

**A New Class of Solvents for TRU Dissolution and Separation: Ionic Liquids**

**Progress Report – Project # 81891**

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**Robin D. Rogers  
Department of Chemistry and Center for Green Manufacturing  
The University of Alabama  
Tuscaloosa, AL 35487**

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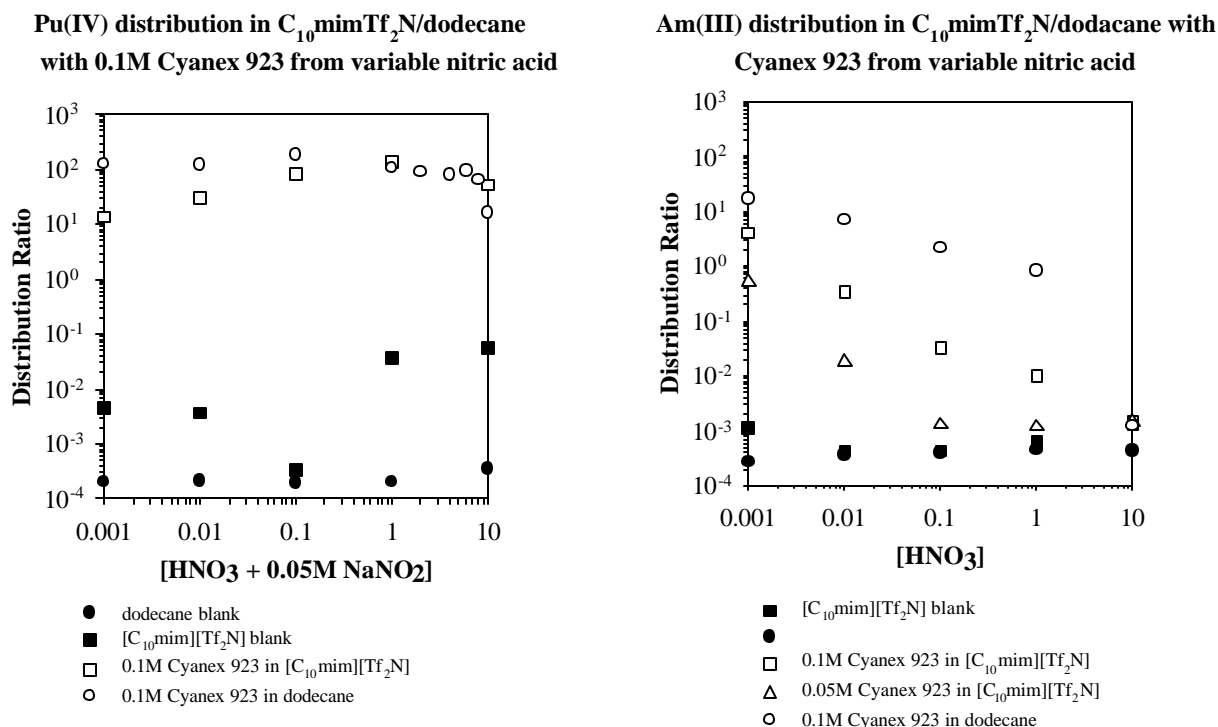
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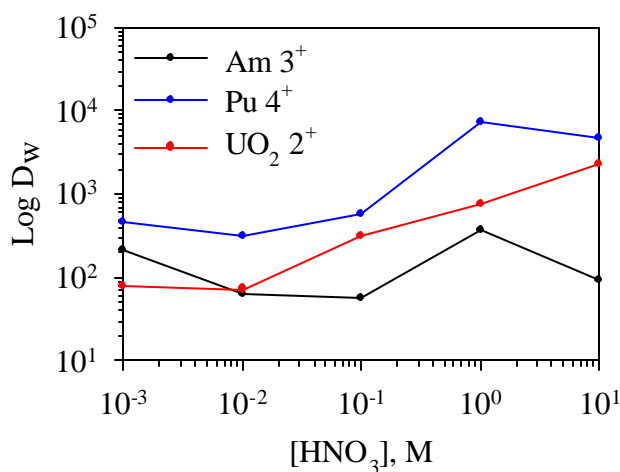
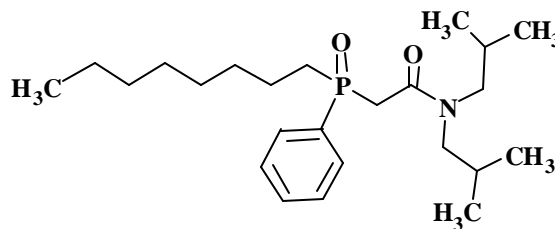
Progress on the study of a New Class of Solvents for TRU Dissolution and Separation: Ionic Liquids is summarized under the headings of the major proposal objectives.

**I. Examine Cs, Sr, Tc, and TRU partitioning in Ionic Liquid/aqueous systems.** Ionic Liquids (ILs) are composed of organic cations and either organic or inorganic anions that remain liquid over a wide temperature range, including room temperature. IL characteristics can be dramatically adjusted (e.g., hydrophobic vs. hydrophilic) by changing the anion type or subtly altered by changing the length or number of alkyl groups appended to the cation. Changing alkyl chain lengths in the 1-alkyl-3-methylimidazolium cation, in combination with  $\text{PF}_6^-$   $\text{N}(\text{SO}_2\text{CF}_3)_2^-$  anions, produces hydrophobic IL with rheological properties suitable for their use in liquid/liquid separations.

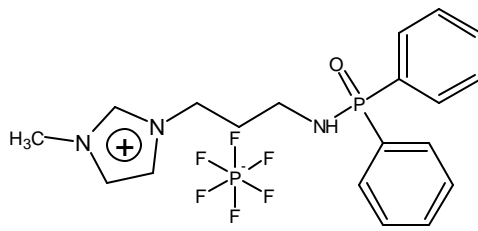
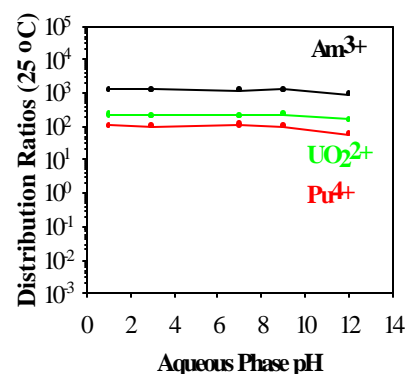
Cyanex 923® (trialky phosphine oxide) has been studied in  $\text{C}_{10}\text{mimTf}_2\text{N}$  for extraction of TRU from nitric acid solutions. Selectivity of Pu(IV) over Am(III) has been observed with a higher distribution from Pu(IV) by 4 orders of magnitude at 1M nitric acid. There is no acid dependency for the extraction of Pu(IV) yet there is for Am(III). Ligand dependency has been illustrated for Pu(IV) and Am(III) having a 1:1 and either 1:0 or 1:3 (M:L), respectively. In the ligand dependency of Am(III) there is a change in the extraction ratio at a concentration of 0.05M Cyanex 923® from 1:0 to 1:3 (M:L). Speciation and ligand dependency is to be studied further. Studies of trialkylphosphine oxides are planned using depleted uranium and natural thorium ore to investigate extraction mode and leaching of the ionic liquid into the acid medium. The study will also confirm the extraction of uranium by the phosphine oxide by the use of IR studies.



The preparation of novel biorenewables modified using ionic liquids was explored. The actinide complexant (complexing agent), octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide, or CMPO can be incorporated into a reconstituted cellulose matrix to provide a solid supported metal extractant. The distribution of several actinides between aqueous nitric acid solutions and modified cellulose materials impregnated with CMPO was studied in relation to the aqueous phase acidity and extractant content in the solid phase. The presence of CMPO was confirmed by enhanced distribution ratios.



**II. Develop new Ionic Liquids for TRU separations.** The success with CMPO as an extractant prompted us to extend the concept of Task Specific Ionic Liquids (TSILs) to actinide separations by including a phosphonamide functional group in the pendant arm of the cation. Such TSILs could help reduce or eliminate extractant loss to the aqueous phase. In collaboration with Prof. Jim Davis at the University of South Alabama a TSIL has been synthesised and extraction of have been conducted in a 1:5 ratio with  $\text{C}_4\text{mimPF}_6$ . High distributions have been shown fro U(VI), Am(III) and Pu(IV) without selectivity. There is no acid dependency for the extraction for the of any of the metal salts. Future studies will include physical properties (viscosity, DSC, TGA, NMR, etc.) and exploration into extraction mode.



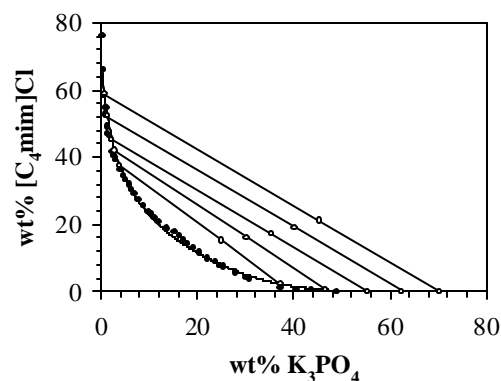
Structure of the  $[\text{TSIL}][\text{PF}_6]$

**III. Study the speciation and coordination of TRU elements in both hydrophilic and hydrophobic ionic liquids.** We are currently investigating the actinide coordination environment in ILs to determine whether unique extractant behavior or solvent effects (e.g., liquid ion exchange) underlie the results shown here. A fundamental understanding of systems based on traditional extractant molecules in ILs is a paramount objective towards optimizing the potential for these novel solvent alternatives in a variety of applications.

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<sub>4</sub>mim][PF<sub>6</sub>] and [C<sub>8</sub>mim][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]. 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<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(CMPO)<sub>2</sub>. 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<sub>2</sub>(NO<sub>3</sub>)(CMPO)<sup>+</sup>. The concentration of the IL cation in the aqueous phase increases in proportion to the amount of UO<sub>2</sub>(NO<sub>3</sub>)(CMPO)<sup>+</sup> in the IL phase, supporting a predominantly cation exchange mechanism for partitioning in the IL systems.

**IV. Investigate how aqueous phase composition affects the liquid/liquid partitioning behavior with particular emphasis on aqueous phases similar to those found in DOE related tank wastes.** By adding 1-butyl-3-

methylimidazolium chloride, [C<sub>4</sub>mim]Cl, a hydrophilic ionic liquid (IL), to concentrated solutions of the water-structuring salt, K<sub>3</sub>PO<sub>4</sub>, an aqueous biphasic system (ABS) is produced, forming an upper IL-rich phase and a lower K<sub>3</sub>PO<sub>4</sub>-rich phase, both of which are aqueous. An entirely new salt-salt ABS has been discovered. The mutual coexistence curve for the [C<sub>4</sub>mim]Cl/K<sub>3</sub>PO<sub>4</sub> 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<sub>4</sub>mim]Cl upon addition of K<sub>3</sub>PO<sub>4</sub>.



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<sub>4</sub>mim]Cl can be formed with a range of kosmotropic salts including KOH, K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>HPO<sub>4</sub>, and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. 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.

**V. Determine the stability of ionic liquids to thermolysis and radiolysis.** Preliminary assessment of radiation stability of [C<sub>n</sub>mim]Cl and [C<sub>4</sub>mim][NO<sub>3</sub>] ILs to α, β, and γ radiation indicated no significant decomposition. The [C<sub>n</sub>mim]Cl and [C<sub>4</sub>mim][NO<sub>3</sub>] ILs appeared to be

much more stable than TBP/kerosene mixtures after similar irradiation conditions. Additional ILs and process conditions need to be investigated.

**VI. Investigate the unique heat transfer properties of ionic liquids for use in other processing steps.** While we currently have no results to report relating to heat transfer properties and actinides, we are posed to begin experiments.

## **VII. Publications and Presentations at Meetings Acknowledging DOE support from the Current Project Period:**

### **A. Refereed Publications**

1. 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.
2. 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.
3. 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.
4. Gutowski, K. E.; Broker, G. A.; Willauer, H. D.; Huddleston, J. G.; Swatoski, 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.

### **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. R. P. Swatoski, A. E. Visser, J. H. Davis, Jr., and R. D. Rogers, "Actinides in room temperature ionic liquids; old elements - new solvents," Presented by R. P. Swatoski before the 223<sup>rd</sup> ACS National Meeting (2002), Orlando, FL, Abstract NUCL 132.
- P2. R. D. Rogers, A. E. Visser, J. H. Davis, Jr., C. Koval, D. L. DuBois, P. Scovazzo, and R. D. Noble, "Choosing ionic liquids for supported ionic liquid membranes," Presented by R. D. Rogers before the 223<sup>rd</sup> ACS National Meeting (2002), Orlando, FL, Abstract I&EC 128. (Invited Symposium Presentation)
- P3. R. D. Rogers and A. E. Visser, "Actinide Chemistry in Novel Solvent Media: Room Temperature Ionic Liquids," Presented by R. D. Rogers before the Thirteenth International Symposium on Molten Salts, part of the 201<sup>st</sup> National Meeting of the Electrochemical Society (2002), Philadelphia, PA, Abstract 1446. (Invited Presentation)

- P4. R. D. Rogers and A. E. Visser, "Room Temperature Ionic Liquids: New Solvents for f-element Separations and Associated Solution Chemistry," Presented by R. D. Rogers before the 23<sup>rd</sup> Rare Earth Research Conference (2002), Davis, CA, Abstract OSE-1-05.
- P5. A. E. Visser, M. P. Jensen, K. L. Nash, and R. D. Rogers, "An investigation of actinide and fission product extraction in room temperature ionic liquids: Liquid/liquid separations and in-situ solution analysis," Presented by A. E. Visser before the 224<sup>th</sup> ACS National Meeting (2002), Boston, MA, Abstract I&EC 88.
- P6. R. D. Rogers, J. D. Holbrey, and A. E. Visser, "Application of Task Specific Ionic Liquids to the Extraction of  $\text{Hg}^{2+}$  and Actinides," Presented by R. D. Rogers before the 54<sup>th</sup> Southeast Regional ACS Meeting (2002), Charleston, SC, Abstract 575 (Invited Symposium Presentation).
- P7. 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.
- P8. 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.
- P9. V. A. Cocalia, N. J. Bridges, S. T. Griffin, S. K. Spear, and R. D. Rogers, "Uranyl Extraction using Cyanex-272 in 1-Decyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide," Presented by V. A. Cocalia before the 27th Actinide Separations Conference (2003), Lemont, IL, Abstract Book p 36.