



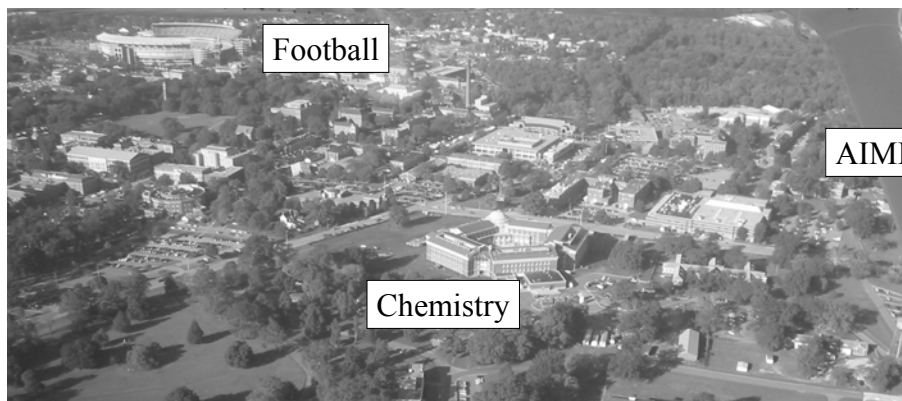
A New Class of Solvents for TRU Dissolution and Separation: Ionic Liquids

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Goal

The proposed research aims to address some of the challenges facing current thrusts in nuclear waste treatment and remediation by understanding and controlling IL properties at the level of cation and anion interactions for the ultimate development and demonstration of viable IL-based technologies for targeted metal ion separations.

This research will provide necessary fundamental information on the factors that facilitate/inhibit competing solvent extraction or cation/anion exchange mechanisms for metal ion partitioning with respect to tank wastes by understanding the influence of the IL components on metal ion coordination environments versus traditional molecular solvents.





Approach

Conduct solvation and coordination studies of metal ions in ILs to understand the nature of the differences with respect to traditional molecular solvents

Develop new ILs that are stable with respect to the harsh, alkaline conditions of tank wastes, and that contain cation/anion pairs that have been consciously chosen or designed to facilitate metal ion transfer

Design improved or enhanced separations schemes based upon the IL solvent effects on extractant efficiency, as well as a better control and understanding of extraction mechanism (ion exchanges, solvent extraction, sacrificial ions).



Primary Tasks



Investigate metal coordination and solvation in IL systems:

- Measure Partition Coefficients, Extend X-ray Absorption Fine Structure (EXAFS)
- Spectroscopy, Optical Spectroscopy, Electron Paramagnetic Resonance (EPR)
- Spectroscopy, Single Crystal X-ray Diffraction

Design and implement new IL systems:

- Assess Synthesis and Availability of Ionic Liquids.
- Investigate Ionic Liquid Systems Containing Aromatic Cations: (1,2,3-trialkylimidazolium, N-alkylpyridinium) and Ionic Liquids with Unsaturated Cations (Tetraalkylphosphonium, quaternary ammonium and N,N-dialkylpyrrolidinium)

Use range of complexants that are more compatible with ILs for waste applications:

- Phosphorus-based extractants, Dicarbolides, Crown ethers/calixarenes, Malonamides/diamides, Solid ion-exchange materials

Investigate salt/salt aqueous biphasic systems:

- Metathesis, Physical properties, Cation/anion control, Liquid/liquid extractions

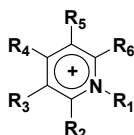
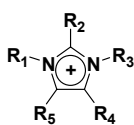




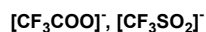
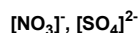
What is an Ionic Liquid?

- Low melting organic salt
- Little/no vapor pressure
- Non-flammable
- Typically has wide liquid range
- Viscous
- Solvent properties are different to molecular solvents
- Solvent properties can be varied (and controlled)

Cations



Anions



Reactive to water

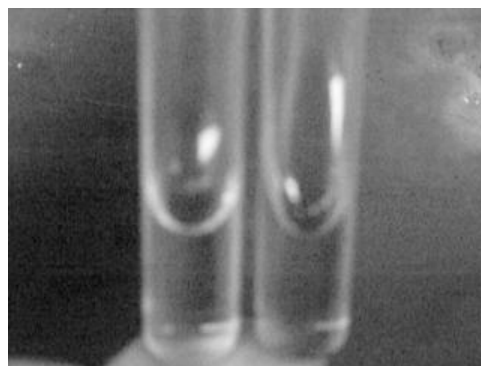
Air and water stable

Decreasing coordinating ability

Increasing hydrophobicity



Viscosity of water vs. IL



Water

Ionic liquid



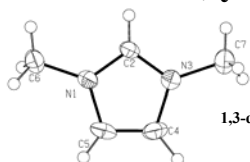


Approaches to Separations with Ionic Liquid Systems

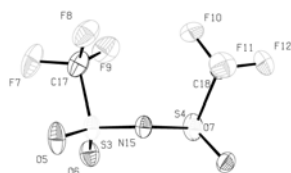
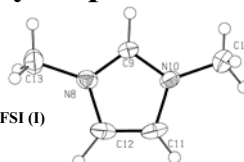
- Hydrophobic IL/aqueous
 - Most widely studied
 - Limited number of hydrophobic ionic liquids
- IL/organic and IL/aromatic clathrates
 - solvent extraction of products from reactions in IL
 - Potentially significant differences in reactivity
- Hydrophilic IL/aqueous salt
 - Phase transfer systems, extraction and recovery of IL components, nuclear waste treatment



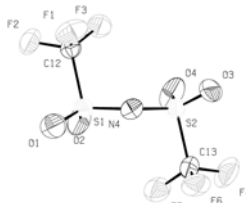
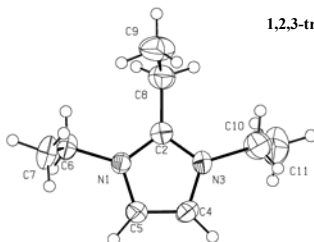
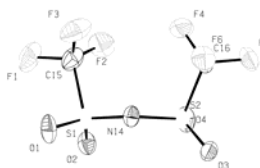
First, you need a hydrophobic IL!



1,3-dimethylimidazolium TFSI (I)

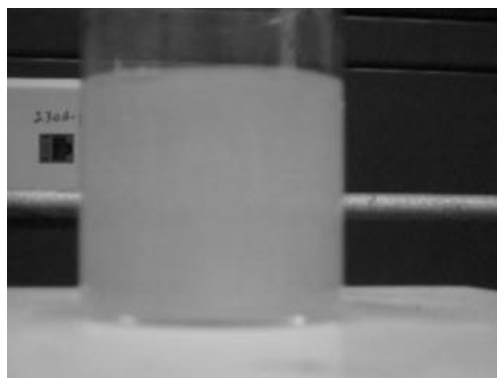


1,2,3-triethylimidazolium TFSI (II)

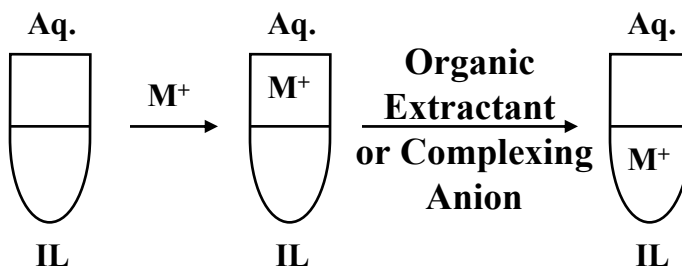




Separation from Water



Metal Ion Separations



We are implementing well-known metal ion extractants to increase the partitioning of highly hydrated metal ions to the RTIL phase

BUT: Recent results in the literature have demonstrated the presence of BOTH solvent extraction AND ion exchange.


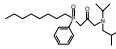

The contributions of each may change with system composition.





Extraction mechanisms in IL/aq vs. org/aq biphasic systems



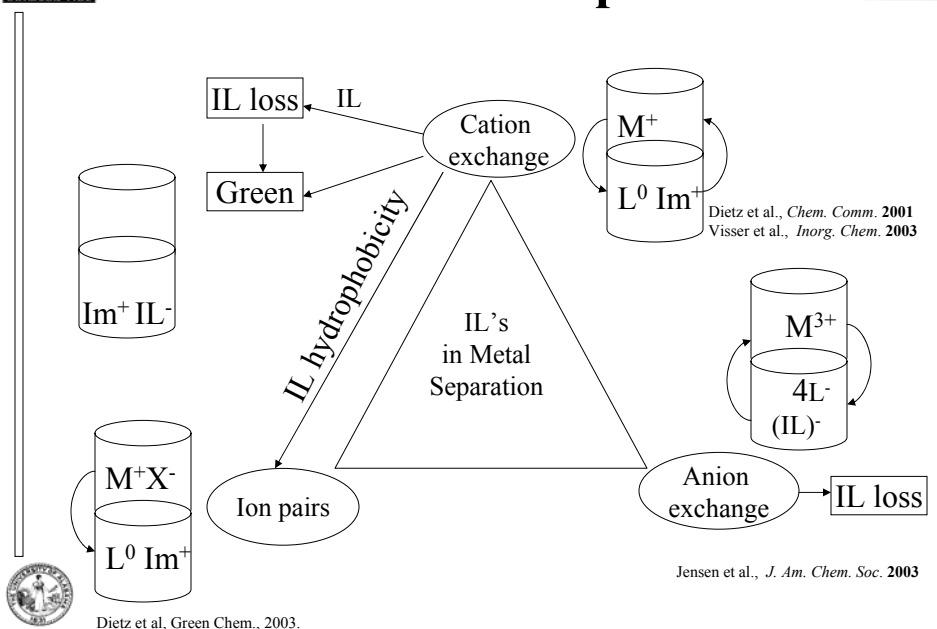
| Eq. Reaction for ILs | Eq. Reaction for Molecular Solvents |
|---|--|
|  | $L = \text{Dicyclohexyl-18-crown-6}$ |
| $1) \text{Sr}^{2+}_{\text{aq}} + L_{\text{IL}} + 2[\text{C}_5\text{mim}]^+_{\text{IL}} + 2\text{H}_2\text{O} \Leftrightarrow [(\text{Sr}L)(\text{H}_2\text{O})_2]^{2+}_{\text{IL}} + 2[\text{C}_5\text{mim}]^+_{\text{aq}}$ <p style="text-align: center;">Or</p> $2) \text{Sr}^{2+}_{\text{aq}} + 2\text{NO}_3^-_{\text{aq}} + L_{\text{IL}} \Leftrightarrow [\text{Sr}L] \cdot (\text{NO}_3)_2_{\text{IL}}$ | $3) \text{Sr}^{2+}_{\text{aq}} + L_{\text{org}} + 2\text{NO}_3^-_{\text{aq}} \Leftrightarrow [\text{Sr}(\text{NO}_3)_2L]_{\text{org}}$ |
|  | $L = \text{CMPO}$ |
| $4) \text{UO}_2^{2+}_{\text{aq}} + [\text{C}_n\text{mim}]^+_{\text{IL}} + \text{NO}_3^-_{\text{aq}} + L_{\text{IL}} \Leftrightarrow [(\text{UO}_2)(\text{NO}_3)L]_{\text{IL}} + [\text{C}_n\text{mim}]^+_{\text{aq}}$ | $5) \text{UO}_2^{2+}_{\text{aq}} + 2\text{NO}_3^-_{\text{aq}} + 2L_{\text{org}} \Leftrightarrow [(\text{UO}_2)(\text{NO}_3)_2L_2]_{\text{org}}$ |
|  | $L = \text{Htta}$ |
| $6) \text{Ln}^{3+}_{\text{aq}} + 4\text{HL}_{\text{IL}} + [\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{\text{IL}} \Leftrightarrow [\text{C}_4\text{mim}]^+ [\text{Ln}L_4]^-_{\text{IL}} + 4\text{H}^+_{\text{aq}} + [\text{Tf}_2\text{N}]^-_{\text{aq}}$ | $7) \text{Ln}(\text{H}_2\text{O})_n^{3+}_{\text{aq}} + 3\text{HL}_{\text{org}} \Leftrightarrow [\text{Ln}L_3(\text{H}_2\text{O})_{n-6}]_{\text{org}} + 3\text{H}^+_{\text{aq}} + 6\text{H}_2\text{O}_{\text{aq}}$ <p style="text-align: center;">and</p> $8) \text{Ln}(\text{H}_2\text{O})_n^{3+}_{\text{aq}} + 4\text{HL}_{\text{org}} \Leftrightarrow \text{Ln}L_3 \cdot \text{HL}_{\text{org}} + 3\text{H}^+_{\text{aq}} + n\text{H}_2\text{O}_{\text{aq}}$ |



- M. L. Dietz and J. A. Dzielawa (2001), Chem. Commun., 20, 2124-2125.
- M. L. Dietz, J. A. Dzielawa, I. Laszak, B. A. Young, and M. P. Jensen (2003), Green Chem., 5, 682-685.
- M. P. Jensen, J. Neufeind, J. V. Beitz, S. Skanthakumar, and L. Soderholm (2003), J. Am. Chem. Soc., 125, 15466-15473.
- A. E. Visser, M. P. Jensen, I. Laszak, K. L. Nash, G. R. Choppin, and R. D. Rogers (2003), Inorg. Chem., 42, 2197-2199.



IL's in Metal Ion Separations





- ◆ **The majority of extraction mechanisms involves loss of either IL's cation or anion to the aq phase.**
- ◆ **Better extraction schemes design are needed for metal ion separation in IL/aqueous system:**
 - ◆ **Control of coordination mode for ligand**
 - ◆ **Control of separation mechanism**



Can Identical Extraction Behavior and Coordination of Actinide Cations be Observed using Ionic Liquid vs. Molecular Solvents?

A Collaborative Study with Mark Jensen, Argonne National Laboratory

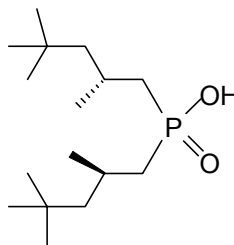




Cyanex 272[®]

(predominantly bis(2,2,4-trimethylpentyl) phosphinic acid)

- ◆ Commercially available from Cytec Inc., Canada
- ◆ Cyanex 272 is used commercially in extraction of Co(II) and Ni(II)⁵
- ◆ Lanthanide⁶⁻¹⁰ and actinide^{6,7,10} extractions have also been studied



Cyanex-272

5. Yu, X.; Gu, G.; Fu, X.; Su, B.; Zhang, H. *Solvent Extract. Ion Exch.* **2001**, 19(5), 939-943.

6. Jensen, M. P.; Bond, Andrew H. *Radiochim. Acta* **2002**, 90(4), 205-209.

7. Jensen, M. P.; Bond, Andrew H.; Nash, K.L. AIP Conference Proceedings **2000**, 532 (Plutonium Futures--The Science), 228-229.

8. Reddy, M. L. P.; Ramamohan, T. R.; Iyer, C. S. P. *Solvent Extraction Research and Development, Japan* **1998**, 5, 1-15.

9. Wang, Z.; Ma, G.; Li, D. *Solvent Extract. Ion Exch.* **1998**, 16(3), 813-828.

10. Rajeswari, B.; Dhawale, B. A.; Bangia, T. R.; Mathur, J. N.; Page, A. G. *J. Radioanal. Nuc. Chem.* **2002**, 254(3), 479-483.

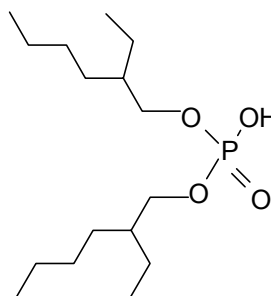


HDEHP

(bis(2-ethylhexyl) phosphoric acid)

Applications:

- ◆ Separation of Ce⁴⁺ from other trivalent lanthanides with excellent separation factors¹¹
- ◆ In mixture with mono(2-ethylhexyl) phosphoric for preconcentration of rare -earth elements from sea water¹²
- ◆ HDEHP gives one of the highest separation factor for separation of adjacent trivalent lanthanides¹³



HDEHP

11. Rehkämper, M.; Gärtner, M.; Galer, S. J. G.; Goldstein, S. L. *Chemical Geology* **1996**, 129, 201

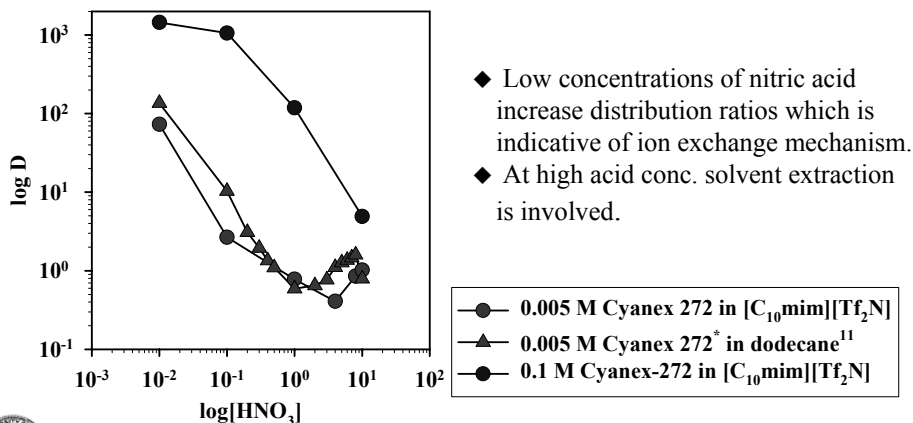
12. Shabani, M. B.; Akagaki, T.; Shimizu, H.; Masuda, A. *Analytical Chemistry* **1990**, 62, 2709.

13. Peppard, D.F.; Mason, G.W.; Maier, J.L.; Driscoll, W.J. *Journal of Inorganic and Nuclear Chemistry* **1957**, 4, 334.





Uranyl Distribution Ratios in Cyanex-272 in [C₁₀mim][Tf₂N]/Dodecane



- ◆ Low concentrations of nitric acid increase distribution ratios which is indicative of ion exchange mechanism.
- ◆ At high acid conc. solvent extraction is involved.

● 0.005 M Cyanex 272 in [C₁₀mim][Tf₂N]
 ▲ 0.005 M Cyanex 272⁺ in dodecane¹¹
 ● 0.1 M Cyanex-272 in [C₁₀mim][Tf₂N]

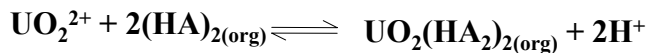


11. Dogmane, S. D.; Singh, R. K.; Bajpai, D. D.; Mathur, J. N. *J. Radioanal. Nuc. Chem.* **2002**, 253(3), 477-482.

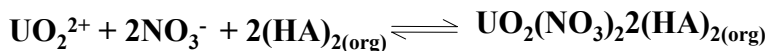


Extraction Equilibrium for UO₂²⁺ in Cyanex 272 in Dodecane

- ◆ Low acidities: Ion Exchange^{2,11}

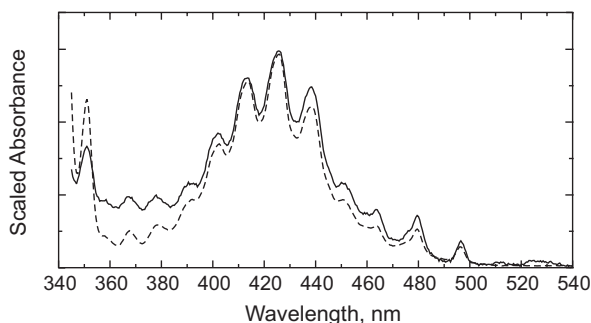


- ◆ High Acidities: Solvent Extraction¹¹





UV-vis spectra of UO_2^{2+} in IL and dodecane

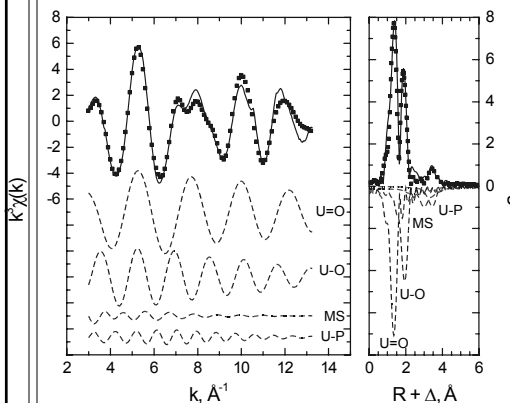


◆ Similar coordination environment is observed in both dodecane and $[C_{10}mim^+][Tf_2N^-]$.

(—) IL and (---) dodecane solutions containing 1 M HDEHP, after contact with 0.06 M UO_2^{2+} /0.25 M HNO_3

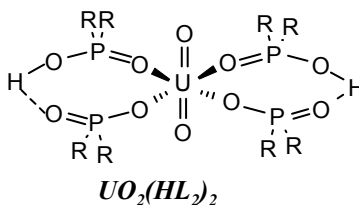


EXAFS data for extracted UO_2^{2+} with HDEHP in IL



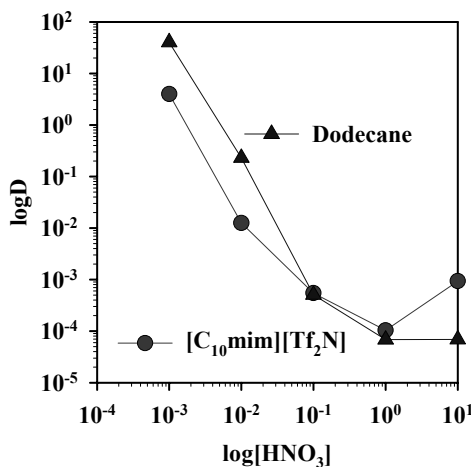
k3-Weighted uranium L3-edge EXAFS (—) and best fit (■) of the UO_2^{2+} -HDEHP complex extracted into $[C_{10}mim^+][Tf_2N^-]$.
(M. Jensen, ANL)

◆ The results show 2 axial oxygens at 1.77Å and 3.5 ± 0.6 oxygens coordinated equatorially to the UO_2^{2+} core at an average U-O distance of 2.38Å .
◆ Uranyl coordination environment is the same as observed in dodecane.





Distribution Ratios for ^{241}Am in 0.1 M Cyanex 272 vs. $[\text{HNO}_3]$



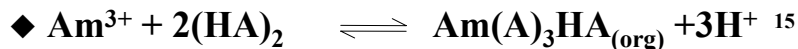
◆ Distribution ratios follow the same trend in both IL and dodecane



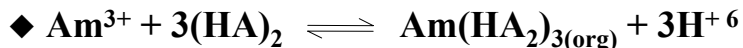
Extraction Equilibrium for ^{241}Am in Cyanex 272/Dodecane



Two equilibrium mechanisms are reported in the literature:



Not taking into consideration aggregation formation.



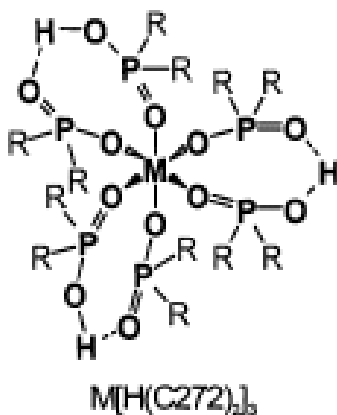
Taking into consideration aggregation formation

15. Hill C. ; Madic C. ; Baron P. ; Ozawa M. ; Tanaka Y. *Journal of Alloys and Compounds*, **1989**, 271-273, 156-162
6. Jensen, M. P.; Bond, Andrew H. *Radiochim. Acta* **2002**, 90(4), 205-209





Structure of Am(III) Complex with Cyanex 272 in Dodecane¹⁴



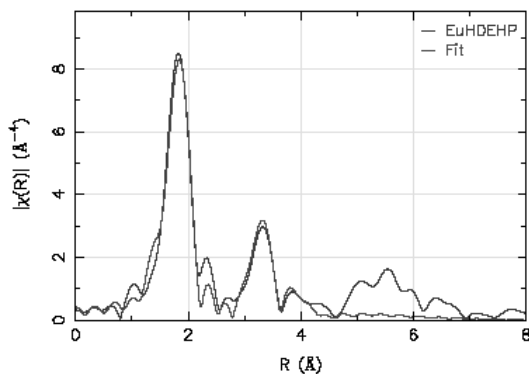
- ◆ EXAFS measurements show a 3:1 ligand : metal ratio in dodecane.¹⁴
- ◆ The complex presents Oh symmetry.



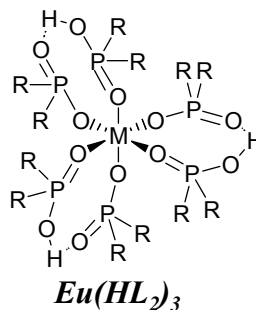
14. Jensen, M. P.; Bond, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 9870-9877.



EXAFS data* for Eu(III) in HDEHP/[C₁₀mim⁺][Tf₂N⁻]



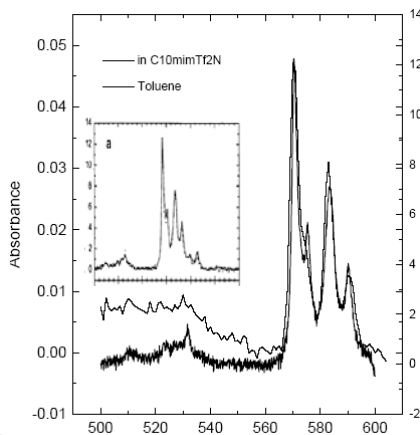
- ◆ The results show ~ 6.2 O atoms at 2.285 Å and 6 P atoms at 3.75 Å and Eu-O-P angles are 160 +/- 5 °.



* Experiment done by Mark Jensen at ANL.



Optical Spectra for Nd(III) in Cyanex 272/[C₁₀mim][Tf₂N] and HDEHP/ toluene*



- ◆ The spectra indicate the same environment for Nd both in [C₁₀mim][Tf₂N] and toluene.
- ◆ Nd appears to be extracted as a dinuclear species.¹⁰



12. Jensen, M. P.; Chiarizia R.; Urban, V. *Solvent Extraction and Ion Exchange* 2001,19(5), 865.
* Spectrum measured by Mark Jensen at ANL.



Can Identical Extraction Behavior and Coordination of Actinide Cations be Observed using Ionic Liquid vs. Molecular Solvents?

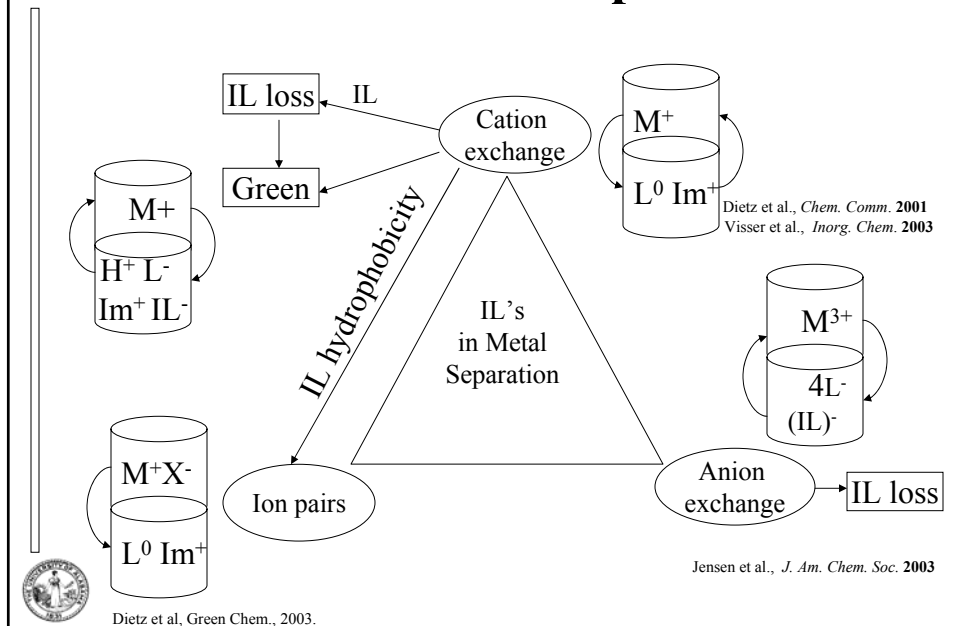
YES!



A Collaborative Study with Mark Jensen, Argonne National Laboratory



IL's in Metal Ion Separations



Approaches to Separations with Ionic Liquid Systems



- Hydrophobic IL/aqueous
 - Most widely studied
 - Limited number of hydrophobic ionic liquids
- IL/organic and IL/aromatic clathrates
 - solvent extraction of products from reactions in IL
 - Potentially significant differences in reactivity
- **Hydrophilic IL/aqueous salt**
 - Phase transfer systems, extraction and recovery of IL components, nuclear waste treatment





Controlling Hydrophobicity

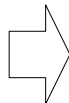


Hydrophobic ILs limited to few cation/anion combinations

Thus, more hydrophilic ILs exist than hydrophobic ones

Controlled by:

- ◆ Anion-selection
- ◆ Alkyl-substitution

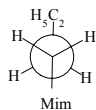
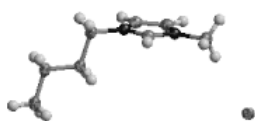


Here, we show hydrophobicity can be controlled by nature of aqueous phase

Hydrophilic ILs can be induced to phase separate from aqueous salt solutions by controlling the kosmotropic nature of the system

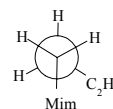
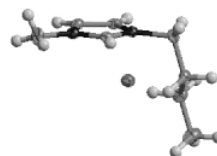


Crystal Structure of [C₄mim][Cl] polymorphs – A Water Soluble IL



monoclinic

Chain conformation angle: 174.12°



orthorhombic

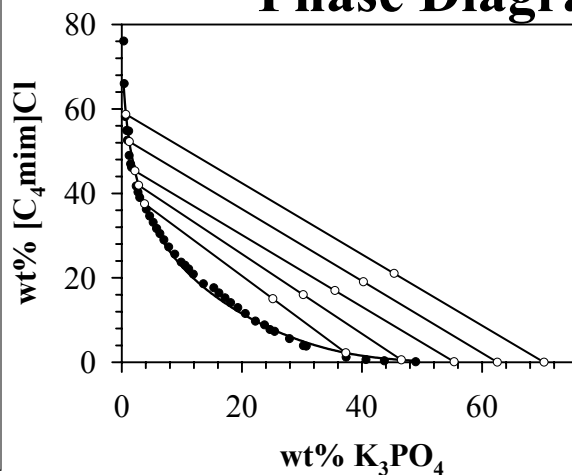
Chain conformation angle: 67.96°
In bromide: 66.21°



Holbrey, John D.; Reichert, W. Matthew; Nieuwenhuyzen, Mark; Johnston, Suzanne; Seddon, Kenneth R.; Rogers, Robin D. *Chem. Comm.* **2003**, 1636-1637



Aqueous [C₄mim]Cl/K₃PO₄ Phase Diagram



Gutowski *et al.*, submitted to *J. Am. Chem. Soc.*, 2003.



Phase Diagram Relationships

Tie Line Length (TLL): Expresses phase divergence



As TLL increases, phase divergence increases

Mathematical relationships:

$$\text{TLL} = (\Delta\text{IL}^2 + \Delta\text{Salt}^2)^{1/2}$$

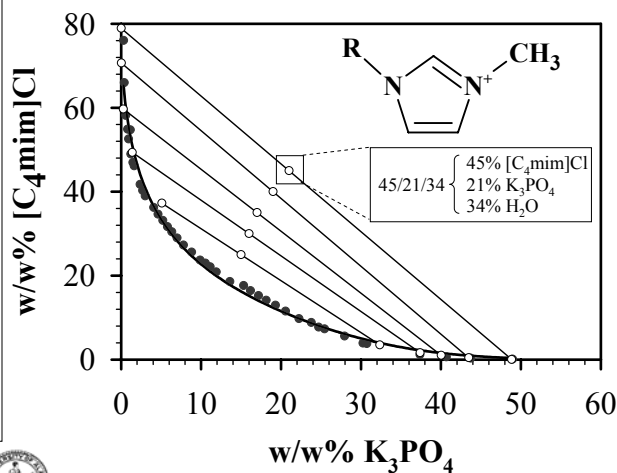
$$\Delta\text{IL} = (\text{Top IL} - \text{Bottom IL})$$

$$\Delta\text{Salt} = (\text{Top Salt} - \text{Bottom Salt})$$





[C₄mim]Cl/K₃PO₄/H₂O Biphasic System Phase Diagram



- ◆ Binodal curve from **cloud point titration method** (dependent upon initial composition of solutions)
- ◆ Compositions **above curve are biphasic**, while those **below the curve are monophasic**
- ◆ Tie lines relate upper and lower phase compositions



Salting-Out of [C₄mim]Cl*

Biphasic

- ◆ K₃PO₄
- ◆ K₂HPO₄
- ◆ Na₂HPO₄
- ◆ K₂CO₃
- ◆ Na₂CO₃
- ◆ KOH
- ◆ NaOH
- ◆ Na₂S₂O₃
- ◆ Na₂S₂O₈

Monophasic

- ◆ KH₂PO₄
- ◆ NaH₂PO₄
- ◆ KNO₃
- ◆ NaNO₃
- ◆ Li₃PO₄
- ◆ CaCl₂
- ◆ ZnSO₄
- ◆ K₂Cr₂O₇
- ◆ KMnO₄
- ◆ NaHSO₄
- ◆ SDS

Precipitate

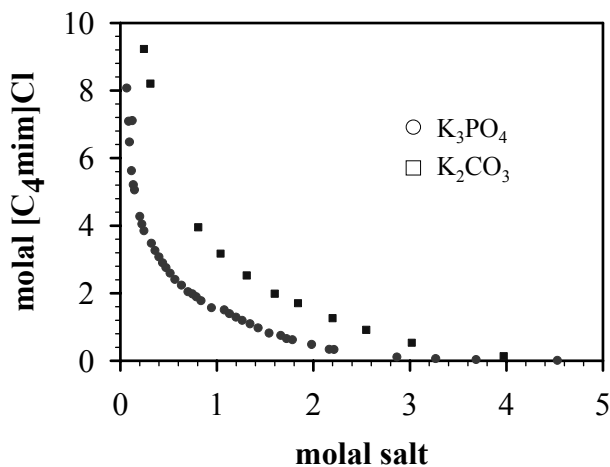
- ◆ Na₂SO₄
- ◆ (NH₄)₂SO₄
- ◆ Li₂CO₃
- ◆ KI
- ◆ NaReO₄
- ◆ NaMoO₄



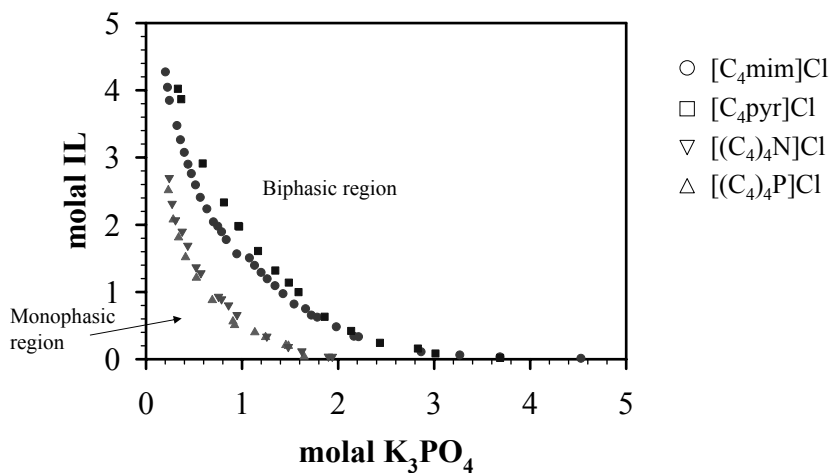
* Not exhaustive



[C₄mim]Cl Biphasic System with K₂CO₃ vs. K₃PO₄



Phase Diagram Comparison





Hydrophilic IL/Aqueous Salt Separations

- ◆ Water soluble ILs can be phase separated from aqueous solutions with water-structuring-salts such as K_3PO_4
- ◆ The most hydrophobic cation (organic) forms a phase with the least kosmotropic anion
- ◆ Phenomena applies to all classes of ILs
- ◆ Drastically increases the number of ILs which can form biphasic systems
- ◆ Potential use in recycling ILs, metathesis and separations applications, including nuclear waste remediation



Conclusions

Separations utilizing ILs as the extracting phase are much more complex than those with simple molecular organic solvents,

BUT,

Understanding the IL systems and choosing appropriate conditions to design targeted extractions IS possible.

One Can Either:

Take advantage of the different extraction mechanisms which ILs afford

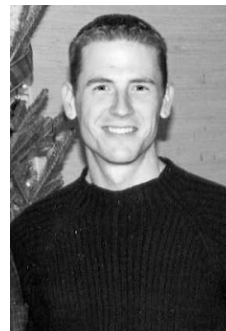
OR

Find those separations/ligands/ILs which afford identical behavior to molecular solvents





The Alabama Green Team!





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References to publications are available at:



<http://bama.ua.edu/~rdrogers/>