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EXAFS Investigations of the Mechanism of Facilitated Ion Transfer into a Room-Temperature Ionic Liquid

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The favorable and readily tunable physicochemical properties of room-temperature ionic liquids (RTILs) have led to intense interest in these materials as alternatives to conventional organic solvents in a range of synthetic, catalytic, and electrochemical applications.[1] Of particular interest in the context of the potential synthetic and catalytic applications of these "neoteric"[2] solvents has been the extent to which reactions conducted in RTILs parallel the corresponding reactions in ordinary organic solvents.[1,3,4] Recent work in this laboratory[5] has concerned 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, a significant issue in phase-transfer catalysis and chemical separations. Our preliminary studies of cation transfer from acidic aqueous phases into a series of *N,N′*-dialkylimidazolium-based RTILs containing a crown ether (CE) suggest that, unlike conventional organic solvents, cation transfer into an RTIL in the presence of a neutral complexing agent may not require anion coextraction.[5] If the ion-transfer properties of ionic liquid-based systems cannot be predicted from the established behavior of conventional organic solvents, the rational design of RTIL-based catalytic and separations processes will only be possible when the mechanisms of ion transfer and the solvation state of ions dissolved in ionic liquids are understood at a fundamental level. With this in mind, 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 SO_4^{2-}), both in a room-temperature ionic liquid, 1-methyl-3-pentylimidazolium bis[(trifluoromethyl)sulfonyl]amide ($C_5mim^+Tf_2N^-$), and in a conventional organic solvent, 1-octanol. Although EXAFS has been used to the examine metal−ligand interactions in a variety of aqueous and organic media, its application to ambient-temperature ionic liquids has thus far been limited.[6,7]

Strontium complexes of 18-crown-6 (18C6) and DCH18C6 were synthesized by two paths. Crystalline $Sr(NO_3)_2(18C6)$ was prepared by literature procedures[8] to be used as a standard. Solution-phase complexes of $Sr(DCH18C6)^{2+}$ were prepared by contacting a solution of 0.5 M DCH18C6 in 1-octanol or 0.2 M DCH18C6 in $C_5mim^+Tf_2N^-$ with aqueous solutions of $Sr(NO_3)_2$, $SrCl_2$, or $SrSO_4$. X-ray absorption measurements at the Sr K-edge (16.105 keV) were conducted at the Advanced Photon Source, beamline 12-BM. Details of sample preparation and data analysis are presented as Supporting Information.

The Sr−O coordination numbers (N_O) derived from the EXAFS of each sample are based on the 10-coordinate $Sr(NO_3)_2(18C6)$ solid. In this compound, the Sr sits inside the 18-crown-6 ring, coordinated by the six crown ether O atoms and by four O atoms from two axially coordinated bidentate nitrate groups.[8] The amplitude reduction factor ($S_0^2 = 1.0$) and the Debye−Waller factor associated with the Sr−O bonds ($\sigma^2 = 0.0136$ Å^2) were obtained by fitting the EXAFS of the $Sr(NO_3)_2(18C6)$ solid using the FEFF8.00 theoretical phase and amplitude functions[9] with fixed coordination numbers. These two parameters were then used to calculate N_O from least-squares fits for all other samples.

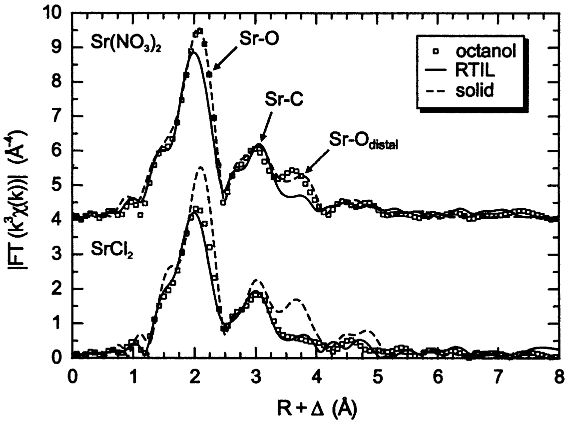

Figure 1. Fourier transform magnitude of the Sr K-edge EXAFS (without phase shift correction), comparing the results of extraction from nitrate media (top) and chloride media (bottom). (Top) $Sr(NO_3)_2(18C6)$ dissolved in $C_5mim^+Tf_2N^-$ (- - -), and extraction of $Sr(NO_3)_2(DCH18C6)$ into 1-octanol (□) 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 $SrCl_2$.

The Sr coordination environment in $Sr(NO_3)_2(18C6)$ does not change when the solid sample is directly dissolved in water-saturated $C_5mim^+Tf_2N^-$. Three major peaks from 10 O atoms 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 are obvious in the Fourier transformed EXAFS (Figure 1). These same three peaks are observed when $Sr(NO_3)_2(DCH18C6)$ is extracted into 1-octanol. Thus, nitrate anions only form inner-sphere complexes with the Sr−CE cations in both a two-phase water-octanol system and in a single-phase water-saturated RTIL.

In contrast, the EXAFS shows that little nitrate is coordinated to the $Sr(DCH18C6)^{2+}$ cation in $C_5mim^+Tf_2N^-$ when the complex is prepared by extraction from an aqueous solution of $Sr(NO_3)_2$. Only 8.5 O atoms are coordinated to the Sr (Table 1). Moreover, the characteristic peak of the distal (uncoordinated) nitrate O atoms at 4.3 Å nearly disappears (Figure 1). The poor coordinating ability of the Tf_2N^- anion toward alkaline earth cations[10] and the large amount of water (1 M)[11] dissolved in $C_5mim^+Tf_2N^-$ make it likely that the coordination sites left vacant by the nitrate are occupied by water molecules in a 1 H_2O:1 NO_3^- ratio (Figure 2).

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Table 1. Average Total Number of Coordinated Oxygen Atoms or 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-DH18C6 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 = $C_5mim^+Tf_2N^-$. [b] Assuming bidentate NO_3^- coordination and two axial ligands. [c] Fixed coordination number. [d] Derived from ion chromatographic measurement of $[SO_4^{2-}]_{org}$.

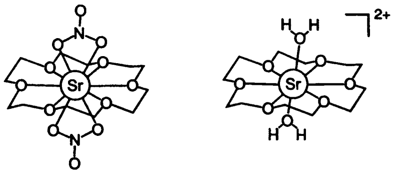

Figure 2. Coordination environments of $Sr(NO_3)_2(DCH18C6)$ in 1-octanol and the $Sr(DCH18C6)(H_2O)_2^{2+}$ cation present in $C_5mim^+Tf_2N^-$.

The EXAFS of the analogous Cl^- and SO_4^{2-} samples also show a decrease in N_O to ~8 (Table 1) The cationic Sr-DCH18C6 complex remains intact in the RTIL, since the 12 crown ether C atoms are still visible in the EXAFS, but features attributable to coordinated Cl^- or SO_4^{2-} ions are not evident. Interestingly, this is true of the Sr-DCH18C6 complex both in 1-octanol and $C_5mim^+Tf_2N^-$. Because two Cl^- must be extracted with the $Sr(DCH18C6)^{2+}$ complex into nonionic solvents such as 1-octanol, the $Sr(DCH18C6)^{2+}\cdot 2Cl^-$ ion pair in 1-octanol must be present as an outer sphere complex where the $Sr(DCH18C6)^{2+}$ cation is solvated by two water or octanol molecules and no Cl^- is directly bound to the Sr. However, the absence of anions in the Sr inner coordination sphere of the two-phase RTIL samples does not, in itself, allow us to unambiguously distinguish between the two possible mechanisms of $Sr(DCH18C6)^{2+}$ transfer from aqueous solutions into the RTIL because NO_3^-, Cl^-, or SO_4^{2-} counterions could be present as outer-sphere ligands in the two-phase RTIL system. Consequently, either ion pair extraction (eq 1) or cation-exchange (eq 2) could account for the EXAFS observations in the RTIL.

$$Sr(CE)^{2+} + nX^{x-} \rightleftharpoons Sr(CE)^{2+}\cdot nX^{x-}{}_{(org)} \quad (n = 2/x) \quad (1)$$

$$Sr(CE)^{2+} + 2C_5mim^+{}_{(org)} \rightleftharpoons Sr(CE)^{2+}{}_{(org)} + 2C_5mim^+ \quad (2)$$

The possibility of significant amounts of NO_3^-, Cl^-, or SO_4^{2-} being present in the Sr outer coordination sphere was addressed by measuring the concentrations of these anions in $C_5mim^+Tf_2N^-$ after Sr-DCH18C6 partitioning reached equilibrium. Direct measurement of the nitrate content of the $C_5mim^+Tf_2N^-$ solution via ^{15}N NMR following extraction of aqueous $Sr(^{15}NO_3)_2$ by DCH18C6 indicates approximately 16% of the NO_3^- required to balance the charge of $Sr(DCH18C6)^{2+}$ is coextracted into the RTIL. Similarly, indirect measurement of the $[NO_3^-]_{org}$, $[Cl^-]_{org}$, and $[SO_4^{2-}]_{org}$ by ion chromatography of the aqueous phase before and after formation of the Sr−DCH18C6 complexes confirms that the amounts of anion coextracted into the RTIL are vastly insufficient to produce neutral Sr complexes (9% NO_3^-, 0% Cl^-, and 16% SO_4^{2-}, with an uncertainty of ±7%). The insignificant coextraction of these counterions in the two-phase RTIL system and the difference in the Sr coordination environment versus the octanol system indicates that the phase-transfer reaction proceeds primarily through the cation-exchange mechanism described by eq 2. Recent work also has shown that two molecules of C_5mim^+ partition to the aqueous phase for every molecule of $Sr(DCH18C6)^{2+}$ extracted.[5] Therefore, in the two-phase RTIL systems studied, the cationic $Sr(DCH18C6)^{2+}$ complex becomes a component of the ionic liquid with its positive charge being balanced by two noncoordinated Tf_2N^- anions.

While a number of reactions have been demonstrated to proceed by similar mechanisms in conventional solvents and RTILs,[7,12] our results show that the coordination compounds formed in 1-octanol and in $C_5mim^+Tf_2N^-$ are distinctly different because the partitioning mechanisms differ. These results, in addition to representing the first direct structural comparison of the coordination environment of a metal ion in an ionic liquid and a conventional molecular solvent, have significant implications for the application of RTILs in separations and catalysis. That is, for catalytic processes dependent on anion transfer (e.g., oxidation of alkenes by MnO_4^- or halide exchange promoted by a phase-transfer catalyst), the poor coextraction of anions into $C_5mim^+Tf_2N^-$ suggests the possibility of low process efficiency in many RTILs. Similarly, for metal-ion separations systems employing RTILs as a substitute for conventional organic solvents, the inefficient extraction of counteranions would be expected to make recovery of extracted cations difficult. Indeed, our preliminary results suggest that in many instances, cation recovery from two-phase RTIL systems can be effected only under conditions that lead to significant solubilization of the ionic liquid in the aqueous phase.

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Supporting Information Available: Experimental procedures, data analysis, k^3-weighted EXAFS, and best fit parameters (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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