Project Title: Fission-Product Separation Based on Room-Temperature Ionic Liquids (OR08SP24–16)

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Annual Progress Report:

Research Objective

The objectives of this project are (a) to synthesize new ionic liquids tailored for the extractive separation of Cs^{+} and Sr^{2+}; (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 second 12 months of a 3-year project. We have measured physical properties of several ionic liquids and the results are listed in Table 1. Extraction experiments using ionic liquids containing calix[4]arene-bis(*tert*-octylbenzo-crown-6) [BoBCalix6] have been extensively studied. The results are listed in Table 2. The selectivities of the Cs^{+} extraction based on ionic liquids have been investigated using aqueous solutions containing competitive Na^{+}, K^{+}, and Sr^{2+}. The selectivity coefficient for the extraction of Cs^{+} in the presence of competitor species can be obtained from the ratios of D_{Cs} values to the corresponding distribution coefficients of the competitive ions. Table 3 shows the results of competitive extraction of Cs^{+} in the presence of Na^{+}, K^{+}, and Sr^{2+}. As seen in the Table 3, the extraction distribution coefficients for Na^{+} and Sr^{2+} using BoBCalixC6 in C_4mim-Tf_2N are too small to be detected. Accordingly, the selectivity for extracting Cs^{+} in the presence of Na^{+} and Sr^{2+} is very high. The concomitant extraction of K^{+} along with Cs^{+} has been observed (see Table 3). The selectivity coefficients determined under various conditions are ~7.9 to ~43.9. Effects of different anions and addition of $NaBPh_4$ have also been studied. Table 4 shows the D_{Cs} values

as a function of the counteranions for Cs^+. From these data, it is clear that the distribution coefficients do not change much with different anions at lower concentrations of BoBCalixC6. This weak dependence of the D_{Cs} values can be partially rationalized by two models: (1) ion-exchange extraction and (2) similar anion solubilities in ionic liquids. Based on the ion-exchange model, only cations are involved in the extraction process. Accordingly, the counteranions have little effect on the D_{Cs} values. The rationalization of the observed weak dependence by the second model requires similar solvation properties of Cl^-, NO_3^-, and Ac^- in ionic liquids. Which factor is dominant is not clear from the present experiment.

Planned Activities

In the next 12 months, we will continue to do extraction experiments in order to select optimum macrocyclic extractants. We will try to develop an efficient process to recycle ionic liquids and crown ethers. We will continue to refine our synthesis techniques to prepare some new ionic liquids containing a crown ether fragment, which can be used both as an extractant and solvent. Extraction experiments using ionic liquids containing crown ethers with Sr^{2+} will be extensively investigated.

Information Access

Makote, R. D.; Luo, H.; Dai, S. "Synthesis of Ionic Liquid and Silica Composites Doped with Dicyclohexyl-18-crown-6 for Sequstration of Metal Ions", Clean Solvents, ACS Symposium Series 819: 26-33, 2002

Luo, H.; Dai S.; Bonnesen, P. V.; Buchanan, A. C. III, "Solvent Extraction of Cesium Nitrate by Room Temperature Ionic Liquids Containing Crown Ethers" Americal Chemical Society Meeting, Boston, August 20-25, 2002

Luo, H.; Dai S., "Solvent Extraction of Alkali and Alkaline Earth Metal Salts by Room Temperature Ionic Liquids Containing Crown Ethers" Americal Chemical Society Meeting, New Orleans, March 22-26, 2003

Luo, H.; Dai, S.; Bonnesen, P. V.; Rogers, R. D. "Extraction of Cesium Ions from Aqueous Solutions Using Calix[4]arene-bis(*tert*-octylbenzo-crown-6) in Ionic Liquids" in preparation.

Table 1. Densities, Solubilities in Water, and Water Contents of 1-Alkyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]-amide

R in Rmim -Tf_2N	Solubilities in water (g/100 mL)	Density (g/mL)		Water contents(ppm)	
		Dried	Wet	Dried	Water Solubility *
Ethyl, C2	1.77	1.5028	1.4561	350	19,361
Propyl, C3	1.16	1.4204	1.3922	312	17,475
Butyl, C4	0.80	1.4198	1.3882	240	13,613
Hexyl, C6	0.34	1.3329	1.2987	167	10,926
Octyl, C8	0.21	1.3074	1.2511	33	8,148

*1 mL of RTILs and 10 mL D.I. H_2O were shaken in a vibrating mixer for one hour.

Table 2. Extraction Results (D_{Cs}) with Ionic Liquids.
The initial aqueous concentration of Cs^+ is 2.5 H 10^{-3} M.

BobCalixC6 Concentration	R in Rmim-Tf_2N					$CHCl_3$
	Ethyl, C2	Propyl, C3	Butyl, C4	Hexyl, C6	Octyl, C8	
0	0.084	0.055	0.024	ud*	ud	ud
9.79×10^{-4} M	1.61	1.36	0.77	0.56	0.45	ud
3.37×10^{-3} M	4.68	3.90	3.67	3.20	2.50	ud
7.71×10^{-3} M	15.3	14.6	13.8	11.5	8.10	ud
1.36×10^{-2}M	nm**	137	131	57.4	17.9	0.034

*ud: undetectable; **nm: not measured because the concentration can not be reached.

Table 3. Extraction Selectivity Results with C_4mim- Tf_2N Containing BoBCalixC6. The initial concentration of each ion is 0.77 mM.

BoBCalixC6 Concentration	Aqueous phase	D_{Cs}	D_K	D_{Na}	D_{Sr}	D_{Cs}/D_K
9.79×10^{-4} M	Cs^++K^++ Na^+	122.7	15.6	~0	N/A	7.9
7.71×10^{-3} M	Cs^++K^++ Na^+	161.9	3.69	~0	N/A	43.9
	Cs^++K^+	118.4	2.75	N/A	N/A	43.1
	Cs^++K^++ Sr^{2+}	101.8	2.95	N/A	~0	34.5
	Cs^++ Sr^{2+}	285.0	N/A	N/A	~0	N/A
3.83×10^{-2} M	Cs^++ Sr^{2+}	524.6	N/A	N/A	~0	N/A

Table 4. Effect of Different Anions on Extraction Results of C_4mim-Tf_2N Containing BoBCalixC6 without and with $NaBPh_4$ (0.12 M).

BoBCalixC6 Concentration	7.71×10^{-3} M		1.0×10^{-2} M		1.38×10^{-2} M		2.0×10^{-2} M	
	Without $NaBPh_4$	With $NaBPh_4$	Without $NaBPh_4$	With $NaBPh_4$	Without $NaBPh_4$	With $NaBPh_4$	Without $NaBPh_4$	With $NaBPh_4$
$CsNO_3$	10.91	9.76	22.36	21.88	97.55	92.65	628.5	608.0
CsCl	12.17	11.37	22.60	22.60	75.33	66.60	956.4	939.5
CsAc	12.75	13.42	24.89	22.55	120.23	85.43	925.4	798.2