Novel Fission-Product Separation Based on Room Temperature Ionic Liquids

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Research Objectives

The overall goal of this project is to develop a new ionic liquid based solvent extraction process for separation of Cs-137 and Sr-90 from tank wastes.

- To synthesize new ionic liquids tailored for the extractive separation of Cs\(^+\) and Sr\(^{2+}\).
- To select optimum macrocyclic extractants through studies of complexation of fission products with macrocyclic extractants and transport in new extraction systems based on ionic liquids.
- To develop efficient processes to recycle ionic liquids and crown ethers via electrochemistry.
- To investigate chemical stabilities of ionic liquids under strong acid, strong base, and high level radiation conditions.
Why Ionic Liquids?

Ionic systems consisting of salts that are liquid at ambient temperatures can act as solvents for a broad spectrum of chemical species.

- Nonvolatility
- Ionicity
- Tunable Hydrophobicity
- Tunable Lewis Acidity
- Large Electrochemical windows
- Thermal Stability
- Nonflammability
- Wide Liquid-Phase Temperature. (-100°C to around 300°C)
Range of Organic Cations and Anions Typically Used to Prepare Room-Temperature Ionic Liquids

Most commonly used cations:

- 1-alkyl-3-methyl-imidazolium
- N-alkyl-pyridinium
- Tetraalkyl-ammonium
- Tetraalkyl-phosphonium

Some possible anions:
- water-insoluble: [PF$_6$]$^-$, [((CF$_3$SO$_2$)$_2$N]$^-$, [BR$_1$R$_2$R$_3$R$_4$]$^-$

Most commonly used alkyl chains:
- ethyl, octyl
- butyl, decyl
- hexyl
Comparison of Solvent Extractions Based on Molecular Solvents and Ionic Liquids

**Molecular Solvents**

- $M^{n+}(aq) \rightarrow M^{n+}(org)$ *Unfavorable*
- $n A^-(aq) \rightarrow n A^-(org)$ *Unfavorable*
- crown(org) + $M^{n+}(org)$ $\rightarrow$ {crown $M^{n+}$}(org) *Favorable*
- {crown $M^{n+}$}(org) + $n A^-(org)$ $\rightarrow$ {crown $M^{n+} nA^-$}(org) *Formation of Ion Pair*

**Ionic Liquids (IL)**

- $M^{n+}(aq) \rightarrow M^{n+}(IL)$ *more favorable*
- $n A^-(aq) \rightarrow n A^-(IL)$ *more favorable*
- crown(org) + $M^{n+}(IL)$ $\rightarrow$ {crown $M^{n+}$}(IL) *Favorable*
- $M^{n+}(aq) + n \text{Org}^+(IL) \rightarrow M^{n+}(IL) + n \text{Org}^+(aq)$ *Ion Exchange – Dietz & Rogers*

**Overall Process:**

- crown(org) + $M^{n+}(aq) + n A^-(aq)$ $\rightarrow$ {crown $M^{n+} nA^-$}(org) *Thermodynamically Unfavorable*
- crown(IL) + $M^{n+}(aq) + n A^-(aq) + n \text{Org}^+(IL)$ $\rightarrow$ {crown $M^{n+}$}(IL) + $n A^-(IL) + n \text{Org}^+(aq)$ *Thermodynamically favorable*
Summary of Completed Research

- Development of Highly Selective Extraction Process for Cs\(^+\) Based on Calixarenes
- Demonstration of Facilitated Sacrificial Ion-Exchange Extraction Processes to Reduce the Loss of ILs and to Increase Extractive Strength of ILs
- Development of Recyclable IL-Based Extraction Systems
- Optimization of Selectivities of Extractants via Systematic Change of ILs
- Development of an Electrochemical Method for Recycling the Ionic Liquid-ionophore Extractant Phase Following the Extraction of Cs\(^+\) and Sr\(^{2+}\)
- Synthesis of New Ethylene-Glycol Functionalized Bis-Imidazolium Ionic Liquids and Sr\(^{2+}\)/Cs\(^+\) Partitioning Studies

### Comparison of Sr-Extraction Results Obtained Using Ionic Liquids and Conventional Solvents.

<table>
<thead>
<tr>
<th>Extract Phase</th>
<th>$K_d$ (^a) With 0.15 M crown ether</th>
<th>$K_d$ Without crown ether</th>
</tr>
</thead>
<tbody>
<tr>
<td>BuMe(_2)ImPF(_6)</td>
<td>4.2</td>
<td>0.67</td>
</tr>
<tr>
<td>BuMeImPF(_6)</td>
<td>2.4 × 10</td>
<td>0.89</td>
</tr>
<tr>
<td>EtMe(_2)ImTf(_2)N</td>
<td>4.5 × 10(^3)</td>
<td>0.81</td>
</tr>
<tr>
<td>EtMeImTf(_2)N</td>
<td>1.1 × 10(^4)</td>
<td>0.64</td>
</tr>
<tr>
<td>PrMe(_2)ImTf(_2)N</td>
<td>1.8 × 10(^3)</td>
<td>0.47</td>
</tr>
<tr>
<td>PrMeImTf(_2)N</td>
<td>5.4 × 10(^3)</td>
<td>0.35</td>
</tr>
<tr>
<td>C(_6)H(_5)CH(_3)</td>
<td>7.6 × 10(^{-1})</td>
<td>nm (^a)</td>
</tr>
<tr>
<td>CHCl(_3)</td>
<td>7.7 × 10(^{-1})</td>
<td>nm</td>
</tr>
</tbody>
</table>

\(^a\) The crown ether used in this experiment is dicyclohexane-18-crown-6.

\(^b\) nm : not measurable.


**Messages:**
- Key Role Played By Crown Ether
- Ion-Exchange Effect

14,000 Enhancement
Very High Capture of Cesium Measured for Ionic Liquid-Based Solvents Containing BOBCalixC6

BOBCalixC6 extractant is > 4000 times more effective in ionic liquid than in conventional solvent!

\[ K_d = 0.034 \]

Calix[4]arene-bis(tert-octylbenzo-crown-6) "BoBCalixC6"
Separation Systems Based on Facilitated Ion-Exchange Recognition

Liquid Membranes Containing NaB(Ph)$_4$ or NaB(Ph-F)$_4$ in Ionic Liquids

<table>
<thead>
<tr>
<th></th>
<th>$K_d$ (Cs)</th>
<th>Initial CsCl Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaB(ph)$_4$</td>
<td>7.69 x 10$^{-3}$ M</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>2.34 x 10$^{-3}$ M</td>
<td>0.32</td>
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</tbody>
</table>

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<tr>
<th></th>
<th>$K_d$ (Cs)</th>
<th>Initial CsCl Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaB(ph-F)$_4$</td>
<td>1.85 x 10$^{-2}$ M</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>5.87 x 10$^{-2}$ M</td>
<td>0.71</td>
</tr>
</tbody>
</table>

Facilitated Transport via Ion-Exchange Recognition

Na$^+$ Sacrificial Ion Exchanger
UV-Visible Spectra of Ionic Liquids Lost to Aqueous Solutions During Extraction with and Without NaBPh$_4$

- Cut Loss of Ionic Liquid by 20%
- Maintain extraction efficiencies for BOBCalixC6
Development of Stripping Protocol to Recycle Macroyclic Extractants

Synthesis of 1-Aza-18-crown-6 Derivatives

\[
\text{HN} \quad + \quad \text{n-RX} \begin{array}{c}
\text{Na}_2\text{CO}_3/\text{CH}_3\text{CN} \\
80^\circ\text{C}, 72 \text{ h}
\end{array}
\]

1. R = ethyl, X = Br
2. R = n-butyl, X = Br
3. R = n-hexyl, X = Br
4. R = n-octyl, X = Br
5. R = n-dodecyl, X = Br
6. R = n-hexadecyl, X = Br
7. R = CF\text{\textsubscript{3}}(CF\text{\textsubscript{2}})\text{\textsubscript{5}}CH\text{\textsubscript{2}}CH\text{\textsubscript{2}}-, X = I
8. R = 9-anthracenylmethyl, X = Cl
Recycling Experimental Results of Recyclable N-Alkylaza-18-crown-6 in [C$_4$mim][NTf$_2$]

$K_{dSr}^{2+}=918.64$, 1 drop 6N HNO$_3$ gave 100% Sr$^{2+}$ recovery
$K_{dCs}^+=23.96$, 1 drop 6N HNO$_3$ gave 100% Cs$^+$ recovery

$K_{dSr}^{2+}=3.77$, 1 drop 6N HNO$_3$ gave 95% Sr$^{2+}$ recovery
$K_{dCs}^+=14.9$, 1 drop 6N HNO$_3$ gave 100% Cs$^+$ recovery
Effect of 1-Akyl Group of ILs on Efficiency and Selectivity of Competitive Sr, K, Na, Cs Cation Extraction from Aqueous Solutions into ILs Containing 1-Octyl-aza-18-crown-6

- For C₂mim-Tf₂N & C₄mim-Tf₂N, the extraction efficiency is Sr²⁺ >> K⁺ > Cs⁺ > Na⁺.
- In C₆mim-Tf₂N & C₈mim-Tf₂N, the order is K⁺ > Sr²⁺ > Cs⁺ > Na⁺.
## Comparison of Extraction Results of 1-Octyl-aza-18-crown-6 with DCH18C6

<table>
<thead>
<tr>
<th>OAZ18C6</th>
<th>DCH18C6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recyclable</td>
<td>Non-recyclable</td>
</tr>
<tr>
<td>Non-commercial available</td>
<td>Commercial available</td>
</tr>
<tr>
<td>$D_{Sr}$: 8426 (in C$_2$) and 1072 (in C$_4$)</td>
<td>$D_{Sr}$: 10734 (in C$_2$) and 935 (in C$_4$)</td>
</tr>
<tr>
<td>$D_{Cs}$: 25.21 (in C$_2$) and 25.73 (in C$_4$)</td>
<td>$D_{Cs}$: 589 (in C$_2$) and 380 (in C$_4$)</td>
</tr>
</tbody>
</table>

Extraction Selectivity:
- Sr$^{2+}$ > K$^+$ > Cs$^+$ > Na$^+$
- K$^+$ > Sr$^{2+}$ > Cs$^+$ > Na$^+$

![Chemical Structure of OAZ18C6](image1)

![Chemical Structure of DCH18C6](image2)
Future Research Plans

1. Synthesis and Optimization of ILs Tailored for Solvent Extraction of Fission Products
2. Synthesis and Study of Recyclable Crown Ethers
3. Optimization of Anions of ILs for Extraction of Fission Products
4. Sacrificial Ion-Exchange Method for Synergistic Extraction of Metal Ions and Reduction of ILs Loss
5. Development of an Electrochemical Method for the Non-Destructive Removal of Extracted Cs\(^+\) and Sr\(^{2+}\)
6. Study of Stabilities of ILs in Harsh Chemical and Radiation Environments
Synthesis and Optimization of Ionic Liquids Tailored for Solvent Extraction of Fission Products

1,3-Dialkylimidazolium-Based

C(2)-Position Substituted Imidazolium-Based

Pyridinium-Based

Quaternary Ammonium-Based

Tetraalkyphosphonium-Based

Metal Complexes-Based
Typical Synthesis of Ionic Liquids Based on Alkylpyridinium and Quaternary Ammonium

\[ \text{Typical Synthesis of Ionic Liquids} \]

\[ \text{Based on Alkylpyridinium and Quaternary Ammonium} \]

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\[ \text{Typical Synthesis of Ionic Liquids} \]

\[ \text{Based on Alkylpyridinium and Quaternary Ammonium} \]
Synthesis of Task-Specific Ionic Liquids Containing an Aza crown Ether Fragment

\[
\text{H}_3\text{C-SO}_3\text{O} - \underset{\text{O}}{\text{O}} - \underset{\text{O}}{\text{O}} - \text{SO}_3\text{CH}_3 + \text{Na}_2\text{CO}_3/\text{CH}_3\text{CN} \xrightarrow{80^\circ \text{C}, 72 \text{ h}} \text{N-(CH}_2)_n\text{N} - \text{N-(CH}_2)_n\text{N} - \text{NH}_2
\]

1. RBr
2. Tf\text{}_2\text{NLi}

\[
\text{N-(CH}_2)_n\text{N} - \text{N-(CH}_2)_n\text{N} - \text{R} + \text{NTf}_2^-
\]
Dependence of $D_{Sr}$ on IL Anions of [C$_4$mim]-based ILs Containing DCH18C6.

- $D_{Sr}$ value increases dramatically as the anion changed from PF$_6$ to NTf$_2$ to BETI. $D_{Sr}$ for BETI is more 200 times larger than that for PF$_6$.
- The increase of $D_{Sr}$ with the hydrophobicity of the counter anions is in sharp contrast to the observation with the cation effect of ILs. In the latter case, $D_{Sr}$ decreases with the hydrophobicity of the IL cations.
Anion Effect on $D_{Cs}$ of $[C_4\text{mim}][X]$ Containing BOBCalixC6

- $D_{Cs}$ values increase slightly as the anion changed from PF$_6$ to NTf$_2$ to BETI.
Detection of Cation Leaching of (a) [C4mim][PF6], (b) [C4mim][NTf2], and (c) [C4mim][BETI] via UV-Vis Spectra of Equilibrium Aqueous Phases

- The loss of the ILs was found to be strongly correlated to the conjugate anions. The more hydrophobic the anions are, the less are the losses of the ILs. The loss of C₄min-BETI is about 25 fold less than that of C₄min-PF₆.
Examples of Alkaline Metal Salts Can be Used to Produce a Variety of Ionic Liquids
Proton-Based Sacrificial Ion Exchangers

\[
\begin{align*}
\text{CH}_3(\text{CH}_2)_7\text{CH}=&\text{CH}(\text{CH}_2)_7\text{COOH} & \text{pKa: 4.8} \\
\text{CH}_3(\text{CH}_2)_7\text{OH} & & \text{pKa: 20} \\
\text{MeR} & & \text{pKa: 8.8} \\
\text{HF}_2\text{C}(\text{CF}_2)_7\text{CH}_2\text{OH} & & \text{pKa: 9.9} \\
\end{align*}
\]

Effect of Carbon Chain Length of ILs and Synergistic Effect of Oleic Acid and Two Different Hydroxy Acids on Extraction Results of Rmim-Tf$_2$N Containing DCH18C6

<table>
<thead>
<tr>
<th>Aq. Phase</th>
<th>Crown Ether</th>
<th>ILs containing Proton Exchanger</th>
<th>R in Rmim-Tf$_2$N</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrCl$_2$</td>
<td>DCH18C6 0.02 M</td>
<td>NO</td>
<td>Ethyl, C2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Oleic acid(1)</td>
<td>466.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fluoro-(2)</td>
<td>465.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Di-tertbutylphenol (3)</td>
<td>419.0</td>
</tr>
</tbody>
</table>
The work is supported by US Department of Energy, EMSP program project 81929.