

Project Title: Fission-Product Separation Based on Room-Temperature Ionic Liquids  
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Progress Report:

### Research Objective

The objectives of this project are (a) to synthesize new ionic liquids tailored for the extractive separation of Cs<sup>+</sup> and Sr<sup>2+</sup>; (b) 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; (c) to develop efficient processes to recycle ionic liquids and crown ethers; and (d) to investigate chemical stabilities of ionic liquids under strong acid, strong base, and high-level-radiation conditions.

### Research Progress and Implications

This report summarizes research for the first 12 months of a 3-year project. We have successfully prepared several ionic liquids tailored specifically for extraction of Cs<sup>+</sup> and Sr<sup>2+</sup>. Several extraction experiments using ionic liquids containing calix[4]arene-bis(*tert*-octylbenzo-crown-6) have been performed. The results are listed in Table 1. Because Cs<sup>+</sup> cannot be analyzed by inductively coupled plasma atomic emission (ICP-AE), we have established a method to analyze Cs<sup>+</sup> and Sr<sup>2+</sup> cations at same time via ion chromatography

(1) **Synthesis of ionic liquids.** The literature methods of preparing 1-alkyl-3-methylimidazolium bromides have been modified. 1-Butyl-3-methylimidazolium bromide can be synthesized by mixing equal molar concentrations of 1-methylimidazole and bromobutane and stirring at room temperature for 3 days. The completion of reaction was monitored by NMR. The advantage of this modified method is that no solvent and refluxing at higher temperature are involved; therefore, it is more environmentally friendly. Using the same method, 1-ethyl-3-methylimidazolium bromide, 1-propyl-3-methylimidazolium bromide, 1-hexyl-3-methylimidazolium bromide, and 1-octyl-3-methylimidazolium bromide have been synthesized. 1-Alkyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]amides ( $\text{RMeIm}^+ \text{Tf}_2\text{N}^-$ ) were obtained by reaction of 1-alkyl-3-methylimidazolium bromides with N-lithiotrifluoromethanesulfonimide. A series of new 1-ester-functionalized-3-methylimidazolium  $\text{Tf}_2\text{N}^-$  salts and 1,3-di-(ester-functionalized) imidazolium  $\text{Tf}_2\text{N}^-$  salts have been synthesized and characterized. The structures of these novel ionic liquids and their NMR data are listed in Table 2. Several reaction routes have been pursued to prepare perfluorinated alkyl imidazolium-based ionic liquids but without success.

(2) **Extraction experiments.** The extraction experiments were performed by contacting 1 mL of ionic liquids containing crown ether with 10 mL of  $\text{CsNO}_3$  ( $2.5 \times 10^{-3} \text{ M}$ , 488 ppm) for about 1 hour in a vibrating mixer. The concentration of BoBCalix C6 in ionic liquid was  $7.7 \times 10^{-3} \text{ M}$ . The upper aqueous phase was separated, and the concentration of  $\text{Cs}^+$  was determined by ion chromatography.

(3) **Analysis of  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  by ion chromatography.** Concentrations of  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  cations were determined by injecting the aqueous phase directly into a Dionex LC20 ion chromatograph equipped with an IonPac CS 12 analytical column. The eluent was 15 mM methanesulfonic acid, and the flow rate was 1 mL/min. Because the retention time for  $\text{Cs}^+$  is 10.45 min and that for  $\text{Sr}^{2+}$  is 13.33 min, the two cations peaks are well separated. The instrument response was calibrated using  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ , and  $\text{Sr}^{2+}$  in the concentration range of 10–500 ppm.

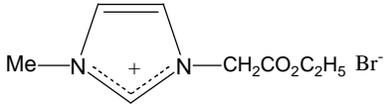
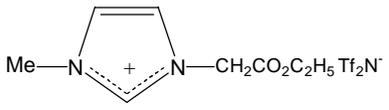
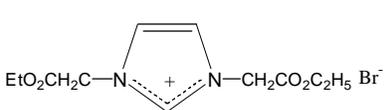
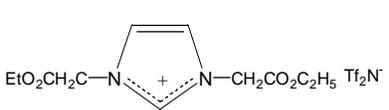
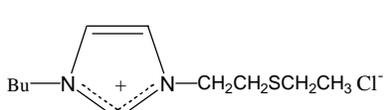
### Planned Activities

In the next 12 months, we will continue to refine our synthesis techniques to prepare more new ionic liquids. Extraction experiments with  $\text{Sr}^{2+}$  will be performed, and other crown ethers will also be tested. Study of electrochemistry of these ionic liquid system will be initiated.

Table 1. Extraction results with ionic liquids ( $\text{RMeIm}^+\text{Tf}_2\text{N}^-$ )

R in $\text{RMeIm}^+\text{Tf}_2\text{N}^-$	$D_{\text{Cs}}$ (with BoBCalix)	$D_{\text{Cs}}$ (without BoBCalix)
Ethyl-	9.1	0.84
Propyl-	12.6	0.58
Butyl-	13.8	0.024
Hexyl-	11.5	No extraction
Octyl-	8.1	No extraction

Table 2. Structures and NMR data of novel ionic liquids

Structures	Proton $^1\text{H}$ NMR	$^{13}\text{C}$ NMR
 <chem>CN1CCN(CCOC(=O)C)C1.[Br-]</chem>	1.29 (3H, t), 4.12 (3H, s) 4.25 (2H, q), 5.51 (2H, s) 7.71 (1H, s), 7.83 (1H, s) 10.08 (1H, s)	13.91 (CH <sub>3</sub> ), 38.40 (CH <sub>3</sub> ) 50.03 (CH <sub>2</sub> ), 62.63 (CH <sub>2</sub> ) 122.91 (CH), 123.67 (CH) 137.70 (CH), 165.75 (CO)
 <chem>CN1CCN(CCOC(=O)C)C1.[Tf2N-]</chem>	1.27 (3H, t), 3.85 (3H, s) 4.22 (2H, q), 4.95 (2H, s) 7.40 (2H, s), 8.48 (1H, s)	14.30 (CH <sub>3</sub> ), 37.08 (CH <sub>3</sub> ) 50.74 (CH <sub>2</sub> ), 63.36 (CH <sub>2</sub> ) 118.20 (CH), 124.37 (CH) 137.93 (CH), 166.97 (CO) 119.75 (CF <sub>3</sub> , q, coupling constant of C-F is 321 Hz)
 <chem>CCN1CCN(CCOC(=O)C)C1.[Br-]</chem>	1.29 (6H, t), 4.25 (4H, q) 5.41 (4H, s), 7.72 (2H, s) 9.98 (1H, s)	14.07 (CH <sub>3</sub> ), 50.46 (CH <sub>2</sub> ) 62.95 (CH <sub>2</sub> ), 123.30 (CH) 138.63 (CH), 165.84 (CO)
 <chem>CCN1CCN(CCOC(=O)C)C1.[Tf2N-]</chem>	1.29 (6H, t), 4.25 (4H, q) 5.02 (4H, s), 7.40 (2H, s) 8.95 (1H, s)	13.87 (CH <sub>3</sub> ), 50.16 (CH <sub>2</sub> ) 63.24 (CH <sub>2</sub> ), 123.31 (CH) 138.47 (CH), 165.35 (CO) 119.70 (CF <sub>3</sub> , q, coupling constant of C-F is 321 Hz)
 <chem>CCN1CCN(CCC)C1.[Cl-]</chem>	0.96 (3H, t), 1.24 (3H, s) 1.40 (2H, m), 1.92 (2H, m) 2.63 (2H, q), 3.09 (2H, t) 4.34 (2H, t), 4.65 (2H, t) 7.57 (1H, s), 7.86 (2H, t) 10.61 (1H, s)	13.17 (CH <sub>3</sub> ), 14.41 (CH <sub>3</sub> ) 19.14 (CH <sub>2</sub> ), 25.63 (CH <sub>2</sub> ) 31.82 (CH <sub>2</sub> ), 48.72 (CH <sub>2</sub> ) 49.49 (CH <sub>2</sub> ), 122.91 (CH) 122.68 (CH), 137.34 (CH)
 <chem>CCN1CCN(CCC)C1.[Tf2N-]</chem>	1.00 (3H, t), 1.27 (3H, s) 1.42 (2H, m), 1.90 (2H, m) 2.59 (2H, q), 2.99 (2H, t) 4.22 (2H, t), 4.42 (2H, t) 7.42 (1H, s), 7.47 (2H, t) 8.85 (1H, s)	13.07 (CH <sub>3</sub> ), 14.33 (CH <sub>3</sub> ) 19.14 (CH <sub>2</sub> ), 25.63 (CH <sub>2</sub> ) 31.48 (CH <sub>2</sub> ), 32.12 (CH <sub>2</sub> ) 49.05 (CH <sub>2</sub> ), 49.84 (CH <sub>2</sub> ) 122.24 (CH), 122.72 (CH), 135.54 (CH), 119.70 (CF <sub>3</sub> , q, coupling constant is 321 Hz)