ACTINIDE CHEMISTRY IN NOVEL SOLVENT MEDIA: ROOM TEMPERATURE IONIC LIQUIDS.

Robin D. Rogers and Ann E. Visser

Department of Chemistry and Center for Green
Manufacturing, The University of Alabama, Box 870336,
Tuscaloosa, AL 35487, Fax: 205-348-0823

Room Temperature Ionic Liquids (RTILs) are composed of organic cations and either organic or inorganic anions that, together, remain liquid at room temperature. RTIL characteristics can be dramatically adjusted by changing the composition; Cl^- anions result in hydrophilic RTILs whereas the $[PF_6]^-$ anions produce hydrophobic RTILs. Changing the length of the alkyl chain on the cation affects the rheological properties and water content. Thus, RTILs can be considered 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.

In liquid/liquid separations systems incorporating 1-alkyl-3-methylimidazolium cations (Figure 1) with $[PF_6]^-$ anions, the highly hydrated UO_2^{2+}, Pu^{4+}, and Am^{3+} ions remain in the aqueous phase.

Using the extractant molecule octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO, Figure 2), we have successfully demonstrated the partitioning of Am^{3+}, Pu^{4+}, UO_2^{2+}, Th^{4+}, and PuO_2^{2+} from water when $[C_4mim][PF_6]$ is used in place of traditional organic solvents as the extracting phase. In addition, Task Specific Ionic Liquids for actinide extraction have been prepared (in collaboration with Jim Davis, South Alabama) and demonstrate that the extractant can be incorporated into the structure of the cation (Figure 3), thus minimizing losses to the aqueous phase.

We have also investigated the coordination environment of f-elements and their complexes in both $[C_4mim][PF_6]$ and $[C_8mim][N(SO_2CF_3)_2]$ using UV-vis, lanthanide fluorescence, and EXAFS spectroscopy for comparison to organic solvents such as dodecane. Fluorescence measurements for Eu^{3+} show fluorescence lifetime differences between the metal ion dissolved in aqueous solution vs. RTIL. Lifetime differences are also observed for Eu^{3+}/PAN complexes in RTILs vs. traditional organic solvents. UV-vis results for Nd^{3+} and UO_2^{2+} complexes with CMPO in RTILs suggest a complex mode of interaction. Initial EXAFS data for Th^{4+}, UO_2^{2+}, and Y^{3+} have also been collected.

This presentation will discuss the choice of RTILs for actinide separations and the liquid/liquid partitioning results for Am^{3+}, Pu^{4+}, Th^{4+}, UO_2^{2+}, and PuO_2^{2+} from aqueous phases to either an RTIL or dodecane extracting phase. Alternative separations strategies and spectroscopic evidence for actinide complexation in RTIL solvents will also be presented.

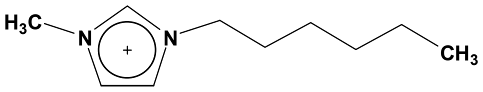

Figure 1. $[C_n mim]^+$ (n = hexyl, $[C_6 mim]^+$).

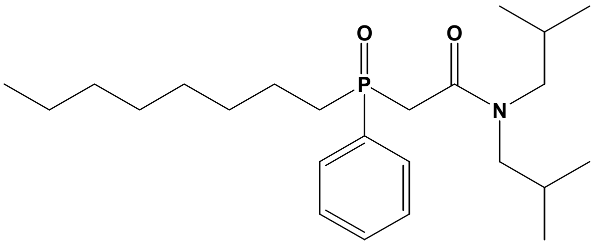

Figure 2. CMPO

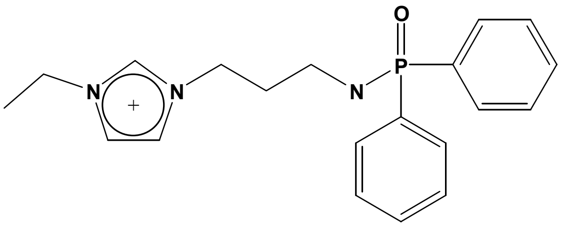

Figure 3. TSIL phosphonamide cation

This research was supported by the Environmental Management Science Program of the Office of Environmental Management, U.S. Department of Energy, Grant DE-FG07-01ER63266.