

Project Title: **Fission-Product Separation Based on Room-Temperature Ionic Liquids**
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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 Sr²⁺; (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 year of a 2-year project. A series of new hydrophobic and protic alkylammonium ionic liquids with bis(trifluoromethanesulfonyl)imide or bis(perfluoroethylsulfonyl)imide as conjugated anions were synthesized in a one-pot reaction with a high yield. The essence of our synthesis method involves the combination of neutralization and metathesis reactions. These new ionic liquids have been characterized by NMR and mass spectroscopy. The thermal properties of these ionic liquids have been investigated by thermogravimetric analysis (TGA). A number of these hydrophobic and protic ionic liquids were liquids at room temperature and therefore investigated as new extraction media for separation of Sr²⁺ and Cs⁺ from aqueous solutions. An excellent extraction efficiency was found for a number of these ionic liquids using dicyclohexano-18-crown-6 and calix[4]arene-bis(*tert*-octylbenzo-crown-6) as extractants. The observed enhancement in the extraction efficiency can be attributed to the greater hydrophilicity of the cations of the protic ionic liquids. The application of the protic ionic liquids as a new solvent system for solvent extraction opens up a new avenue in searching for simple and efficient ionic liquids for tailored separation processes.

Basic physical property data, including density and mutual solubilities with water, are shown in Table 1.

Table 1. Synthesis and physical properties of quaternary ammonium ionic liquids

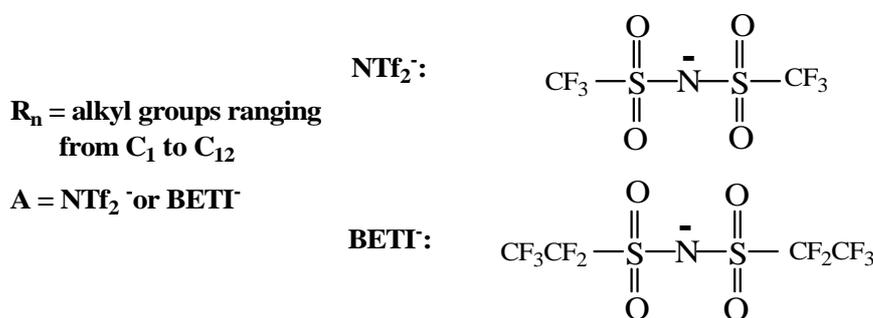
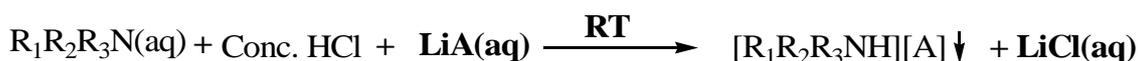
Molecular Formula	Synth. Yield (%)	MP (°C)	T _{onset} ^a (°C)	IL solubility in H ₂ O (mM)	Water content (ppm)	
					Dried	Wet ^b (*100)
[(CH ₃) ₂ (i-C ₃ H ₇)NH][NTf ₂]	94	NM ^c	360	153	219	319
[(CH ₃) ₂ (i-C ₃ H ₇)NH][BETI]	95	NM	340	31.2	193	241
[(CH ₃)(C ₂ H ₅) ₂ NH][NTf ₂]	93	NM	360	117	634	384
[(CH ₃)(C ₂ H ₅) ₂ NH][BETI]	97	NM	340	25.1	448	197
[(CH ₃) ₂ (n-C ₄ H ₉)NH][NTf ₂]	97	NM	360	87.3	284	346
[(CH ₃) ₂ (n-C ₄ H ₉)NH][BETI]	94	36	300	NM	NM	NM
[(C ₂ H ₅) ₃ NH][NTf ₂]	97	NM	360	95.7	453	278
[(C ₂ H ₅) ₃ NH][BETI]	97	NM	340	14.1	131	227
[(CH ₃)(n-C ₃ H ₇) ₂ NH][NTf ₂]	96	NM	350	20.6	530	136
[(CH ₃)(n-C ₃ H ₇) ₂ NH][BETI]	98	64	300	NM	NM	NM
[(C ₂ H ₅) ₂ (n-C ₄ H ₉)NH][NTf ₂]	94	NM	335	35.4	299	356
[(C ₂ H ₅) ₂ (n-C ₄ H ₉)NH][BETI]	96	NM	310	27.6	220	171
[(i-C ₃ H ₇) ₂ (C ₂ H ₅)NH][NTf ₂]	91	NM	350	52.9	220	217
[(i-C ₃ H ₇) ₂ (C ₂ H ₅)NH][BETI]	96	36	330	NM	NM	NM
[(n-C ₃ H ₇) ₃ NH][NTf ₂]	93	49	350	NM	NM	NM
[(n-C ₄ H ₉) ₃ NH][NTf ₂]	93	37	335	NM	NM	NM
[(i-C ₄ H ₉) ₃ NH][NTf ₂]	95	62	315	NM	NM	NM
[(n-C ₆ H ₁₃) ₃ NH][NTf ₂]	93	NM	345	37.0	429	130
[(n-C ₈ H ₁₇) ₃ NH][NTf ₂]	99	NM	360	19.6	232	116
[(CH ₃) ₂ (n-C ₁₂ H ₂₅)NH][NTf ₂]	98	NM	378	6.55	1396	191
[(n-C ₄ H ₉) ₂ NH ₂][NTf ₂]	92	62	310	NM	NM	NM
[(n-C ₆ H ₁₃) ₂ NH ₂][NTf ₂]	92	87	320	NM	NM	NM
[(n-C ₈ H ₁₇)NH ₃][NTf ₂]	95	NM	350	96.0	2285	631
[(n-C ₈ H ₁₇)NH ₃][BETI]	96	NM	325	17.9	608	173

^a T_{onset} : Onset decomposition temperature based on TGA measurement. ^b The water partition experiments were conducted by contacting 1 mL of ionic liquid with 10 mL of D.I. H₂O for one hour. ^c NM: Not measured.

Though a large number of quaternary tetraalkylammonium compounds (R₄N⁺) have been investigated as media for various applications ranging from electrochemistry to catalysis, few

trialkylammonium, dialkylammonium, and monoalkylammonium salts have been explored for similar purposes. The reaction used for synthesizing trialkylammonium compounds (R_3NH^+) used in our current study is illustrated in Scheme 1. The essence of this synthesis method is the combination of neutralization and metathesis reactions and thereby avoids the use of more expensive reagents (e.g. HTFSI). Similar combinational reactions were also employed to synthesize protic ILs based on dialkylammonium and monoalkylammonium.

Scheme 1



Twenty trialkylammonium (R_3NH^+), two dialkylammonium ($R_2NH_2^+$), and two monoalkylammonium (RNH_3^+) compounds were successfully synthesized in a high yield (Table 1). The melting points of the solid compounds (eight of them) were measured to all be below 100°C . The thermal properties of these ILs were investigated by thermogravimetric analysis (TGA). As seen from Table 1, these ILs are stable up to about 300°C , giving rise to wide liquidus temperature ranges. The thermal stabilities of these ILs seem to be essentially independent of the carbon chain length of alkyl groups on ammonium ions. However, there does appear to be a systematic correlation between the anion and the onset decomposition temperature of a specific IL. For the same cation, the ILs with BETI^- as the conjugate anion have slight lower thermal stabilities (20 degrees lower) than the ILs with NTf_2^- as the conjugate anion. This observation is unexpected, considering the structure and basicity similarities between BETI^- and NTf_2^- . As seen from Table 1, the solubilities of these protic ILs in aqueous phases are inversely proportional to the alkyl chain length, indicating that the hydrophobicity of the protic ILs with the same anion is dominated by the alkyl substituent groups. Accordingly, the hydrophobicity of the longer chain alkyl substituents should significantly reduce the solubilities of the resulting neutral salts in water. As also seen from Table 1, the solubilities of the protic ILs in water could be cut by two thirds through change of anions from NTf_2^- to BETI^- . The water contents of these protic ILs under dried conditions are comparable to those of aprotic imidazolium-based ILs. However, the water contents of the wet protic ILs (equilibrated with water phase for 1 hr) are considerably higher than those of aprotic imidazolium-based ILs, indicating that the cations of the former ILs are more hydrophilic than those of the latter ILs.

The viscosities of these protic ILs were measured at three different temperatures and are summarized in Table 2. The viscosities decrease appreciably when the temperatures increase from room temperature to 40°C and 100°C. There seems to be little correlation between the cation compositions of this series of the protic ILs and the viscosities measured. For ILs with shorter carbon chain length, they have the comparable viscosities with those of aprotic imidazolium-based ILs. As expected, the ILs with BETI⁺ are more viscous than the ILs with NTf₂⁻ for the same cations.

Table 2. Density and viscosity of ionic liquids

Molecular Formula	Molecular Weight	Density (g/mL)	Viscosity (cP)		
			23°C	40°C	100°C
[(CH ₃) ₂ (i-C ₃ H ₇)NH][NTf ₂]	368.3	1.42	67.72	29.93	6.194
[(CH ₃) ₂ (i-C ₃ H ₇)NH][BETI]	468.3	1.53	216.7	81.19	9.967
[(CH ₃)(C ₂ H ₅) ₂ NH][NTf ₂]	368.3	1.43	46.42	23.31	5.328
[(CH ₃)(C ₂ H ₅) ₂ NH][BETI]	468.3	1.51	159.4	64.66	8.924
[(CH ₃) ₂ (n-C ₄ H ₉)NH][NTf ₂]	382.3	1.39	55.69	25.97	5.246
[(C ₂ H ₅) ₃ NH][NTf ₂]	382.3	1.36	49.20	25.21	5.862
[(C ₂ H ₅) ₃ NH][BETI]	482.3	1.48	163.4	67.09	9.281
[(CH ₃)(n-C ₃ H ₇) ₂ NH][NTf ₂]	396.3	1.34	61.40	27.95	5.434
[(C ₂ H ₅) ₂ (n-C ₄ H ₉)NH][NTf ₂]	410.3	1.33	67.12	31.34	6.090
[(C ₂ H ₅) ₂ (n-C ₄ H ₉)NH][BETI]	510.3	1.42	158.4	64.28	8.773
[(i-C ₃ H ₇) ₂ (C ₂ H ₅)NH][NTf ₂]	410.3	1.32	191.7	77.82	10.88
[(n-C ₆ H ₁₃) ₃ NH][NTf ₂]	550.6	1.12	170.4	71.60	9.690
[(n-C ₈ H ₁₇) ₃ NH][NTf ₂]	634.7	1.06	219.3	89.43	11.74
[(CH ₃) ₂ (n-C ₁₂ H ₂₅)NH][NTf ₂]	494.5	1.17	158.6	63.87	8.767
[(n-C ₈ H ₁₇)NH ₃][NTf ₂]	410.3	1.32	331.4	125.0	14.20
[(n-C ₈ H ₁₇)NH ₃][BETI]	510.3	1.38	763.2	265.4	26.77

The Sr-extraction experiments based on the protic ILs were performed as single-species (i.e., noncompetitive) extractions from SrCl₂ aqueous solutions at five different acidities. Table 3 summarizes the Sr-extraction results under these five different acidic conditions. As seen in Table 3, the D_{Sr} values are inversely proportional to the alkyl (R₁, R₂, R₃) chain length on the corresponding ammonium cations. For example, the D_{Sr} value (0.418) of the [(n-C₈H₁₇)₃NH][NTf₂]-based extraction system is significantly less than that (12300) of the [(CH₃)(C₂H₅)₂NH][NTf₂] based extraction system under neutral conditions. This observation is again consistent with the previous results concerning the imidazolium-based IL extraction system reported previously. This trend can be again attributed to the synergistic effect of the ion-

exchange capability of the IL cations and the unique ionic solvation environment of the ILs for the charged macrocyclic complexes. The ammonium cations with long alkyl chains are more hydrophobic than those with short alkyl chains. Accordingly, both ion-exchange and solvation capabilities decrease with the alkyl chain length. The correlations between IL anions and D_{Sr} values are obvious and the ILs with BETI⁻ as anions give rise to much higher D_{Sr} values than the ILs with NTf₂⁻ as anions.

Table 3. Effects of acidities of aqueous solution on extraction efficiency of ionic liquids containing 0.10M DCH18C6

Molecular Formula	D_{Sr} at different pH conditions				
	1.5 mM SrCl ₂				
	D.I. H ₂ O	0.1 N HCl	0.2 N HCl	0.5 N HCl	1.0 N HCl
[(CH ₃) ₂ (<i>i</i> -C ₃ H ₇)NH][NTf ₂]	8460	613	282	106	55.7
[(CH ₃) ₂ (<i>i</i> -C ₃ H ₇)NH][BETI]	194000	911	369	129	66.9
[(CH ₃)(C ₂ H ₅) ₂ NH][NTf ₂]	12300	655	287	107	54.6
[(CH ₃)(C ₂ H ₅) ₂ NH][BETI]	229000	904	363	126	64.5
[(CH ₃) ₂ (<i>n</i> -C ₄ H ₉)NH][NTf ₂]	2520	193	90.2	35.5	20.0
[(C ₂ H ₅) ₃ NH][NTf ₂]	13800	571	270	104	53.9
[(C ₂ H ₅) ₃ NH][BETI]	159000	604	256	94.9	50.8
[(CH ₃)(<i>n</i> -C ₃ H ₇) ₂ NH][NTf ₂]	1750	128	62.1	25.1	14.7
[(C ₂ H ₅) ₂ (<i>n</i> -C ₄ H ₉)NH][NTf ₂]	870	82.3	34.4	17.6	10.6
[(C ₂ H ₅) ₂ (<i>n</i> -C ₄ H ₉)NH][BETI]	7520	107	49.6	21.3	13.4
[(<i>i</i> -C ₃ H ₇) ₂ (C ₂ H ₅)NH][NTf ₂]	2680	218	94.2	40.2	25.1
[(<i>n</i> -C ₆ H ₁₃) ₃ NH][NTf ₂]	0.810	0.268	0.280	0.313	0.398
[(<i>n</i> -C ₈ H ₁₇) ₃ NH][NTf ₂]	0.571	0.329	0.222	0.161	0.235
[(CH ₃) ₂ (<i>n</i> -C ₁₂ H ₂₅)NH][NTf ₂]	0.341	0.448	0.442	0.310	0.483

Planned Activities

With the continued support of the DOE-ERSP program, we will complete studies needed to turn the promising results achieved to date into advanced solvent systems that can be effectively employed for the separation of fission products from high-level tank wastes. The studies will be aimed at: (1) development of ionic liquid solvents that are stable in highly caustic solutions and which have enhanced extraction efficiency and selectivity for Sr²⁺ and Cs⁺, (2) synthesis of recyclable aza-substituted calixarene crown ethers for selective separation of Cs⁺ in ionic liquids and new task-specific regenerable *ionic liquids* tailored for the extractive separation of Sr²⁺, (3) investigation of sacrificial ion-exchange processes to enhance extraction efficiency and

reduce the loss of ionic liquids, (4)development of electrochemical regeneration of ionic liquids loaded with fission products for exceptional volume reduction, (5)investigation of the stabilities of ionic liquids under aggressive chemical and high-level radiation conditions. We believe that this work will lead to the discovery and development of a new and very versatile class of solvent systems that will improve processes for separation of fission products by reducing hazards and process complexity.

Information Access

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