

Separations of Metal Ions Using Ionic Liquids: The Challenges of Multiple Mechanisms*

Violina A. Cocalia, John D. Holbrey, Keith E. Gutowski,
Nicholas J. Bridges, Robin D. Rogers**

Department of Chemistry and Center for Green Manufacturing,
The University of Alabama, Tuscaloosa, AL 35487, USA

Abstract: Ionic liquids are a distinct sub-set of liquids, comprising only of cations and anions, often with negligible vapor pressure. As a result of the low or non-volatility of these fluids, ionic liquids are often considered in liquid/liquid separation schemes where the goal is to replace volatile organic solvents. Unfortunately, it is often not yet recognized that the ionic nature of these solvents can result in a variety of extraction mechanisms, including solvent ion-pair extraction, ion exchange, and simultaneous combinations of these. This paper discusses current ionic liquid-based separations research where the effects of the nature of the solvent ions, ligands, and metal ion species were studied in order to be able to understand the nature of the challenges in utilizing ionic liquids for practical applications.

Key words: metal ion; liquid-liquid separation; ionic liquid; solvent extraction

Introduction

Ionic liquids (ILs) are proving to be increasingly interesting fluids for application in soft-matter materials systems from electrochemistry to energetic materials, and are also studied as potential solvents in separation processes^[1-19]. Properties, including low melting points, wide liquid ranges, and negligible vapor-pressure, have encouraged researchers to explore the uses of ILs to replace volatile organic solvents (VOCs).

Seddon^[20] has remarked that over 10^{18} simple organic salts that might be potential ILs could be prepared by varying the substitution patterns and anion

choices, even just within imidazolium and pyridinium systems. High symmetry pseudo-spherical, non-coordinating anions are commonly regarded as optimal for formation of ILs. Common examples of cations and anions which have been most widely investigated with regard to ionic liquid phase formation are shown in Fig. 1. Common anions that yield ILs include hexafluorophosphate ($[\text{PF}_6]^-$), tetrafluoroborate ($[\text{BF}_4]^-$), bis(triflyl)imide ($[(\text{SO}_2\text{CF}_3)_2\text{N}]^-$ or $[\text{Tf}_2\text{N}]^-$), and chloride (Cl^-).

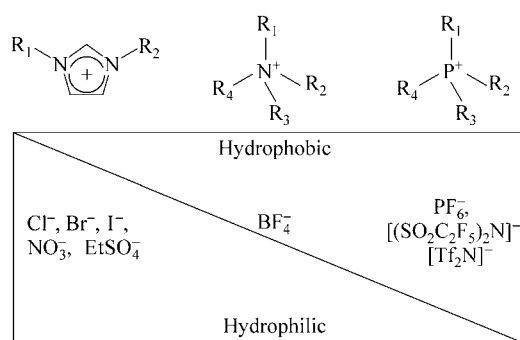


Fig. 1 Examples of IL cations and anions.

Received: 2005-10-09

* Supported by U.S. Department of Energy, Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Research (No. DE-FG02-96ER14673), and Office of Environmental Management, Environmental Management Science Program (No. DE-FG07-01ER63266).

** To whom correspondence should be addressed.

E-mail: rdrogers@bama.ua.edu

Differences in solvent behavior of ILs and conventional organic solvents, especially for hydrophobic ILs, have been manifested in different and enhanced distribution of metal extractant complexes in two phase systems. The presence of two charged species from the ionic solvent itself, in an IL/aqueous biphasic system, makes metal ion separation a much more complex process than in traditional solvents. This does not necessarily mean that ILs are not suitable for separation processes (although for some ILs that is the case), but one needs to find the right combination of IL and ligand to obtain similar behavior as in organic solvents or one needs to use the differences from organic solvents for achieving more advantageous separations.

The first investigations of metal ion extraction in IL/aqueous systems showed extremely high metal ion partitioning to the IL phase^[8,16]. It was the success of these initial studies that led to conjecture that ILs could also be used for the removal of hazardous actinide ions

and fission products from aqueous media. Further studies of different IL-based separation systems followed to elucidate the cause of the very high distribution ratios for metal ions. Dietz showed that the high distributions in IL/aqueous systems were due to a change in extraction equilibria in comparison to the octanol/aqueous system^[17]. In octanol, Sr²⁺ is extracted as a strontium nitrate-crown ether complex (Fig. 2, Eq. (3)), whereas in ILs, the two axial bound nitrates are substituted with two water molecules bound to the metal ion, and the charged Sr(CE)(H₂O)₂²⁺ species, where CE is dicyclohexano-18-crown-6-ether, is transferred to the IL phase^[18]. The neutrality of the system is maintained through the migration of two imidazolium cations to the aqueous phase for each extracted metal ion. The loss of the IL components in the aqueous phase would be a major limitation for practical applications of ILs in separations (Fig. 2, Eq. (1)).

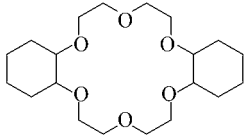
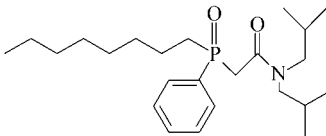
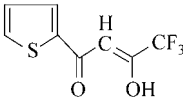
Equilibrium reaction for M ⁿ⁺ separation in ILs	Equilibrium reaction for M ⁿ⁺ separation in molecular solvents
 <p>L = Dicyclohexyl-18-crown-6</p>	
(1) $\text{Sr}^{2+}_{\text{aq}} + \text{L}_{\text{IL}} + 2[\text{C}_5\text{mim}]^+_{\text{IL}} + 2\text{H}_2\text{O} \Leftrightarrow [(\text{SrL})(\text{H}_2\text{O})_2]^{2+}_{\text{IL}} + 2[\text{C}_5\text{mim}]^+_{\text{aq}}$ ^[17] or (2) $\text{Sr}^{2+}_{\text{aq}} + 2\text{NO}_3^-_{\text{aq}} + \text{L}_{\text{IL}} \Leftrightarrow [\text{SrL} \cdot (\text{NO}_3)_2]_{\text{IL}}$ ^[21]	(3) $\text{Sr}^{2+}_{\text{aq}} + \text{L}_{\text{org}} + 2\text{NO}_3^-_{\text{aq}} \Leftrightarrow [\text{Sr}(\text{NO}_3)_2\text{L}]_{\text{org}}$ ^[17]
 <p>L = CMPO</p>	
(4) $\text{UO}_2^{2+}_{\text{aq}} + [\text{C}_n\text{mim}]^+_{\text{IL}} + \text{NO}_3^-_{\text{aq}} + \text{L}_{\text{IL}} \Leftrightarrow [(\text{UO}_2)\text{NO}_3\text{L}]^+_{\text{IL}} + [\text{C}_n\text{mim}]^+_{\text{aq}}$ ^[22]	(5) $\text{UO}_2^{2+}_{\text{aq}} + 2\text{NO}_3^-_{\text{aq}} + 2\text{L}_{\text{org}} \Leftrightarrow [(\text{UO}_2)(\text{NO}_3)_2\text{L}_2]_{\text{org}}$ ^[22]
 <p>L = Htta</p>	
(6) $\text{Ln}^{3+}_{\text{aq}} + 4\text{HL}_{\text{IL}} + [\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{\text{IL}} \Leftrightarrow [\text{C}_4\text{mim}]^+ [\text{LnL}_4]^-_{\text{IL}} + 4\text{H}^+_{\text{aq}} + [\text{Tf}_2\text{N}]^-_{\text{aq}}$ ^[23]	(7) $\text{Ln}(\text{H}_2\text{O})_n^{3+}_{\text{aq}} + 3\text{HL}_{\text{org}} \Leftrightarrow [\text{LnL}_3(\text{H}_2\text{O})_{n-6}]_{\text{org}} + 3\text{H}^+_{\text{aq}} + 6\text{H}_2\text{O}_{\text{aq}}$ ^[23] and (8) $\text{Ln}(\text{H}_2\text{O})_n^{3+}_{\text{aq}} + 4\text{HL}_{\text{org}} \Leftrightarrow \text{LnL}_3 \cdot \text{HL}_{\text{org}} + 3\text{H}^+_{\text{aq}} + n\text{H}_2\text{O}_{\text{aq}}$ ^[23]

Fig. 2 Extraction mechanisms in IL/aqueous vs. organic/aqueous biphasic systems.

Further investigations on the same system, but using the more lipophilic IL, $[C_{10}mim][Tf_2N]$, demonstrated that the extraction mechanism in ILs can be the same as in octanol (Fig. 2, Eq. (2)). However, the coordination environment of the metal ion was found to be different from that observed in 1-octanol/water biphasic systems with nitrate ions lying outside of the metal ion's inner coordination sphere^[21].

The nature of the IL is not the only factor which determines the metal extraction pathway; ligand type also has a very important contribution. Lanthanide(III) salts were shown to follow an anion exchange mechanism (Fig. 2, Eq. (6)) when extracted in an IL/aqueous system using Htta; in contrast to the cation exchange observed in molecular solvents (Fig. 2, Eqs. (7) and (8))^[23]. Here, changing the lipophilicity of the IL did not change the partitioning mechanism.

Another example of different behavior of metal ion extraction in ILs was observed by Visser et al. who showed that the high extraction of UO_2^{2+} with the well studied CMPO ligand to an IL phase, was due to a different mechanism (Fig. 2, Eqs. (4) and (5)) than observed in molecular organic solvents^[22]. Further, it was demonstrated that the metal ion coordination environment in the extracted species was also different from that observed in organic solvents. The coordination environment of uranyl nitrate with CMPO and TBP in a series of hydrophobic ILs was probed using both ultra-violet and visible (UV/Vis) spectroscopy and extended X-ray absorption fine structure (EXAFS) spectroscopy. Differences in UV/Vis peak location and intensity patterns (Fig. 3) in ILs vs. dodecane illustrated their inequivalence.

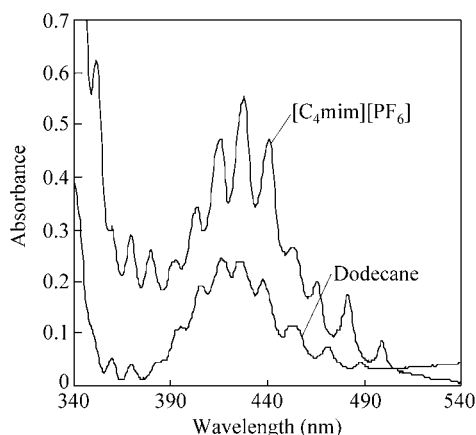


Fig. 3 Absorption spectra of dodecane and $[C_4mim][PF_6]$ solutions containing 0.1 mol/L CMPO and 1 mol/L TBP, after contact with 20 mmol/L $UO_2(NO_3)_2$ in 1 mol/L HNO_3 from Ref. [22].

The coordination environment around the metal ion in each instance was further clarified using EXAFS (Fig. 4). The EXAFS data for the uranyl-CMPO complex in dodecane was consistent with a hexagonal bipyramidal $UO_2(NO_3)_2(CMPO)_2$ complex, while the data in $[C_4mim][PF_6]$ and $[C_8mim][Tf_2N]$ suggested an average equatorial coordination number of 4.5, yielding a net stoichiometry of $UO_2(NO_3)(CMPO)^+$. The differences observed between the two types of solvents (ILs and molecular) illustrated the importance of elucidating the unique coordination interactions that occur in the ILs to optimize separations performance.

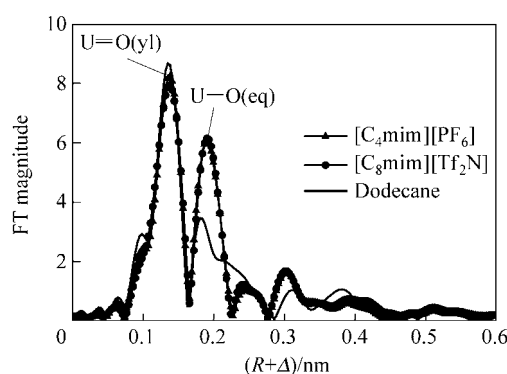


Fig. 4 Fourier transform magnitude of the k^3 weighted L_3 EXAFS of the UO_2^{2+} complexes in dodecane, $[C_4mim][PF_6]$, and $[C_8mim][Tf_2N]$ from Ref. [22].

Clearly, coordination, speciation, and extraction mechanism can and do vary from those in conventional solvent systems. The challenge is now to use the differences from traditional solvents efficiently and develop unique and more advantageous separation schemes, or to find the combinations of ILs and ligands which behave in an identical manner to molecular organic solvents. In our current work, we have studied a range of separation schemes in order to gain a better understanding of the relative roles and importance of complexant, metal, and IL ions to achieve these tasks. Here, we review some of the preliminary data coming from these studies.

1 Results and Discussion

1.1 Ligand assisted metal ion partitioning

We have investigated Cyanex-923 as an extractant for actinide ions in liquid/liquid separations using the hydrophobic IL $[C_{10}mim][Tf_2N]$ as the extracting phase. mixture of tri-alkyl-phosphine oxides of varying

mixture of tri-alkyl-phosphine oxides of varying chain lengths (hexyl- and octyl-) and has been used for actinide extraction into molecular solvents^[24]. Distribution ratio measurements for Pu⁴⁺ and Am³⁺ showed little acid dependency (HNO₃) for Pu⁴⁺, but strong acid dependency for the trivalent actinide. In addition, ligand dependency studies seem to support 1:1 metal-to-ligand binding for Pu⁴⁺, but significantly different binding ratios for Am³⁺, again supporting the notion that ILs can provide different coordination environments.

The high distribution ratios for Pu⁴⁺ and lack of acid dependency (Fig. 5) preclude stripping using a pH or concentration swing. Since oxalate has a high affinity for tetravalent actinides such as plutonium, forming hydrophobic anion complexes, the ability to strip extracted Pu⁴⁺ from the IL using oxalate as a stripping agent was investigated. The stripping of Pu⁴⁺ from dodecane system (85%) was more efficient than in the IL (70%) (Fig. 6), although conditions were not optimized.

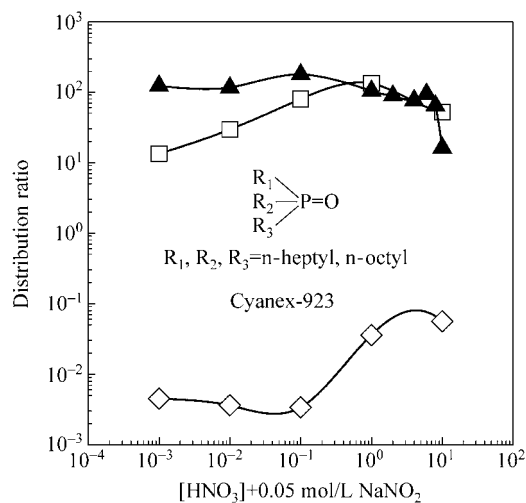


Fig. 5 Distribution of Pu⁴⁺ to 0.10 mol/L Cyanex-923 in [C₁₀mim][Tf₂N] (□), 0.10 mol/L Cyanex-923 in dodecane (▲), and [C₁₀mim][Tf₂N] blank (◇) versus [HNO₃].

A second class of complexants that we are currently investigating are closely related to siderophores. Siderophores are molecules produced by bacteria to bind Fe³⁺ in iron-deficient environments. The binding constants for Fe³⁺ can be as high as 10⁵² in some cases and their relative affinities for a series of metals is based on charge-to-size ratio. Due to the similarities in charge-to-size ratio between Fe³⁺ and Pu⁴⁺, siderophores can be highly effective sequestering

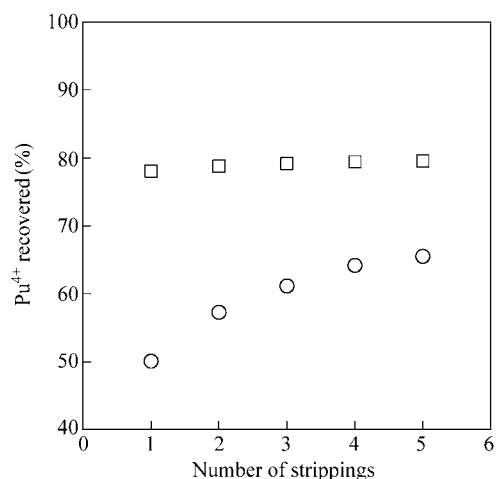


Fig. 6 Pu⁴⁺ stripping from 0.1 mol/L Cyanex-923 in dodecane (□) and [C₁₀mim][Tf₂N] (○).

agents for Pu⁴⁺ from solution. The siderophore-derived molecule, 1-hydroxy-6-N-octylcarboxamide-2(1H)-pyridinone (octyl-1,2-HOPO), has been studied by Raymond for the extraction of plutonium species from acidic media into octanol^[25].

We have studied the partitioning of Pu⁴⁺ with octyl-1,2-HOPO in IL/aqueous systems incorporating the hydrophobic ILs [C₄mim][Tf₂N] and [C₈mim][Tf₂N] (Fig. 7). Effects of cation hydrophobicity and lipophilicity (controlled by variation in the length of the alkyl-chain substituents) could be observed and can be related to changes in extraction mechanism following the observations made by Dietz et al.^[21]

Interestingly, the IL with the butyl chain (least lipophilic) resulted in Pu⁴⁺ distribution ratios which were nearly acid independent, whereas the IL with the octyl chain showed extraction behavior that was strongly acid dependent; the latter most closely paralleled the distribution ratios obtained from the octanol system. In both ILs, however, the ligand dependency observed was significantly different from those in octanol. In octanol, four octyl-1,2-HOPO ligands are bound to each Pu⁴⁺ ion in the extracting phase, whereas in the IL, a lower ligand:metal ratio was observed, with, presumably, nitrate anions filling the remainder of the plutonium coordination sphere.

Most importantly, it can be seen that the IL environment can greatly affect the degree to which an extractant molecule interacts with a metal ion, thus supporting the need for more targeted studies aimed at elucidating the nuances of IL coordination chemistry for the ultimate design of better, tailored ILs for

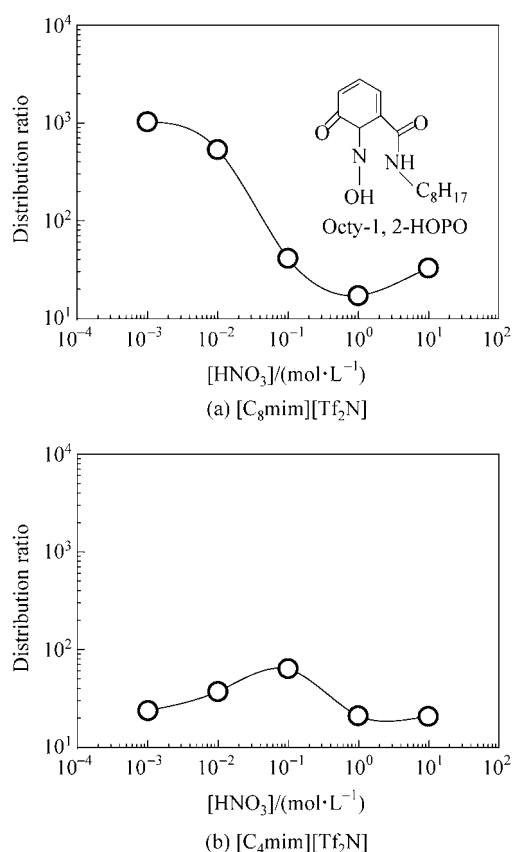


Fig. 7 Pu⁴⁺ distribution ratios for 0.003 mol/L octyl-1,2-HOPO in [C₄mim][Tf₂N] and [C₈mim][Tf₂N] versus [HNO₃].

application to more complex systems. These studies are now underway.

1.2 Hydrophilic ILs in liquid/liquid separation

Hydrophobic ILs are not the only choice for liquid/liquid IL-based separation of metal ions. We recently showed that hydrophilic ILs such as 1-butyl-3-methylimidazolium chloride ([C₄mim]Cl), can also be induced to form biphasic systems that are wholly aqueous in nature via the addition of concentrated aqueous solutions of water-structuring salts such as K₃PO₄ (Fig. 8)^[26]. These aqueous biphasic systems (ABS) can be formed from a wide range of IL types, including imidazolium-, pyridinium-, phosphonium-, and ammonium-based salts, as well as, with a variety of inorganic salts including phosphates, carbonates, hydroxides, and sulfates. These systems contain two aqueous phases: the upper phase is more lipophilic (containing organic cations), whereas the lower, more dense phase consists of a concentrated inorganic salt solution.

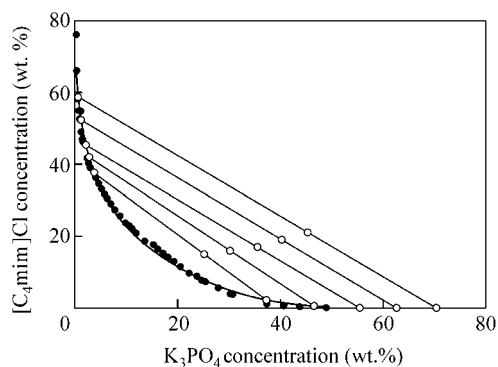


Fig. 8 The mutual coexistence curve for the aqueous [C₄mim]Cl/K₃PO₄ system from Ref. [26]. System compositions below the binodal are monophasic, compositions above the binodal are biphasic.

It is important to note that many of these inorganic salts are present in large amounts in nuclear tank wastes. As a result, these salt-salt biphasic systems are excellent models to critically investigate the behavior and sustainability of ILs with regard to stability and ion exchange under tank waste conditions. For example, it was found that distribution ratios for TcO₄⁻ from a concentrated K₃PO₄ solution to the IL-rich phase will exceed 700 and increase with increasing tie line length, without the need for an extractant. This is similar to polyethylene glycol-based aqueous biphasic systems where TcO₄⁻ was found to partition to the polyethylene glycol-rich phase^[27]. This offers the potential to remove TcO₄⁻ from tank waste using IL technology. In addition, further studies of the role of the IL anion and cation in these systems will aid in developing new ILs that are better suited for tank waste applications.

2 Conclusions

Separations utilizing ILs as the extracting phase are much more complex than those with simple molecular organic solvents. However, understanding the IL systems and choosing appropriate conditions to design targeted extractions is possible. One can either take advantage of the different extraction mechanisms which ILs afford, or one can find those separations, ligands, and ILs which afford identical behavior to molecular solvents. Our preliminary results show that separation schemes in ILs can indeed utilize the same extraction mechanism while preserving the same metal ion coordination found in traditional solvents, but only when an appropriate metal ion/ligand/IL system is used.

This argues once again, for a more complete fundamental understanding of IL systems in general.

Acknowledgements

The authors thank Cytec Inc. and 3M for gifts of Cyanex (272[®] and 923[®]) and Li[Tf₂N], respectively.

References

- [1] Rogers R D, Seddon K R, eds. *Ionic Liquids as Green Solvents: Progress and Prospects*. ACS Symposium Series 856. Washington, DC: American Chemical Society, 2003.
- [2] Rogers R D, Seddon K R, eds. *Ionic Liquids: Industrial Applications to Green Chemistry*. ACS Symposium Series 818. Washington, DC: American Chemical Society, 2002.
- [3] Welton T. *Chem. Rev.*, 1999, **99**: 2071-2084.
- [4] Holbrey J D, Seddon K R. *Clean Prod. Proc.*, 1999, **1**: 223-236.
- [5] Wasserscheid P, Keim W. *Angew. Chem. Int. Ed.*, 2000, **39**: 3772.
- [6] Dupont J, de Souza R F, Suarez P A Z. *Chem. Rev.*, 2002, **102**: 3667-3692.
- [7] Visser A E, Swatloski R P, Reichert W M, Griffin S T, Rogers R D. *Ind. Eng. Chem. Res.*, 2000, **39**: 3596-3604.
- [8] Chun S, Dzyuba S V, Bartsch R A. *Anal. Chem.*, 2001, **73**: 3737-3741.
- [9] Huddleston J G, Willauer H D, Swatloski R P, Visser A E, Rogers R D. *Chem. Commun.*, 1998, **16**: 1765-1766.
- [10] Visser A E, Swatloski R P, Rogers R D. *Green Chem.*, 2000, **1**: 1-4.
- [11] Visser A E, Swatloski R P, Reichert W M, Mayton R, Sheff S, Wierzbicki A, Davis J H, Jr., Rogers R D. *Chem. Commun.*, 2001, **1**: 135-136.
- [12] Visser A E, Swatloski R P, Griffin S T, Hartman M P, Rogers R D. *Sep. Sci. Technol.*, 2001, **36**: 785-804.
- [13] Blanchard L A, Gu Z, Brennecke J F. *J. Phys. Chem. B.*, 2001, **105**: 2437-2444.
- [14] Fadeev A G, Meagher M M. *Chem. Commun.*, 2001, **3**: 295-296.
- [15] Branco L C, Crespo J G, Alfonso C A M. *Angew. Chem. Int. Ed.*, 2002, **41**: 2771-2773.
- [16] Dai S, Ju Y H, Barnes C E. *Dalton Trans.*, 1999, **8**: 1201-1202.
- [17] Dietz M L, Dzielawa J A. *Chem. Commun.*, 2001, **20**: 2124-2125.
- [18] Jensen M P, Dzielawa J, Ricket P, Dietz M L. *J. Am. Chem. Soc.*, 2002, **124**: 10 664-10 665.
- [19] Visser A E, Griffin S T, Hartman D H, Rogers R D. *J. Chromatogr. B: Biomed. Sci. Appl.*, 2000, **743**: 107-114.
- [20] Seddon K R. In: Boghosian S, Dracopoulos V, Kontoyannis C G, Voyiatzis G A, eds. *The International George Papatheodorou Symposium: Proceedings*. Patras: Institute of Chemical Engineering and High Temperature Chemical Processes, 1999: 131.
- [21] Dietz M L, Dzielawa J A, Laszak I, Young B A, Jensen M P. *Green Chem.*, 2003, **5**: 682-685.
- [22] Visser A E, Jensen M P, Laszak I, Nash K L, Choppin G R, Rogers R D. *Inorg. Chem.*, 2003, **42**: 2197-2199.
- [23] Jensen M P, Neuefeind J, Beitz J V, Skanthakumar S, Soderholm L. *J. Am. Chem. Soc.*, 2003, **125**: 15 466-15 473.
- [24] Zhu Y, Jiao R. *Nuclear Technology*, 1994, **108**: 361-369.
- [25] Romanovski V V, White D J, Xu J, Hoffman D C, Raymond K N. *Solvent Extr. Ion Exch.*, 1999, **17**: 55-71.
- [26] Gutowski K E, Broker G A, Willauer H D, Huddleston J G, Swatloski R P, Holbrey J D, Rogers R D. *J. Am. Chem. Soc.*, 2003, **125**: 6632-6633.
- [27] Rogers R D, Bond A H, Bauer C B, Zhang J, Rein S D, Chomko R R, Roden D M. *Solv. Extr. Ion Exch.*, 1995, **13**(4): 689-713.