

Novel Fission-Product Separation based on Room-Temperature Ionic Liquids

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Overview

U.S. DOE's underground storage tanks at Hanford, SRS, and INEEL contain liquid wastes with high concentrations of radioactive cesium-137 and strontium-90. Because the primary chemical components of alkaline supernatants are sodium nitrate and sodium hydroxide, the majority of this could be disposed of as low level waste if radioactive cesium-137 and strontium-90 could be selectively removed.

The underlying goal of this project was to investigate the application of ionic liquids as novel solvents for new solvent extraction processes for separation of cesium-137 and strontium-90 from tank wastes. Ionic liquids are a distinct sub-set of liquids, comprising only of cations and anions they are proving to be increasingly interesting fluids for application in systems from electrochemistry to energetic materials, and are also rapidly establishing their promise as viable media for synthesis and separations operations. Properties including low melting points, *electrochemical conductivity*, *wide liquid ranges*, *lack of vapor-pressure*, and chemical *tunability* have encouraged researchers to explore the uses of ILs in place of volatile organic solvents. The most promising current developments arise from control of the unique combinations of chemical and physical properties characteristic of ionic liquids.

This project has demonstrated that Sr^{2+} and Cs^{+} can be selectively extracted from aqueous solutions into ionic liquids using crown ethers and that unprecedentedly large distribution coefficients can be achieved for these fission products. The volume of secondary wastes can be significantly minimized with this new separation technology. Through the current EMSP funding, the solvent extraction technology based on ionic liquids has been shown to be viable and can potentially provide the most efficient separation of problematic fission products from high level wastes. The key results from the current funding period are the development of highly selective extraction process for cesium ions based on crown ethers and calixarenes, optimization of selectivities of extractants via systematic change of ionic liquids, and investigation of task-specific ionic liquids incorporating both complexant and solvent characteristics.

The collaboration between established groups at Oak Ridge National Laboratory (ORNL), the University of Alabama, and the University of Mississippi has been shown to be a successful partnership, combining expertise in synthesis, solvent extraction and characterization of ionic liquids. We believe that the study of fission product chemistry and separations in ionic liquid solvent systems has had an important role in the investigation, understanding, discovery and development of a new and very versatile solvent systems targeted for the separation of important fission products from high-level tank wastes

Background and Significance

The overall goal of the proposed research was to investigate solvent extraction process for separation of cesium-137 and strontium-90 from tank wastes based on **ionic liquids**.

Research Rationale

Crown ethers and related macrocycles have found wide application in the design of novel solvent extraction systems that are *selective* for fission products, such as Cs^+ and Sr^{2+} . Difficulties in increasing the solvent extraction efficiency of conventional solvent extraction systems using crown ethers as extractants lie in the unfavorable transport of the cation and counter anions from aqueous phases to organic phases and limited solubilities of ionic species in nonionic organic solvents. A number of strategies have been proposed to address this problem, including the addition of hydrophobic anions to the aqueous solution or the addition of hydrophilic solvents to the organic phase. The obvious drawback to these approaches is that more chemicals would have to be added to the system thereby increasing the complexity of the aqueous solution.

These deficiencies associated with current extraction processes based on crown ethers prompted the search for alternative extraction media that could convert the solvation of ionic species into a more favorable process using ionic liquid solvents as the extracting phases. Unlike the conventional solvents currently in use, they are nonvolatile and therefore do not emit noxious vapors, which can contribute to air pollution and health problems for process workers. The very unusual intrinsic property of these melts is that they consist *only of ions* and that they can be made *hydrophobic*! The novel dual properties of these new ionic liquids make them efficient solvents for the extraction of *ionic species* from aqueous solutions.

However, in contrast to molecular solvents used as extracting phases, ionic liquids comprise of two ions, rather than a single neutral molecule, and the ions can participate in the extraction process. Understanding, control and utilization of the different solvent extraction, and cation and anion exchange mechanisms possible in any one ionic liquid solvent system are both the challenge and the key to exploiting ionic liquids in separations schemes. By adjusting the nature of the ionic liquid extracting phase through choice or modification of the cationic or anionic components, the roles of solvent extraction and ion exchange mechanisms in the metal-ion separation process can be controlled.

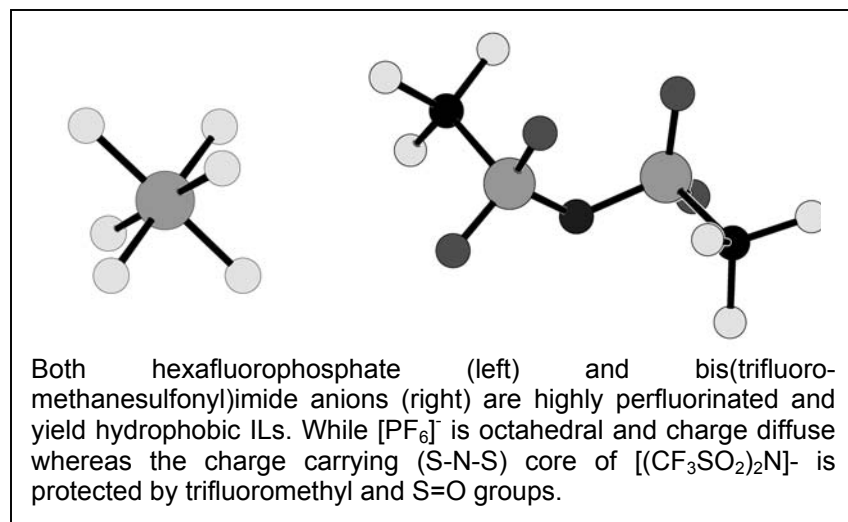
Fundamental chemical studies towards developing ionic liquid-based separation methods for removing cesium and strontium with high selectivity have been undertaken. Noteworthy advantages of the proposed ionic-liquid-based separation methods, especially applicable to meeting EMSP objectives include: (a) methods with very high separation factors that would permit the effective removal of Sr^{2+} and Cs^+ from high level wastes, (b) methods that enable the concentration of Sr^{2+} and Cs^+ into small volumes for sensitive analyses, (c) methods which do not need a large inventory of expensive macrocyclic ligands and permit recovery of the extractant ligands, (d) methods which separate Sr^{2+} and Cs^+ in solid salt forms with the minimal expenditure of energy (no need to evaporate large volumes of water), (e) methods based on solvent systems with no measurable vapor pressure, significantly reducing air pollution and

health problems for process workers, and (f) methods using nonflammable solvents, promising significant safety benefits.

Our current studies indicated that both Sr^{2+} and Cs^+ can be efficiently (quantitatively) removed from high-level waste simulants. Crown and calixarene-crown ethers have been used to extract strontium and cesium ions from various types of aqueous media. Use of crown ethers for strontium ion extraction, and calixarene crown-ethers for cesium ion extraction, in ionic liquid media, can greatly increase the strontium and cesium distribution ratios to 10^4 or more. The separation selectivities for these two target ions can be achieved via rational choice of macrocyclic ligands and further enhanced via proper choice of ionic liquids. A key methodology to significantly reduce the loss of ILs and increase the extraction efficiency through a sacrificial cation-mediated ion exchange has been proposed and demonstrated preliminarily. Furthermore, we have developed several ligands, which can be readily recycled and highly selective toward Sr^{2+} in ILs. Our current research has clearly addressed the important factors that are involved in development of the scientific basis as well as the potentials of the IL-based extraction technology for efficient separation of problematic fission products from high level wastes.

Progress on the UA portion of this collaborative study with scientists at ORNL of Novel Fission-Product Separation Based on Room Temperature Ionic Liquids is summarized under the headings of the major proposal objectives.

Using ILs as direct replacements for organic solvents in organic/aqueous liquid-liquid biphasic systems is currently limited to hydrophobic ILs that form biphasic systems when contacted with aqueous solutions. These ILs usually contain perfluorinated anions such as in $[\text{C}_n\text{mim}][\text{PF}_6]$ or $[\text{C}_n\text{mim}][(\text{CF}_3\text{SO}_2)_2\text{N}]$ ILs, where $[\text{C}_n\text{mim}]^+$ is the common 1-alkyl-3-methylimidazolium cation (but can also include pyridinium, ammonium, and phosphonium salts). Fundamental studies of hydrophobic ILs typically involve $[\text{PF}_6]^-$ ILs as a standard, but it's implementation in practical separations schemes is hindered by its susceptibility to hydrolysis and the formation of HF (Swatloski, R. P.; Holbrey, J. D.; Rogers, R. D. *Green Chem.* **2003**, 5, 361). As a result, the focus for hydrophobic ILs has recently largely shifted to the bis(trifluoromethanesulfonyl)imide anion, $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$, that offers much more stability to



hydrolysis and acidic conditions but is much more expensive. A later section will center on the use of more environmentally friendly cations that form the basis of hydrophilic ILs in novel IL-based aqueous biphasic systems.

We have investigated the use of hydrophobic ILs in IL/aqueous biphasic separations systems for the uptake of both actinides and

fission products from acidic media using traditional extractants, with a principle focus on radiotracer studies to determine distribution behavior under infinite dilution conditions, as a function of extractant, acid, or salt concentrations in the systems. Liquid-liquid samples containing equal volumes of the extractant-containing IL and salt or acid solution (varying between 10^{-3} M and 10^1 M) are contacted and spiked with a desired activity of a given radiotracer. Partitioning of fission products (^{137}Cs , ^{85}Sr , ^{99}Tc , and ^{125}I) have been investigated. Partitioning of radiotracers between the two phases is analyzed either by gamma counting or scintillation counting (for alpha and beta emitters respectively) and distribution ratios for a given radiotracer due to partitioning by the extractant can be calculated.

Analysis of distribution data from both nitric acid dependency and ligand dependency experiments allows for the elucidation of the nature of the extraction mechanism. Solvent extraction mechanisms involve the formation of adducts where metal cations bind with the extractant, along with certain anions to maintain charge neutrality, and are collectively transferred to the diluent phase as a neutral species. Ion exchange, on the other hand, is dependent upon the mutual exchange of cationic or anionic components between the phases to facilitate the transfer of a desired charged complex and maintain electroneutrality of each phase.

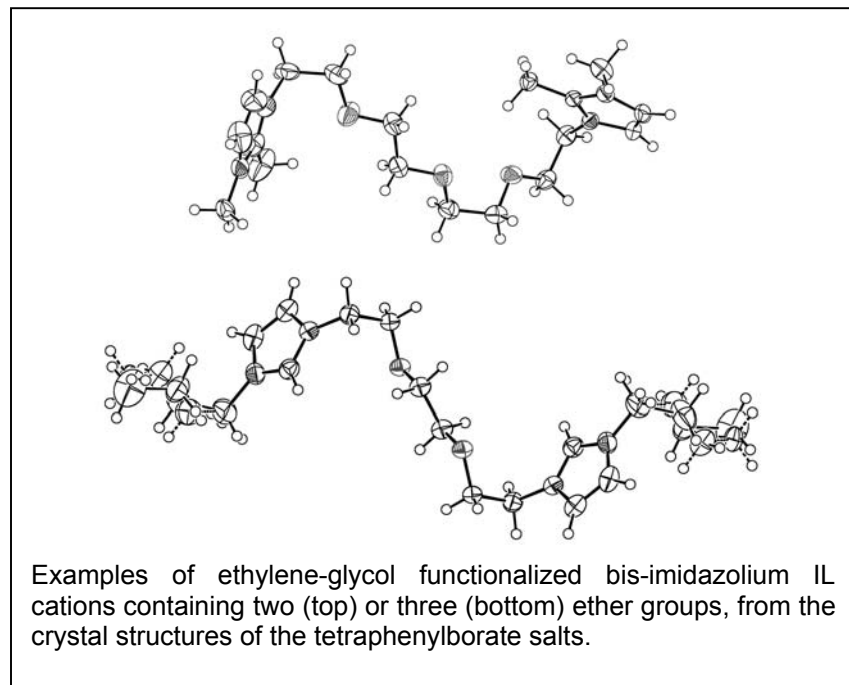
I. Synthesize new Ionic Liquids tailored for the extractive separation of Cs and Sr.

The tunable nature of ILs allows for the covalent attachment of extractant functionalities to the cation component in the rational design of ILs aimed at performing specific tasks. TSILs can be viewed as either (i) appending complexing functionality onto the IL components, or (ii) addition of an ionic moiety (IL component) to an extractant to increase affinity with an IL diluent. Incorporation of an extractant functionality into the ILs itself provides opportunities to develop new and novel chemistries with ILs while at the same time bypassing the need to add the extractant itself. In doing so, the favorable properties of the extractant can be maintained, leading to a “loaded” solvent environment with high extractive ability.

Our interest in metal–ether complexants (*e.g.*, with Group 1–2 metals of relevance to electrochemistry), salt-induced phase separation and structuring in polyethylene glycol (PEG)-based aqueous biphasic systems (ABS), and separation and extraction of heavy metals, led us to investigate a range of ILs incorporating ether functionality as extraction media. Initial results for an IL containing the bis-imidazolium cation, 1,1A-[1,2-ethanediylbis(oxy-1,2-ethanediyl)]bis[3-methyl-1*H*-imidazolium-1-yl], in which a proto-extractant functionality (an ethylene glycol unit) is incorporated between the two cationic groups are reported.

New bis-imidazolium ILs which contains a polyether spacer has been synthesized, characterized, and metal partitioning studies between the IL and water have been investigated. The initial studies were made single prototype single example, and partitioning of mercury and cesium ions from aqueous salt and acid and base solutions were studied. As anticipated, the incorporation of 'task-specific' extracting functionalities into the cationic core of the IL lead to enhanced partitioning of mercury to the IL phase, when compared to conventional ILs, and is comparable to that of IL containing specific metal extractants. This simple, new IL demonstrated the proof of concept, that polyether-coordinating functions can be easily

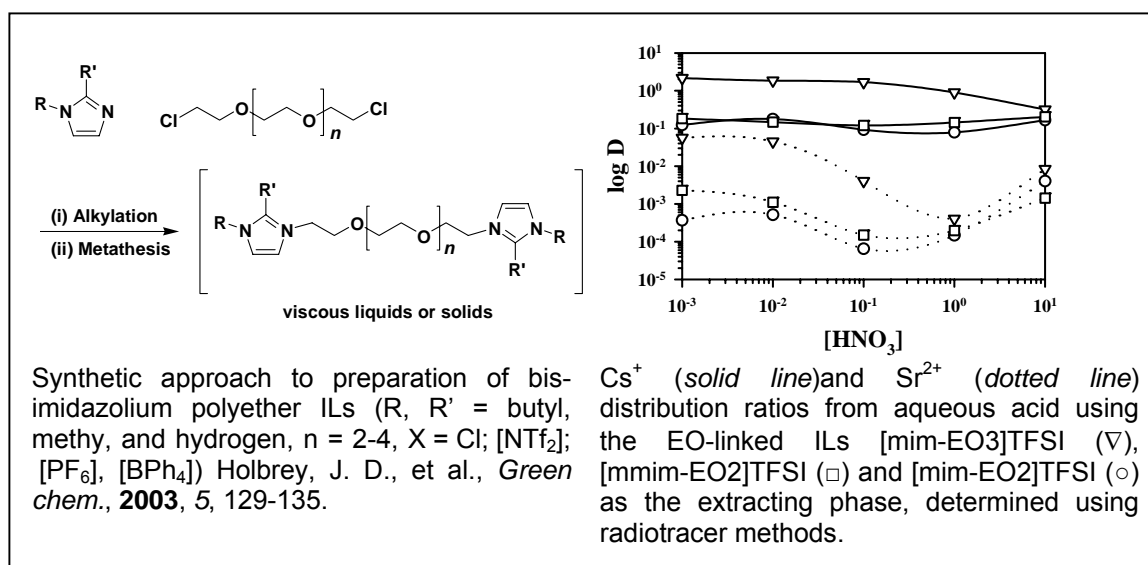
incorporated and used to facilitate metal extraction, though at present, the mechanism for extraction has not been fully elucidated.



The distribution ratios between 1,1A-[1,2-ethanediyl-bis(oxy-1,2-ethanediyl)] bis[3-methyl-1*H*-imidazolium-1-yl] bis(trifluoromethanesulfonyl)imide, and pure H₂O for Cs⁺ and Hg²⁺ are 0.33 and 54, respectively. The Cs⁺ distribution ratios remain essentially invariant between 0.13–0.33 with the concentration of acid, base, or salt in the aqueous phase, perhaps indicating the inability of the short PEG moiety to completely wrap up and dehydrate the large, hard Cs⁺ coordination sphere. This is consistent

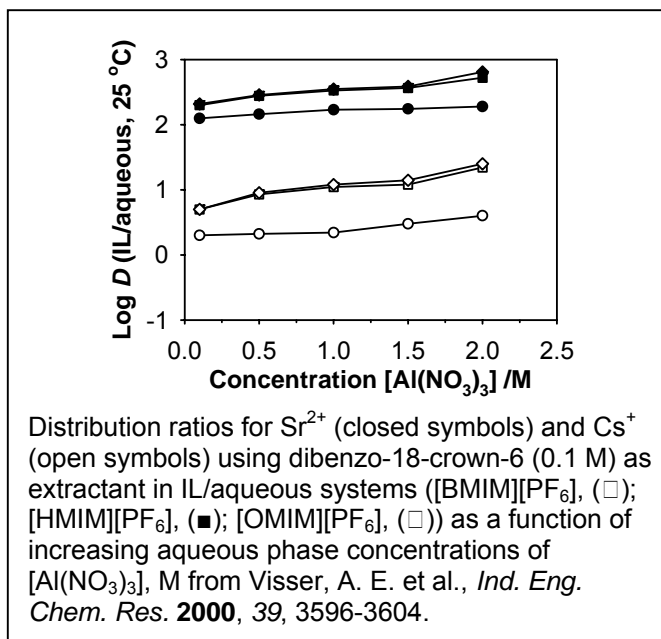
with data for other hydrophobic IL-aqueous systems in which Cs⁺ remains in the aqueous phase in the absence of complexants (*e.g.*, crown ethers).

Further examples of this type of new ionic liquid have been prepared, with differing polyether spacers and functionality on the cation head groups. Partitioning results for Cs⁺ and Sr²⁺ from acid show increased *D*s to the IL phase with increasing length of the EO-spacer.



II. Select optimum macrocyclic extractants through studies of complexation of fission products with macrocyclic extractants and transport in new extraction systems based in Ionic Liquids.

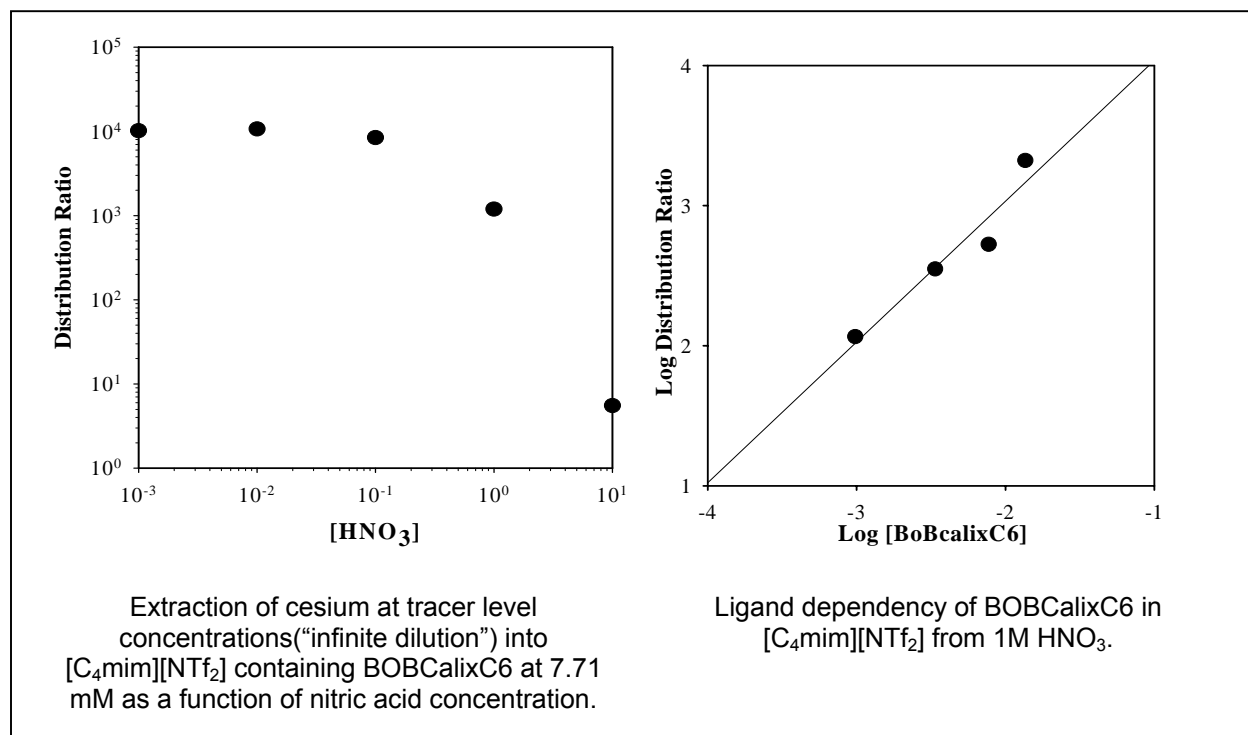
The applications of ionic liquids (ILs) as new separation media have been actively investigated recently. Macrocyclic ligands such as crown ethers have been widely used for metal ion extraction, with the structure and cavity size of the crown ether as the basis for metal ion selectivity. By attaching alkyl or aromatic ligands to the crown, the hydrophobicity of the ligand can be adjusted. Impressive results have been obtained using dicyclohexano-18-crown-6 as an extractant for Sr^{2+} in [RMIM][NTf₂] IL/aqueous systems [Dai, S.; Ju, Y. H.; Barnes, C. E. *J. Chem. Soc., Dalton Trans.* **1999**, 1201.] and 18-crown-6, dicyclohexano-18-crown-6, and 4,4'-(5')-di-(*t*-butylcyclohexano)-18-crown-6 in [RMIM][PF₆]/aqueous systems [Visser, A. E.; Swatoski, R. P.; Reichert, W. M.; Griffin, S. T.; Rogers, R. D. *Ind. Eng. Chem. Res.* **2000**, 39, 3596-3604.] as extractants for Sr^{2+} , Cs^{+} , and Na^{+} . Metal ion extraction to the ILs is greatest at high anion concentration in the aqueous phase, but decrease with increasing acid concentration, in contrast to typical solvent extraction where the higher distribution ratios are obtained with increasing acid concentrations.



Recent studies 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 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. 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 [C₅mim][N(SO₂CF₃)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 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.

We extended our investigation of the solvent extraction and ion exchange properties of ILs to the extraction of cesium ions. A lipophilic derivative of a calix[4]-bis-crown-6, calix[4]arene-bis(*tert*-octylbenzo-crown-6) (“BOBCalixC6”) as shown in Figure 3 was utilized as a cation acceptor. These studies were directed primarily toward acquiring an understanding of the mechanism of extraction in the complex IL solvents, and secondarily to determining if a Cs-removal technology utilizing ILs is possible. The cations of the ILs used in this work were 1- C_n -3-methylimidazolium ($C_n\text{mim}^+$), where $C_n = C_2$ (ethyl), C_4 (butyl), C_6 (hexyl), and C_8 (octyl). The anion is bis[(trifluoromethyl)sulfonyl]amide (NTf_2^-).



The D_{Cs} values of the plain ILs in the absence of an extractant are very low. The small amount of Cs^+ which does partition into the ILs correlates with the observed hydrophobicities of the IL organic cations. The hydrophobicity is also inversely related to the solubility of the corresponding 1-alkyl-3-methylimidazolium cation ($[\text{C}_n\text{mim}]^+$) in the aqueous phase, and thus its ion-exchange capability. Accordingly, the selectivity of this solvent is dominated by the hydrophobicity of the metal ions extracted (i.e., their Hofmeister selectivity). The solubilities of BOBCalixC6 in the ILs are quite high, even though this complexant was designed specifically for use in an organic extracting phase. As seen in Table 1, the distribution coefficients (D_{Cs}) of Cs^+ from water to IL with BOBCalixC6 strongly depend on the concentration of BOBCalixC6 in the ILs and increase with the concentration of the extractant. This observation is very similar to that noted in the extraction of Sr^{2+} with *cis*-dicyclohexano-18-crown-6 (DCH18C6) in ILs, indicating that the complexation of Cs^+ plays a key role in the partitioning processes.

The distribution of Cs^+ to the IL phase was observed to decrease with increasing chain length of the substituted alkyl group (R) in the organic cation of the IL. This observation is consistent with a mechanism of ion-exchange during the extraction. The longer the alkyl chain is, the more hydrophobic the organic cation becomes, and accordingly the less the IL will partition to the aqueous phase. From infinite dilution distribution studies as a function of nitric

acid concentrations in the aqueous phase, at $[\text{HNO}_3] < 0.1 \text{ M}$, BOBCalixC6 shows virtually quantitative extraction of cesium. At acid concentrations greater than 0.1 M, an acid dependency occurs lowering the distribution ratio, and the ligand dependency of 1:1 was determined from what was measured from 1 M HNO_3 solution.

Table 1. Distribution ratios (D_{Cs}) between the ILs and 2.5 mM CsNO_3							
[BOBCalixC6] (mM)	$n\text{-R in } [\text{Rmim}][\text{Tf}_2\text{N}]$						CHCl_3
	2	3	4	4*	6	8	
0	0.084	0.055	0.024	0.19	ud	ud	ud
1.00	1.61	1.36	0.77	0.95	0.56	0.45	ud
3.40	4.68	3.90	3.67	2.92	3.20	2.50	ud
7.71	15.3	14.6	13.8	11.7	11.5	8.10	ud
13.6	nm	137	131	63.8	57.4	17.9	0.034

*Work conducted using radiotracer technique. ud: Undetectable via ion chromatography.
nm: Not measured because concentration of BOBCalixC6 could not be reached.

The selectivity for Cs^+ was investigated using aqueous solutions containing competitive Na^+ , K^+ , and Sr^{2+} ions in contact with BOBCalixC6-loaded $[\text{C}_4\text{mim}][\text{NTf}_2]$. The selectivity coefficient for Cs^+ in the presence of competitor cations can be obtained from the ratios of the D_{Cs} values to the corresponding distribution coefficients of the competitive ions. The distribution coefficients for Na^+ and Sr^{2+} using BOBCalixC6 in $[\text{C}_4\text{mim}][\text{NTf}_2]$ were too small to be detected by ion chromatography. This observation is consistent with what has previously been observed for BOBCalixC6 and related calixarene-crown ethers in conventional solvents. Coextraction of K^+ along with Cs^+ has been observed, however, using BOBCalixC6 in conventional solvents. The concomitant extraction of K^+ along with Cs^+ is also observed in our studies. The selectivity coefficients determined under various conditions range from ~ 3.94 to ~ 68.7 , which are lower than the selectivities of ca. 220 seen in organic solvents such as 1,2-dichloroethane. The lower selectivity of cesium over potassium maybe attributable to the greater polarity of the ionic liquid than 1,2-dichloroethane (dielectric constant 10.19 at 25°C).

III. Develop efficient processes to recycle ionic liquids and crown ethers.

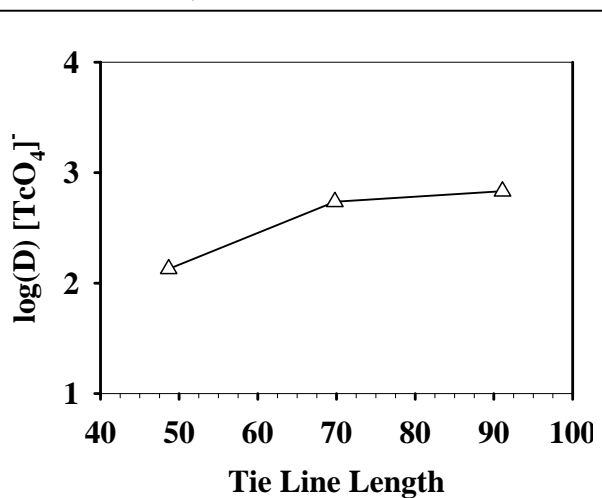
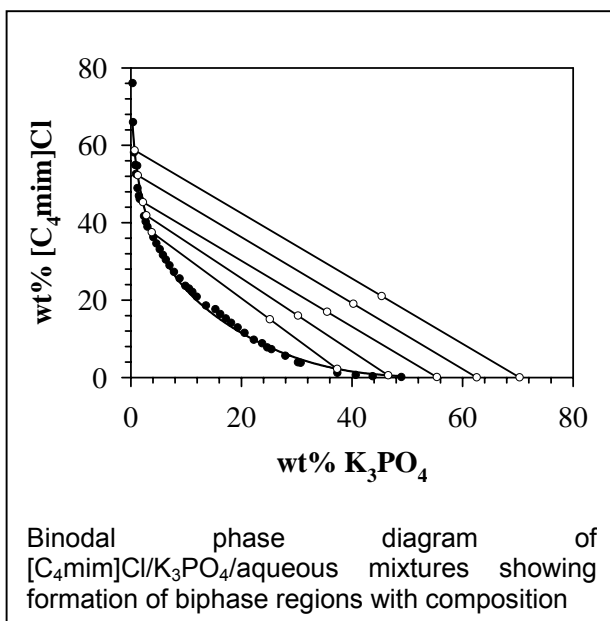
The use of ILs as direct replacements for organic solvents in organic/aqueous liquid-liquid separations schemes is largely restricted to hydrophobic ILs containing anions that are usually both perfluorinated and expensive. As a result, implementation of these types of ILs on a large scale will be limited due to cost or environmental impact. The potential environmental impact of the $[\text{PF}_6]^-$ anion in ILs was recently established; hydrolysis and degradation at high acidity of this anion leads to the formation of toxic, environmentally non-benign compound, HF. The potential to use hydrophilic ILs in separations schemes is particularly appealing due to the availability of 'greener' anions, cheaper costs, and broader range.

We have shown (Gutowski, K. E.; et al., *J. Am. Chem. Soc.* **2003**, *125*, 6632) that aqueous solutions of hydrophilic ILs can be induced to form biphasic systems in contact with concentrated solutions of water-structuring (i.e., kosmotropic) salts, such as in the example of $[\text{C}_4\text{mim}]\text{Cl}$ and K_3PO_4 .

By adding 1-butyl-3-methylimidazolium chloride, $[C_4mim]Cl$, a hydrophilic ionic liquid (IL), to concentrated solutions of the water-structuring salt, K_3PO_4 , an aqueous biphasic system (ABS) is produced, forming an upper IL-rich phase and a lower K_3PO_4 -rich phase, both of which are aqueous. An entirely new salt-salt ABS has been discovered. The mutual coexistence curve for the $[C_4mim]Cl/K_3PO_4$ system was determined by the cloud point method at room temperature, and shows that aqueous biphasic systems can be formed over a large composition range from monophasic, aqueous solutions of $[C_4mim]Cl$ upon addition of K_3PO_4 .

By considering the use of other water-structuring salts to salt-out the IL ions from aqueous solution, a generalization on the formation of ABS of this type can be made. We have found that a large number of ABS of $[C_4mim]Cl$ can be formed with a range of kosmotropic salts including KOH , K_2CO_3 , Na_2HPO_4 , and $Na_2S_2O_3$. These new ABS can be utilized to recycle or concentrate hydrophilic ILs from aqueous solution, to carry out metathesis in the formation of new IL salts, and for separations, including reactive separations.

This phenomenon is not limited to imidazolium-based ILs, and has also been observed previously with quaternary tetraalkylammonium salts. Further investigation has shown that this is indeed, a general phenomenon that occurs for other classes of ILs including pyridinium-, phosphonium-, and ammonium-based systems. Hence, the expansion of IL-based separations systems to include hydrophilic ILs is a distinct possibility. In fact, these aqueous biphasic systems possess a sufficient chemical potential between the phases to allow organics, such as short-chain alcohols, and inorganics such as $[TcO_4]^-$ to partition to the IL-rich phase without the need for an extractant. Partitioning is observed to increase with both phase divergence as well as the number of carbons in the alcohol alkyl chain. Shown is partitioning of $[^{99}TcO_4]^-$ to IL-rich upper phase of IL/salt aqueous biphasic of $[C_4mim]Cl/K_3PO_4$ as a function of tie-line length.



IV. Investigate chemical stabilities of Ionic Liquids under strong acid, strong base, and high-level radiation conditions.

Preliminary assessment of radiation stability of [C_nmim]Cl and [C₄mim][NO₃] ILs to α , β , and γ radiation indicated no significant decomposition. The [C_nmim]Cl and [C₄mim][NO₃] ILs appeared to be much more stable than TBP/kerosene mixtures after similar irradiation conditions. Additional ILs and process conditions need to be investigated.

V. Publications and Presentations at Meetings Acknowledging DOE support from the Project:

A. Refereed Publications

1. Gutowski, K. E.; Bridges, N. J.; Cocalia, V. A.; Spear, S. K.; Visser, A. E.; Holbrey, J. D.; Davis Jr., J. H.; Rogers, R. D. "Ionic Liquid Technologies for Utilization in Nuclear-based Separations," in *Ionic Liquids III, Fundamentals, Progress, Challenges and Opportunities*, Rogers, R. D.; Seddon K. R., Eds, ACS Symposium Series, 901, *in press*.
2. Holbrey, J. D. "Industrial Applications of Ionic Liquids" *Chim. Oggi*, **2004**, 22, 35-37.
3. Luo, H.; Dai, S.; Bonnesen, P. V.; A. C. Buchanan, III, Holbrey, J. D.; Bridges, N. J.; and Rodger, R. D. "Extraction of Cesium Ions from Aqueous Solutions Using Calix[4]arene-bis(*tert*-octylbenzo-crown-6) in Ionic Liquids" *Anal. Chem.*, **2004**, 76, 3078-3083.
4. Rogers, R. D.; Gutowski, K. E.; Griffin, S. T.; Holbrey, J. D. "Aqueous biphasic systems based on salting-out polyethylene glycol or ionic liquid solutions: strategies for actinide or fission product separations. Preprints of Extended Abstracts presented at the ACS National Meeting, American Chemical Society, Division of Environmental Chemistry **2004**, 44, 403-407.
5. Visser, A. E.; Rogers, R. D. "Actinide Chemistry in Novel Solvent Media: Room Temperature Ionic Liquids," In *Molten Salts XIII*; Delong, H. C.; Bradshaw, R. W.; Matsunaga, M.; Stafford, G. R.; Trulove, P. C., Eds.; Electrochemical Society: Pennington, NJ, 2002; pp 516-529.
6. Visser, A. E.; Jensen, M. P.; Laszak, I.; Nash, K.L.; Choppin, G. R.; Rogers, R. D. "Uranyl Coordination Environment in Hydrophobic Ionic Liquids: An In Situ Investigation," in *Inorg. Chem.* **2003**, 42, 2197-2199.
7. Visser, A. E.; Rogers, R. D. "Room Temperature Ionic Liquids: New Solvents for f-Element Separations and Associated Solution Chemistry," *J. Solid State Chem.* **2003**, 171, 109-113.
8. Gutowski, K. E.; Broker, G. A.; Willauer, H. D.; Huddleston, J. G.; Swatloski, R. P.; Holbrey, J. H. "Controlling the aqueous miscibility of ionic liquids: Aqueous biphasic systems of water-miscible ionic liquids and water-structuring salts for recycle, metathesis, and separations," *J. Am. Chem. Soc.* **2003**, 125, 6632-6633.
9. Holbrey, J.D.; Visser, A.E.; Spear, S.K.; Reichert, W.M.; Swatloski, R.P.; Broker, G. A.; Rogers, R. D. "Mercury(II) partitioning from aqueous solutions with a new, ethylene-glycol functionalized bis-imidazolium ionic liquid," *Green Chem.* **2003**, 5, 129-135.

B. Thesis Completed

1. A. E. Visser, "Metal Ion Separations in Aqueous Biphasic Systems and Room Temperature Ionic Liquids," Ph.D., The University of Alabama, 2002.

C. Presentations before National and International Meetings

- P1. Robin D. Rogers, John D. Holbrey, Scott K. Spear, Keith E. Gutowski, Nicholas J. Bridges, Violina A. Cocalia, and Richard P. Swatloski Application of Ionic Liquid Technologies to Nuclear Separations ACS National Meeting, New York, NY, USA, 7-11 Sept. 2003. (NUCL-)
- P2. Keith E. Gutowski, John D. Holbrey, Scott K. Spear, Nicholas, J. Bridges, Robin D. Rogers Approaches to Nuclear Separations Using Room Temperature Ionic Liquids Global 2003, New Orleans, LA, USA, 16-20 Nov. 2003.
- P3. Keith E. Gutowski, Grant A. Broker, Heather D. Willauer, Jonathan G. Huddleston, Richard P. Swatloski, John D. Holbrey, and Robin D. Rogers, "Controlling the Aqueous Miscibility of Hydrophilic Ionic Liquids Via the Addition of Water-Structuring Salts," Presented by K. E. Gutowski before the 13th Symposium on Separation Science and Technology, Oct. 27-30, 2003, Gatlinburg, TN, Abstract Book p 68.
- P4. Nicholas J. Bridges and Robin D. Rogers, "Comparative Study of Cyanex-923R in Ionic Liquids versus Traditional Organic Solvents," Presented by N. J. Bridges before the 13th Symposium on Separation Science and Technology, Gatlinburg, TN, USA, 27-30 Oct. 2003.
- P5. Cocalia, V. A.; Bridges, N. J.; Griffin, S. T.; Spear, S. K.; Rogers, R. D.; "Actinide Partitioning Using the Traditional Extractant Cyanex 272 in a Room Temperature Ionic Liquid as a Novel Medium for Liquid/Liquid Extraction," Presented by V. A. Cocalia before the 13th Symposium on Separation Science and Technology, Oct. 27-30, 2003, Gatlinburg, TN, Abstract Book p 80.
- P6. W. Matthew Reichert, John D. Holbrey, Scott T. Griffin, Violina A. Cocalia, Nicholas J. Bridges, Joe Chambers, and Robin D. Rogers, Task specific ionic liquids that incorporate poly (ethylene glycols) functionality for the extraction of metal ions ACS National Meeting, Anaheim, CA, 28 March- 1 April 2004. (IEC-228)
- P7. Robin D. Rogers; Nicholas J. Bridges, John D Holbrey, H. Luo, Sheng Dai, and Peter V. Bonnesen The role of ion exchange vs solvent extraction processes in metal ion partitioning in ionic liquid/aqueous systems: Cesium Extractions with Calix[4]arene-bis(tert-octylbenzo-crown-6) in imidazolium bistriflylimide ionic liquids ACS National Meeting, Anaheim, CA, 28 March-1 April 2004 (IEC-227)
- P8. R. D. Rogers, "A New Class of Solvents for TRU Dissolution and Separation: Ionic Liquids," Presented by R. D. Rogers before the Department of Energy Environmental Management Sciences Program Principal Investigators Workshop (2003), Richland, WA, no abstract.
- P9. R. D. Rogers, J. D. Holbrey, S. K. Spear, K. E. Gutowski, N. J. Bridges, V. A. Cocalia, and R. P. Swatloski, "Application of Ionic Liquid Technologies to Nuclear Separations," Presented by R. D. Rogers before the 27th Actinide Separations Conference (2003), Lemont, IL, AbstractBook p 12.

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