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

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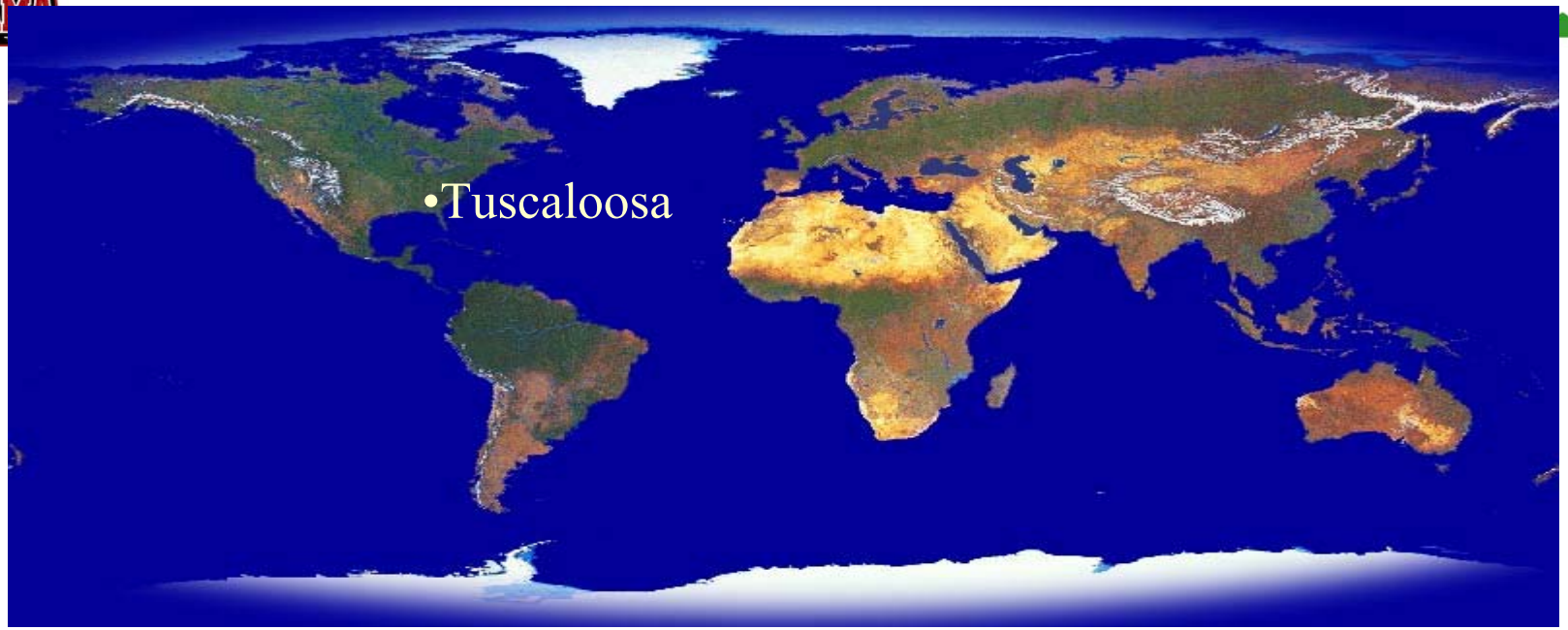
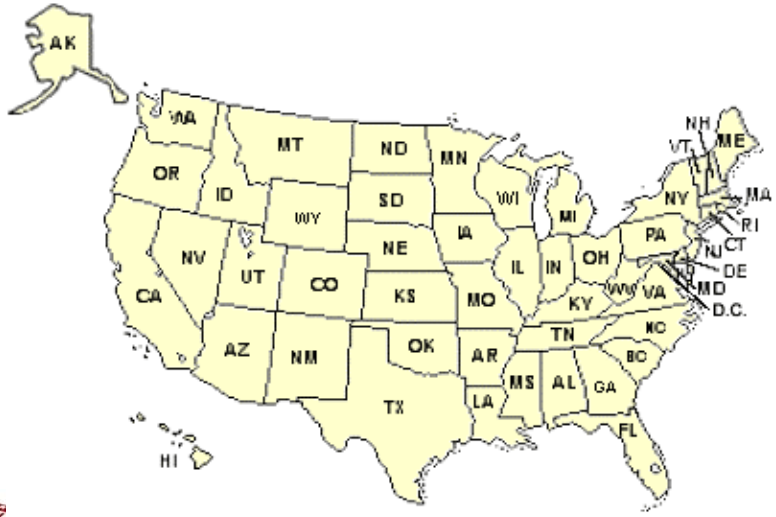
Project number: 81891 **Award period: 09/15/01 – 09/14/04**

EMSP

Environmental Management Science Program


•Tuscaloosa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Overall Research Goals

- The investigation of ionic liquids (ILs) as new solvents for dissolution and separation of transuranic elements (TRU)

Current Major Objectives

- Examine Cs, Sr, Tc, I^-, and TRU partitioning in IL/aqueous systems
- Develop new ILs for TRU separations
- Study speciation and coordination of TRU elements
- Investigate aqueous phase composition on liq./liq. partitioning behavior with emphasis on tank wastes.

Specific Objectives for 2002-2003

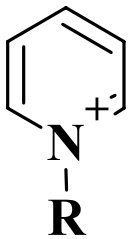
- Examine liquid/liquid partitioning using common extractants in ILs with comparison to traditional organics.
- Synthesize and study new ILs with extracting functionality.
- Investigate novel Aqueous Biphasic Systems formed by IL/salt mixtures with emphasis on tank waste.
- Studies of solid phase analogues of these polymeric systems.

Structure of Presentation

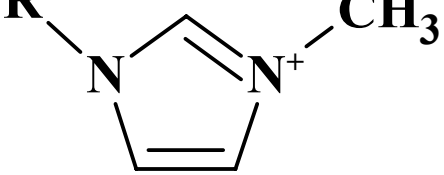
- Ionic liquid concepts in liquid/liquid separations
- Metal ion partitioning
- Added crown ether extractant for Cs/Sr
- Added CMPO extractant for Am/Pu/U/Th
- Added Cyanex™ extractants for Am/Pu/U
- UV/Vis and EXAFS Spectroscopy
- 'Task Specific Ionic Liquids'
- CMPO impregnated cellulose for Am/Pu/U
- Am^{3+} partitioning from waste tank simulants
- Aqueous phase compositions - Salt/salt studies

Ionic Liquids

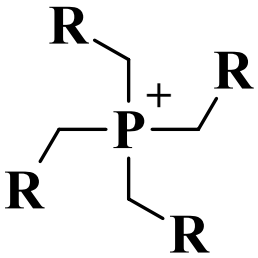
Most commonly used cations:



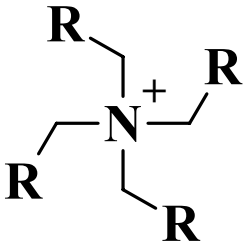
N-alkyl-pyridinium



1-alkyl-3-methyl imidazolium



Tetraalkyl-phosphonium



Tetraalkyl-ammonium

Some possible anions:

Water immiscible → **Water miscible**

Water immiscible		Water miscible
$[PF_6^-]$	$[BF_4^-]$	$[CH_3CO_2^-]$
$[N(SO_2CF_3)_2^-]$	$[CF_3SO_3^-]$	$[CF_3SO_2^-]$
$[BR_1R_2R_3R_4^-]$		$[NO_3^-]$, $[Cl^-]$

Most common alkyl chains: Ethyl, Butyl, Hexyl, Octyl, Decyl

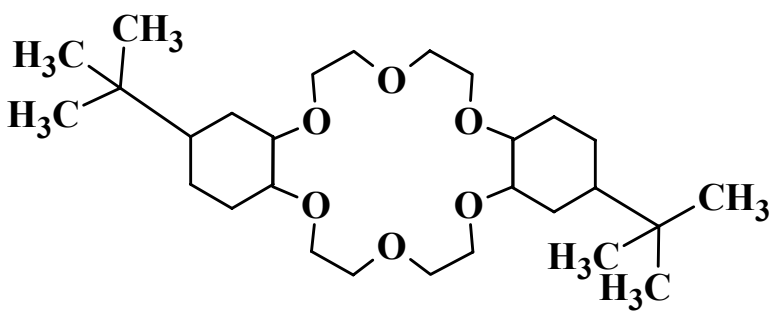
Ionic Liquid Systems for Separations

- **Advantages**
  - Nonvolatile
  - Nonflammable
  - Many IL combinations
  - Recyclable
  - High thermal stability
  - Wide liquidus range
- **Disadvantages**
  - Intellectual Properties restricts availability
  - Unknown toxicity and BOD
  - Cost
  - Large variability in ionic liquid properties requires lengthy characterization and appraisal

Metal Ions Extractants in RTIL

- Distribution ratios for Am, Pu, Th, and UO_2 to IL are all less than 0.01
  - Marked preference for the aqueous phase
  - Highly hydrated nature of many metal ions
  - To achieve partitioning, it is necessary to change the ion's hydration environment
    - Add complexing extractants

Crown ether in Liquid/Liquid Systems



dtb18C6

- 4,4'-(5')-di-(*tert*-butylcyclohexano)-18-crown-6
- Established Cs^+ and Sr^{2+} extractant
- A neutral extractant for the separation of Cs^+ and Sr^{2+} from nitrate media

Horwitz, Deitz, and Fisher *Solv. Extr. Ion Exch.*., 1990, *8*, 557

- Distribution ratios with dtb18C6 in $[C_n mim][PF_6]$ for Cs^+ and Sr^{2+} are greater than less hydrophobic crown ethers

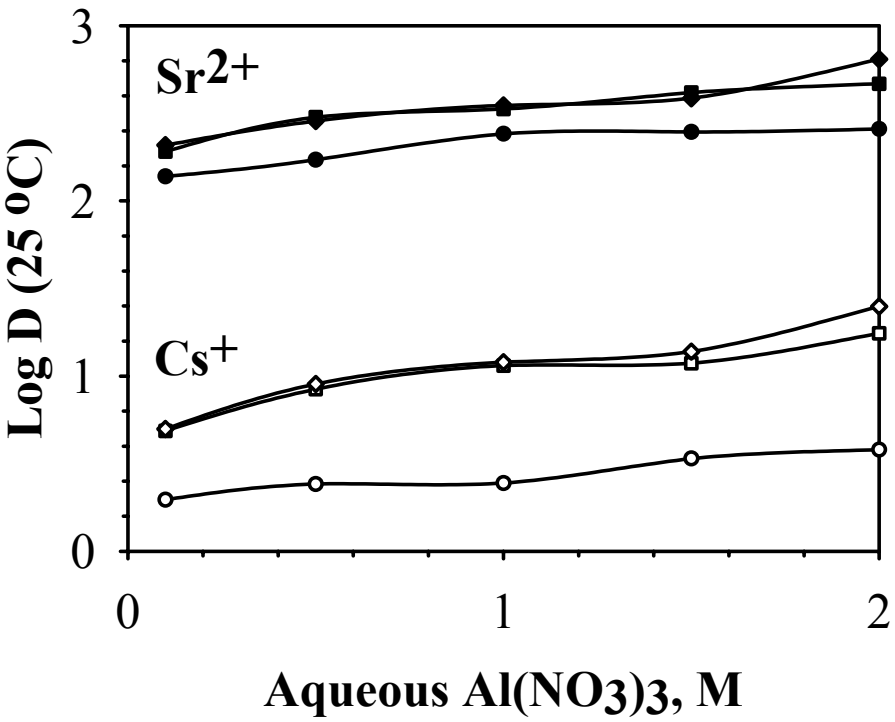
  Visser, Swatloski, Reichert, Griffin, and Rogers *Ind. Eng. Chem. Res.*, 2000, *39*, 3596

- Distribution ratios with dicyclohexyl-18-crown-6 for Sr^{2+} in $[C_n mim][Tf_2N]$ were reported 'unprecedentedly large'

  Dai, Ju, and Barnes *J. Chem. Soc., Dalton Trans.*, 1991, 1201

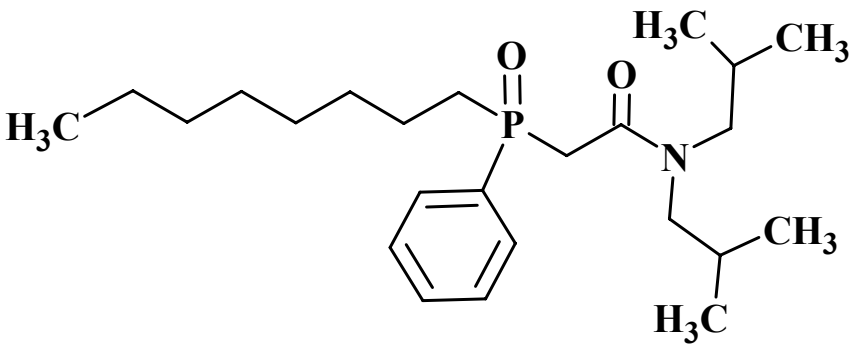
Crown ether in Liquid/Liquid Systems

- High acid concentrations (> 1 M HNO_3) in the aqueous phase promoted the conversion of the $[PF_6]^-$ anion into $[PO_4]^{3-}$
- $[PF_6]^-$ ILs for metal ion separations will thus be limited to lower acid concentrations
- $Al(NO_3)_3$ can be used as a convenient source of nitrate[1]



[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**.

CMPO in Liquid/Liquid Systems



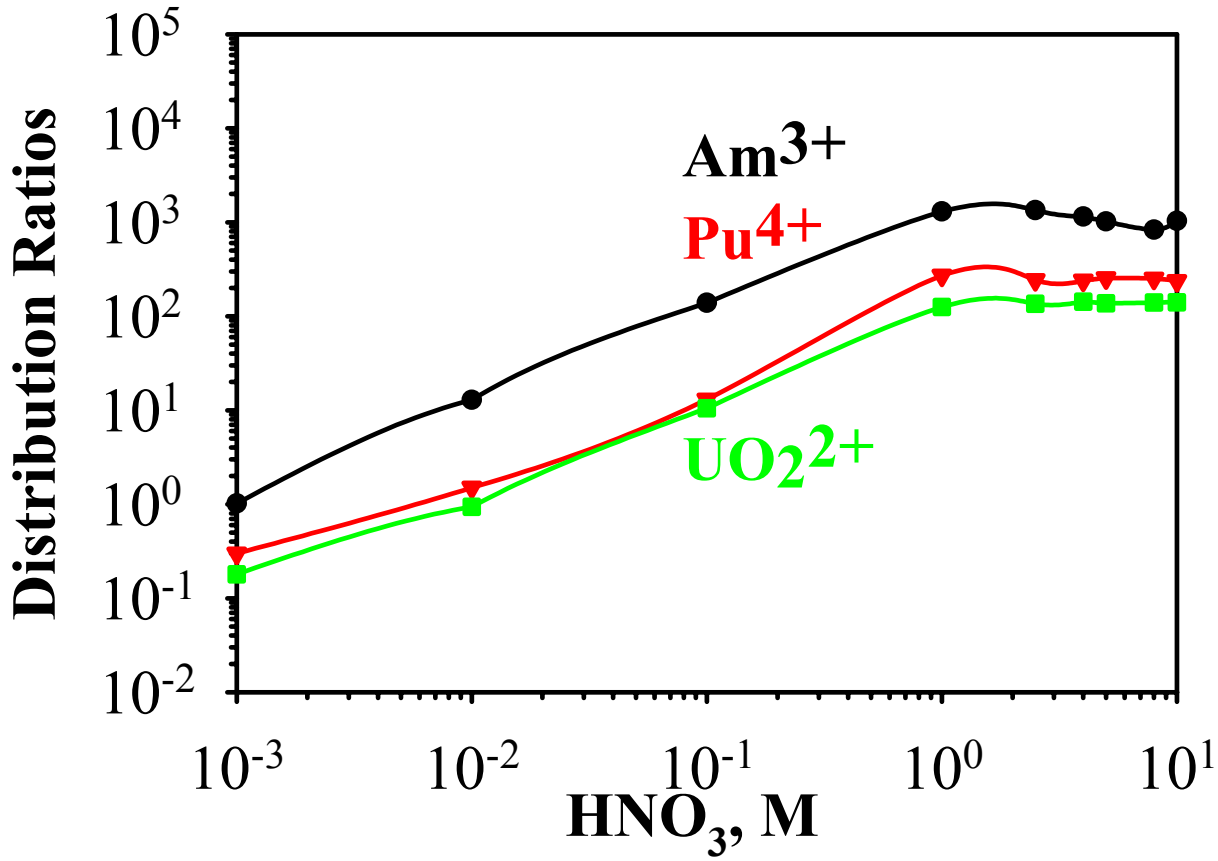
CMPO

Octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide
Established actinide extractant remains quantitatively in IL phase as determined by UV-VIS

- A neutral extractant for the separation of +3, +4, and +6 chloride and nitrate actinide complexes
- Distribution ratios with 0.2 M CMPO & 1.2 M TBP (dodecane) increase with increasing HNO_3: $Pu4^+$ 20,000 (5 M), UO_2^{2+} 3,000 (6 M), Am^{3+} 10 (6 M)
- Am^{3+} stripping can be achieved at < 0.1 M HNO_3

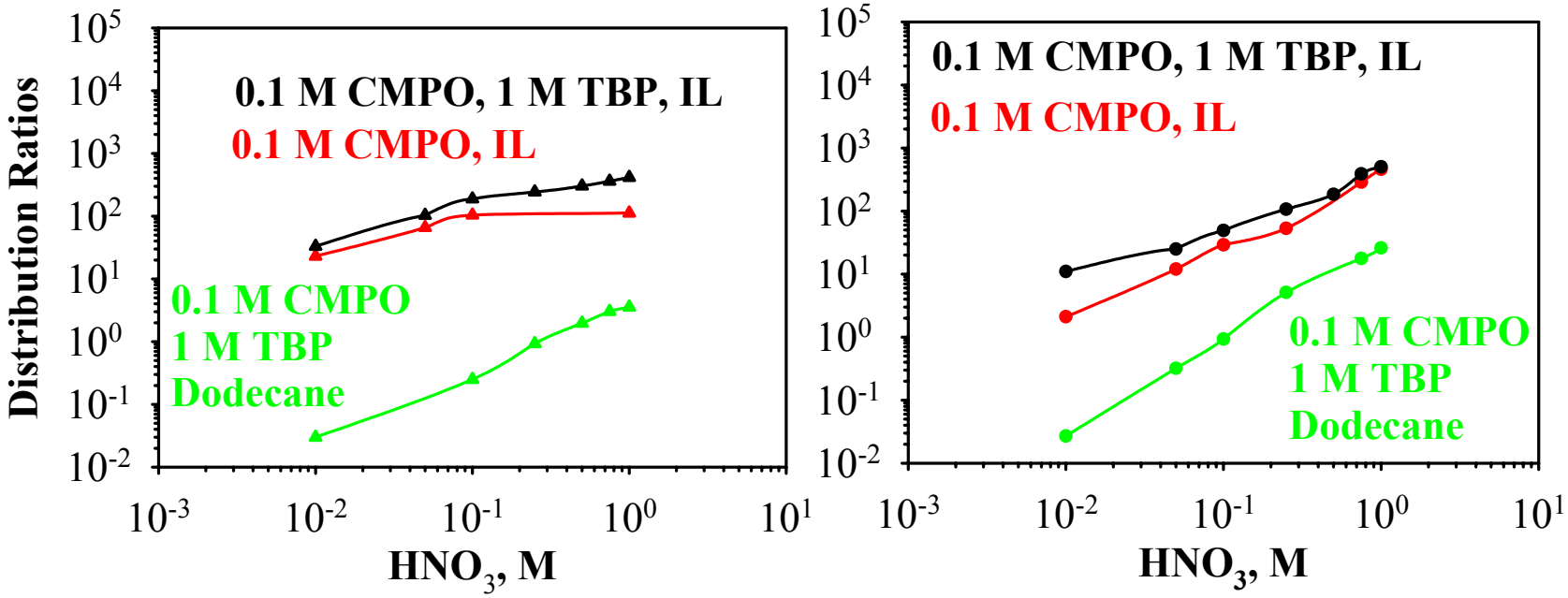
Schulz and Horwitz, *Sep. Sci. Technol.*, 1988, *12/13*, 1191

Metal Ion Distribution Ratios with 0.1 M CMPO in $[C_6mim][N(SO_2CF_3)_2]$[2]



[2]Visser, A. E.; Rogers, R. D. "Room Temperature Ionic Liquids: New Solvents for f-Element Separations and Associated Solution Chemistry," *Journal of Solid State Chemistry*, In Press

$^{241}Am^{3+}$ and $^{234}Th^{4+}$ Distribution Ratios with 0.1 M CMPO and 1 M TBP[1,2]



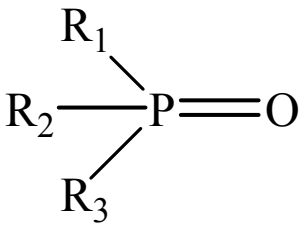
CMPO as an Extractant in IL

- Incorporating in IL significantly increases the distribution ratios with CMPO/TBP compared to dodecane
- Presence of TBP enhances the extraction
- Slope analysis does not support An-NO_3 neutral extraction

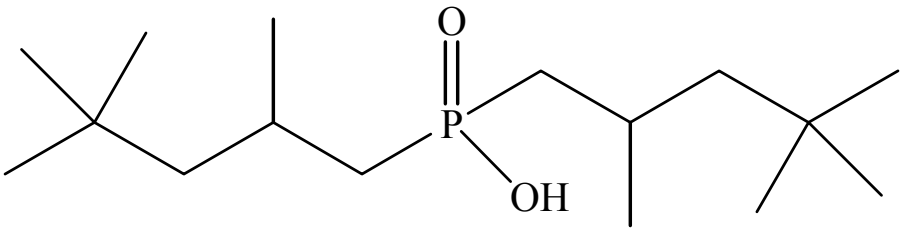
$$An^{n+} + nNO_3^- \rightarrow An(NO_3)_n$$

- High distribution ratios at low acid concentrations may hinder stripping
- Ion exchange mechanism may be possible

Cyanex™ Extractants in Liquid/Liquid Systems



(R_1, R_2, R_3: n-hexyl and n-octyl groups)



Cyanex 923

- Mixture of trialkylphosphine oxides
- Established actinide extractant
- A neutral extractant for the separation of +3, +4, and +6 chloride and nitrate actinide complexes

Cyanex 272

- Bis (2,4,4-trimethylpentyl) phosphinic acid
- Established for the separation of Co, Ni, Fe, and Zn from chloride and sulfate media

Cyanex™ extractants are products of Cytec, Inc., Canada.

Other Common Extractants in ILs

Pu(IV) – Cyanex 923

- No acid dependency for IL. Possibly strip with oxalic acid.
- At 10 M HNO_3 extraction to IL blank similar to dodecane w/Cyanex 923.
- Extraction using 0.001M Cyanex 923 in dodecane is acid dependent.
- Ligand dependency for Pu(IV):Cyanex 923 is 1:1 in $[C_{10}mim][NTf_2]$.

Other Common Extractants in ILs

Am(III) – Cyanex 923

- Strong acid dependency for IL.
- Extraction of Am(III) using 0.1M Cyanex 923 in[C_{10}mim][NTf_2] is possibly acid strippable.

Other Common Extractants in ILs

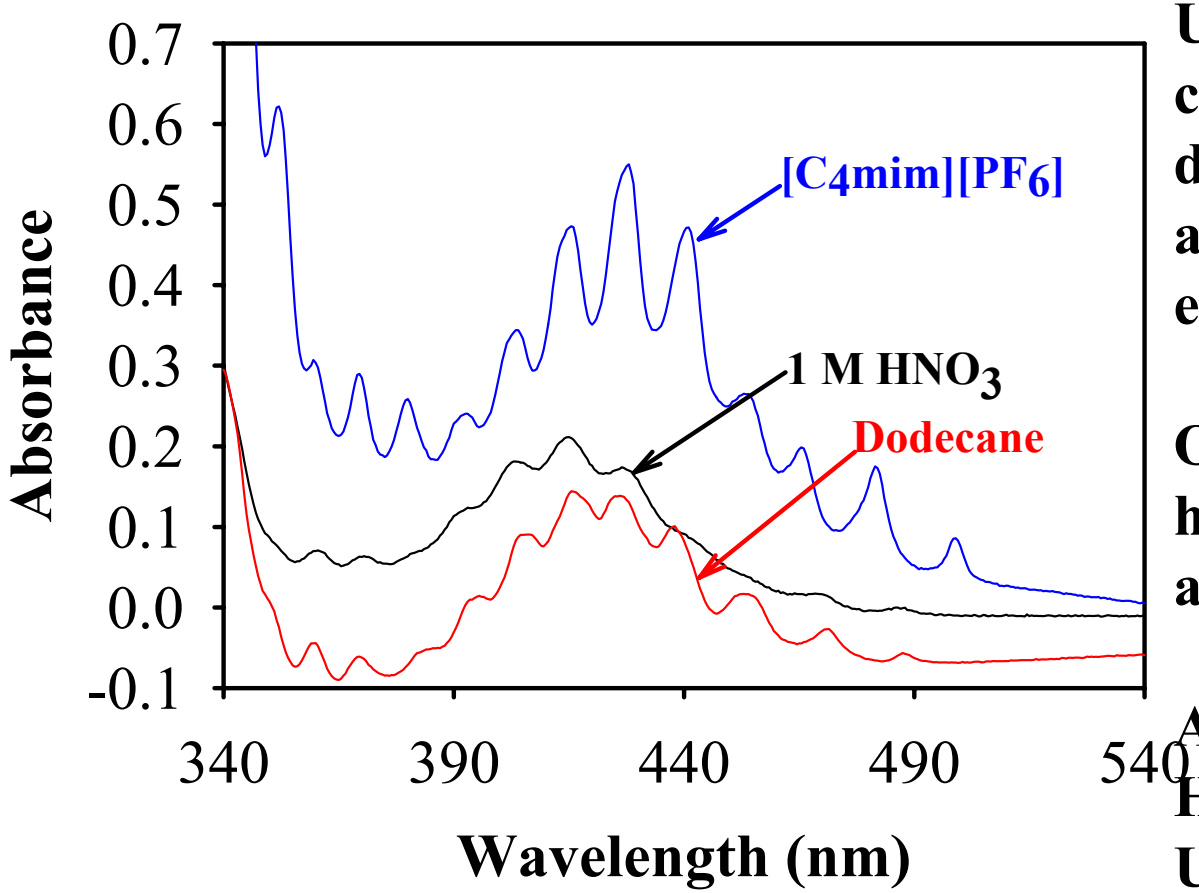
Am(III) - Cyanex 923

- Ligand dependency for Am(III):Cyanex 923 is complicated in $[C_{10}mim][NTf_2]$.
- 0.001 to 0.05M slope is 0.18.
- 0.05 to 0.1M slope is 3.
- Possibly chemical change occurring.

Cyanex™ Extractants in ILs

- Incorporating in IL significantly increases the distribution ratios with Cyanex 923 compared to dodecane
- 1:1 ligand dependency for Pu(IV):Cyanex 923
- Ligand dependency for Am(III) does not suggest 1:1 Ratio
- High distribution ratios at low and high acid concentrations may hinder stripping
- No $[C_{10}mim]^+$ is leached to the aqueous phase by U(VI) from Cyanex 272 $[C_{10}mim][Tf_2N]$

UO_2^{2+} VIS Spectroscopy



UO_2^{2+} - CMPO complexes in dodecane and ILs are not equivalent[3]

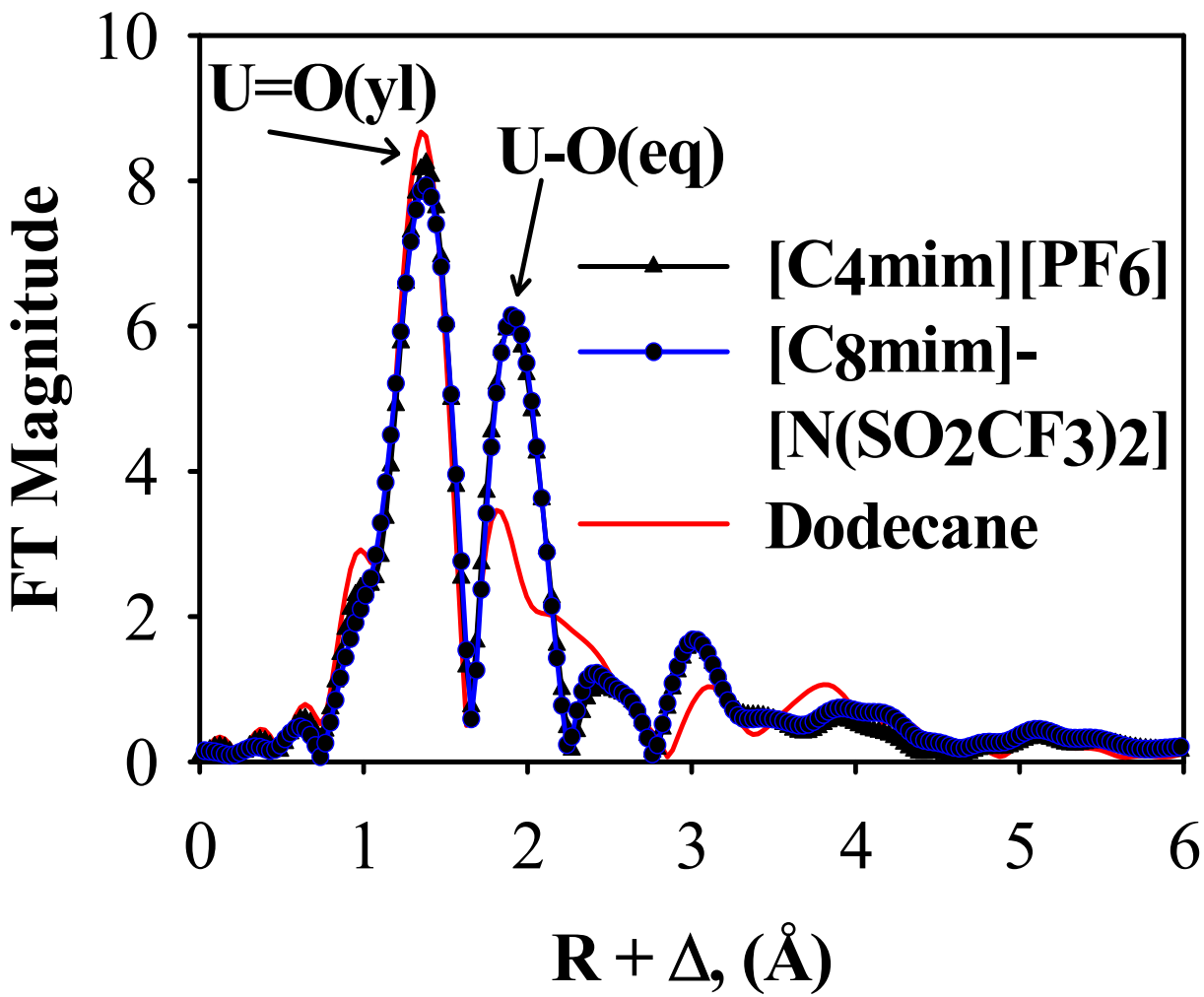
Organic or IL has 0.1 M CMPO and 1 M TBP

Aqueous is 2 M HNO_3 and 20 mM $UO_2(NO_3)_2$

~ 5mM $UO_2(NO_3)_2$

[3]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.

UO_2^{2+} EXAFS



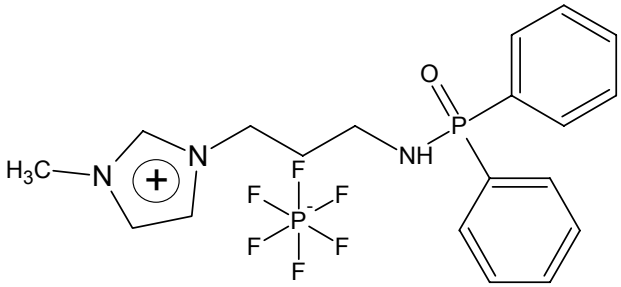
In dodecane, $UO_2(NO_3)_2 \cdot (CMPO)_2$ complexes are hexagonal bipyramidal[3]

In ILs, $UO_2(NO_3)_2$ form complexes with CMPO which exhibit a coordination number of ~ 4.5[3]

TSIL

- The identity of ionic liquids can be designed to target “Task Specific” applications
- Facilitated introduction of the metal ion extractant group onto the cation further demonstrates the fine-tunable nature of ionic liquids
- Combining two ionic liquids illustrates how mixtures of ionic liquids can be used to minimize cost and overcome difficult properties

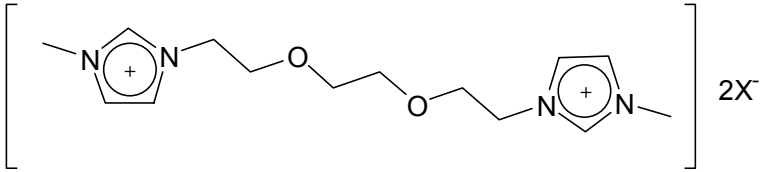
TSIL for TRU Extraction

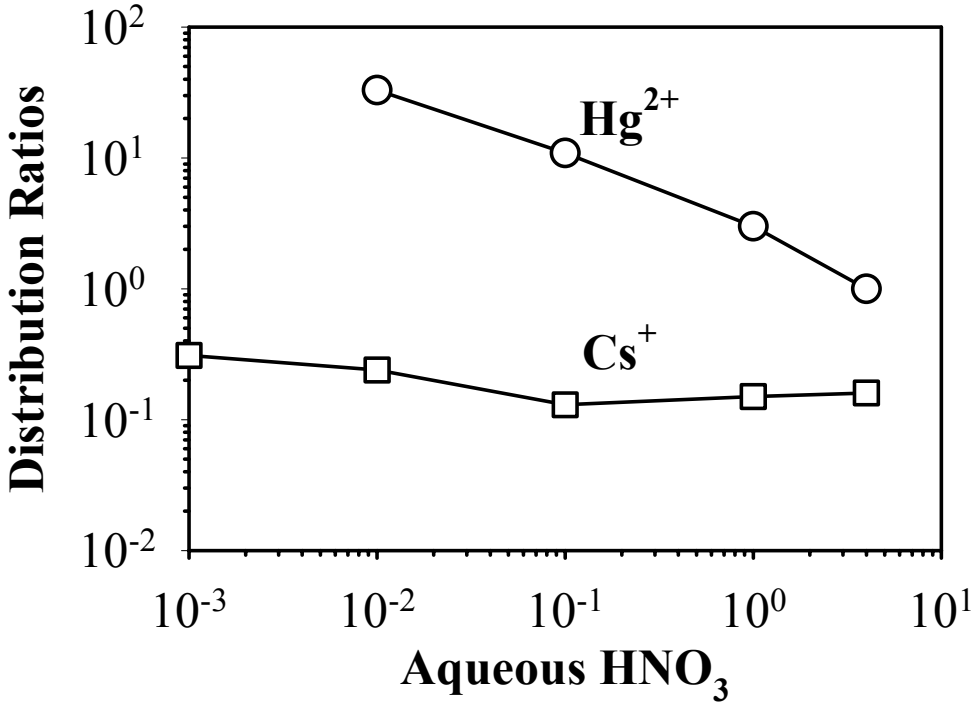


- In collaboration with Prof. Jim Davis at USA, a TSIL with phosphonamide functional group has been synthesized.
- 1:5 ratio with $[C_4mim][PF_6]$.
- High distributions have been shown for U(VI), Am(III) and Pu(IV) without selectivity.
- No acid dependency.

TSIL for Cs and Sr Extraction

- We have synthesized a TSIL with polyether functionality.[4]
- Screened as [NTf_2].
- Cs is not extracted, but Hg shows acid dependency.
- Sr extraction experiments planned.

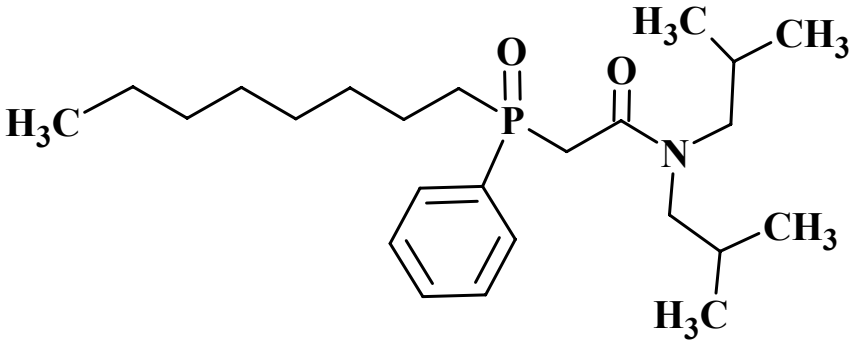




[4]Holbrey, J.D.; Visser, A.E.; Spear, S.K.; Reichert, W.M.; Swatloski, R.P.; Broker, G. A.; Rogers, R. D. *Green Chem.* 2003, *5*, 129-135.

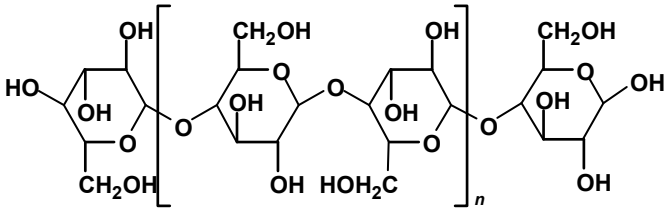
Solid Supports for TRU Separations
CMPO for the Separation of *f*-elements

The actinide complexant (complexing agent), carbamoyl methyl phosphine oxide, or CMPO can be incorporated into a reconstituted cellulose matrix to provide a solid supported metal extractant



Cellulose Dissolution in ILs

- Cellulose can be dissolved without pretreatment in molten $[C_4mim]Cl$ at ~120°C
- Dissolution is enhanced by microwave heating
- Other ionic liquids can be used - require anion activity



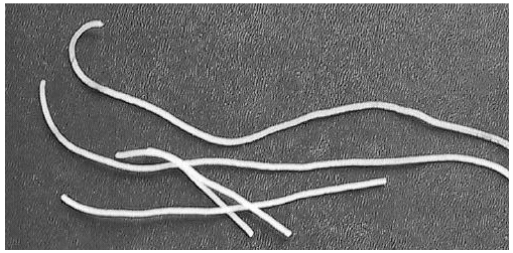
Molecular structure of the cellulose polymer chain, *n* is typically 400-750

Swatloski *et al.*, *J. Am. Chem. Soc.*, **2002**, *124*, 4974.
Rogers et al., *Pat. Appl.*, 2002.
Swatloski *et al.*, in *Molten Salts XIII*, Electrochemical Society, 2002.

Regeneration

Threads can be prepared by extruding the cellulose/ IL solution from a disposable syringe into a beaker of water

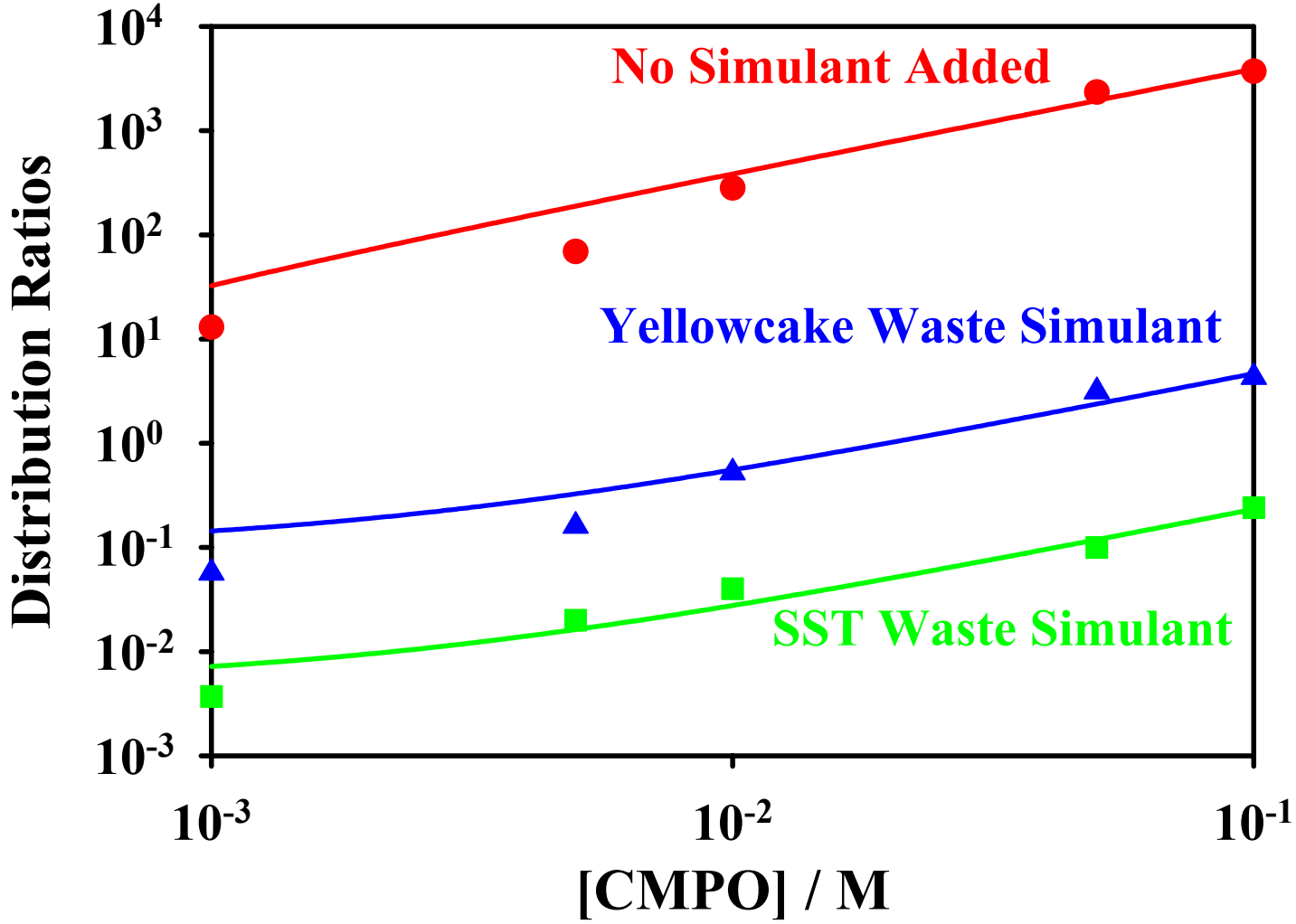
Water



DOE Waste Characteristics

- $NaOH$ or Na_2CO_3 added to minimize tank corrosion, aqueous
  - pH > 14 and high salt (~ 5M Na^+)
- Quantitative description of each tank composition is difficult due to complex speciation, radiolysis, and natural decay reactions
- A majority of the tanks contain salt solution, salt cake, and sludge

Am^{3+} Partitioning with CMPO/ $[C_6mim][N(SO_2CF_3)_2]$



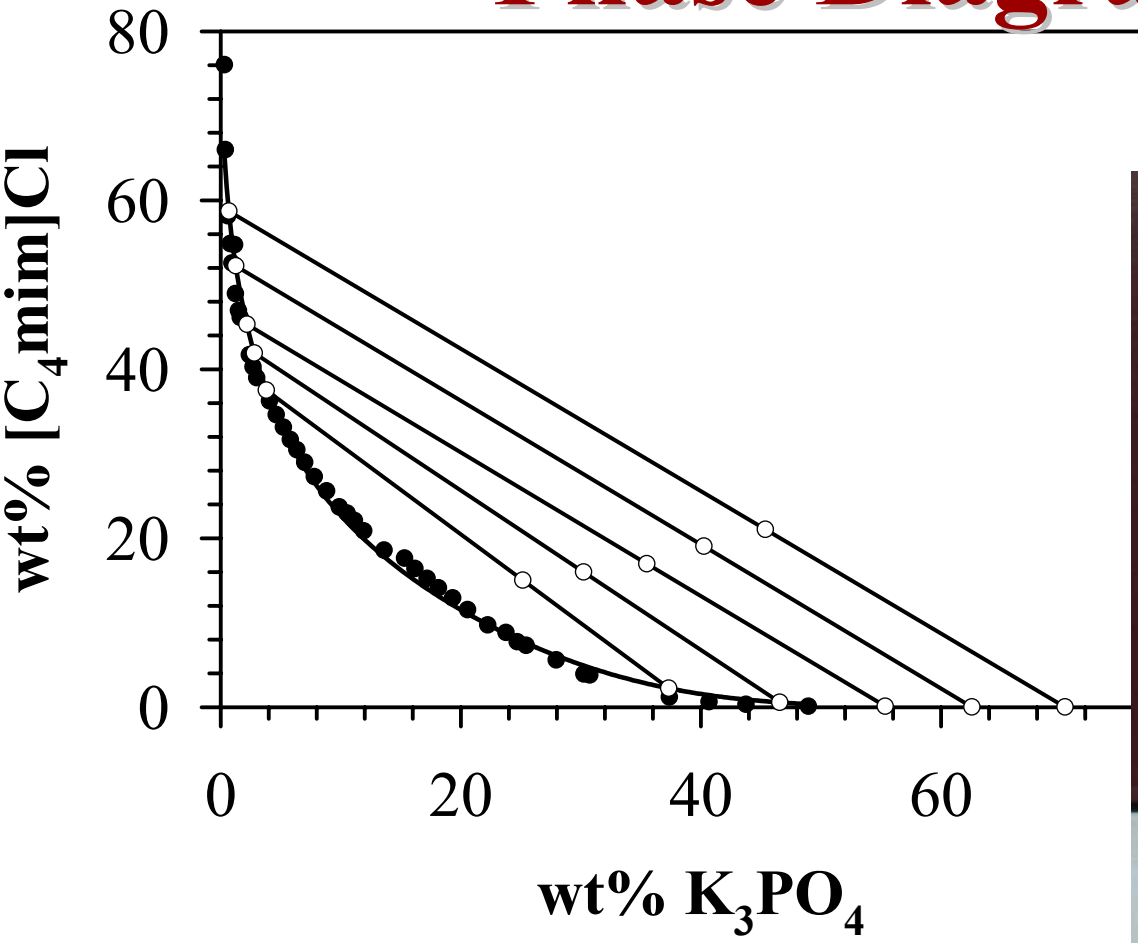
Waste Simulants

- Am^{3+} extraction to ionic liquid is suppressed by other metal ions in waste matrix - competition
- Ionic liquids containing $[N(SO_2CF_3)_2]^-$ anions may be better suited for contact with acidic waste systems than $[PF_6]^-$

Approaches to 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

Aqueous $[C_4mim]Cl/K_3PO_4$ Phase Diagram



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

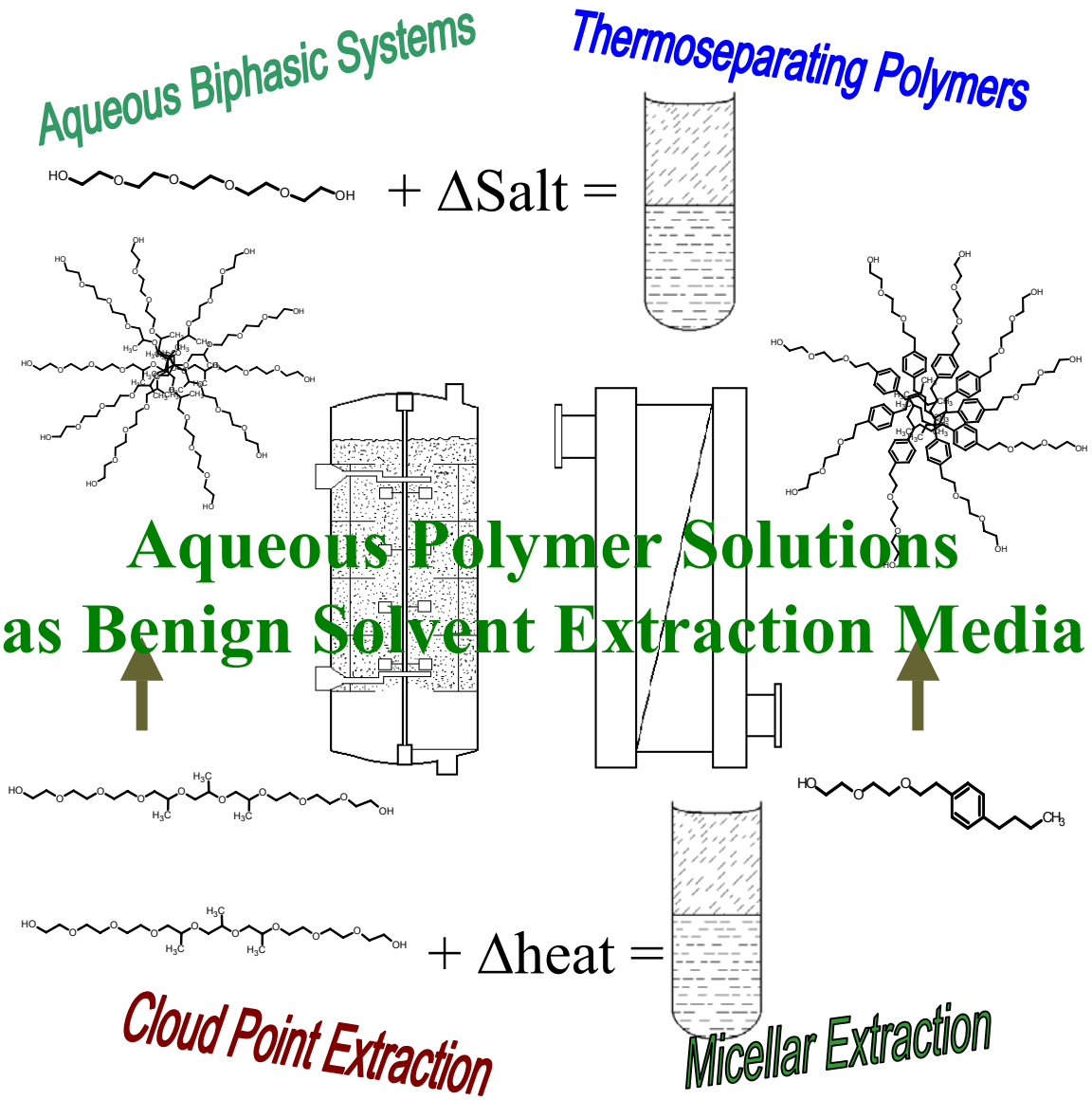
Hydrophilic Ionic Liquids/Aqueous Systems

- Hydrophobicity scales
  - Changes in hydrophobicity with anion, and cation
- Salt-salt partitioning and kosmotropic ion effects
  - uses in recycling
  - metathesis/recovery of IL cations
  - separation systems based on kosmotropic anions

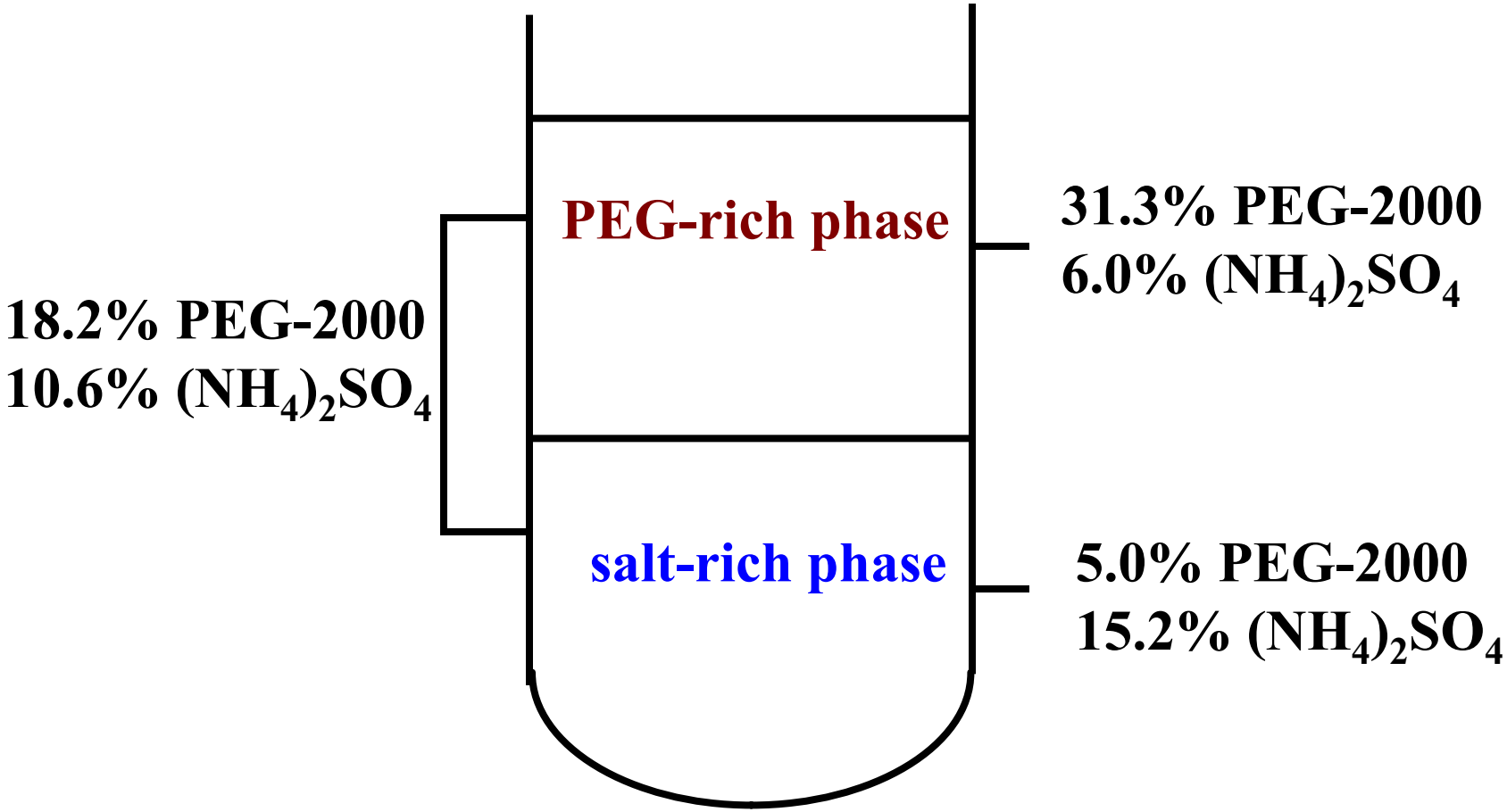
Range of Salting-out Systems

- $[C_4mim]Cl$ with
  - K_3PO_4
  - K_2CO_3
  - KOH
  - Na_2HPO_4
  - $Na_2S_2O_3$
- $[C_4mim][BF_4]$ with
  - KCl
  - NaCl
  - $CaCl_2$
- Brennecke has observed separation of ILs from aqueous solution with CO_2 pressures
  - possible mechanism for separation from carbonate formation

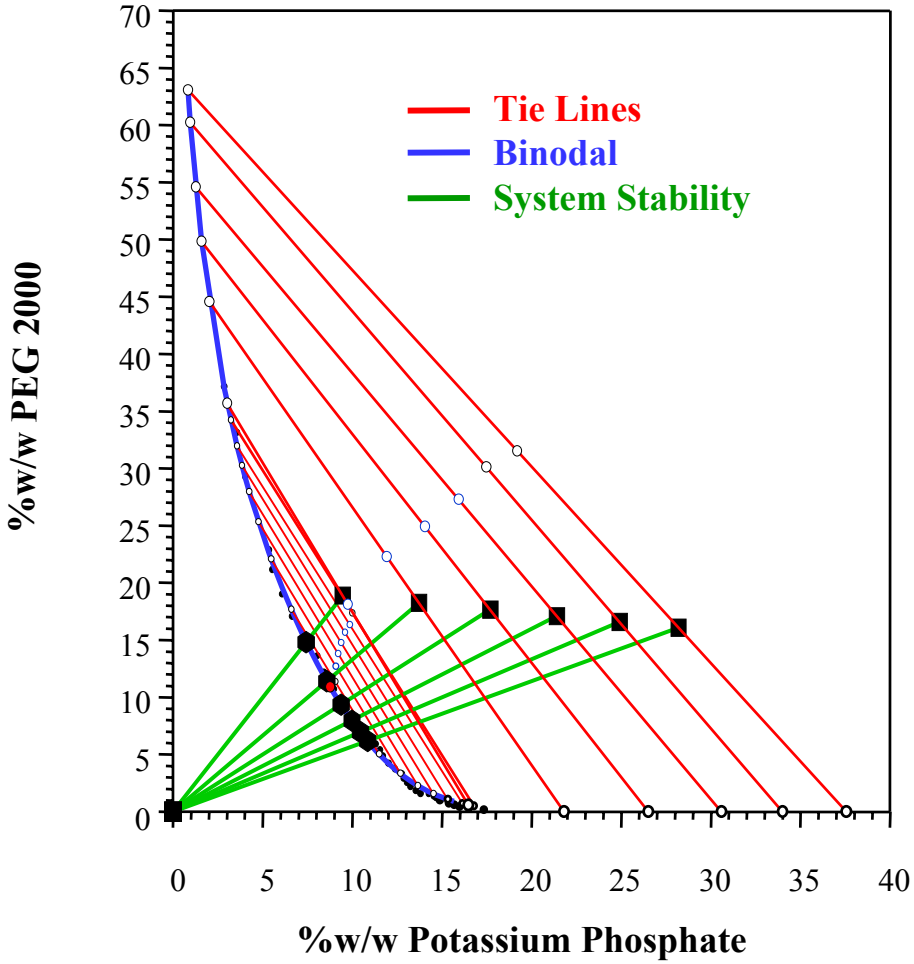
Aqueous Polymer Solutions as Benign Solvent Extraction Media



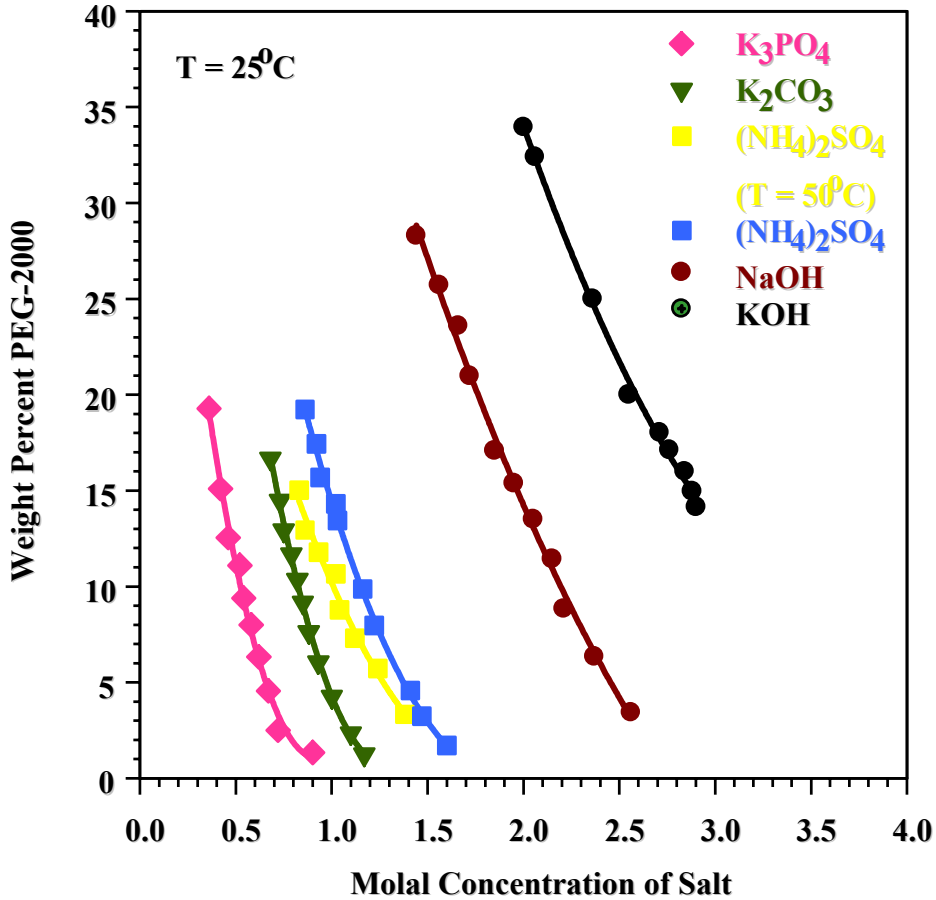
Typical Phase Compositions



PEG-2000/Potassium Phosphate Phase Diagram



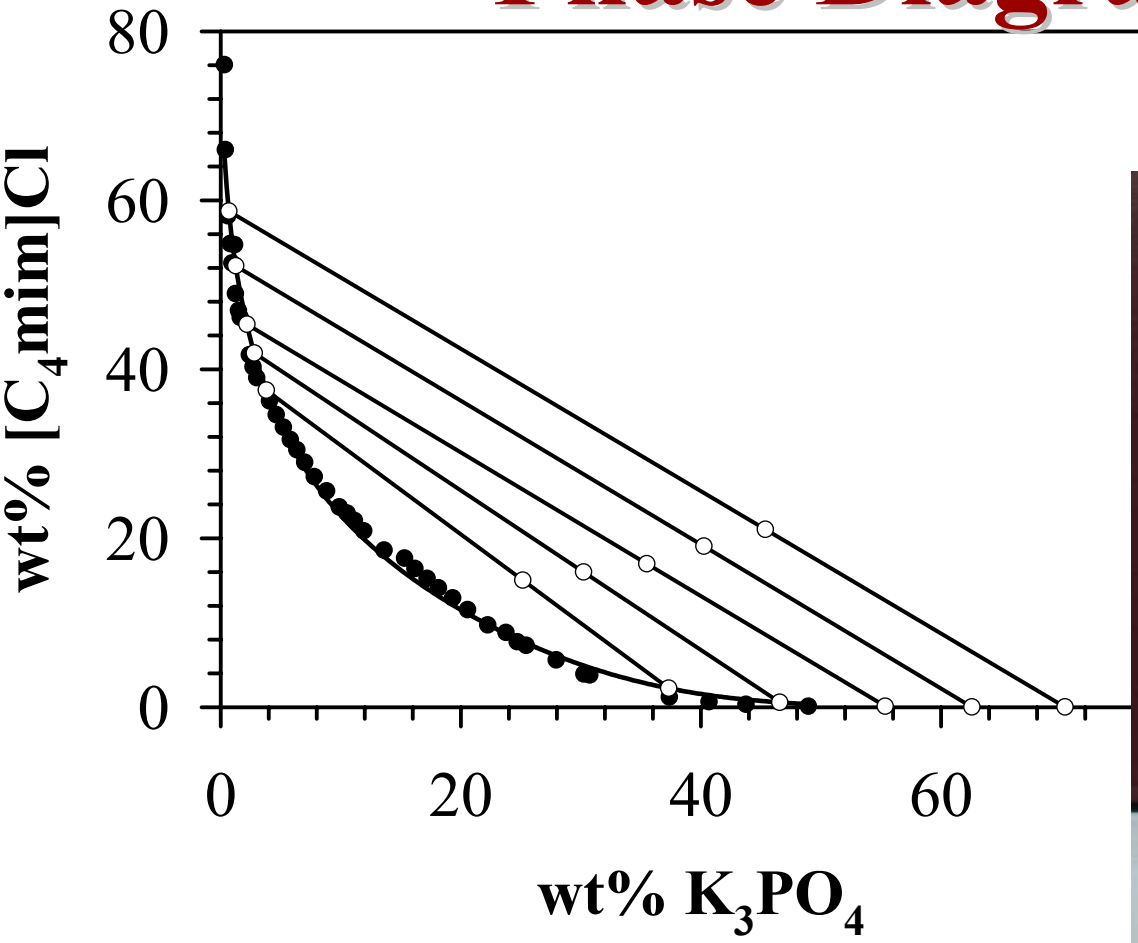
Phase diagrams for six common PEG-2000/salt ABS determined by turbidimetric titration



Phase-forming ability increases as the Gibbs free energies of hydration for the salt anion become more negative:

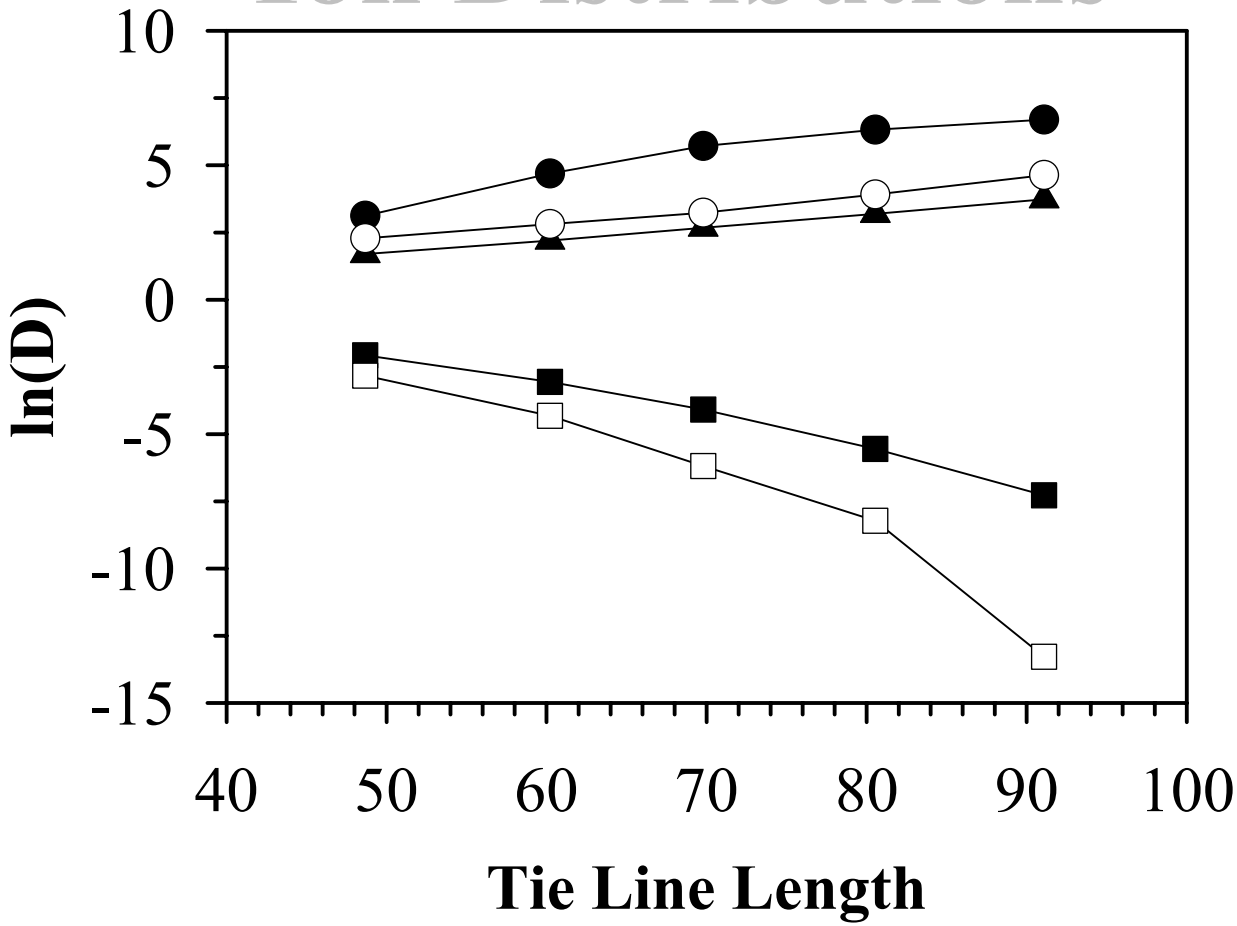
Anion	ΔG_{hyd} (kJ/mol)
F^-	-345
OH^-	-345
SeO_4^{2-}	-1110
CrO_4^{2-}	-1120
SO_4^{2-}	-1145
SO_3^{2-}	-1230
S^{2-}	-1280
CO_3^{2-}	-1300
PO_4^{3-}	-2835

Aqueous $[C_4mim]Cl/K_3PO_4$ Phase Diagram



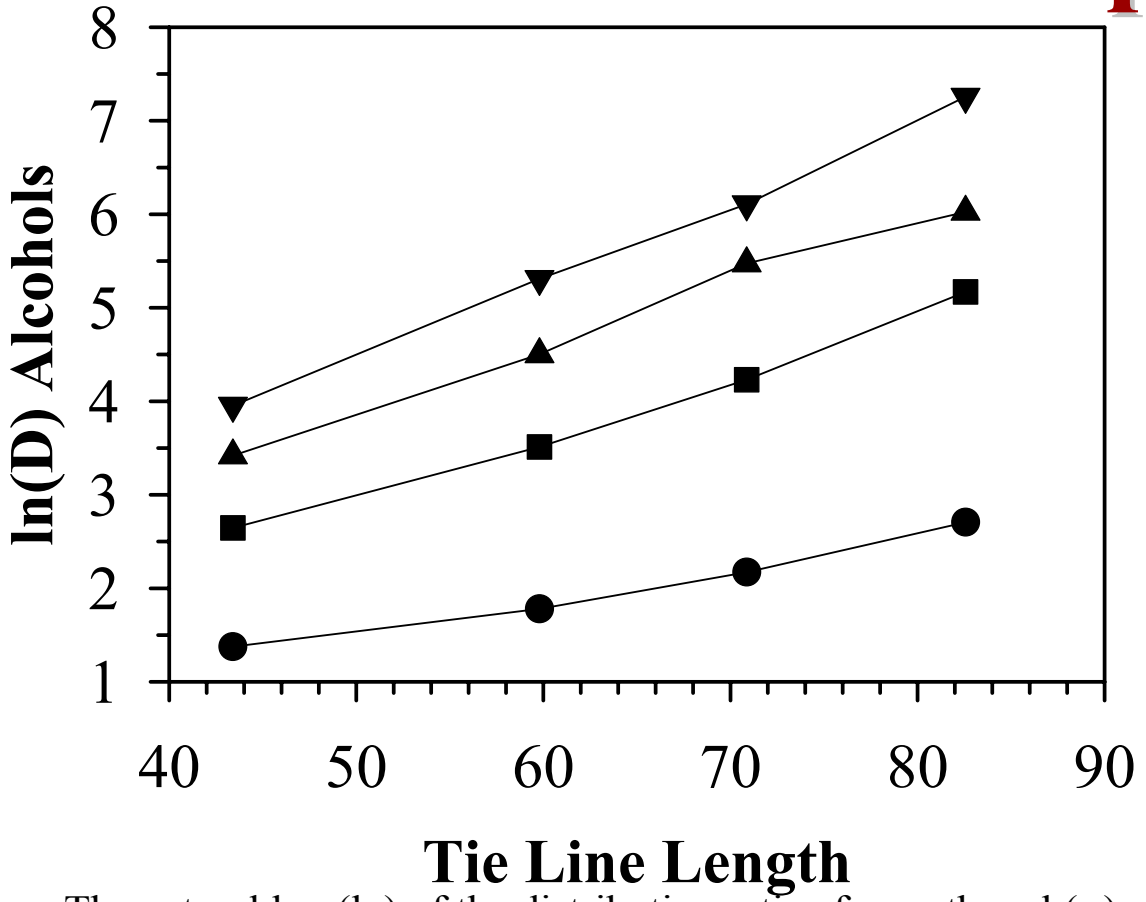
Gutowski *et al.*, *submitted to J. Am. Chem. Soc.*, 2003.

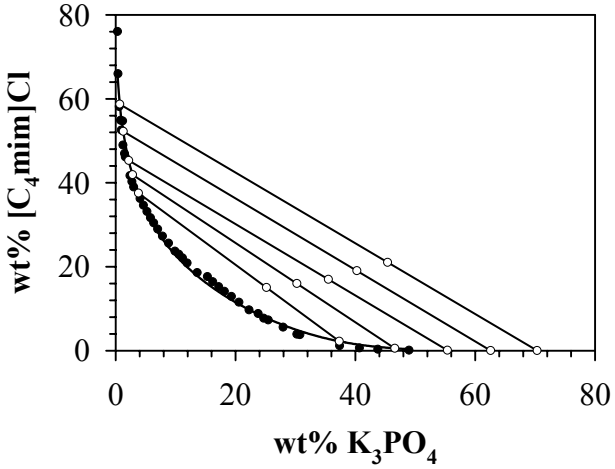
Ion Distributions



Plot of the log of the distribution ratio as a function of tie line length for ^{36}Cl (▲), ^{14}C (●), and ^{32}P (■) tracer species and for $[C_4mim]Cl$ (○) and K_3PO_4 (□) determined from the phase diagram.

Distribution Ratios for Linear Alcohols in the Biphase





The natural log (ln) of the distribution ratios for methanol (●), propanol (■), butanol (▲), and pentanol (▼) in the $[C_4mim]Cl/K_3PO_4$ biphasic system at four different tie line lengths

Range of Salting-out Systems

- $[C_4mim]Cl$ with
  - K_3PO_4
  - K_2CO_3
  - KOH
  - Na_2HPO_4
  - $Na_2S_2O_3$
- $[C_4mim][BF_4]$ with
  - KCl
  - NaCl
  - $CaCl_2$
- Brennecke has observed separation of ILs from aqueous solution with CO_2 pressures
  - possible mechanism for separation from carbonate formation

Waste Simulant Composition

- **PNNL #1***
  - $NaNO_3$ – 1.758M
  - $NaNO_2$ – 0.8238M
  - NaOH – 2.294M
  - NaF – 0.06742M
  - Na_3PO_4 – 0.00534M
  - Na_2SO_4 – 0.00526M
  - NaCl – 0.0001M
- **Ionic Liquids that salted out in PNNL #1***
  - $[C_4mim][Cl]$
  - $[C_4mim][OTf]$
  - $[C_4mim][SCN]$
  - [1-butyl-4-dimethylaminopyridinium][Cl]
  - $[C_{10}mim][Cl]$
  - [1-butyl-4-picolinium][Br]
  - $[C_4mim][NO_3]$

*Sharma, A.K.; Clauss, S.A.; Mong, G.M.; Wahl, K.L.; Campbell, J.A. *J. Chromatogr. A* 1998, *805*, 101-107.

Advantages/Disadvantages

Advantages	Disadvantages
• Biphases can be formed with addition of wide range of salts • Avoid expensive or environmentally harmful anions (fluorine-containing) • Potential applications in metathesis and recycling • Expands number of ILs that can be used for separations • Fluorinated anions are NOT necessarily required for biphase-formation	• High salt concentrations required to form biphase • Not totally clean two-phase system due to salt contamination • Biphase formation dictated by phase diagram – must be cognizant of phase compositions • Potentially unwanted metathesis

Summary

- $[C_4mim]Cl$ can be induced to form aqueous biphasic systems concentrated K_3PO_4
- The water-structuring nature of the $[PO_4]^{3-}$ anion increasing electroconstriction in the lower aqueous phase, forcing the low dielectric $[C_4mim]^+$ cations to the upper phase with concurrent Cl^- transfer
- Increasing salt concentration enhances the phase separation. Analogous to PEG/salt aqueous biphasic systems
- The solvophobic nature indicates that bulky hydrophilic IL organic cations can be salted-out by addition of a *more* kosmotropic anion
- ABS of $[C_4mim]Cl$ have been formed with a range of kosmotropic salts including KOH, K_2CO_3, Na_2HPO_4, and $Na_2S_2O_3$
- This offers the potential to exploit these systems for metathesis, recycling, and separations

Initial Conclusions

- IL can be used as alternatives to traditional solvents in l/l separations
- Results with CMPO indicate different underlying complexations and partitioning mechanisms in IL systems
- Composition of the IL and aqueous phases should be considered when complex matrices or harsh conditions may be encountered

Future Work

- Investigate the coordination environment for An-extractant in IL
- Determine the stability of IL under conditions similar to those encountered in waste processing systems
- Continue to explore other IL cations and anion combinations
- Determine solubility of salts in IL and capacity of IL for An-extractant complexes

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References to publications are available at:

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

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