Inorg. Chem. **2003**, *42*, 2197–2199

Inorganic Chemistry
Communication

Uranyl Coordination Environment in Hydrophobic Ionic Liquids: An in Situ Investigation

Ann E. Visser,[†] Mark P. Jensen,*,[‡] Ivan Laszak,[‡] Kenneth L. Nash,[‡] Gregory R. Choppin,[§] and Robin D. Rogers*,[†]

Department of Chemistry and Center for Green Manufacturing, The University of Alabama, Tuscaloosa, Alabama 35487, Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, and Department of Chemistry, Florida State University, Tallahassee, Florida 32306

Received December 24, 2002

Different inner-sphere coordination environments are observed for the uranyl nitrate complexes formed with octyl-phenyl-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide and tributyl phosphate in dodecane and in the hydrophobic ionic liquids (ILs) $[C_4mim][PF_6]$ and $[C_8mim][N(SO_2CF_3)_2]$. Qualitative differences in the coordination environment of the extracted uranyl species are implied by changes in peak intensity patterns and locations for uranyl UV–visible spectral bands when the solvent is changed. EXAFS data for uranyl complexes in dodecane solutions is consistent with hexagonal bipyramidal coordination and the existence of $UO_2(NO_3)_2(CMPO)_2$. In contrast, the complexes formed when uranyl is transferred from aqueous nitric acid solutions into the ILs exhibit an average equatorial coordination number of approximately 4.5. Liquid/liquid extraction results for uranyl in both ILs indicate a net stoichiometry of $UO_2(NO_3)(CMPO)^+$. The concentration of the IL cation in the aqueous phase increases in proportion to the amount of $UO_2(NO_3)(CMPO)^+$ in the IL phase, supporting a predominantly cation exchange mechanism for partitioning in the IL systems.

Ionic liquids (ILs) are currently being investigated as alternative reaction media to replace conventional organic solvents in numerous applications, including chemical synthesis and catalysis[1] and nuclear fuel reprocessing,[2] and as alternatives to traditional organic solvents for metal ion separations in liquid/liquid systems.[3] These salts, which by definition melt below 100 °C, are composed of an organic cation, like quaternary ammonium, 1-alkyl-3-methylimidazolium (Figure 1), or *n*-alkyl-pyridinium derivatives, and one of a variety of anions. The length of the alkyl chain substituents of the cation subtly affects the physical properties,[4] while both anion selection (e.g., Cl^-, NO_3^-, PF_6^-, or $N(SO_2CF_3)_2^-$) and the alkyl chain length of the cation control the water miscibility of the IL.

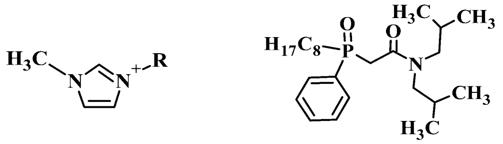

Figure 1. 1-Alkyl-3-methylimidazolium cation ($[C_nmim]^+$), where *n* designates the number of carbons in the alkyl chain (e.g., $[C_4mim]^+$ indicates *n*-butyl) and the ligand CMPO.

When an IL is sufficiently hydrophobic to form a two-phase aqueous/IL system, solutes partition between the aqueous and IL phases according to their relative solubility in the solvents. Aqueous metal ions are poorly soluble in ILs[5,6] except when coordinated with, or solvated by, hydrophobic molecules added to the IL phase,[3,5,7–9] or with hydrophilic complexing anions[6] that can facilitate metal ion transport into the IL phase. Given the substantial differences between ILs and conventional molecular solvents, it is conceivable that the complexes found in ILs are considerably different from the complexes known to exist in molecular solvents.

Recent studies[3,5,7] of Sr^{2+} and Cs^+ complexes with crown ether ligands in two-phase aqueous/IL systems have shown that the transfer of the metal ion complex into the IL phase occurs by a significantly different and more efficient biphasic mechanism than is observed when these ions partition into a molecular solvent containing a crown ether. For Sr^{2+} the phase transfer reaction changes from ion-pairing/solvation

---

* Authors to whom correspondence should be addressed. E-mail: mjensen@anl.gov; rdrogers@bama.ua.edu (R.D.R.).

[†] The University of Alabama.

[‡] Argonne National Laboratory.

[§] Florida State University.

(1) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772.

(2) Pitner, W. R.; Rooney, D. W.; Seddon, K. R.; Thied, R. C. Nuclear Fuel Processing, World Patent 99/41752, 2000.

(3) Dietz, M. L.; Dzielawa, J. A. *Chem. Commun.* **2001**, 2124.

(4) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, *3*, 156.

(5) Visser, A. E.; Swatloski, R. P.; Reichert, W. M.; Griffin, S. T.; Rogers, R. D. *Ind. Eng. Chem. Res.* **2000**, *39*, 3596.

(6) Visser, A. E.; Swatloski, R. P.; Griffin, S. T.; Hartman, D. H.; Rogers, R. D. *Sep. Sci. Technol.* **2001**, *36*, 785.

(7) Dai, S.; Ju, Y. H.; Barnes, C. E. *J. Chem. Soc., Dalton Trans.* **1999**, 1201.

(8) Visser, A. E.; Rogers, R. D. In *Molten Salts XIII*; De Long, H. C., Ed.; The Electrochemical Society: Philadelphia, 2002.

(9) Visser, A. E.; Rogers, R. D. *J. Solid State Chem.*, in press.

10.1021/ic026302e CCC: $25.00

in 1-octanol to cation exchange in some ILs and can be accompanied by an obvious change in the coordination environment of the Sr^{2+}−crown ether complex.[10] Two water molecules replaced two axially coordinated nitrate anions to give a cationic Sr^{2+}−crown complex when the solvent was changed from 1-octanol to $[C_5mim][N(SO_2CF_3)_2]$.

The increase in the fraction of Cs^+ and Sr^{2+} transferred into the IL phases relative to conventional solvents is potentially important, but it does not establish that this is a general phenomenon linked to changes in the coordination environment of the metal ion. The highly ionic character and high water content[4] of the ILs are at least partly responsible for the change in the phase transfer mechanism from ion-pairing/solvation to cation exchange, but the low charge density of Cs^+ and Sr^{2+} may be an important factor. To address this issue, we have examined the UO_2^{2+} complexes formed through contact with the well-studied hydrophobic ligand, CMPO (Figure 1), in the $[C_4mim][PF_6]$ and $[C_8mim][N(SO_2CF_3)_2]$ ILs, and the conventional solvent *n*-dodecane. Dodecane is the preferred solvent for the industrial scale separation of actinides from nuclear waste by the TRUEX process.[11]

Each of the these studies used 0.1 M CMPO and 1 M tri(*n*-butyl)phosphate (TBP) in the organic phase. Though TBP is known to form complexes with $UO_2(NO_3)_2$, it is employed in the TRUEX process to provide a more polar organic medium that will accommodate higher concentrations of actinides. Extensive previous work has demonstrated that the interaction of TBP with the uranium is minimal despite the 10:1 mole ratio of TBP:CMPO, largely because the phosphine oxide donor group of CMPO is a significantly stronger Lewis base than the phosphate oxygen of TBP. Though TBP might not be necessary in the CMPO−IL system, it was also added to both ILs to keep the conditions as comparable to those in dodecane as possible. The TBP does not directly interact with the extracted UO_2^{2+} in the ILs, since increasing the TBP concentration does not alter the partitioning equilibria of the uranium complexes.

Coordination of linear dioxo actinyl ions like UO_2^{2+} in the conventional aqueous nitric acid/dodecane-based system results in a neutral, hexagonal bipyramidal complex with two coordinated bidentate nitrate anions and two monodentate (P═O coordinated) CMPO molecules coordinated equatorially.[12] As was the case for Sr^{2+} and Cs^+ extraction by crown ethers, the fraction of UO_2^{2+} transferred out of the aqueous phase is consistently higher for IL/aqueous systems relative to dodecane/aqueous systems.[8] In principle, this could indicate either the formation of different complexes in the IL or improved compatibility of the same complexes with ILs.

Absorption spectroscopy has been used previously to investigate uranium in $AlCl_4^-$ ILs and systems wherein Cl^- is the only ligand, and unique interactions and speciation have been reported.[13−15] In our case, the spectra of the phases containing 0.1 M CMPO and 1 M TBP after contact with 20 mM $UO_2(NO_3)_2$ in 1 M HNO_3 (Figure 2) demonstrate that the uranyl−CMPO complexes in dodecane and the ILs are not equivalent. Particularly notable features are the change in the relative intensity of the peaks in the UO_2^{2+} fingerprint region and the red-shift in the longer wavelength peaks of the $[C_4mim][PF_6]$ sample.

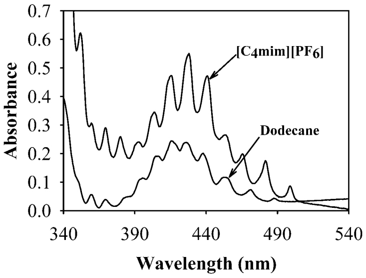

Figure 2. Absorption spectra of dodecane and $[C_4mim][PF_6]$ solutions containing 0.1 M CMPO and 1 M TBP, after contact with 20 mM $UO_2(NO_3)_2$ in 1 M HNO_3.

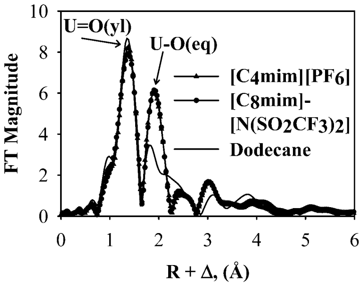

Figure 3. Fourier transform magnitude of the k^3 weighted U L_3 EXAFS (without phase shift correction) of the UO_2^{2+} complexes in dodecane (solid line), $[C_4mim][PF_6]$ (triangles), and $[C_8mim][N(SO_2CF_3)_2]$ (circles).

Changes in the UO_2^{2+} inner sphere coordination environment were investigated by extended X-ray absorption fine structure (EXAFS) measurements. The Fourier transform magnitudes of the EXAFS are shown in Figure 3, and the results of fitting the EXAFS data to the single scattering theoretical phase and amplitude functions generated by FEFF7.02[16] are summarized in Table 1 and included as Supporting Information. In the dodecane (TRUEX) sample, the coordination numbers for the UO_2^{2+} complex were fixed at the values derived from previous work[12] with two monodentate CMPO molecules (P═O bound) and two bidentate nitrate anions coordinated to the linear UO_2^{2+} moiety (i.e., $UO_2(NO_3)_2(CMPO)_2$). In this complex, the U−O distances of the CMPO ligand and nitrate anions are distinct. The two CMPO oxygen atoms are 2.38 ± 0.02 Å from the U center while the four U−O(nitrate) distances are 2.53 ±

---

(10) Jensen, M. P.; Dzielawa, J. A.; Rickert, P.; Dietz, M. L. *J. Am. Chem. Soc.* **2002**, *124*, 10664.

(11) Horwitz, E. P.; Chiarizia, R. In *Separation Techniques in Nuclear Waste Management*; Carleson, T. E., Chipman, N. A., Wai, C. M., Eds.; CRC Press: New York, 1996; p 1.

(12) Horwitz, E. P.; Diamond, H.; Martin, K. A. *Solvent Extr. Ion Exch.* **1987**, *5*, 447.

(13) Dai, S.; Shin, Y. S.; Toth, L. M.; Barnes, C. E. *Inorg. Chem.* **1997**, *36*, 4900.

(14) Anderson, C. J.; Deakin, M. R.; Choppin, G. R.; D'Olieslager, W.; Heerman, L. *Inorg. Chem.* **1991**, *30*, 4013.

(15) Anderson, C. J.; Choppin, G. R.; Pruett, D. J.; Costa, D.; Smith, W. *Radiochim. Acta* **1999**, *84*, 31.

(16) Zabinsky, S. I.; Rehr, J. J.; Ankudinov, A.; Albers, R. C.; Eller, M. J. *Phys. Rev. B* **1995**, *52*, 2995.

Table 1. Results from Fitting Four Shells (Dodecane) and Two Shells (ILs) of the k^3 Weighted U L_3 Edge EXAFS with Uncertainties in the Last Digits of the Fit Parameters Indicated in Parentheses

	CN	R, Å	σ^2, Å^2	ΔE, eV
dodecane				
U═O(yl)	2^a	1.779(6)	0.0014(3)	9.6
U−O(P)$_{eq}$	2^a	2.38(2)	0.0040(15)	(2.1)
U−O(N)$_{eq}$	4^a	2.53(2)	0.0038(16)	
U−N	2^a	2.97(3)	0.0029(15)	
[C$_4$mim][PF$_6$]				
U═O(yl)	2^a	1.785(9)	0.0017(5)	9.3
U−O$_{eq}$	4.6(5)	2.40(1)	0.0038(15)	(1.7)
[C$_8$mim][N(SO$_2$CF$_3$)$_2$]				
U═O(yl)	2^a	1.784(7)	0.0019(7)	9.4
U−O$_{eq}$	4.1(5)	2.40(1)	0.0029(17)	(2.1)

[a] Fixed parameter.

Table 2. Aqueous Concentration of C$_n$mim$^+$ after Contact of IL with Aqueous Phases

aqueous phase composition	aqueous phase [C$_4$mim]$^+$, M	aqueous phase [C$_8$mim]$^+$, M
water	0.024	0.011
1 M HNO$_3$	0.520	0.290
20 mM UO$_2$(NO$_3$)$_2$ + 1 M HNO$_3$	0.537	0.317
40 mM UO$_2$(NO$_3$)$_2$ + 1 M HNO$_3$	0.553	0.334
60 mM UO$_2$(NO$_3$)$_2$ + 1 M HNO$_3$	0.571	0.352

0.02 Å. These values are similar to those observed in other $UO_2(OPR_3)_2(NO_3)_2$ complexes.[17,18]

In contrast to the dodecane sample, only a single equatorial U−O bond distance at 2.40 ± 0.01 Å is observed in the EXAFS of the U−CMPO complexes in ILs. The axial uranyl oxygen distances remain unchanged, within experimental error, as expected. At the same time, the average number of oxygen atoms equatorially coordinated to U decreases from 6 in dodecane to approximately 4−4.5 in [C$_4$mim][PF$_6$] and [C$_8$mim][N(SO$_2$CF$_3$)$_2$]. Within the uncertainty of the observation, the number of coordinated equatorial oxygen atoms in the IL samples reported in Table 1 can be assumed to be identical for the two samples. In fact, when σ^2 is constrained to be 0.0038 in the [C$_8$mim][N(SO$_2$CF$_3$)$_2$] sample, the coordination number of the equatorial oxygen atoms increases from 4.1 to 4.5 ± 0.3. The similarity of the results for the complexes in ILs with different anions, [C$_4$mim][PF$_6$] vs [C$_8$mim][N(SO$_2$CF$_3$)$_2$] (Figure 3), also indicates that the IL anions are not present in the inner-sphere of UO_2^{2+} in these systems.

To determine the stoichiometry of the hydrophobic complexes, the partitioning of uranyl between the phases was measured as a function of [CMPO] and [HNO$_3$]. A log−log plot of the uranium distribution ratios as a function of [HNO$_3$] (at constant [CMPO]) and of [CMPO] (at constant [HNO$_3$]) defines the stoichiometry of the predominant species present in the organic phase as the slope of the resulting linear relationships (setting aside differences in activity coefficients). In both ILs, the unit slopes indicate the predominance of the species $UO_2(NO_3)(CMPO)^+$. Furthermore, the data in Table 2 demonstrate that the formation of this complex coincides with a one-for-one exchange of the IL cation into the aqueous phase. Since [C$_8$mim][N(SO$_2$CF$_3$)$_2$] is more hydrophobic than [C$_4$mim][PF$_6$], less of the [C$_8$mim]$^+$ cation is leached into the aqueous phase and a smaller amount of the cationic UO_2^{2+} complex can partition to the IL phase, resulting in lower distribution ratios.

Combining the oxygen coordination numbers derived from the EXAFS of the IL samples (Table 1) with this 1:1:1 (UO_2^{2+}:NO_3^-:CMPO) stoichiometry, it is still difficult to determine the denticity of the nitrate anion and the CMPO molecule because of the high water content of the ILs. If the nitrate and CMPO are both monodentate, two to three water molecules would also be extracted with the UO_2^{2+}. At the other extreme, if nitrate and CMPO are both bidentate, as observed in crystalline samples with UO_2^{2+},[17] a maximum of one additional water molecule (0.5 ± 0.5 H_2O) would be present in the UO_2^{2+} inner coordination sphere.

These results combined with the previous Sr^{2+} and Cs^+ studies indicate that if ILs are to be used as alternatives to traditional organic solvents in liquid/liquid separations of metal salt complexes, greater attention to the design of appropriate ILs and selection of ligand systems will be required. Although ILs have demonstrated their niche in many applications, the observed loss of the [C$_n$mim]$^+$ cation to the aqueous phase due to exchange with cationic metal complexes presents unique challenges for future use of ILs in metal ion separations. To prevent a cation exchange mechanism from occurring upon metal ion coordination, there is a need to design more hydrophobic cations for IL composition, possibly through fluorination of the alkyl chain. More research is needed not only in extraction, exchange, and solvation mechanisms but also to realize the true potential of ultimately "tunable" solvents.

Acknowledgment. This research is supported by the EMSP of the OEM, U.S. DOE, under Grants DE-FG07-01ER63266 and DE-FG07-01ER63296. The ANL staff and use of the Advanced Photon Source and are supported by the U.S. DOE, Offices of Science and Basic Energy Sciences, under Contract No. W-31-109-Eng-38. The authors gratefully acknowledge the infrastructure provided by BESSRC-CAT and the Argonne Actinide Facility.

Supporting Information Available: Experimental procedures, k^3 weighted EXAFS and fits, and details of data analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

IC026302E

---

(17) Caudle, L. J.; Duesler, E. N.; Paine, R. T. *Inorg. Chim. Acta* **1985**, *110*, 91.

(18) (a) Burns, J. H.; Brown, G. M.; Ryan, R. R. *Acta Crystallogr. C* **1985**, *41*, 1446. (b) Den Auwer, C.; Charbonnel, M. C.; Presson, M. T.; Madic, C.; Guillaumont, R. *Polyhedron* **1998**, *17*, 4507.