

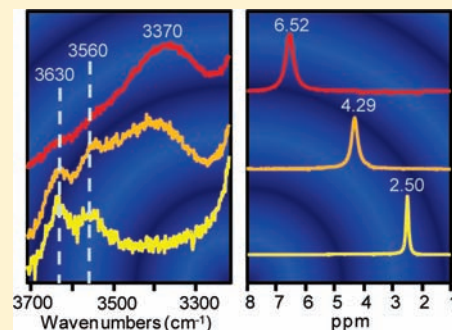
Effect of Nitrate, Perchlorate, and Water on Uranyl(VI) Speciation in a Room-Temperature Ionic Liquid: A Spectroscopic Investigation

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Supporting Information

ABSTRACT: Room-temperature ionic liquids form potentially important solvents in novel nuclear waste reprocessing methods, and the solvation, speciation, and complexation behaviors of lanthanides and actinides in these solvents are of great current interest. In the study reported here, the coordination environment of uranyl(VI) in solutions of the room-temperature ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][Tf₂N]) containing perchlorate, tetrabutylammonium nitrate, and water was investigated using Raman, ATR-FTIR, and NMR spectroscopies in order to better understand the role played in uranyl(VI) solution chemistry in room-temperature ionic liquids by water and other small, weakly complexing ligands. The ²H NMR chemical shift for water in a solution of uranyl perchlorate hexahydrate in [EMIM][Tf₂N] appears at 6.52 ppm, indicating that water is coordinated to uranyl(VI). A broad ν(OH) stretching mode at 3370 cm⁻¹ in the ATR-FTIR spectrum shows that this coordinated water is engaged in hydrogen bonding with water molecules in a second coordination sphere. A significant upfield shift in the ²H NMR signal for water and the appearance of distinct ν_{as}(HOH) (at 3630 cm⁻¹) and ν_s(HOH) (at 3560 cm⁻¹) vibrational bands in the ATR-FTIR spectra show that coordinated water is displaced by nitrate upon formation of the UO₂(NO₃)₂ and UO₂(NO₃)₃⁻ complexes. The Raman spectra indicate that perchlorate complexed to uranyl(VI) is also displaced by nitrate. Our results indicate that perchlorate and water, though weakly complexing ligands, do have a role in uranyl(VI) speciation in room-temperature ionic liquids and that Raman, infrared, and NMR spectroscopies are valuable additions to the suite of tools currently used to study the chemical behavior of uranyl(VI)–ligand complexes in these solvents.



INTRODUCTION

Reprocessing of spent nuclear fuel with recycling of fissile isotopes is important for optimizing energy extraction from actinide resources and minimizing waste product production. A wide variety of solvent extraction processes have been used to separate plutonium and uranium from fission products in spent nuclear fuel, and novel reprocessing methods are under development. There is much interest in the use of room-temperature ionic liquids (RTILs) in nuclear fuel reprocessing schemes, as they have low melting points and volatilities and can solubilize actinide and lanthanide complexes. In addition, RTIL physicochemical properties, and perhaps even radiation stabilities,^{1,2} can be manipulated through judicious choice or design of the RTIL cation and anion. A great deal of work evaluating these interesting and flexible solvents for use in the separations of actinides and fission products from nuclear wastes has been completed.^{3–5}

The chemical behavior of the actinide and lanthanide elements in RTILs is likewise an area of active investigation, and several review articles discussing the speciation and coordination chemistry of actinides and lanthanides in RTILs have been published in the past few years.^{6–8} The chemistry of the uranyl(VI) nitrate system in RTILs has been especially well-studied because of the importance of nitrate in radioactive waste processing. Previous workers have used UV–visible absorption spectrometry^{9–12} and

EXAFS^{9,11} to show that the major species in solutions of RTILs containing tetrabutylammonium nitrate (TBAN) and uranyl(VI) are UO₂(NO₃)⁺, UO₂(NO₃)₂, and UO₂(NO₃)₃⁻. Servaes et al.¹¹ and Georg et al.¹² have shown that UO₂(NO₃)₃⁻ is the major species in RTIL solutions when nitrate is present in excess. Gaillard et al.¹³ have used EXAFS, UV–visible absorption spectrometry, and molecular dynamics calculations to show that uranyl(VI) can form a variety of complexes containing both chloride and nitrate when both anions are present in an RTIL solution.

Raman and infrared spectroscopies can also be used to study the solution speciation of actinides and lanthanides. These techniques are particularly suitable for the investigation of actinides having oxo ligands, such as uranyl(VI). The infrared-active ν_{as}(UO₂) and Raman-active ν_s(UO₂) modes are sensitive to changes in the uranyl(VI) coordination environment, shifting to lower wavenumber when complexation of uranyl(VI) by a ligand weakens the O=U=O bonds. These modes can thus be used to track uranyl(VI) speciation in solution. In an earlier spectroscopic study using attenuated total reflectance FTIR (ATR-FTIR) spectrometry, we used the ν_{as}(UO₂) vibrational mode to track

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uranyl(VI) nitrate complex formation in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][Tf₂N]).¹⁴ In that study, we found that both UO₂(NO₃)₂ and UO₂(NO₃)₃⁻ species ($\nu_{\text{as}}(\text{UO}_2)$ 951 and 944 cm⁻¹, respectively) were formed when TBAN was used as a nitrate source, but only UO₂(NO₃)₂ was detected in the infrared spectrum when HNO₃ was used. UV–visible absorption spectrometry showed that UO₂(NO₃)₃⁻ was present as a minor species. One major difference between the TBAN/[BMIM][Tf₂N] and the HNO₃/[BMIM][Tf₂N] systems in the above-mentioned study was the amount of H₂O introduced into solution in each case, as a solution of 70 wt % HNO₃ was used as a nitrate source in the HNO₃/[BMIM][Tf₂N] system. Kaplan et al.¹⁵ studied the formation of the UO₂(NO₃)₃⁻ complex in organic solvents using UV–visible spectrometry and suggested that a nitrate ion and water molecules compete for a coordination position around the uranyl(VI) ion. Billard et al.¹⁶ also noted that the formation of the UO₂(NO₃)₃⁻ complex in [BMIM][Tf₂N] is affected by the presence of water. However, water does not displace NO₃⁻ or otherwise affect the O=U=O bond strength.¹⁴ In this current work, we use Raman, infrared, and ²H and ¹⁷O NMR spectroscopies to further investigate the effect of water and other weakly complexing ligands on uranyl(VI) speciation in the RTIL 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][Tf₂N]).

EXPERIMENTAL SECTION

Chemicals and Reagents. Uranyl perchlorate hexahydrate, UO₂(ClO₄)₂·6H₂O was purchased from International Bio-Analytical Industries, Inc. (Boca Raton, FL). Tetrabutylammonium nitrate (97%) and ¹⁷O enriched H₂O (20.0–24.9 atom % ¹⁷O) were purchased from Sigma-Aldrich (Milwaukee, WI). 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (99%) (water and halides < 100 ppm) was purchased from IoLiTec Ionic Liquid Technologies Inc. (Tuscaloosa, AL). Acetonitrile and acetone were purchased from Fisher Scientific (Pittsburgh, PA). Deuterated acetone (*d*-6, 99.8% D) and D₂O (99.8% D) were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA).

Instruments. A Bruker Avance 500 MHz NMR spectrometer was used to acquire the NMR spectra. Raman spectra were acquired using a Renishaw Ramascope Raman microscope with a 785 nm laser. The spectral resolution was 4 cm⁻¹. ATR-FTIR spectra were acquired using a Nicolet Magna 760 FTIR spectrometer equipped with a DTGS detector. ATR-FTIR measurements were made with a SplitPea attenuated total reflection accessory (Harrick Scientific Corporation). A silicon internal reflection element was used as a reflection medium. ATR-FTIR spectra were acquired using 500 coadded scans at 2 cm⁻¹ resolution with Happ–Genzel apodization. A single-beam reference spectrum of the silicon ATR internal reflection element was acquired at the start of each experiment, and each single-beam sample spectrum collected was ratioed against this background reference spectrum. Spectra were not otherwise corrected. Each sample spectrum required ~17 min to collect.

Sample Preparation. Commercially purchased uranyl perchlorate hexahydrate was used as received. Deuterated uranyl perchlorate hexahydrate used in the ²H NMR experiments was prepared by recrystallizing uranyl perchlorate hexahydrate from D₂O. The ¹H NMR spectra indicated that approximately 60% of the protons in the uranyl perchlorate hexahydrate were replaced by deuterons during the recrystallization step. ¹⁷O-enriched uranyl(VI) was prepared by dissolving uranyl perchlorate hexahydrate in warm ¹⁷O-enriched water to make a saturated solution, exposing the solution to 254 nm light for ~48 h, and allowing the resulting uranyl perchlorate complex to crystallize. The water/uranyl mole ratio in the uranyl perchlorate hexahydrate

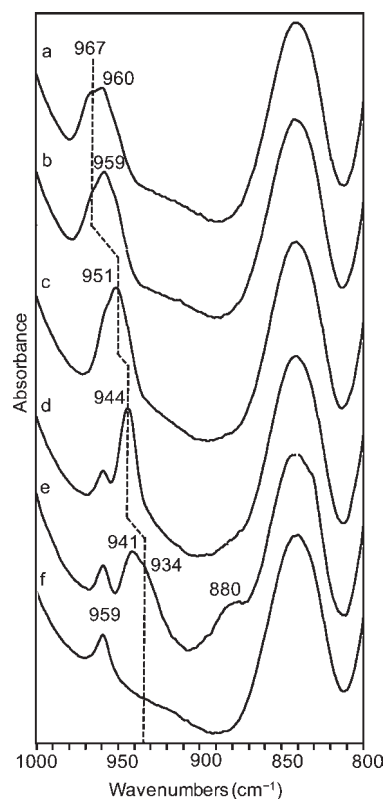


Figure 1. ATR-FTIR spectra showing the $\nu_{\text{as}}(\text{UO}_2)$ region for solutions containing [EMIM][Tf₂N] and (a) 0.1 M UO₂(ClO₄)₂·6H₂O and no TBAN, (b) 0.1 M UO₂(ClO₄)₂·6H₂O and 0.1 M TBAN, (c) 0.1 M UO₂(ClO₄)₂·6H₂O and 0.2 M TBAN, (d) 0.1 M UO₂(ClO₄)₂·6H₂O and 0.3 M TBAN, (e) 0.1 M UO₂(ClO₄)₂·6H₂O and 0.4 M TBAN, and (f) 1 M H₂O.

compounds was estimated as described in the Supporting Information. Samples for spectroscopic analysis were prepared by dissolving either uranyl(VI) perchlorate hexahydrate or its deuterated form in [EMIM][Tf₂N] to a final concentration of 0.1 M. Nitrate was added in the form of TBAN. Nitrate concentrations ranged from 0.05 to 0.5 M in [EMIM][Tf₂N]. The samples were sonicated to completely homogenize all solutes in the ionic liquid. For analyses using ATR-FTIR, a small droplet of sample was placed directly on the silicon internal reflection element. The sample stage was covered and kept under dry air during analysis. Samples for Raman and ²H and ¹⁷O NMR analyses were placed in 5 mm NMR tubes. A coaxial NMR tube insert containing acetone-*d*₆ was inserted into each sample tube before NMR analysis and used for the magnetic field lock. ¹⁷O NMR spectra were acquired at 30 °C and referenced to an external H₂¹⁷O signal at 0 ppm. The ²H NMR spectra were also acquired at 30 °C but were referenced to an external acetone-*d*₆ C²H₃ signal (2.5 ppm).

Caution! Uranyl perchlorate is a radioactive oxidizer and may cause fire or explosion if heated with organic matter or strong reducing agents. Rubber gloves and safety glasses or a face shield should be used when working with this compound. In addition, metal perchlorate salts are shock-sensitive. Precautions for handling metal perchlorate salts may be found in ref 17.

RESULTS AND DISCUSSION

Figure 1 shows the $\nu_{\text{as}}(\text{UO}_2)$ region of the infrared spectra acquired from solutions containing 0.1 M uranyl perchlorate hexahydrate in [EMIM][Tf₂N] to which increments of TBAN have been added. As the concentration of TBAN in solution

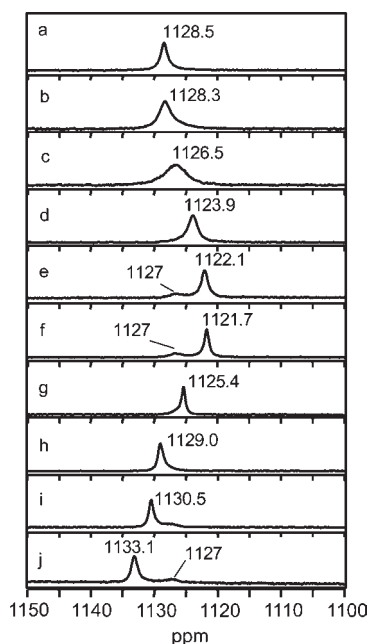


Figure 2. ^{17}O NMR spectra acquired from $[\text{EMIM}][\text{Tf}_2\text{N}]$ solutions containing 0.1 M $\text{UO}_2(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and (a) no TBAN, (b) 0.05 M TBAN, (c) 0.1 M TBAN, (d) 0.2 M TBAN, (e) 0.25 M TBAN, (f) 0.3 M TBAN, (g) 0.35 M TBAN, (h) 0.4 M TBAN, (i) 0.45 M TBAN, and (j) 0.5 M TBAN. Spectra were acquired at 30 °C and referenced to an external H_2^{17}O signal.

increases from 0 to 0.4 M, major changes are seen in the spectra.

In an earlier study,¹⁴ we examined the effect of TBAN addition to a 0.1 M solution of uranyl(VI) bis(trifluoromethylsulfonyl)imide ($\text{UO}_2(\text{Tf}_2\text{N})_2$) in $[\text{BMIM}][\text{Tf}_2\text{N}]$. In that study, $\nu_{\text{as}}(\text{UO}_2)$ vibrational modes assigned to uranyl(VI) coordinated by Tf_2N^- , to $\text{UO}_2(\text{NO}_3)_2$, and to $\text{UO}_2(\text{NO}_3)_3^-$ appeared at 968, 951, and 944 cm^{-1} , respectively. In a solution of 0.1 M uranyl perchlorate hexahydrate in $[\text{EMIM}][\text{Tf}_2\text{N}]$, we note the presence of two overlapping vibrational modes at 967 and 960 cm^{-1} in the infrared spectrum (Figure 1, spectrum a). Here, we assign the mode at 967 cm^{-1} to $\nu_{\text{as}}(\text{UO}_2)$ for uranyl(VI) coordinated by Tf_2N^- , perchlorate anions, and water. Perchlorate is a weakly coordinating anion and does not form strong complexes with uranyl(VI) in some RTILs.¹⁸ However, a study using extended X-ray absorption fine structure spectroscopy and molecular dynamic simulations has shown that the uranyl(VI) perchlorate salt does not completely dissociate upon dissolution in $[\text{BMIM}][\text{Tf}_2\text{N}]$ and that perchlorate in a $\text{UO}_2(\text{ClO}_4)_2$ complex may be coordinated to uranyl(VI) in a monodentate fashion.⁹

The mode at 960 cm^{-1} has previously been assigned to the C–C stretching mode arising from the EMIM cation¹⁹ and is a constant feature in all the spectra. The presence of $\nu_{\text{as}}(\text{UO}_2)$ vibrational modes at 951 cm^{-1} (Figure 1, spectrum c) and 944 cm^{-1} (Figure 1, spectrum d) indicates that $\text{UO}_2(\text{NO}_3)_2$ and $\text{UO}_2(\text{NO}_3)_3^-$ form in these solutions at the expected uranyl(VI)/nitrate ratios (1:2 and 1:3, respectively). These results match those we obtained previously in solutions prepared using $\text{UO}_2(\text{Tf}_2\text{N})_2$.¹⁴ Upon a change in the uranyl(VI)/nitrate mole ratio from 1:3 to 1:4 (0.3 M TBAN to 0.4 M TBAN), $\nu_{\text{as}}(\text{UO}_2)$ broadens, shifts slightly to 941 cm^{-1} , and develops

a shoulder at $\sim 934 \text{ cm}^{-1}$ (Figure 1, spectrum e). This is an indication that a new uranyl(VI) complex has formed in this solution. The nature of this complex is as yet unknown. A new, as yet unassigned, vibrational mode at 880 cm^{-1} likely to relate to this species also appears in the spectrum. These features do not relate to the use of uranyl perchlorate hexahydrate as a source of uranyl(VI), as they also appear in the infrared spectra when $\text{UO}_2(\text{Tf}_2\text{N})_2$ is used as a source of uranyl(VI). ATR-FTIR spectra showing the growth of the shoulder at 934 cm^{-1} as uranyl(VI)/nitrate mole ratios are varied incrementally from 1:3 to 1:5 are given in Figure 1, Supporting Information. The spectra were deconvoluted, and $\nu_{\text{as}}(\text{UO}_2)$ peak areas were determined (Figure 2, Supporting Information).

Further evidence for the formation of a new complex at a uranyl(VI)/nitrate mole ratio of 1:4 is given by the ^{17}O NMR spectra shown in Figure 2. The ^{17}O chemical shift for uranyl oxygens in ^{17}O NMR spectra acquired from a 0.1 M solution of uranyl(VI) perchlorate hexahydrate in $[\text{EMIM}][\text{Tf}_2\text{N}]$ is observed at 1128.5 ppm (Figure 2, spectrum a). As the concentration of TBAN increases to 0.1 M, the uranyl(VI) oxygen ^{17}O chemical shift moves upfield and broadens (Figure 2, spectra b and c). The line broadening may be due to the change in the uranyl(VI) chemical environment resulting from a rapid nitrate exchange between uranyl(VI) species. Line broadening can also result from a decrease in the symmetry of the uranyl(VI) complex. Because the exchange rate is fast on the chemical shift time scale, separate signals for individual uranyl(VI) nitrate species are not seen, but the position of each NMR peak in Figure 2 corresponds to the weighted chemical shift average of the chemical forms of uranyl(VI).

The ^{17}O chemical shift arising from uranyl(VI) oxygens in a solution where the $\text{UO}_2(\text{NO}_3)_2$ complex is the predominant species (0.1 M uranyl(VI) and 0.2 M TBAN) is observed at 1123.9 ppm (Figure 2, spectrum d), whereas that for uranyl(VI) oxygens in a solution where $\text{UO}_2(\text{NO}_3)_3^-$ is the predominant species (0.1 M uranyl(VI) and 0.3 M TBAN) is observed at 1121.7 ppm (Figure 2, spectrum f). As the uranyl(VI)/nitrate mole ratio is increased from 1:3 to 1:5 (0.3 M TBAN to 0.5 M TBAN), the ^{17}O resonances shift downfield (Figure 2, spectra f–j). When the TBAN concentration reaches 0.5 M, the chemical shift is 1133.1 ppm. This increase in chemical shift with increasing nitrate concentration most likely results because of an equilibrium reaction between $\text{UO}_2(\text{NO}_3)_3^-$ and a second uranyl nitrate species. The ATR-FTIR spectra show that at least one new uranyl(VI) species (with $\nu_{\text{as}}(\text{UO}_2)$ at 934 cm^{-1}) forms at nitrate concentrations greater than 0.3 M (Figure 1, spectrum e, and the Supporting Information). The presence of other uranyl(VI) nitrate species in an ionic liquid is not unexpected at high uranyl(VI) and nitrate concentrations. Bradley et al.²⁰ have isolated a $[\text{UO}_2(\text{NO}_3)_4]^{2-}$ alkyl imidazolium salt from an ionic liquid, and Cocalia et al.²¹ have isolated a $[(\text{UO}_2)_2(\mu\text{-OH})_2(\text{NO}_3)_4]^{2-}$ alkyl imidazolium salt, also from an ionic liquid.

The small ^{17}O resonance visible at a constant chemical shift of 1127 ppm in Figure 2, spectra e, f, i, and j, is unassigned, but likely arises from a uranyl(VI) species. The constant chemical shift indicates that the exchange rate for this species is much slower than those of the various uranyl(VI) nitrate species; thus, it is unlikely to be a uranyl(VI) nitrate species. No $\nu_{\text{as}}(\text{UO}_2)$ mode that can be assigned to this species is seen in the ATR-FTIR spectra shown in Figure 1; whatever the source of this species, it is present at low concentration.

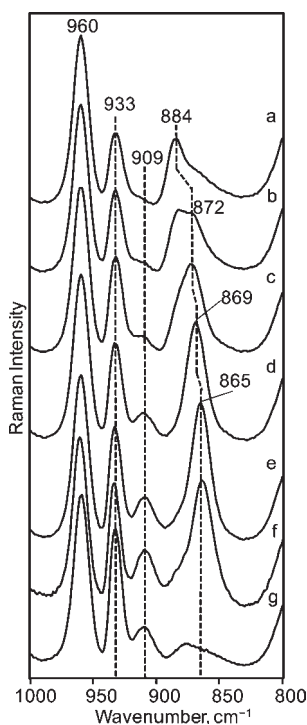


Figure 3. Raman spectra showing the $\nu_s(\text{UO}_2)$ region for solutions containing $[\text{EMIM}][\text{Tf}_2\text{N}]$ and (a) 0.1 M $\text{UO}_2(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and no TBAN, (b) 0.1 M $\text{UO}_2(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 0.05 M TBAN, (c) 0.1 M $\text{UO}_2(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 0.1 M TBAN, (d) 0.1 M $\text{UO}_2(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 0.2 M TBAN, (e) 0.1 M $\text{UO}_2(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 0.3 M TBAN, (f) 0.1 M $\text{UO}_2(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 0.4 M TBAN, and (g) 0.2 M tetra-butylammonium perchlorate.

Figure 3 shows the $\nu_s(\text{UO}_2)$ region of the Raman spectra acquired from solutions containing 0.1 M uranyl perchlorate hexahydrate in $[\text{EMIM}][\text{Tf}_2\text{N}]$ to which increments of TBAN have been added. The $\nu_s(\text{UO}_2)$ modes appear at 884–865 cm^{-1} in these spectra. Modes at 933 and 909 cm^{-1} arise from perchlorate; the mode at 960 cm^{-1} has previously been assigned to a C–C stretching mode^{19,22} or a ring in-plane asymmetric stretching mode²² arising from the EMIM cation. The $\nu_s(\text{UO}_2)$ mode at 884 cm^{-1} corresponds to the same species giving rise to $\nu_{\text{as}}(\text{UO}_2)$ at 967 cm^{-1} in the infrared spectrum and is likewise assigned to uranyl(VI) coordinated by Tf_2N^- , perchlorate anions, and water. The shoulder at $\sim 860 \text{ cm}^{-1}$ is due to a weak vibrational mode arising from the ionic liquid. As the concentration of TBAN increases to 0.2 and 0.3 M, we note the growth of modes at 869 and 865 cm^{-1} , which can be assigned to $\text{UO}_2(\text{NO}_3)_2$ and $\text{UO}_2(\text{NO}_3)_3^-$, respectively (Figure 3, spectra d and f). While a small ($\sim 1 \text{ cm}^{-1}$) shift to lower wavenumber can be discerned, no new $\nu_s(\text{UO}_2)$ vibrational mode is seen in the Raman spectrum when the TBAN concentration is increased from 0.3 to 0.4 M (Figure 3, spectrum f), unlike in the ATR-FTIR spectrum (Figure 1, spectrum e). This may be due to the broad nature of the $\nu_s(\text{UO}_2)$ Raman bands and the spectral resolution of the spectrometer.

Uncoordinated perchlorate ion has four vibrational modes, all of which are Raman-active. The symmetric stretching mode, $\nu_s(\text{ClO}_4)$, appears at 932 cm^{-1} , whereas the asymmetric stretching mode, $\nu_{\text{as}}(\text{ClO}_4)$, appears at 1110 cm^{-1} .²³ These modes shift and split upon coordination to uranyl(VI).²⁴ The vibrational modes at 933 and 909 cm^{-1} in Figure 3 can be assigned to

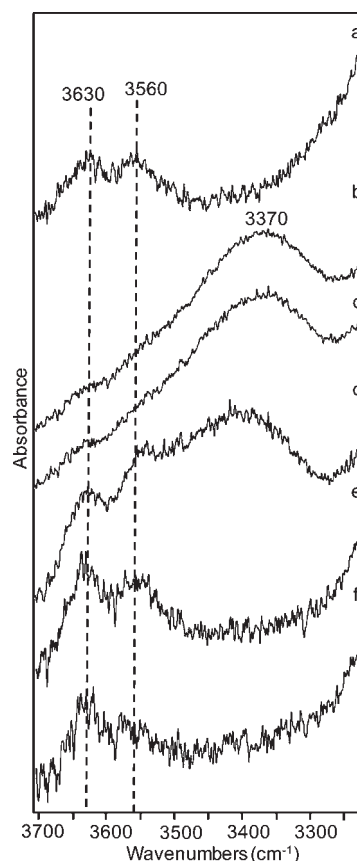


Figure 4. ATR-FTIR spectra showing the $\nu(\text{OH})$ region for solutions containing $[\text{EMIM}][\text{Tf}_2\text{N}]$ and (a) 1 M H_2O , (b) 0.1 M $\text{UO}_2(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and no TBAN, (c) 0.1 M $\text{UO}_2(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 0.1 M TBAN, (d) 0.1 M $\text{UO}_2(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 0.2 M TBAN, (e) 0.1 M $\text{UO}_2(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 0.3 M TBAN, and (f) 0.1 M $\text{UO}_2(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 0.4 M TBAN.

$\nu_s(\text{ClO}_4)$ and to an overtone of $\delta(\text{OCIO})$,²⁵ respectively. The presence of the $\nu_s(\text{ClO}_4)$ mode at 933 cm^{-1} in our Raman spectra (Figure 3, spectra a–g) is clear evidence for the presence of uncoordinated perchlorate in our solutions. We note, however, that the intensity of this mode increases relative to that of the mode at 960 cm^{-1} as the concentration of nitrate in our solution increases, implying that at least one perchlorate moiety is complexed to the uranyl(VI) dication and is displaced by nitrate, which is a stronger ligand. The expected infrared and Raman vibrational modes arising from coordinated perchlorate²⁴ are not observed, but may be buried under the more intense modes arising from $[\text{EMIM}][\text{Tf}_2\text{N}]$.

Water is an integral part of the systems we are studying because we use uranyl perchlorate hexahydrate as a source of uranyl(VI). Therefore, although the water concentration in our commercially purchased $[\text{EMIM}][\text{Tf}_2\text{N}]$ is relatively low ($<100 \text{ ppm}$, $<0.01 \text{ M}$), the concentration of water in our uranyl(VI)-containing solutions is $\sim 0.6 \text{ M}$. It is interesting to examine how the interactions of water with uranyl(VI) and $[\text{EMIM}][\text{Tf}_2\text{N}]$ are affected by addition of a ligand, such as nitrate. The OH stretching modes for water, $\nu_{\text{as}}(\text{HOH})$ and $\nu_s(\text{HOH})$, which appear in the region from ~ 3700 to 3500 cm^{-1} , are sensitive indicators of intermolecular interactions and have been used to study water–water bonding interactions in RTILs, as well as those between water molecules and RTIL cations and

anions.^{26–36} Thus, an examination of the water OH stretching modes should provide some information about the behavior of water in RTIL solutions containing uranyl(VI) and potential ligands.

Figure 4 shows the $\nu(\text{OH})$ region of the infrared spectrum for solutions of $[\text{EMIM}][\text{Tf}_2\text{N}]$ and uranyl(VI) in which TBAN concentrations vary from 0 to 0.4 M. Because uranyl perchlorate hexahydrate was used as a source of uranyl(VI), the solutions also contain 0.2 M perchlorate and 0.6 M water. Figure 4a shows a spectrum of 1 M H_2O in $[\text{EMIM}][\text{Tf}_2\text{N}]$. In this spectrum, the OH stretching modes for water, $\nu_{\text{as}}(\text{HOH})$ and $\nu_{\text{s}}(\text{HOH})$, appear at 3630 and 3560 cm^{-1} , respectively. The intermolecular interactions of water with RTILs have been extensively investigated.^{26–37} The presence of distinct $\nu_{\text{as}}(\text{HOH})$ and $\nu_{\text{s}}(\text{HOH})$ modes in Figure 4, spectrum a, indicates that the water molecules are not engaged in hydrogen bonding with each other, but are “isolated” in the RTIL at this concentration.²⁶ Several studies have shown that such “isolated” water molecules engage in hydrogen bonding with RTIL anions.^{27,28,34}

In a solution of $[\text{EMIM}][\text{Tf}_2\text{N}]$ containing only uranyl(VI), perchlorate, and water, the $\nu_{\text{as}}(\text{HOH})$ and $\nu_{\text{s}}(\text{HOH})$ modes are broadened and shifted to lower wavenumber, resulting in a single broad vibrational band at 3370 cm^{-1} (Figure 4, spectrum b). A molecular dynamics study has shown that the “naked” uranyl(VI) dication will coordinate water in a water-saturated RTIL to form a $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$ complex and that unsaturated uranyl(VI) chloride complexes complete their inner coordination shell with water molecules.³⁸ A uranyl(VI) perchlorate species in $[\text{EMIM}][\text{Tf}_2\text{N}]$ will also coordinate water. The presence of a single broad $\nu(\text{OH})$ mode at 3370 cm^{-1} (Figure 4, spectrum b) shows that these coordinated water molecules take part in hydrogen-bonding interactions with other water molecules,²⁶ possibly in a second coordination sphere. Figure 4, spectra b–e, shows the spectra at various uranyl(VI)/TBAN mole ratios. No distinct changes in the spectra are apparent until the uranyl(VI)/TBAN mole ratio reaches 1:2 (0.2 M TBAN), shown in Figure 4, spectrum d. At this uranyl(VI)/TBAN mole ratio, $\text{UO}_2(\text{NO}_3)_2$ is the predominant species in solution.¹⁴ In Figure 4, spectrum d, the $\nu(\text{OH})$ mode at 3370 cm^{-1} can be seen to have decreased in intensity when compared to spectra b and c in Figure 4, and distinct $\nu_{\text{as}}(\text{HOH})$ and $\nu_{\text{s}}(\text{HOH})$ modes at 3630 and 3560 cm^{-1} also appear. The presence of all three vibrational bands indicates that both “isolated” and hydrogen-bonded forms of water are present in this solution. At a uranyl(VI)/TBAN mole ratio of 1:3 (0.3 M TBAN), where $\text{UO}_2(\text{NO}_3)_3^-$ is the predominant species, all water–water hydrogen-bonding interactions have been disrupted, and water exists completely in the “isolated” form (Figure 4, spectrum e). No additional changes in the spectrum are seen when the uranyl(VI)/TBAN mole ratio reaches 1:4 (0.4 M TBAN) (Figure 4, spectrum f). It is expected that some “isolated” water should be present at a uranyl(VI)/TBAN mole ratio of 1:1 (0.1 M TBAN), as well (Figure 4, spectrum b). However, the expected $\nu_{\text{s}}(\text{HOH})$ and $\nu_{\text{as}}(\text{HOH})$ modes are small and likely buried under the large and very broad $\nu(\text{OH})$ mode.

It is possible to infer from the infrared spectra discussed above that, in $[\text{EMIM}][\text{Tf}_2\text{N}]$, water coordinated to uranyl(VI) is involved in hydrogen-bonding interactions with water molecules in an outer coordination sphere. Because nitrate forms stronger complexes with uranyl(VI) than does water, the addition of nitrate displaces water from the first coordination sphere and disrupts these interactions. To gain a better understanding of the

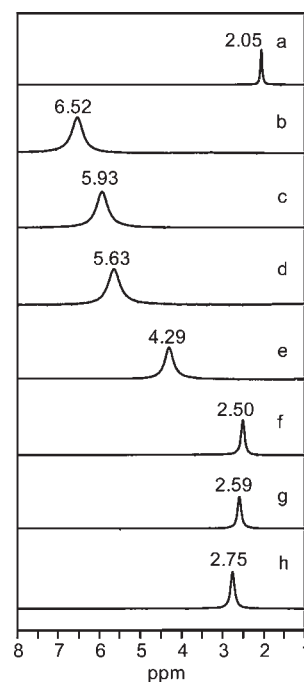


Figure 5. ^2H NMR spectra of solutions of $[\text{EMIM}][\text{Tf}_2\text{N}]$ containing (a) 0.6 M D_2O , (b) 0.1 M DUPH and no TBAN, (c) 0.1 M DUPH and 0.05 M TBAN, (d) 0.1 M DUPH and 0.1 M TBAN, (e) 0.1 M DUPH and 0.2 M TBAN, (f) 0.1 M DUPH and 0.3 M TBAN, (g) 0.1 M DUPH and 0.4 M TBAN, and (h) 0.6 M D_2O and 0.1 M TBAN. DUPH indicates deuterated uranyl perchlorate hexahydrate. Spectra were acquired at $30\text{ }^\circ\text{C}$ and referenced to an external d_6 -acetone signal.

effect of nitrate on the coordination of water to uranyl(VI), we used ^2H NMR spectroscopy to study solutions of uranyl(VI) in $[\text{EMIM}][\text{Tf}_2\text{N}]$ prepared using deuterated uranyl perchlorate hexahydrate (Figure 5). TBAN concentrations in these solutions vary from 0 to 0.4 M. ^2H NMR was used instead of ^1H NMR in order to avoid overlap with the strong ^1H signal arising from $[\text{EMIM}][\text{Tf}_2\text{N}]$. The ^2H NMR spectra represent a fast exchange limit between uncomplexed or “free” water at 2.05 ppm and water complexed to uranyl(VI) at ~ 6.5 ppm. The position of each NMR band in Figure 5 corresponds to the weighted chemical shift average of the two chemical forms of water.

In a 0.6 M solution of D_2O in $[\text{EMIM}][\text{Tf}_2\text{N}]$, the ^2H NMR signal of “isolated” water molecules is observed at 2.05 ppm at $30\text{ }^\circ\text{C}$ (Figure 5, spectrum a). In a 0.1 M solution of uranyl(VI) prepared using deuterated uranyl perchlorate hexahydrate, the ^2H NMR signal due to water is broadened and shifted downfield to 6.52 ppm (Figure 5, spectrum b), strong evidence that water is coordinated to uranyl(VI) in $[\text{EMIM}][\text{Tf}_2\text{N}]$. As TBAN is added to this solution, the ^2H NMR signal shifts only slightly upfield until the uranyl(VI)/nitrate ratio reaches 1:2, at which point $\text{UO}_2(\text{NO}_3)_2$ becomes the major species in solution and there is a large upfield shift in the ^2H NMR signal to 4.29 ppm, approximately halfway between the “free” and “bound” signal (Figure 5, spectrum e). This corroborates our interpretation from our infrared data that, although some water molecules are displaced by nitrate from the uranyl(VI) coordination sphere, some remain coordinated. When the uranyl(VI)/nitrate ratio reaches 1:3 and $\text{UO}_2(\text{NO}_3)_3^-$ becomes predominant in solution, the ^2H chemical shift for water is at 2.50 ppm, close to that for “free” water (Figure 5, spectrum f). Again, this corroborates

our conclusion from the infrared data that water is completely displaced from the uranyl coordination sphere and is in a “free” state at this point. The ^2H NMR signal shifts slightly upfield to 2.59 ppm as the uranyl(VI)/nitrate mole ratio increases from 1:3 to 1:4 (Figure 5, spectrum g). In a solution containing only 0.1 M TBAN, the ^2H NMR signal appears at 2.75 ppm (Figure 5, spectrum h).

CONCLUSIONS

We have conducted a detailed Raman, infrared, and NMR spectroscopic examination of uranyl(VI) speciation in solutions of [EMIM][Tf₂N] containing perchlorate, TBAN, and water. Dissolution of uranyl(VI) perchlorate hexahydrate in [EMIM]-[Tf₂N] results in a uranyl complex containing both perchlorate and water. The presence of $\nu_s(\text{ClO}_4)$ at 933 cm^{-1} is evidence that some uncoordinated perchlorate is present in solution, however. Water coordinated to uranyl(VI) is engaged in hydrogen bonding with molecules in a second coordination sphere, as shown by the appearance of a broad $\nu(\text{HOH})$ stretching mode at 3370 cm^{-1} and the presence of a ^2H NMR chemical shift at 6.52 ppm, both indicative of the presence of complexed water. Upon addition of nitrate to form the $\text{UO}_2(\text{NO}_3)_2$ and $\text{UO}_2(\text{NO}_3)_3^-$ species, distinct $\nu_{\text{as}}(\text{HOH})$ (at 3630 cm^{-1}) and $\nu_s(\text{HOH})$ (at 3560 cm^{-1}) vibrational bands appear, indicating that coordinated water is displaced by nitrate. In addition, the ^2H NMR signal for water shifts significantly upfield, confirming the displacement of water. Uranyl(VI) in the $\text{UO}_2(\text{NO}_3)_2$ complex can accommodate water in its coordination sphere, but water is completely displaced upon formation of the $\text{UO}_2(\text{NO}_3)_3^-$ species. More research is needed to examine the role that water and other potentially competing species play in uranyl(VI) solution chemistry in RTILs; however, our overall results indicate that Raman, infrared, and NMR spectroscopies are valuable additions to the suite of tools currently used to study the chemical behavior of uranyl(VI) in RTILs.

ASSOCIATED CONTENT

S Supporting Information. Additional experimental information and infrared spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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