Abs. 2425, 206th Meeting, © 2004 The Electrochemical Society, Inc.

PARTITIONING OF TRANSURANIC METAL IONS TO IONIC LIQUIDS CONTAINING THE IONIZABLE COMPLEXANT CYANEX-272

V. Cocalia,[a] J. D Holbrey,[a] S. K. Spear,[a]
M. P. Jensen,[b] and R. D. Rogers[a]

[a]Center for Green Manufacturing and Department of
Chemistry, The University of Alabama,
Tuscaloosa, AL 35487
[b]Chemistry Division, Argonne National Laboratory,
Argonne, IL 60439

Extraction mechanisms in Ionic Liquid (IL) based separations systems for metal ions are potentially much more complex that those with simple organic solvents as extracting phases. This arises from the potential for either, or, both cations and anions from the IL to contribute in the extraction processes. In contrast to organic extracting phases, ionic liquids can not necessarily be considered to be passive carrier fluids. Solvent extraction and cation, anion, or sacrificial ion exchange mechanisms have been observed, and the significance of each varies depending on the nature of the ionic liquid components and of the complexants used. Recognition and application of this knowledge allows potential control of the complexation and extraction mechanisms.

The solvent system Cyanex-272 (a dialkylphosphinic acid) and the hydrophobic IL 1-decyl-3-methylimidazolium *bis* (trifluoromethanesulfonyl)imide ($[C_{10}mim][NTf_2]$) has been investigated for the complexation and separation of Am^{3+}, Nd^{3+} and Eu^{3+} from aqueous solution. The metal complex environment and structure have been studied in detail by uv/vis spectroscopy and by EXAFS, and metal ion partitioning has been studied from nitric acid solutions as a function of acid concentration using radiotracer labelling.

Partitioning of Am^{3+} between aqueous acidic solutions and $[C_{10}mim][NTf_2]$, using Cyanex-272 as an extractant, has been investigated. Distribution ratios and partitioning behavior is comparable to that of the analogous liquid/liquid system using dodecane as the extractant phase, and the partitioning data for Am^{3+} in the two systems IL/Cyanex-272 and dodecane/Cyanex-272 are shown in figure 1, with the ligand dependency in figure 2. Leaching and solubility of the imidazolium cation from the ionic liquid to the aqueous phase as a function of nitric acid pH has been measured and does not appear to be a significant contributing factor to the observed metal ion distribution coefficients. Cyanex-272 is an ionizable complexant; the role of the ionized proton, as a sacrificial cation exchanger for metal ions, and changes in the IL composition are currently under study.

UV/Vis absorption spectra for Nd^{3+}, a stand-in element for Am^{3+}, in both Cyanex-272/$[C_{10}mim][NTf_2]$ and bis (diethylhexylphosphoric acid (HDEHP)/toluene overlap perfectly in the range 560-600 nm, suggesting identical coordination environments in both the IL and toluene. This is confirmed by EXAFS data collected on Eu^{3+} (as a non-radioactive stand-in for Am^{3+}) in HDEHP/ $[C_{10}mim][NTf_2]$ and Am^{3+} in Cyanex-272/dodecane indicate identical coordination environments with coordination numbers of six in an octahedral environment for both the IL and dodecane systems.

Further work is being undertaken to probe the nucleation of the complex (i.e., mononuclear vs. dinuclear) as well as aggregation effects of the extractant. This data shows an example where ILs can provide an environment that is identical to molecular solvents, presumably because of dominating coordination effects from the ionized complexant. Thus, it become critical to elucidate the interactions that are important in ILs with regard to extractant binding and coordination. Additionally, investigations with lanthanide analogs as stand-in elements will continue to be important and require further study, especially with regard to macroscopic studies for TRU elements.

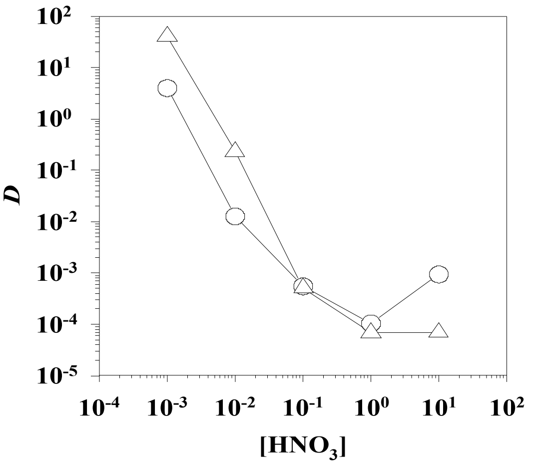

Figure 1. Distribution Ratios for ^{241}Am in 0.1 M Cyanex-272 vs. $[HNO_3]$. Δ Dodecane, ○ $[C_{10}mim][NTf_2]$.

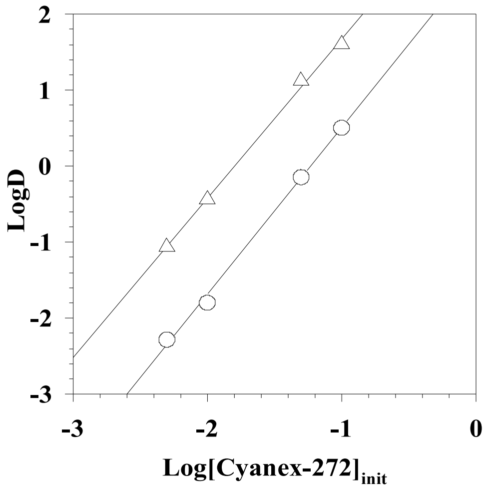

Figure 2. Ligand Dependency for ^{241}Am in in $[C_{10}mim][NTf_2]$ (○, slope = 2.19) and dodecane (Δ, slope = 2.09) from 0.001M HNO_3.

This research was supported by the US Department of Energy, Office of Environmental Management, Environmental Management Science Program (Grants DE-FG07-01ER63266 and DE-FG07-01ER63296).