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

Progress Report

For Period September 15, 2001 – September 14, 2002

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June 2002

Prepared for

**The U. S. DEPARTMENT OF ENERGY
AWARD NO. DE-FG07-01ER63266**

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 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. Actinides exhibit significant partitioning to these ILs from aqueous solutions with the addition of an extractant (e.g., octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO)) to the IL. Ionic liquids can thus, be considered for actinide chemistry as a new class of materials with adjustable solvent characteristics, unique properties, and the potential for enhancing the principles of “green” chemistry in various chemical processes. Here we highlight the unique physical properties of some ILs and their use in liquid/liquid separations.

CMPO and CMPO/TBP in ILs do enhance distribution ratios for selected actinide elements from low HNO_3 concentrations. At the studied concentrations, there is an enhancement of actinide distribution ratios to the ILs over dodecane as the diluent. Nonetheless, there are several facets of this work which will require much further study.

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 phosphine oxide functional group in the pendant arm of the cation. Such TSILs could help reduce or eliminate extractant loss to the aqueous phase. Our initial results in collaboration with Prof. Jim Davis at the University of South Alabama with such a moiety appear promising, but the mechanism of the extraction process is still unclear.

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.

We have performed preliminary experiments with EXAFS to investigate the coordination environment of actinide-CMPO complexes in ILs compared to traditional solvents. This will help 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.

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. Despite the positive results for actinide separations, stripping the actinides from the IL phase has not been addressed and, as the results in Figure 1 show, a simple change in aqueous phase pH may not be sufficient to induce stripping. Further research is needed to understand the mechanism, responsible for the results observed here, and to use the results to find appropriate conditions for stripping.

Figure 1. Distribution ratios for $^{241}\text{Am}^{3+}$, $^{233}\text{UO}_2^{2+}$, $^{238}\text{Pu}^{4+}$, and $^{232}\text{Th}^{4+}$ in $[\text{C}_4\text{mim}][\text{PF}_6]$ /aqueous (solid symbols) or dodecane/aqueous (open symbols) liquid/liquid systems. The extracting phase is either 0.1 M CMPO in $[\text{C}_4\text{mim}][\text{PF}_6]$ (dashed lines) or 0.1 M CMPO and 1 M TBP in $[\text{C}_4\text{mim}][\text{PF}_6]$ (solid lines).

V. Determine the stability of ionic liquids to thermolysis and radiolysis. A recent report in the literature indicates that due to the ability of aromatic rings to absorb energy, radiolysis of $[\text{C}_n\text{mim}]^+$ cations does not appear to present a problem.¹ The preliminary assessment of radiation stability of $[\text{C}_n\text{mim}]\text{Cl}$ and $[\text{C}_4\text{mim}][\text{NO}_3]$ ILs to α , β , and γ radiation indicated no significant decomposition. The $[\text{C}_n\text{mim}]\text{Cl}$ and $[\text{C}_4\text{mim}][\text{NO}_3]$ 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 poised to begin experiments.

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

A. Refereed Publications

¹ D. Allen, G. Baston, A. E. Bradley, T. Gorman, A. Haile, I. Hamblett, J. E. Hatter, M. J. F. Healey, B. Hodgson, R. Lewin, K. V. Lovell, B. Newton, W. R. Pitner, D. W. Rooney, D. Sanders, K. R. Seddon, H. E. Sims, and R. C. Thied, *Green Chem.*, 2002, **4**, 152-158.

1. Visser, A. E.; Rogers, R. D. "Actinide Chemistry in Novel Solvent Media: Room Temperature Ionic Liquids," in Molten Salts XIII, H. C. De Long (Ed.), The Electrochemical Society, Philadelphia, **2002**, In Press.
2. Visser, A. E.; Rogers, R. D. "Room Temperature Ionic Liquids: New Solvents for f-Element Separations and Associated Solution Chemistry," in *Journal of Solid State Chemistry*, Submitted.

B. Presentations before National and International Meetings

- P1. R. D. Rogers, and A. E. Visser "Actinide Chemistry in Novel Solvent Media: Room Temperature Ionic Liquids," Presented by R. D. Rogers before the 13th Molten Salt Meeting of The Electrochemical Society (2002), Philadelphia, PA, Abstract #1446.
- P2. R. D. Rogers, A. E. Visser, and J. H. Davis, Jr., "Actinide Separations Utilizing Room Temperature Ionic Liquids," Presented by A. E. Visser at the Actinides-2001 International Conference (2001), Hayama, Japan, Abstract 4O10.
- P3. E. Visser, M. P. Jensen, K. L. Nash, and R. D. Rogers, "Investigation of Actinide Complexation and Solvation in Room Temperature Ionic Liquids," Presented by A. E. Visser at the Actinides-2001 International Conference (2001), Hayama, Japan, Abstract 2O15.
- P4. E. Visser, R. P. Swatloski, W. M. Reichert, and R. D. Rogers, "Actinide Separations in Room-Temperature Ionic Liquids," Presented by A. E. Visser before the Twelfth Symposium on Separations Science and Technology for Energy Applications (2001), Gatlinburg, TN, Abstract Book p 88.

VIII. Statement of Unexpended Funds.

Salaries and Benefits	\$63,399.49
Operational Expenditures	\$18,389.34
Travel	\$1,840.33
<u>Indirect Costs (Overhead)</u>	<u>\$34,514.01</u>
Total Funds Available	\$118,143.17