_3:C_2mim BF_3$, only these radicals were observed by EPR at 77 K,²¹ suggesting that reaction 10 prevailed over reaction 4. Thus, the extraction of the nitric acid from the aqueous solutions may not necessarily result in the directed damage to the CE in these ionic liquids. The latter conclusion, however, remains conjectural and requires further studies for validation.

We expect that mechanistic insights such as those provided by this study will be of significant value to separations chemists in their pursuit of ionic liquid-based separations systems that exhibit high extraction efficiency and satisfactory radiation stability.

■ ASSOCIATED CONTENT

S Supporting Information. Figures 1S–8S showing EPR results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ REFERENCES

- (1) Plechkova, N. V.; Seddon, K. R. *Chem. Soc. Rev.* **2008**, 37, 123–150.
- (2) Wishart, J. F. *Energy Environ. Sci.* **2009**, 2, 956–961.
- (3) Tan, S. S. Y.; MacFarlane, D. R. In *Ionic Liquids*; Springer-Verlag: Berlin, 2009; pp 311–339.
- (4) Dietz, M. L. *Sep. Sci. Technol.* **2006**, 41, 2047–2063. Dietz, M. L.; Stepinski, D. C. *Green Chem.* **2005**, 7, 747–750. Dietz, M. L.; Dzielawa, J. A.; Laszak, I.; Young, B. A.; Jensen, M. P. *Green Chem.* **2003**, 5, 682–685. Dietz, M. L.; Dzielawa, J. A. *Chem. Commun.* **2001**, 2124–2125.
- (5) Luo, H.; Dai, S.; Bonnesen, P. V.; Haverlock, T. J.; Moyer, B. A.; Buchanan, A. C., III *Solvent Extr. Ion Exch.* **2006**, 24, 19–???. Luo, H.; Dai, S.; Bonnesen, P. V. *Anal. Chem.* **2004**, 76, 2773–2779. Dai, S.; Ju, Y. H.; Barnes, C. E. *J. Chem. Soc., Dalton Comm.* **1999**, 1201–1202. Luo, H.; Dai, S.; Bonnesen, P. V.; Buchanan, A. C., III *J. Alloys Comp.* **2006**, 418, 195–199.
- (6) Jensen, M. P.; Neufeind, J.; Beitz, J. V.; Skanthakumar, S.; Soderholm, L. *J. Am. Chem. Soc.* **2003**, 125, 15466.
- (7) Stepinski, D. C.; Young, B. A.; Jensen, M. P.; Rickert, P. G.; Dzielawa, J. A.; Dilger, A. A.; Rausch, D. J.; Dietz, M. L. In *Separations for the Nuclear Fuel Cycle in the 21st Century*; Lumetta, G.; Nash, K. L., Clark, S. B., Friese, J. L., Eds. American Chemical Society: Washington, DC, 2006; p 233.
- (8) Vendilo, A. G.; Djigailo, D. I.; Smirnova, S. V.; Torocheshnikova, I. I.; Popov, K. I.; Krasovsky, V. G.; Pletnev, I. V. *Molecules* **2009**, 14, 5001–5016.
- (9) Dietz, M. L.; Dzielawa, J. A.; Jensen, M. P.; Beitz, J. V.; Borkowski, M. In *Ionic Liquids IIb: Fundamentals, Progress, Challenges and Opportunities: Transformations and Processes*; American Chemical Society: Washington, DC, 2005; Vol. 902, pp 2–18.
- (10) Nash, K. L. In *Separations for the Nuclear Fuel Cycle in the 21st Century*; Lumetta, G. J.; Nash, K. L.; Clark, S. B.; Friese, J. L., Eds.; American Chemical Society: Washington, DC, 2006; Vol. 933, pp 21–40.
- (11) Cocalia, V. A.; Gutowski, K. E.; Rogers, R. D. *Coord. Chem. Rev.* **2006**, 250, 755–764.
- (12) Cocalia, V. A.; Jensen, M. P.; Holbrey, J. D.; Spear, S. K.; Stepinski, D. C.; Rogers, R. D. *Dalton Trans.* **2005**, 1966–1971.
- (13) Chaumont, A.; Wipff, G. *J. Phys. Chem. B* **2010**, 114, 13773–13785.
- (14) Chun, S.; Dzyuba, S. V.; Bartsch, R. A. *Anal. Chem.* **2001**, 73, 3737–3741.

- (15) For example: Chen, P. Y.; Hussey, C. L. *Electrochim. Acta* **2004**, *49*, 5125–5138.
- (16) Stepinski, D. C.; Vandegrift, G. F., III; Shkrob, I. A.; Wishart, J. F.; Kerr, K.; Dietz, M. L.; Qadah, D. T. D.; Garvey, S. L. *Ind. Eng. Chem. Res.* **2010**, *49*, 5863–5868.
- (17) Berthon, L.; Nikitenko, S. I.; Bisel, I.; Berthon, C.; Faucon, M.; Saucrotte, B.; Zorz, N.; Moisy, P. *Dalton Trans.* **2006**, 2526–2534. Bosse, E.; Berthon, L.; Zorz, N.; Monget, J.; Berthon, C.; Bisel, I.; Legand, S.; Moisy, P. *Dalton Trans.* **2008**, 924–931. Le Rouzo, G.; Lamouroux, C.; Dauvois, V.; Dannoux, A.; Legand, S.; Durand, D.; Moisy, P.; Moutiers, G. *Dalton Trans.* **2009**, 6175–6184. Allen, D.; Baston, G.; Bradley, A. E.; Gorman, T.; Haile, A.; Hamblett, I.; Hatter, J. E.; Healey, M. J. F.; Hodgson, B.; Lewin, R.; Lovell, K. V.; Newton, B.; Pitner, W. R.; Rooney, D. W.; Sanders, D.; Seddon, K. R.; Sims, H. E.; Thied, R. C. *Green Chem.* **2002**, *4*, 152–158.
- (18) (a) Yuan, L. Y.; Peng, J.; Xu, L.; Zhai, M. L.; Li, J. Q.; Wei, G. S. *J. Phys. Chem. B* **2009**, *113*, 8948–8952. Qi, M.; Wu, G.; Chen, S.; Liu, Y. *Radiat. Res.* **2007**, *167*, 508–514. Yuan, L. Y.; Peng, J.; Xu, L.; Zhai, M. L.; Li, J. Q.; Wei, G. S. *Radiat. Phys. Chem.* **2009**, *78*, 737–739. Yuan, L. Y.; Peng, J.; Xu, L.; Zhai, M. L.; Li, J. Q.; Wei, G. S. *Dalton Trans.* **2008**, 6358–6360. (b) Yuan, L. Y.; Xu, C.; Peng, J.; Xu, L.; Zhai, M. L.; Li, J. Q.; Wei, G. S.; Shen, X. H. *Dalton Trans.* **2009**, 7873–7875.
- (19) Wishart, J. F. *J. Phys. Chem. Lett.* **2010**, *1*, 3225–3231.
- (20) Shkrob, I. A.; Chemerisov, S. D.; Wishart, J. F. *J. Phys. Chem. B* **2007**, *111*, 11786–11793.
- (21) Shkrob, I. A.; Marin, T. W.; Chemerisov, S. D.; Wishart, J. F. *J. Phys. Chem. B* **2011**, DOI: 10.1021/jp2003062.
- (22) Shkrob, I. A.; Marin, T. W.; Chemerisov, S. D.; Hatcher, J.; Wishart, J. F. *J. Phys. Chem. B* **2011**, DOI: 10.1021/jp200305b.
- (23) Berthon, L.; Chabronnel, M.-C. In *Ion Exchange and Solvent Extraction, A Series of Advances*; Moyer, B. A., Ed.; CRC Press: Boca Raton, FL, 2010; Vol. 19, pp 429–513.
- (24) Shkrob, I. A.; Marin, T. W. *Chem. Phys. Lett.* **2008**, *465*, 234–237.
- (25) Egorov, G. F. *Radiation Chemistry of Extraction Systems*; Energizdat: Moscow, 1986.
- (26) Wishart, J. F.; Shkrob, I. A. In *Ionic Liquids: From Knowledge to Application*; Rogers, R. D.; Plechkova, N. V.; Seddon, K. R., Eds.; American Chemical Society: Washington, DC, 2009; pp 119–134.
- (27) Belevskii, V. N.; Belopushkin, S. I.; Feldman, V. I.; Rakitin, Yu. V. *Dokl. Akad. Nauk USSR* **1985**, *282*, 1161–1165. Belevskii, V. N.; Belopushkin, S. I.; Chuvylkin, N. D. *High Energy Chem.* **1998**, *32*, 171–180. Naumov, S.; Janovsky, I.; Knolle, W.; Mehnert, R. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3133–3139.
- (28) Zatonsky, S. V.; Povolotskaya, O. S. *J. Radioanal. Nucl. Chem.* **1987**, *117*, 361–367.
- (29) Selivestrov, A. F.; Ershov, B. G. *High Energy Chem.* **1987**, *22*, 203–206.
- (30) Grigor'ev, E. I.; Myasoedova, T. G.; Nesterov, S. V.; Trakhtenberg, L. I. *High Energy Chem.* **1987**, *21*, 437–440.
- (31) Grigor'ev, E. I.; Nesterov, S. V. *High Energy Chem.* **1992**, *26*, 381–385.
- (32) Makhlyachuk, V. V.; Zatonski, S. V. *Russ. Chem. Rev.* **1992**, *61*, 484–499.
- (33) Grigor'ev, E. I.; Nesterov, S. V.; Mikhailsyna, O. V.; Trakhtenberg, L. I.; Myasoedova, T. G. *High Energy Chem.* **1992**, *26*, 311–316.
- (34) Grigor'ev, E. I.; Nesterov, S. V.; Vorontsov, P. S.; Mikhailsyna, O. V.; Trakhtenberg, L. I. *Radiat. Phys. Chem.* **1995**, *46*, 553–556.
- (35) Abashkin, V. M.; Wester, D. W.; Campbell, J. A.; Grant, K. E. *Radiat. Phys. Chem.* **1996**, *48*, 463–472.
- (36) Nesterov, S. V.; Panov, O. Yu. *J. Radioanal. Nucl. Chem.* **1998**, *231*, 87–93.
- (37) Kucuyavuz, S.; Nesterov, S. V.; Onal, A. M. *J. Radioanal. Nucl. Chem.* **1998**, *230*, 39–44.
- (38) Zakudraeva, O. A.; Nesterov, S. V.; Feldman, V. I. *High Energy Chem.* **2007**, *41*, 65–69.
- (39) Shkrob, I. A.; Wishart, J. F. *J. Phys. Chem. B* **2009**, *113*, 5582–5592. see also Chandrasekhar, N.; Unterreiner, A.-N. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1698–1708.
- (40) Shkrob, I. A.; Chemerisov, S. D. *J. Phys. Chem. C* **2009**, *113*, 17138–17150.
- (41) Lunazzi, L.; Placucci, G.; Grossi, L. *Tetrahedron* **1983**, *39*, 159–163. Gaze, C.; Gilbert, B. C. *J. Chem. Soc., Perkin Trans. II* **1977**, 754–759.
- (42) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (43) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, rev. A.1; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (44) Sharma, R. B.; Blades, A. T.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 510–516.
- (45) Shchori, E.; Jagur-Grodzinski, J. *J. Am. Chem. Soc.* **1972**, *94*, 7957–7962.
- (46) Kolthoff, I. M.; Wang, W.-J.; Chantooni, M. K., Jr. *Anal. Chem.* **1983**, *55*, 1202–1204. Amini, M. K.; Shamsipur, M. *J. Solution Chem.* **1992**, *21*, 275–288. Chantooni, M. K., Jr.; Kolthoff, I. M. *J. Solution Chem.* **1992**, *21*, 683–697.
- (47) Makrlík, E.; Vanura, P.; Budka, J. *Monatsh. Chem.* **2009**, *140*, 583–585.
- (48) Chenevert, R.; Rodrigue, A.; Beauchesne, P.; Savoie, R. *Can. J. Chem.* **1984**, *62*, 2293–2298. Chenevert, R.; Rodrigue, A. *J. Chem. Educ.* **1984**, *61*, 465–466.
- (49) Thomazeau, C.; Olivier-Bourbigou, H.; Magna, L.; Luts, S.; Gilbert, B. *J. Am. Chem. Soc.* **2003**, *125*, 5264–5265.
- (50) Marin, T. W.; Shkrob, I. A.; Dietz, M. L. *J. Phys. Chem. B* **2011**, jp-2011-01193f.
- (51) Yasaka, Y.; Wakai, C.; Matubayasi, N.; Nakahara, M. *Anal. Chem.* **2009**, *81*, 400–407.
- (52) Wang, Y.; Li, H.; Han, S. *J. Phys. Chem. B* **2006**, *110*, 24646–24651.
- (53) Gjika, M.; Brockner, W.; Namyslo, J.; Adam, A. *CrystEngComm* **2008**, *10*, 103–110.