

Separation of fission products based on ionic liquids: Task-specific ionic liquids containing an aza-crown ether fragment

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Abstract

A new class of task-specific ionic liquids (TSILs) based on the covalent attachment of imidazolium cations to a monoaza-crown ether fragment has been synthesized and characterized. The efficacy of these TSILs for the biphasic extraction of Cs⁺ and Sr²⁺ from aqueous solutions has been evaluated. The extraction properties of these TSILs can be influenced by the structures of the covalently attached imidazolium cations, which highlight the possibilities to enhance or tune the selectivities of crown ethers toward target ionic species through the covalent coupling with the imidazolium cations.

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1. Introduction

The applications of ionic liquids (ILs) as replacement solvents for various catalytic reactions and separation processes have been extensively explored [1–8]. The structure templates for the two most common classes of room-temperature ionic liquids are shown in Fig. 1. The cation is usually a heterocyclic cation, such as a dialkyl imidazolium ion or an *N*-alkylpyridinium ion. The relatively large size of these organic cations compared to simple inorganic cations accounts for the low melting points observed for these organic cations when paired with a variety of anions, such as BF₄[−], PF₆[−], CF₃SO₃[−], or other complex anions [1]. These ion pairs or salts are usually liquids from around −100 °C and are thermally stable to around 200 °C, depending on the specific structures of the anions and cations. Unlike conventional solvents currently in use, these ionic liquids are nonflammable, chemically tunable, and have no detectable vapor pressure [1].

We [4,5,9,10] and others [3,7,11–15] have been interested in the development of IL-based solvent extraction methods for the separation of fission products (e.g. Cs-137 and Sr-90). In

contrast to the high-temperature inorganic ionic liquids (molten salts), room-temperature ionic liquids can be made hydrophobic while retaining ionicity [16]. This dual property forms the basis for using room-temperature ionic liquids as unique separation media for the solvent extraction of ionic species. Large distribution coefficients (D_M) for the extraction of metal ions have been observed with ionic liquids containing complexing ligands [5]. For example, whereas conventional solvent extraction of Sr²⁺ using dicyclohexano-18-crown-6 can deliver practical D_M values of less than one, our experiments with ionic liquids as extraction solvents delivered values of D_M on the order of 10⁴ [5]. The enhanced distribution coefficients can be attributed to three major synergistic factors: (1) ion-recognition capabilities of complexing ligands; (2) unique ionic solvation environments provided by ILs for ionic species; (3) ion-exchange capabilities of ILs. The last factor has been revealed in detail by Dietz and Dzielawa [8].

More recently, Davis and co-workers [13,17] have introduced the term task-specific ionic liquids (TSILs) to describe ILs prepared using the concept of increasing the IL affinities of extractants toward a given target species through the incorporation of complexing functionalities as an integral part of ILs. Thus, a new class of ILs with strong extracting abilities can be prepared through the tailored modification of IL-cation structures via covalent attachment. For example, the ionic liquids

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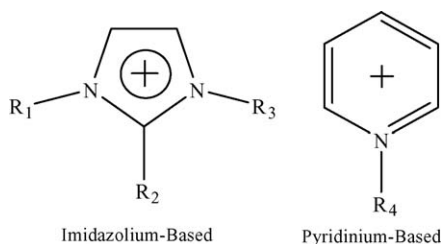


Fig. 1. Structures of two most common ionic liquid cations.

containing amine, thiol, and amide functional groups have been successfully prepared and evaluated for separation of metal ions [13] and CO₂ [18]. We have recently demonstrated that *N*-alkyl monoaza-crown ethers can be a highly effective class of ionophores for extraction of Sr²⁺ in ILs [10]. The protonation capability of the aza group provides a facile stripping methodology to recycle the ILs containing crown ethers. This success with the ionic liquids containing aza-crown ethers prompted us to investigate the possibilities to form TSILs with crown ethers covalently attached to imidazolium cations. Herein, we report the synthesis and characterization of four new TSILs containing an aza-crown ether fragment. These new TSILs can function as both extractants and solvents.

2. Experimental procedure

2.1. Materials and methods

All chemicals and solvents were reagent grade and used without further purification unless noted otherwise. Aqueous solutions were prepared using deionized water with a specific resistance of 18.0 MΩ-cm or greater. ¹H and ¹³C NMR spectra were obtained in CDCl₃ with a Bruker MSL-400 NMR spectrometer, operating at 400.13 MHz for proton and 100.61 MHz for carbon. Proton and carbon chemical shifts were reported relative to tetramethylsilane (TMS). The molecular weights were confirmed using a matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (Voyager DE MALDI-TOF). The matrices used are 4-nitroaniline (99%, Aldrich) and 2,5-dihydroxybenzoic acid (Sigma). Concentrations of Sr²⁺ were determined using a Dionex LC20 ion chromatograph equipped with an IonPac CS-12 analytical column.

2.2. Extraction experiments

The extraction experiments were performed in duplicate for each RTIL by contacting 1 mL of RTIL containing various concentrations of a specific extractant with 10 mL of cation-containing aqueous solution (1.5 mM) for 60 min in a vibrating mixer. After centrifugation, the upper aqueous phase was separated. The concentration of the corresponding cations was determined by ion chromatography.

2.3. Recycling experiments

The recycling experiments were conducted by adjusting the pH values of the extraction solutions with HCl solution (6N) to ~2 for the protonation of the monoaza-crown ethers. The mixture was subsequently agitated for 60 min in a vibrating mixer. After centrifugation, the upper aqueous phase was separated and its pH value was verified to remain ~2. The concentrations of the recovered cations were determined by ion chromatography. This IL phase could be reused in subsequent extraction experiments after the protonated monoaza-crown ethers were deprotonated by addition of a saturated LiOH solution into the extraction systems.

2.4. Synthesis of *N*-histamine aza-18-crown-6 ether (1)

Penta(ethylene glycol) dimesylate (6.42 g, 14.6 mmol), histamine dihydrochloride (2.70 g, 14.6 mmol), and sodium carbonate (15.5 g, 146 mmol) were mixed in acetonitrile. The mixture was heated at 80 °C for 3 days. The resulting cloudy solution was filtered and the solvent removed by rotary evaporation. The pure compound **1** (1.03 g, yield 20%) was obtained by purification with column chromatography [silica gel, hexane:acetone:Et₃N, R_f = 0.5 (acetone with 2% Et₃N)]. ¹H NMR: δ, 7.72 (s, 1H), 6.76 (s, 1H), 7.71 (s, 1H), 3.70–3.54 (m, 21H), and 2.74–2.70 (m, 8H). ¹³C NMR: δ, 135.21 (CH), 132.72 (CH), 122.67 (CH), 70.95 (CH₂), 70.25 (CH₂), 70.01 (CH₂), 69.39 (CH₂), 68.64 (CH₂), 54.37 (CH₂), 53.85 (CH₂), and 22.64 (CH₂). MS *m/z* (M⁺) Calcd. 357.20; found 357.67.

2.5. Synthesis of *N*-(1-imidazolepropyl) aza-18-crown-6 ether (2)

The same procedure for synthesizing compound **1** was used. From penta(ethylene glycol) dimesylate (4.56 g, 10.4 mmol) and 1-(3-aminopropyl)-imidazole (1.30 g, 10.4 mmol), compound **2** (0.53 g, yield 14%) was obtained by purification with column chromatography [silica gel, hexane:acetone:Et₃N, R_f = 0.5 (acetone with 2% Et₃N)]. ¹H NMR: δ, 7.55 (s, 1H), 6.98 (s, 1H), 6.97 (s, 1H), 4.08 (t, 2H, *J* = 6.80 Hz), 3.70–3.65 (m, 16H), 3.59 (t, 4H, *J* = 5.60 Hz), 2.72 (t, 4H, *J* = 5.60), 2.45 (t, 4H, *J* = 6.62 Hz), and 1.93 (t, 2H, *J* = 6.62 Hz). ¹³C NMR: δ, 137.38 (CH), 129.09 (CH), 118.82 (CH), 70.75 (CH₂), 70.61 (CH₂), 70.48 (CH₂), 70.21 (CH₂), 69.94 (CH₂), 69.51 (CH₂), 54.09 (CH₂), 53.81 (CH₂), 51.53 (CH₂), 44.18 (CH₂), 29.16 (CH₂), and 28.79 (CH₂). MS *m/z* (M⁺) Calcd. 371.20; found 370.87.

2.6. Synthesis of *N*-(*N,N*-diethyl)-histamonium aza-18-crown-6 ether bromide (TSIL 1)

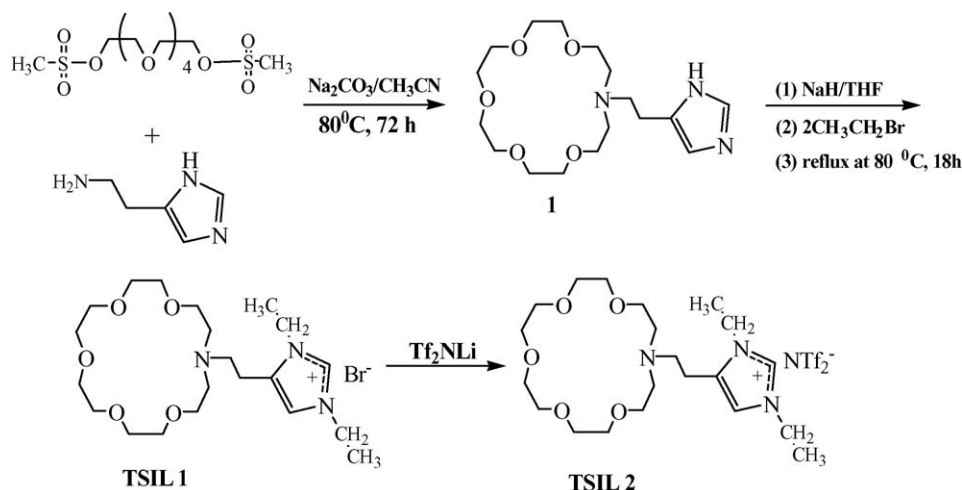
Compound **1** (750 mg, 2.1 mmol) in THF (4 mL) was added dropwise to 95% sodium hydride powder (53 mg, 95%, 2.1 mmol) in THF (3 mL) at 0 °C. The ice bath was removed and the mixture was stirred for 2 h at room temperature. Following dropwise addition of the ethyl bromide (500 mg, 4.5 mmol) at room temperature, the mixture was heated to reflux for 18 h. The precipitate was filtered and thoroughly rinsed with THF, followed by dichloromethane. The filtrate was evaporated in vacuum and the residue was rinsed with diethyl ether and dried under vacuum to give 0.93 g of TSIL 1 (1.88 mmol, 90%) as an oil. ¹H NMR: δ, 10.15 (s, 1H), 7.95 (s, 1H), 4.38 (m, 6H), 3.80–3.54 (m, 20H), 3.25 (m, 6H), and 1.63 (t, 6H, *J* = 7.32 Hz). ¹³C NMR: δ, 135.57 (CH), 119.49 (CH), 114.74 (CH), 70.43 (CH₂), 70.27 (CH₂), 69.84 (CH₂), 67.65 (CH₂), 66.25 (CH₂), 55.99 (CH₂), 44.58 (CH₂), 42.05 (CH₂), 25.31 (CH₂), and 16.07 (CH₃).

2.7. Synthesis of *N*-(*N,N*-diethyl)-histamonium aza-18-crown-6 ether bis[(trifluoromethyl)sulfonyl]imide (TSIL 2)

The TSIL 1 (930 mg, 1.88 mmol) was dissolved in 5 mL D.I. water and heated to 70 °C, and *N*-lithiotrifluoromethanesulfonylimide (540 mg, 1.88 mmol) was dissolved in 10 mL D.I. water and heated to 70 °C. The two solutions were combined and stirred to mix well. The resulting cloudy solution was cooled and then extracted with dichloromethane three times. The combined organic phases were washed four times successively with D.I. water to ensure that all the Li⁺ was removed. Evaporation of the solvent produced the TSIL 2 as a brown oil (815 mg, 62.3%). ¹H NMR: δ, 8.63 (s, 1H), 7.53 (s, 1H), 4.21 (m, 6H), 3.81–3.48 (m, 20H), 2.83 (m, 6H), and 1.53 (t, 6H, *J* = 7.34 Hz). ¹³C NMR: δ, 135.54 (CH), 119.86 (CH), 119.67 (CF₃, q, *J* = 321 Hz), 116.04 (CH), 70.58 (CH₂), 70.28 (CH₂), 69.42 (CH₂), 68.29 (CH₂), 67.59 (CH₂), 54.37 (CH₂), 44.83 (CH₂), 42.28 (CH₂), 21.20 (CH₂), and 14.88 (CH₃).

2.8. Synthesis of *N*-(3-butylimidazolium propyl) aza-18-crown-6 ether bromide (TSIL 3)

The compound **2** (380 mg, 1.02 mmol) and butyl bromide (690 mg, 5.03 mmol) mixed and stirred at room temperature for 24 h. The evaporation of excess butyl bromide gave 490 mg of TSIL 3 (0.97 mmol, 94%). ¹H NMR: δ, 9.85 (s, 1H), 7.92 (s, 1H), 7.74 (s, 1H), 4.61 (t, 2H, *J* = 6.44 Hz), 4.35 (t, 2H,



$J=7.38$ Hz), 3.77–3.55 (m, 20H), 2.72 (m, 4H), 2.15 (m, 2H), 1.91 (m, 2H), 1.40 (m, 2H), 1.25 (m, 2H), and 0.97 (t, 3H, $J=7.32$ Hz). ^{13}C NMR: δ , 137.47 (CH), 129.23 (CH), 118.87 (CH), 70.84 (CH₂), 70.69 (CH₂), 70.58 (CH₂), 70.31 (CH₂), 69.60 (CH₂), 54.21 (CH₂), 51.68 (CH₂), 49.12 (CH₂), 46.10 (CH₂), 44.62 (CH₂), 44.27 (CH₂), 31.25 (CH₂), 28.90 (CH₂), and 14.04 (CH₃).

2.9. Synthesis of *N*-(3-butylimidazolium propyl) aza-18-crown-6 ether bis[(trifluoromethyl)sulfonyl]imide (TSIL 4)

Using the same procedure as the synthesis of TSIL 2, 580 mg of TSIL 4 (0.83 mmol, 85%) was obtained from the TSIL 3 (490 mg, 0.97 mmol) and LiTf_2N (277 mg, 0.97 mmol). ^1H NMR: δ , 8.98 (s, 1H), 7.50 (s, 1H), 7.36 (s, 1H), 4.50 (t, 2H, $J=6.65$ Hz), 4.20 (t, 2H, $J=7.46$), 3.67–3.54 (m, 20H), 2.75 (m, 4H), 2.04 (m, 2H), 1.85 (m, 2H), 1.38 (m, 2H), 1.25 (m, 2H), and 0.96 (t, 3H, $J=7.36$ Hz). ^{13}C NMR: δ , 136.40 (CH), 122.64 (CH), 121.80 (CH), 119.60 (CF₃, q, $J=321$ Hz), 70.05 (CH₂), 69.78 (CH₂), 69.72 (CH₂), 69.54 (CH₂), 67.84 (CH₂), 54.88 (CH₂), 53.08 (CH₂), 49.25 (CH₂), 48.98 (CH₂), 47.38 (CH₂), 46.41 (CH₂), 31.77 (CH₂), 19.16 (CH₂), and 13.08 (CH₃).

3. Results and discussion

3.1. Synthesis

The task-specific ionic liquids containing the aza-crown ether fragment were synthesized in order to investigate the poten-

tial applications of these TSILs in the solvent extractions of both Cs^+ and Sr^{2+} . The concept of TSILs was originally proposed by Davis and co-workers [13]. The reactions used for synthesizing these TSILs are illustrated in Schemes 1 and 2. Precursor compounds **1** and **2** were synthesized by using a similar method developed by Gokel and co-workers for the synthesis of *N*-histamine aza-15-crown-5 [19]. The yields for TSIL precursor compounds **1** and **2** were low and the resulting products had to be purified by column chromatography. Both compounds contain a monoaza-18-crown-6 with the imidazole groups covalently attached. Based on these precursor compounds, four new TSILs containing the monoaza-crown ether fragment were synthesized in relative good yield through alkylation and metathesis reactions. The structural differences among these four TSILs lie in the imidazolium fragments and conjugated anions. TSIL 1 and 3 contain bromide as anions while the conjugate anions of TSIL 2 and 4 are bis[(trifluoromethyl)sulfonyl]imide (NTf_2^-). The latter two TSILs are considerably more hydrophobic than the formers and can form two phases in contact with water because of the enhanced hydrophobicity from NTf_2^- . TSIL 1 and 2 have the attachment of the monoaza-crown ether through position C(4) in imidazolium while the attachment position for TSIL 3 and 4 is N(3).

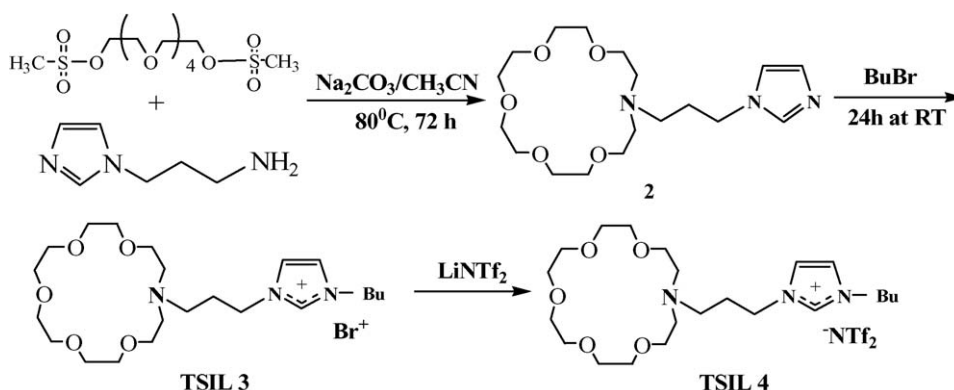


Table 1
Extraction results of TSILs in [C₄mim][NTf₂] and comparison with DCH18C6 and *N*-octylaza18C6

TSILs concentration in [C ₄ mim][NTf ₂] (M)	Aqueous phase (1.5 mM)	D_M			
		TSIL 2	TSIL 4	DCH18C6	<i>N</i> -octylaza18C6
0.02	CsCl	5.53	5.98	16.8	NM ^a
	SrCl ₂	22.9	9.06	74.1	NM
0.10	CsCl	14.5	23.9	380	25.7
	SrCl ₂	447	213	935	1070

^a NM: not measured.

Table 2
Recycling experimental results of [C₄mim][NTf₂] containing recyclable TSIL

TSIL concentration in [C ₄ mim][NTf ₂] (M)	TSIL	D_M in different aqueous phases (1.5 mM)			
		CsCl	+6N HCl (recovery) ^a	SrCl ₂	+6N HCl (recovery) ^a
0.02	2	5.53	1.36 (88)	22.9	0.79 (93)
	4	5.98	1.98 (84)	9.06	1.11 (90)
0.10	2	14.5	1.71 (85)	447	0.12 (99)
	4	23.9	1.77 (85)	213	0.47 (96)

Values in parentheses are in percent.

^a Calculated by following equation: recovery = C_s/C_i , where C_s and C_i represent concentration of M^{n+} stripped back from ILs phase and initial concentration of M^{n+} in aqueous phase.

3.2. Solvent extraction and recycling experimental results

Because of their limited quantities, the TSILs were only evaluated as extractants in a commonly used ionic liquid ([C₄mim][NTf₂]). The distribution coefficients (D_M) for extraction of M^{n+} are defined in Eq. (1) as:

$$D_M = \left\{ \frac{C_i - C_f}{C_f} \right\} \times \frac{\{\text{Volume of aqueous solution}\}}{\{\text{Volume of IL}\}} \quad (1)$$

where C_i and C_f represent the initial and final concentrations of M^{n+} in the aqueous phase. Although the value of D_M depends on the concentration of free extractants, the extraction trend reflected in D_M should be the same as that of the corresponding equilibrium constant for a given initial extractant concentration. A volume ratio is needed in calculation of distribution coefficients (Eq. (1)) to account for the difference in volume between two phases. Thus, a distribution ratio for M^{n+} greater than 1 ($D_M > 1$) represents an overall preference of M^{n+} to the IL phase. The values of D_M were measured in duplicate with uncertainty within 5%.

The extraction efficiencies of TSIL 2 and 4 in [C₄mim][NTf₂] have been investigated at two different concentrations and the results are listed in Table 1.

Experiments were performed with single species extractions, using either CsCl or SrCl₂. Table 1 compares the extraction results from four IL extraction systems with comparable extractant concentrations: (1) TSIL 2; (2) TSIL 4; (3) DCH18C6; (4) *N*-octylaza18C6 in [C₄mim][NTf₂]. The D_M values for TSIL 2 and 4 increase with the concentrations of TSIL 2 and 4, which is consistent with the extraction assisted through the complexation by TSIL 2 and 4. As seen from Table 1, the values of D_M for TSIL 2 and 4 are lower than those for DCH18C6 or *N*-

octylaza18C6. Both TSILs have similar extraction efficiency for Cs⁺ while TSIL 2 exhibits higher extraction efficiency for Sr²⁺ than TSIL 4. For Sr²⁺, the extraction capabilities follow the order of *N*-octylaza18C6 > DCH18C6 > TSIL 2 > TSIL 4. The order for the extraction of Cs⁺ is DCH18C6 > *N*-octylaza18C6 > TSIL 4 > TSIL 2. The reduction of the extraction capabilities for TSIL 2 and 4 in comparison with those of DCH18C6 and *N*-octylaza18C6 can be attributed to the cationic imidazolium groups in both compounds, which repel the binding of cationic species, such as Cs⁺ and Sr²⁺. As also seen from Table 1, TSIL 2 has a greater uptake for Sr²⁺ than TSIL 4. The reverse is true for the extraction of Cs⁺. This observation indicates that the binding capability of monoaza-crown ether can be remotely tuned through the substitution of the functional groups in the imidazolium groups. Accordingly, the covalent coupling between extractant and imidazolium groups has a synergistic effect on the selectivity of the corresponding extractant group.

As demonstrated previously, the key structural feature of monoaza-crown ethers is their facile stripping capability through the protonation reaction of the aza group. The stripping capabilities of TSIL 2 and 4 were evaluated by the protonation of the monoaza-crown ether with hydrochloric acid. The recycling experiments with TSIL 2 and 4 in [C₄mim][NTf₂] for extraction of metal ions from the aqueous solution containing CsCl and SrCl₂ were also conducted at two different concentrations. The experimental results are listed in Table 2. It is clear from the table that the recovery for Cs ion is around 85% while the recovery for Sr ion is around 92%. The recovery efficiencies for both systems are lower than the recovery efficiency for *N*-octyl monoaza-18-crown-6 in the same IL. The extraction efficiency for the latter system can normally reach more than 98% [10].

4. Conclusion

Four new task-specific ionic liquids containing a monoaza-crown ether fragment have been synthesized and characterized. Solvent extraction experiments indicated that these TSILs gave lower extraction efficiency than the IL extraction systems using DCH18C6 or *N*-octylaza18C6 as extractant. These decreased extraction efficiencies can be attributed to the coulombic repulsion from the covalently attached imidazolium cation. The recyclabilities of TSIL 2 and 4 are also inferior as compared with that of the IL extraction system containing *N*-octylaza18C6. The selectivity of these TSILs is dependent on the structure of substituents on the imidazolium ring.

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