EXAFS Investigation of Strontium Complexes in Room-temperature Ionic Liquids

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Introduction

Room-temperature ionic liquids (RTILs) are a new class of solvents, most easily thought of as low-melting salts [1]. In the liquid state the individual cations and anions of RTILs are dissociated, usually producing liquids that possess high electrical conductivities, high thermal stabilities, and low vapor pressures. These favorable and readily tunable physicochemical properties have caused considerable interest in RTILs as alternatives to conventional organic solvents for many synthetic, catalytic, and electrochemical applications. Today large organic cations, such as quaternary ammonium, pyridinium, or 1,3-dialkylimidazolium cations, are commonly used as the cations of RTILs (Fig. 1). The RTIL anion could be a halide, acetate, or BF_4^-, but RTILs containing the anions PF_6^- or $N(SO_2CF_3)_2^-$ (bis[(trifluoro-methyl)sulfonyl] imide, abbreviated Tf_2N^-) form water immiscible ionic liquids that are suitable for liquid-liquid extraction or biphasic chemical synthesis.

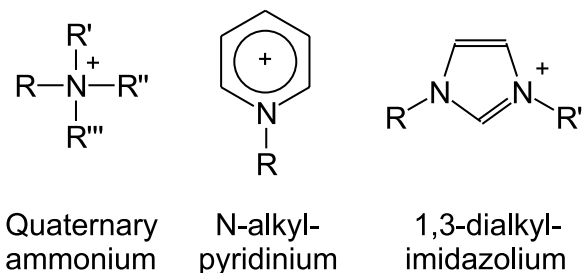Quaternary ammonium   N-alkyl-pyridinium   1,3-dialkyl-imidazolium

FIG. 1. Cations commonly used in RTILs.

Recent work in this laboratory has examined the mechanism of metal ion transfer between aqueous solutions and water-immiscible RTILs containing neutral complexing agents and its relationship to the transfer mechanism in conventional solvent systems [2]. From this work, it appears that, unlike conventional organic solvents, metal cation transfer into an RTIL in the presence of a neutral complexing agent may not require coextraction of an appropriate number of anions to balance the charge of the extracted metal ion. We used extended x-ray absorption fine structure (EXAFS) measurements to directly probe the interaction of an alkaline earth cation, Sr(II), with a representative neutral complexing agent, *cis-syn-cis*-dicyclohexyl-18-crown-6 (DCH18C6) and various counterions (NO_3^-, Cl^-, or $SO4_2^-$), both in a room-temperature ionic liquid, 1-methyl-3-pentylimidazolium bis[(trifluoromethyl)-sulfonyl]amide ($C_5mim^+Tf2N^-$), and in a conventional organic solvent, 1-octanol, to compare the Sr complexes formed and to understand the chemical mechanisms that operate in this RTIL system.

Methods and Materials

Samples of the Sr–DCH18C6 complexes in 1-octanol and $C_5mim^+Tf2N^-$ were prepared by contacting an equal volume of 0.5 M DCH18C6 in 1-octanol or 0.2 M DCH18C6 in $C_5mim^+Tf2N^-$ with an aqueous phase containing 0.03 M $Sr(NO_3)_2$, 0.03 M $SrCl_2$, or saturated $SrSO_4$ at the appropriate acidity. The resulting liquid organic phases were packages in 1 cm polymethyl-methacrylate cuvettes. $Sr(NO_3)_2$(18-crown-6) was prepared as a crystalline standard by crystallization from water [3]. It was ground with boron nitride, and packaged in a 3 mm path-length cell with kapton windows. A portion of the solid was also directly dissolved in water saturated $C_5mim^+Tf2N^-$ for comparison X-ray absorption measurements at the Sr K edge (16.105 keV) were conducted at the Advanced Photon Source, beamline 12-BM. Transmission and fluorescence data were collected simultaneously at ambient temperature using an Ar-filled ionization chamber or a 13-element detector (Canberra), respectively. The monochromator energy was calibrated against the first inflection point of the K edge of metallic Y (17.038 keV).

The transmission spectrum of the more concentrated $Sr(NO_3)_2$(18C6) solid standard was used, while the fluorescence spectra of the liquid samples were used. The fluorescence spectrum of each sample (except for the 0.001 M $Sr(DCH18C6)^{2+}$-$SO4^{2-}$ sample) displayed a small attenuation in the normalized k^3-weighted EXAFS amplitude from sample self-absorption as compared to the EXAFS simultaneously collected in the transmission mode. Therefore, each set of fluorescence EXAFS data was renormalized with a single scaling factor (1.05-1.21) to match the amplitude of its transmission EXAFS. The EXAFS were then fit in R space to the FEFF 8.00 theoretical phase and amplitude functions [4] using IFEFFIT [5] ($\Delta k = 2.25 - 12.0$ Å^{-1}, $\Delta R = 1.5 - 4.3$ Å).

The coordination numbers of the various coordination shells of the $Sr(NO_3)$(18-crown-6)

crystalline standard were fixed at the known values. The Debye-Waller factor for the Sr-O shell at 2.67 Å derived from the fitting of the standard was then used as a fixed parameter while N_O was allowed to vary in the fitting of the liquid samples.
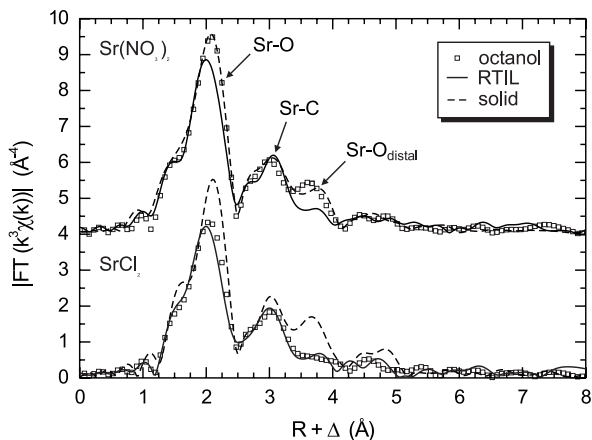

FIG. 2. *Fourier transform magnitude of the Sr K-edge EXAFS (without phase-shift correction), comparing the results of extraction from nitrate media (top) and chloride media (bottom). Top: $Sr(NO_3)_2$(18C6) dissolved in $C_5mim^+Tf_2N^-$ (- -), and extraction of $Sr(NO_3)_2$(DCH18C6) into 1-octanol (□) or $Sr(DCH18C6)2+$ into $C_5mim^+Tf_2N^-$ (—) from aqueous $Sr(NO_3)_2$. Bottom: $Sr(NO_3)_2$(18C6) solid (- -), and extraction of $Sr(DCH18C6)^{2+} \cdot 2Cl^-$ into 1-octanol (□) or $Sr(DCH18C6)2+$ into $C_5mim^+Tf_2N^-$ (—) from aqueous $SrCl_2$. © 2002 by the American Physical Society.*

Results

The EXAFS measurements are consistent with a change in the Sr coordination environment (Fig. 2). The coordinated oxygen atoms and the twelve carbon atoms of the crown ether ring are clearly visible in the Fourier transformed EXAFS of each sample. The presence of coordinated nitrate anions was obvious in some samples because of the prominent Sr-N-O multiple scattering peak at 4.32 Å. However, coordinated nitrate, chloride, and sulfate were not apparent in any of the samples created by extraction from water into $C_5mim^+Tf_2N^-$. These samples also showed consistently lower coordination numbers in the first (Sr-O) coordination shell (Table 1) and Sr-O distances that were 0.02-0.05 Å shorter than in the neutral Sr-crown ether-nitrato complexes.

Discussion

The EXAFS data show clear differences in the Sr coordination environment. The Sr coordination environment is the same for the crystalline

TABLE 1. *Average total number of coordinated oxygen atoms and anions coordinated to Sr derived from EXAFS measurements.*

Anion	Solvent[a]	N_O	Coordinated anions/Sr[b]
Standard Sr–18C6 Complexes			
NO_3^-	solid	10[c]	2[c]
NO_3^-	RTIL	10.4	2.2 ± 0.4
Extracted Sr–DCH18C6 Complexes			
NO_3^-	1-octanol	10.2	2.1 ± 0.4
NO_3^-	RTIL	8.5	0.3 ± 0.4
Cl^-	1-octanol	7.8	0.2 ± 0.7
Cl^-	RTIL	7.5	0.5 ± 0.7
SO_4^{2-}	RTIL	7.8	0.2 ± 0.1[d]

[a]RTIL = $C_5mim^+Tf2N^-$. [b]Assuming bidentate NO_3^- coordination and two axial ligands. [c]Fixed coordination number. [d]Derived from ion chromatographic measurement of $[SO_4^{2-}]_{org}$.

$Sr(NO_3)_2$(18-crown-6) standard, the crystalline standard dissolved directly in water saturated $C_5mim^+Tf2N^-$, and $Sr(NO_3)_2$(DCH18C6) in 1-octanol. Three major peaks from 10 O atoms (6 crown ether O and 4 nitrate O) at 2.7 Å, 12 crown ether C atoms at 3.5 Å, and the 2 distal (uncoordinated) O atoms of the NO_3^- at 4.3 Å [3] are obvious in the Fourier transformed EXAFS (Fig. 2). Thus, nitrate anions form bidentate, inner sphere complexes with the Sr–crown ether cations in both a two-phase water–octanol system and in a single phase water-saturated RTIL.

In contrast, when we *attempted* to extract $Sr(NO_3)_2$(DCH18C6) from water into $C_5mim^+Tf2N^-$, the number of oxygen atoms in the first coordination shell decreased from ca. 10 to 8.5 (Table 1) and the characteristic peak for the distal oxygen of bidentate nitrate anions at ca. 4.3 Å disappeared. Chemical analyses of the solutions before and after the extraction confirm that significant amounts of nitrate anions are not extracted into the RTIL when the Sr partitions from the water phase into the ionic liquid. The poor coordinating ability of the $Tf2N^-$ anion toward alkaline earth cations and the large amount of water (1 M) dissolved in $C_5mim^+Tf2N^-$ make it likely that the coordination sites left vacant by the missing nitrates are occupied by water molecules in a 1 H_2O:1 NO_3^- ratio, giving $N_O = 8$, and formula for the Sr complex of $Sr(DCH18C6)(H_2O)_2^{2+}$.

The EXAFS of the RTIL samples extracted from Cl^- and SO_4^{2-} media also show a decrease in N_O to ≈ 8 (Table 1). The cationic $Sr(DCH18C6)^{2+}$ complex remains intact in the RTIL, since the 12 crown ether C atoms are still observed in the EXAFS, but features

attributable to coordinated Cl^- or SO_4^{2-} ions are not evident. Attempts to fit the data using coordination shells involving chloride, sulfate, or $Tf2N^-$ containing species were completely unsuccessful. This was also true of the Sr–DCH18C6 complex in 1-octanol. Because two Cl^- *must* be extracted with the $Sr(DCH18C6)^{2+}$ complex into non-ionic solvents like 1-octanol, the Sr complex must be present as an outer sphere $Sr(DCH18C6)^{2+} \cdot 2Cl^-$ ion pair in 1-octanol. In this case, the $Sr(DCH18C6)^{2+}$ cation could be solvated by two water or octanol molecules and no Cl^- is directly bound to the Sr. Chemical analysis of the RTIL solutions confirms, as with the nitrate-RTIL solution, that significant concentrations of Cl^- or SO_4^{2-} are not extracted with the $Sr(DCH18C6)^{2+}$ cation. Schematic structures of the two Sr complexes are shown in Fig. 3.
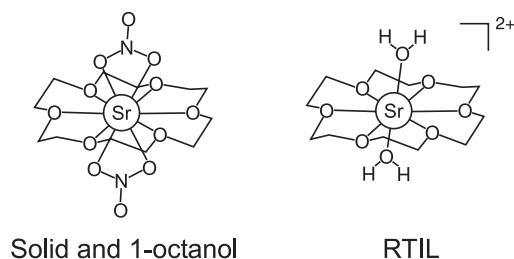

Solid and 1-octanol   RTIL

FIG. 3. Schematic structures of the Sr coordination environments of $Sr(NO_3)_2(DCH18C6)$ in 1-octanol and the $Sr(DCH18C6)(H_2O)_2^{2+}$ cation present in $C_5mim^+Tf_2N^-$ with the crown ether's cyclohexyl groups omitted for clarity. © 2002 by the American Physical Society.

These data are only consistent with a change in the Sr extraction mechanism when the solvent is changed from the conventional, molecular organic solvent, 1-octanol, to the ionic liquid $C_5mim^+Tf2N^-$. With 1-octanol, the neutral $Sr(NO3)_2(DCH18C6)$ complex is extracted, as expected, according to the equilibrium

$$Sr^{2+} + 2\ NO_3^- + DCH18C6_{org} = Sr(NO_3)_2(DCH18C6)_{org}$$

where the subscript *org* indicates species present in the 1-octanol or RTIL phases. In contrast, the EXAFS data show that the extraction of Sr^{2+}-DCH18C6 complexes into $C_5mim^+Tf2N^-$ proceeds by a cation exchange mechanism according to the equilibrium

$$Sr^{2+} + 2C_5mim^+_{org} + DCH18C6_{org} =$$
$$Sr(DCH18C6)^{2+}_{org} + 2\ C_5mim^+.$$

In this reaction, the required charge balance is conserved by the partitioning of two RTIL cations into the aqueous phase, and the $Sr(DCH18C6)^{2+}$ cation becomes part of the RTIL. This change in extraction mechanism, which is accompanied by a change in the Sr coordination environment, provides an explanation for the more efficient extraction of Sr into some RTILs [2,6].

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