

# Solvent extraction of strontium nitrate by a crown ether using room-temperature ionic liquids †

Sheng Dai,<sup>\*a</sup> Y. H. Ju<sup>b</sup> and C. E. Barnes<sup>b</sup>

<sup>a</sup> Chemical Technology Division, Oak Ridge National Laboratory, PO Box 2008, Oak Ridge, TN 37831-6181, USA. E-mail: i9d@ornl.gov

<sup>b</sup> Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600, USA

Received 10th December 1998, Accepted 2nd February 1999

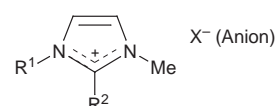
The preliminary results described here show that unprecedentedly large distribution coefficient (*D*) values can be achieved using ionic liquids as extraction solvents for the separation of metal ions by crown ethers. This work highlights the vast opportunities in separation applications for ionic liquids with crown ethers.

The discovery of crown ethers has led to a new class of ligands for alkaline and alkaline earth metal cations.<sup>1</sup> They have found wide applications in designing novel solvent extraction systems that are selective for certain metal ions based on the sizes of the crown-ether rings.<sup>2</sup> These systems utilize organic phases containing crown ethers to extract target metal ions from aqueous solutions through the complexation of the targeted radio-nuclides and the specific crown ethers. The efficiency of such extraction processes is strongly dependent not only on cations but also counter anions.<sup>3</sup> The alkaline and alkaline earth cations which coexist with hydrophobic counter anions in aqueous solutions are more readily extracted into the organic phases than those with hydrophilic anions.<sup>3</sup> In fact, the distribution coefficient (*D*) for the extraction of strontium nitrate into organic phases from its aqueous solutions by crown ethers is always less than one, even though the thermodynamic driving force for the complexation of Sr<sup>2+</sup> with a number of crown ethers is very favorable.<sup>3</sup> This distribution coefficient is low because the solvation free energies for simple inorganic anions such as nitrate by organic solvents are not favored thermodynamically.<sup>2</sup> Accordingly, difficulty in increasing solvent extraction efficiency using crown ethers as extractants lies in the unfavorable transport of anions from organic phases to inorganic phases. Limited solubilities of ionic species in non-ionic organic solvents are the main problem associated with conventional solvent extractions. A number of strategies have been proposed to address this problem including the addition of hydrophobic anions to aqueous solutions.<sup>2,3</sup> The obvious drawback to this approach is that more chemicals would be added to the system thereby possibly increasing the toxicities and complexity of the original aqueous solutions. We have been interested in developing ambient-temperature and high-temperature ionic liquids as new separation media for actinides and fission products.<sup>4</sup> In this communication, we report the use of a number of room-temperature ionic liquids as extraction solvents to remove strontium nitrate from aqueous phases into ionic liquids by a crown ether. The distribution coefficients for these ionic liquid extraction systems are several orders of magnitude better than those observed for current extraction systems based on organic solvents.

The use of ionic liquids to separate toxic metal ions and

organic molecules has been previously investigated by us<sup>4</sup> and others.<sup>5</sup> Notably, Rogers and co-workers have reported the successful extraction of organic acids from aqueous solutions into an ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate).<sup>5</sup> However, the distribution values for a number of organic acids are normally similar or less than those of the corresponding extraction systems based on non-ionic organic solvents. In this case,<sup>5</sup> the main advantage of using this particular room-temperature ionic liquid as an extraction solvent is the low vapor pressure of the ionic liquid as compared to most conventional organic solvents. The unique solvation capability of the room-temperature ionic liquid has not been used to full advantage. The very intrinsic property of the ionic liquid is that it consists only of ions, and that it can be made hydrophobic.<sup>6</sup> The novel dual properties of these new ionic liquids make them efficient solvents for the extraction of ionic species from aqueous solutions. From a thermodynamic perspective, the solvation of ionic species, such as crown-ether complexes, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>, in the ionic liquids, should be much more favored thermodynamically than those of conventional solvent extractions. This is one of the key advantages of using ionic liquids in separations involving ionic species. This prompted us to consider using these ionic liquids as extraction solvents for ionic species. In this report, we describe the effects ionic liquids have on improving the ability of crown ethers to remove metal ions from aqueous solutions. To our knowledge, no solvent-extraction system based on mixtures of ionic liquids and crown ethers has been reported in the literature.

The room-temperature ionic liquids (see below) used in



this work were 1-R<sup>1</sup>-2-R<sup>2</sup>-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]amide (R<sup>1</sup>R<sup>2</sup>MeIm<sup>+</sup>Tf<sub>2</sub>N<sup>-</sup>), where R<sup>1</sup> = ethyl, propyl, or butyl and R<sup>2</sup> = H, or methyl, and 1-R<sup>1</sup>-2-R<sup>2</sup>-3-methylimidazolium hexafluorophosphate (R<sup>1</sup>R<sup>2</sup>MeIm<sup>+</sup>PF<sub>6</sub><sup>-</sup>). These ionic liquids were synthesized as described in the literature and are known to be immiscible in water.<sup>4,5,7,8</sup> The concentration of water in the ionic liquids was too low to be measurable by FTIR, as reported previously.<sup>8</sup> The metal compound used in this work was strontium nitrate, because <sup>90</sup>Sr is a fission product and there is no efficient extraction methodology available for its removal from radioactive waste sites. The crown ether chosen was dicyclohexyl-18-crown-6 (2,3,11,12-dicyclohexano-1,4,7,10,13,16-hexaoxacyclooctadecane), which is known to form a strong complex with Sr<sup>2+</sup>.<sup>2</sup>

The extraction experiments were conducted by contacting 1 mL of an ionic liquid with a 10 mL aqueous solution of Sr(NO<sub>3</sub>)<sub>2</sub> (1.5 × 10<sup>-3</sup> M) for about 2 hours in a vibrating mixer. The pH value of the initial aqueous solution was 4.10. The concentration of the crown ether in the ionic liquids was 0.15 M. For comparison purposes, identical extraction experiments were conducted in which strontium nitrate was extracted from

† The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-96OR22464. Accordingly, the U.S. Government retains a paid-up, nonexclusive, irrevocable, worldwide license to publish or reproduce the published form of this contribution, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, or allow others to do so, for U.S. Government purposes.

**Table 1** Comparison of the extraction results obtained using ionic liquids and conventional solvents

Extract phase	$D^a$ (with crown ether in melts)	$D$ (without crown ether in melts)
BuMe <sub>2</sub> ImPF <sub>6</sub>	4.2	0.67
BuMeImPF <sub>6</sub>	$2.4 \times 10^1$	0.89
EtMe <sub>2</sub> ImTf <sub>2</sub> N	$4.5 \times 10^3$	0.81
EtMeImTf <sub>2</sub> N	$1.1 \times 10^4$	0.64
PrMe <sub>2</sub> ImTf <sub>2</sub> N	$1.8 \times 10^3$	0.47
PrMeImTf <sub>2</sub> N	$5.4 \times 10^3$	0.35
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	$7.6 \times 10^{-1}$	nm <sup>b</sup>
CHCl <sub>3</sub>	$7.7 \times 10^{-1}$	nm

<sup>a</sup> The  $D$  value is defined as  $D = [\text{Molten salt concentration of Sr}^{2+}] / [\text{aqueous solution concentration of Sr}^{2+}]$ . <sup>b</sup> nm = not measurable.

an aqueous phase into conventional organic extraction solvents such as toluene and chloroform containing 0.15 M of the same crown ether. Uptake of strontium nitrate by the ionic liquid or organic phases was measured by determining the remaining Sr<sup>2+</sup> in the aqueous solutions with inductively coupled plasma atomic emission (ICP-AE).

Table 1 gives extraction results for the six ionic liquids and two conventional extraction solvents tested. It is clear that the distribution coefficients of the ionic liquids using the crown ether as an extractant are all greater than those of the organic solvents. Without the crown ether, the partitioning of Sr(NO<sub>3</sub>)<sub>2</sub> into the ionic liquid phases is very small indicating that the crown ether plays an important role as a complexing extractant. This is consistent with our assertion that the solvation free energies of ion pairs by the ionic liquids are very favorable, thereby increasing the extraction coefficients. The highest distribution coefficient value is over 10,000, which is four orders of magnitude greater than those of the conventional extraction systems.<sup>2</sup>

The concentration ratio of Sr<sup>2+</sup> in the ionic liquid phase versus the aqueous phase  $D$ , is strongly dependent on the R<sup>1</sup> and R<sup>2</sup> groups. The  $D$  values of the ionic liquids with R<sup>2</sup> = H are always larger than those with R<sup>2</sup> = Me. This is consistent with our previous observation that the solubility of ionic uranium compounds in ionic liquids<sup>4</sup> is highly influenced by the R<sup>2</sup> group through the ionic interaction between the solvent cationic molecules and ionic solutes. When R<sup>2</sup> = H, we expect that hydrogen bonding interactions will be much stronger than when R<sup>2</sup> = Me. Accordingly, higher solubility and distribution coefficients result for the ionic liquids with R<sup>2</sup> = H.

The  $D$  values of the ionic liquids with bis[(trifluoromethyl)sulfonyl]amide anion are much larger than those with hexafluorophosphate anion. This indicates that the anion also plays a key role in solvation of the crown ether complex. This difference, which is induced by the solvent anions, can be rationalized by considering the difference in the anion size of two ionic liquid systems. The cationic complex of Sr<sup>2+</sup> and the crown ether form a large cation, which is stabilized when solvated by a big anionic species. Since the bis[(trifluoromethyl)sulfonyl]amide anion is larger in size than that of the hexafluorophosphate anion, the  $D$  values of the former extraction systems are larger than those of the latter. Support for this rationale can be found by comparing the corresponding distribution values of Sr<sup>2+</sup> for the ionic liquids without the crown ether. The  $D$  values of the plain ionic liquids with Tf<sub>2</sub>N<sup>−</sup> anion are very close to those of the plain ionic liquids with PF<sub>6</sub><sup>−</sup> anion. Under this condition, the strontium cation, whose size is much smaller

than that of its complex with the crown ether, will be directly solvated by the solvent anions. Accordingly, there are no solvation advantages in this case. The same argument has been employed in explaining the differences in clathrate formation induced by crown ethers.<sup>9</sup>

In conclusion, the preliminary results described here show that unprecedentedly large  $D$  values can be achieved using ionic liquids as extraction solvents for the separation of metal ions by crown ethers. Furthermore, the distribution coefficient values can be easily tailored by varying the substituting groups in the imidazolium cation and the counter anions. This work highlights the vast opportunities in separation applications for ionic liquids with crown ethers. Based on the same principle, we also envision the potential future uses of the ionic liquids containing crown ethers as a selective liquid membrane and liquid ion-selective electrodes.

## Acknowledgements

The authors wish to thank Mr M. C. Burleigh for his help to run ICP-AE analyses of the samples and Mr Y. S. Shin for his assistance with synthesizing ionic liquid precursors. The authors also wish to thank Dr P. V. Bonnesen and Dr B. A. Moyer for helpful discussions. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

## References

- 1 C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017; C. J. Pedersen, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1021; D. J. Cram, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1009; J. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 89.
- 2 M. Hiraoka, *Crown Compounds: Their Characteristics and Applications*, Elsevier, Amsterdam, 1982; L. F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, Cambridge, 1990; B. A. Moyer, *Complexation and Transport*, in *Molecular Recognition: Receptors for Cationic Guests*, ed. G. W. Gokel, in *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle and J.-M. Lehn, Pergamon, Elsevier, Oxford, 1996, vol. 1, ch. 10, pp. 377–416.
- 3 W. J. McDowell, *Sep. Sci. Technol.*, 1988, **23**, 1251; W. J. McDowell and R. R. Shoun, *Proceedings of ISEC'77*, 1977, **1**, 95.
- 4 S. Dai, Y. Shin, L. M. Toth and C. E. Barnes, *Inorg. Chem.*, 1997, **36**, 4900; S. Dai, L. M. Toth, G. D. Del Cul and D. H. Metcalf, *J. Phys. Chem.*, 1996, **100**, 220; S. Dai, L. M. Toth, G. D. Del Cul and D. H. Metcalf, *Inorg. Chem.*, 1995, **34**, 412.
- 5 J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser and R. D. Rogers, *Chem. Commun.*, 1998, 1765.
- 6 C. L. Hussey, *Adv. Molten Salt Chem.*, 1983, **5**, 185; C. L. Hussey, in *Chemistry of Nonaqueous Solvents*, ed. A. Popov and G. Mamantov, VXH Publishers, New York, 1994, ch. 4; R. T. Carlin and J. S. Wilkes, in *Chemistry of Nonaqueous Solvents*, ed. A. Popov and G. Mamantov, VXH Publishers, New York, 1994, ch. 5; K. R. Seddon, *J. Chem. Technol. Biotechnol.*, 1997, **68**, 351; Y. Chauvin and H. Olivier-Bourbigou, *CHEMTECH*, 1995, **25**, 26.
- 7 J. S. Wilkes and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1992, 965.
- 8 P. Bonhote, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Gratzel, *Inorg. Chem.*, 1996, **35**, 1168; N. Papageorgiou, Y. Athanassov, M. Armand, P. Bonhote, H. Pettersson, A. Azam and M. Gratzel, *J. Electrochem. Soc.*, 1996, **143**, 3099.
- 9 H. Hassaballa, J. Steed, P. C. Junk, M. R. J. Elsegood, *Inorg. Chem.*, 1998, **37**, 4666.

Communication 8/09672D