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Solvent Extraction of Sr^{2+} and Cs^{+} Based on Room-Temperature Ionic Liquids Containing Monoaza-Substituted Crown Ethers

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A series of *N*-alkyl aza-18-crown-6 ethers were synthesized and characterized by NMR spectroscopy and mass spectrometry. These monoaza-substituted crown ethers in ionic liquids were investigated as recyclable extractants for separation of Sr^{2+} and Cs^{+} from aqueous solutions. The pH-sensitive complexation capability of these ligands allows for a facile stripping process to be developed so that both macrocyclic ligands and ionic liquids can be reused. The extraction efficiencies and selectivities of these monoaza-substituted crown ethers for Na^{+}, K^{+}, Cs^{+}, and Sr^{2+} were studied in comparison to those of dicyclohexano-18-crown-6 under the same conditions. The extraction selectivity order for dicyclohexano-18-crown-6 in the ionic liquids investigated here was $K^{+} \gg Sr^{2+} > Cs^{+} > Na^{+}$. The extraction selectivity order for *N*-alkyl aza-18-crown-6, in which the alkyl group is varied systematically from ethyl to *n*-dodecyl, was $Sr^{2+} \gg K^{+} > Cs^{+} > Na^{+}$ in 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]amide and 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]amide and $K^{+} > Sr^{2+} > Cs^{+} > Na^{+}$ in 1-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl] amide and 1-octyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]amide. The strong dependence of selectivity on the type of ionic liquid indicates an important role played by solvation in solvent extraction processes based on ionic liquids. The optimization of macrocyclic ligands and ionic liquids led to an extraction system that is highly selective toward Sr^{2+}.

The application of ionic liquids (ILs) as replacement solvents for various catalytic reactions and separation processes is being extensively explored.[1−11] Figure 1 gives the cationic structure templates of the two most common classes of ambient-temperature ionic liquids. The cation is usually a heterocyclic cation, such as a dialkylimidazolium 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 BF_4^-, PF_6^-, $CF_3SO_3^-$, or other complex anions. These ion pairs or salts can be liquids down to ∼−100 °C and are thermally stable to ∼200 °C, depending on the specific structures of the anions and cations. Unlike conventional solvents currently in use for solvent extaction applications, these ionic liquids are nonflammable, are chemically tunable, and have no detectable vapor pressure.

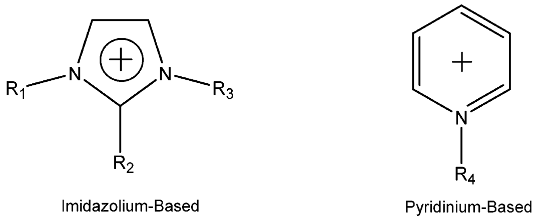

Figure 1. Structures of the two most common ionic liquid cations.

We[11] and others[5,7,10,12] have been interested in the development of IL-based solvent extraction methods for the separation of fission products. In contrast to the high-temperature inorganic molten salts, room-temperature ILs can be made hydrophobic while retaining ionicity.[12] This dual property forms the basis for using ILs as unique separation media for the solvent extraction of ionic species.[11] Large distribution coefficients (D_M) for the extraction of metal ions have been observed by ionic liquids containing complexing ligands.[7−11] For example, whereas conventional solvent extraction of Sr^{2+} using dicyclohexano-18-crown-6 can give

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practical D_M values of less than 1, our experiments[11] with ionic liquids as extraction solvents gave values of D_M on the order of 10^4. The enhanced distribution coefficients can be attributed to the unique solvation properties of ionic liquids for ionic species. Ion-exchange processes also play an important role as revealed by Dietz et al. and Visser et al. [7,10] However, the large D_M values observed for fission products using IL-based extraction processes make it very difficult to strip extracted metal ions, so that crown ethers could be recycled. Another drawback associated with all solvent extraction processes based on dicyclohexano-18-crown-6 for extraction of Sr^{2+} is the significant coextraction of K^+. The affinity of dicyclohexano-18-crown-6 toward K^+ is greater than that toward Sr^{2+}, limiting the direct application of dicyclohexano-18-crown-6 in removal of Sr^{2+} in nuclear wastes. These deficiencies associated with crown ether and IL-based extraction processes for metal ions prompted us to explore other macrocycle ligands, incorporating a switchable binding site. To allow stripping of cations for recycle of macrocycle extractants, we have synthesized several *N*-alkyl aza crown ethers where one of the oxygen atoms is replaced by an aza group. The aza group provides a pH switchable site for binding metal cations that can be readily achieved via protonation and deprotonation of the aza group.[13,14] The extraction abilities of these recyclable crown ethers and their comparison with dicyclohexano-18-crown-6 in ILs are presented here.

EXPERIMENTAL SECTION

Materials and Methods. All chemicals and solvents were reagent grade and used without further purification unless noted otherwise. Dicyclohexano-18-crown-6 (DCH18C6) was purchased from Aldrich and is a mixture of cis−syn−cis and cis−anti−cis isomers. Four 1-alkyl-3-methylimidazolium bis[(trifluoromethyl)-sulfonyl]amide ($[C_n\text{mim}][NTf_2]$) ionic liquids, in which the alkyl groups were ethyl (C_2), *n*-butyl (C_4), *n*-hexyl (C_6), and *n*-octyl (C_8), were synthesized by modified literature procedures[12] and the details are given in Supporting Information. The solubility of ILs in water was determined by combining 1 mL of IL and 10 mL of deionized (DI) water and shaking for 60 min in a vibrating mixer. A 0.5-mL aliquot of the aqueous phase was removed and diluted to 5 mL with DI water. The absorbance at 211 nm was measured using a Varian UV−visible−NIR spectrometer (model 5000).[8b] The solubility of each IL in water was calculated by the comparison of the measured absorbance with that obtained from dissolving a known amount (2−20 mg) of IL in 5 mL of DI water. The density of ILs was measured by filling a 1.0-mL volumetric flask to the mark with each IL and weighing. The water content of the ILs was measured using a Metronm 652 KF coulometer. These physical properties of the ILs are listed in Table 1. Aqueous solutions were prepared using DI water with a specific resistance of 18 MΩ·cm or greater. ^1H, ^{13}C, and ^{19}F NMR spectra were obtained in $CDCl_3$ with a Bruker MSL-400 NMR spectrometer, operating at 400.13 MHz for proton, 100.61 MHz for carbon, and 376.49 MHz for fluorine. Proton and carbon chemical shifts are reported relative to tetramethylsilane. Fluorine chemical shifts are reported relative to fluorotrichloromethane. The molecular weights of monoaza crown ethers were confirmed using a matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (Voyager DE MALDI-TOF). The matrixes used are 4-nitroaniline (99%, Aldrich) and 2,5-dihydroxybenzoic acid (Sigma). Concentrations of Na^+, K^+, Cs^+, and Sr^{2+} were determined using a Dionex LC20 ion chromatograph equipped with an IonPac CS-12 analytical column. In some cases, D_{Sr} values were verified by measuring strontium concentrations using inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Table 1. Solubilities in Water, Water Contents, and Densities of $[C_n\text{mim}][NTf_2]$

alkyl group in $[C_n\text{mim}][NTf_2]$	solubility in water (g/100 mL)	water content (ppm) dried	water content (ppm) wet[a]	density (g/mL) dried	density (g/mL) wet[a]
ethyl, C_2	1.77	350	19 400	1.50	1.46
butyl, C_4	0.80	240	13 600	1.42	1.39
$[C_4\text{mim}][PF_6]$[b]	2.46	513	20 700	1.37	1.35
hexyl, C_6	0.34	167	10 900	1.33	1.30
octyl, C_8	0.21	33	8 150	1.31	1.25

[a] One milliliter of RTIL and 10 mL of DI H_2O were shaken in a vibrating mixer for 1 h to maximize the water content of the IL. [b] $[C_4\text{mim}][PF_6]$ was purchased from Aldrich.

Extraction Experiments. The extraction experiments were performed in duplicate for each IL by contacting 1 mL of IL containing various concentrations of the 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 and the concentrations of cations were determined by ion chromatography. In order not to complicate the extraction systems, no buffer solution was added to control pH. The initial pH of all three aqueous solutions is 6.4. The final pH values of aqueous phases increase to 6.7 for the extraction system containing DCH18C6 but change to ∼11.2 for the systems containing recyclable monoaza crown ethers because of the basicity associated with monoaza crown ethers.

The distribution coefficients (D_M) for extraction of M^{n+} are defined in eq 1 as

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

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%.

Recycling Experiments. Following the extraction experiments, one drop of 6 N HNO_3 solution was added to the extraction systems to protonate the monoaza crown ethers and the pH value of the aqueous phase changed to 2.1. The mixture was agitated

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for 60 min again in a vibrating mixer. After centrifugation, the upper aqueous phase was separated, pH was checked to ensure that remained around 2, and the concentrations of the recovered cations were determined by ion chromatography. The IL phase was rinsed with DI H_2O several times until the aqueous phase was neutral. This IL phase could be reused in subsequent extraction experiments after the protonated monoaza crown ethers were deprotonated by addition of one drop of saturated LiOH solution into the extraction systems.

General Procedure for Synthesis of *N*-Alkyl Aza-18-crown-6 Ethers. The protocol for synthesizing monoaza-substituted crown ethers is based on the literature methodology.[15] Briefly, 1-aza-18-crown-6, primary alkyl halide, sodium carbonate (10 times of mole ratio of alkyl halide), and acetonitrile were mixed in a flask. The mixture was heated to reflux at 80 °C for 3 days. The resulting cloudy solution was filtered and the solvent removed by rotary evaporation. A copious amount of DI water was added to the residue, and the aqueous phase was extracted twice with dichloromethane. The organic phase was dried ($MgSO_4$) and the dichloromethane removed to afford the desired compound as a yellow oil.

***N*-Ethyl Aza-18-crown-6 (1).** From 1-aza-18-crown-6 (0.56 g, 2.13 mmol) and bromoethane (0.38 g, 3.49 mmol), 0.48 g (1.66 mmol) of *N*-ethyl aza-18-crown-6 was obtained (yield 78%): ^{1}H NMR δ, 3.86−3.60 (m, 20H), 2.76 (t, 4H, $J = 5.9$ Hz), 2.60 (q, 2H, $J = 7.1$ Hz), and 1.04 (t, 3H, $J = 7.1$ Hz); ^{13}C NMR δ, 70.83 (CH_2), 70.74 (CH_2), 70.37 (CH_2), 69.86 (CH_2), 53.35 (CH_2), 49.50 (CH_2), 49.24 (CH_2), and 11.89 (CH_3). The NMR data agree with those reported in the literature.[16] MS m/z (M^+) calcd 291.41, found 291.32.

***N*-Butyl Aza-18-crown-6 (2).** From 1-aza-18-crown-6 (0.59 g, 2.25 mmol) and 1-bromobutane (0.37 g, 2.70 mmol), 0.66 g (2.05 mmol) of *N*-butyl aza-18-crown-6 was obtained (yield 91%): ^{1}H NMR δ, 3.85−3.60 (m, 20H), 2.76 (t, 4H, $J = 5.9$ Hz), 2.49 (m, 2H), 1.45 (m, 2H), 1.42(m, 2H), and 0.92 (t, 3H, $J = 7.3$ Hz); ^{13}C NMR δ, 70.83 (CH_2), 70.74 (CH_2), 70.38 (CH_2), 69.90 (CH_2), 55.79 (CH_2), 54.01 (CH_2), 29.28 (CH_2), 20.61 (CH_2), and 14.05 (CH_3). The NMR data agree with those reported in the literature.[17] MS m/z (M^+) calcd 319.46, found 319.21.

***N*-Hexyl Aza-18-crown-6 (3).** From 1-aza-18-crown-6 (0.63 g, 2.37 mmol) and 1-bromohexane (0.45 g, 2.72 mmol), 0.54 g (1.69 mmol) of *N*-hexyl aza-18-crown-6 was obtained (yield 71%): ^{1}H NMR δ, 3.85−3.52 (m, 20H), 2.76 (t, 4H, $J = 5.9$ Hz), 2.48 (m, 2H), 1.42 (br peak, 2H), 1.30 (br peak, 6H), and 0.88 (t, 3H, $J = 7.1$ Hz); ^{13}C NMR δ, 70.81 (CH_2), 70.72 (CH_2), 70.35 (CH_2), 69.87 (CH_2), 55.10 (CH_2), 53.97 (CH_2), 31.77 (CH_2), 27.14 (CH_2), 27.03 (CH_2), 22.62 (CH_2), and 14.04 (CH_3). The NMR data agree with those reported in the literature.[18] MS m/z (M^+) calcd 347.52, found 347.08.

***N*-Octyl Aza-18-crown-6 (4).** From 1-aza-18-crown-6 (0.68 g, 2.59 mmol) and 1- bromoctane (0.67 g, 3.48 mmol), 0.79 g (2.11 mmol) of *N*-octyl aza-18-crown-6 was obtained (yield 82%): ^{1}H NMR δ, 3.86−3.67 (m, 16H), 3.62 (t, 4H, $J = 5.5$ Hz), 2.73 (t, 4H, $J = 5.5$ Hz), 2.52 (m, 2H), 1.44 (br peak, 2H), 1.27 (br peak, 10H), and 0.88 (t, 3H, $J = 7.0$ Hz); ^{13}C NMR δ, 70.46 (CH_2), 69.86 (CH_2), 69.58 (CH_2), 68.58 (CH_2), 55.05 (CH_2), 53.28 (CH_2), 31.59 (CH_2), 29.34 (CH_2), 29.03 (CH_2), 27.25 (CH_2), 26.20 (CH_2), 22.41 (CH_2), and 13.87 (CH_3). The NMR data agree with those reported in the literature.[19] MS m/z (M^+) calcd 375.56, found 375.11.

***N*-Dodecyl Aza-18-crown-6 (5).** From 1-aza-18-crown-6 (0.73 g, 2.78 mmol) and 1-bromododecane (0.70 g, 2.79 mmol), 0.93 g (2.15 mmol) of *N*-dodecyl aza-18-crown-6 was obtained (yield 77%): ^{1}H NMR δ, 3.79−3.63 (m, 16H), 3.60 (t, 4H, $J = 5.9$ Hz), 2.74 (t, 4H, $J = 5.7$ Hz), 2.50 (m, 2H), 1.25 (br peak, 20H), and 0.88 (t, 3H, $J = 7.0$ Hz); ^{13}C NMR δ, 70.76 (CH_2), 70.67 (CH_2), 70.30 (CH_2), 69.82 (CH_2), 56.04 (CH_2), 53.93 (CH_2), 33.95 (CH_2), 32.75 (CH_2), 31.83 (CH_2), 29.55 (CH_2), 29.27 (CH_2), 28.97 (CH_2), 28.68 (CH_2), 28.09 (CH_2), 27.42 (CH_2), 22.60 (CH_2), and 14.04 (CH_3). The NMR data agree with those reported in the literature. MS m/z (M^+) calcd 431.68, found 431.36.

***N*-Hexadecyl Aza-18-crown-6 (6).** From 1-aza-18-crown-6 (0.392 g, 1.49 mmol) and 1-bromohexadecane (0.45 g, 1.49 mmol), 0.66 g (1.35 mmol) of *N*-hexadecyl aza-18-crown-6 was obtained (yield 91%): ^{1}H NMR δ, 3.69−3.60 (m, 20H), 2.74 (t, 4H, $J = 5.9$ Hz), 2.50 (m, 2H), 1.43−1.19 (m, 28H), and 0.88 (t, 3H, $J = 7.0$ Hz); ^{13}C NMR δ, 70.77 (CH_2), 70.69 (CH_2), 70.32 (CH_2), 69.85 (CH_2), 56.05 (CH_2), 53.96 (CH_2), 49.14 (CH_2), 33.86 (CH_2), 32.75 (CH_2), 31.83 (CH_2), 29.59 (CH_2), 29.27 (CH_2), 28.68 (CH_2), 28.09 (CH_2), 27.41 (CH_2), 27.07 (CH_2), 22.59 (CH_2), and 14.03 (CH_3). The NMR data agree with those reported in the literature.[19] MS m/z (M^+) calcd 487.78, found 487.67.

***N*-(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl) Aza-18-crown-6 (7).** From 1-aza-18-crown-6 (0.30 g, 1.15 mmol) and 1*H*,1*H*,2*H*,2*H*-perfluorooctyl iodide (0.54 g, 1.15 mmol), 0.23 g (0.38 mmol) of *N*-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl) aza-18-crown-6 was obtained (yield 33%): ^{1}H NMR δ, 3.71−3.60 (m, 24H) and 2.90−2.70 (m, 4H); ^{13}C NMR δ, 70.55 (CH_2), 70.45 (CH_2), 70.26 (CH_2), 69.64 (CH_2), 58.49 (CF_3), 53.79 (CH_2), 49.14 (CH_2), 47.97 (CF_2), 46.65 (CF_2), and 28.71 (t, CH_2 next to CF_2); ^{19}F NMR δ, −79.85 (t, 3F), −112.97 (m, 2F), −120.98 (br peak, 2F), −121.93 (br peak, 2F), −122.55 (br peak, 2F), and −125.19 (m, 2F). The NMR data agree with those reported in the literature.[20]

***N*-(9-Anthracenylmethyl) Aza-18-crown-6 (8).** From 1-aza-18-crown-6 (0.152 g, 0.58 mmol) and 9-(chloromethyl)anthracene (0.13 g, 0.58 mmol), 0.22 g (0.49 mmol) of *N*-(9-methyl)anthracenyl aza-18-crown-6 was obtained (yield 85%): ^{1}H NMR δ, 8.55 (d, 2H, $J = 8.9$ Hz), 8.40 (s, 1H), 7.96 (d, 2H, $J = 8.8$ Hz), 7.49 (m, 4H), 4.58 (s, 2H), 3.68−3.57 (m, 20H), and 2.89 (t, 4H, $J = 5.7$ Hz); ^{13}C NMR δ, 131.25 (C), 130.39 (C), 128.74 (CH), 127.26 (CH), 127.06 (C), 125.37 (CH), 125.17 (CH), 124.65 (CH), 70.31 (CH_2), 70.65 (CH_2), 70.54 (CH_2), 70.06 (CH_2), 70.02 (CH_2), 53.75 (CH_2), and 51.91 (CH_2). The NMR data agree with those reported in the literature.[21] MS m/z (M^+) calcd 453.60, found 453.30.

RESULTS AND DISCUSSION

Synthesis. Syntheses of *N*-alkyl aza crown ethers have been previously investigated.[22−24] The typical synthesis in the literature

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Scheme 1

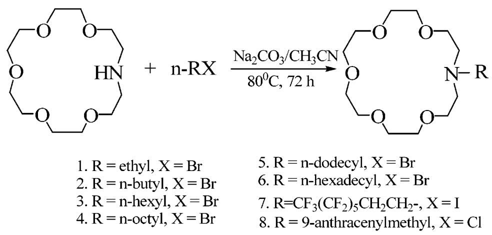

Table 2. Extraction Results of [C$_4$mim][NTf$_2$]Containing Recyclable *N*-Alkyl Aza-18-crown-6 (0.1 M)[a]

R substituents in *N*-alkyl aza-18-C6	D_M in different aqueous phases (1.5 mM)			
	CsNO$_3$	CsCl	Sr(NO$_3$)$_2$	SrCl$_2$
ethyl, C$_2$	2.68	2.48	56.0	55.8
butyl, C$_4$	14.1	13.7	333	381
hexyl, C$_6$	22.0	22.0	470	518
octyl, C$_8$	24.0	25.7	919	1070
dodecyl, C$_{12}$	30.8	30.5	793	982
hexadecyl, C$_{16}$	17.4	20.2	453	742
9-anthracenylmethyl	14.9	nm[b]	3.77	nm
fluorinated octyl	nm	17.5	129	215

[a] Single-species extraction. [b] nm, not measured.

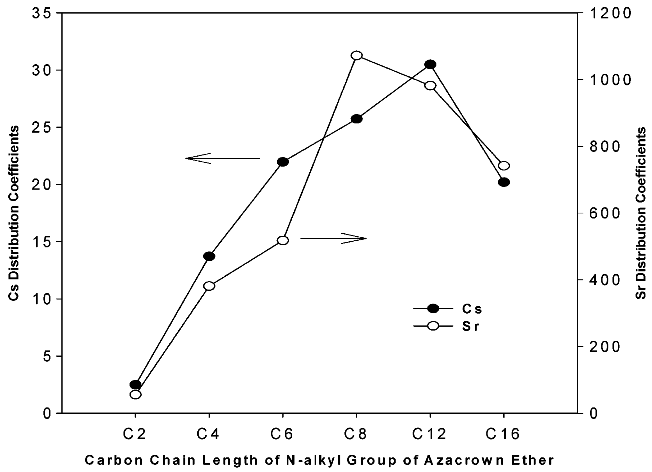

Figure 2. Effect of *N*-alkyl group variation of monoaza crown ethers on extraction efficiency of [C$_4$mim][NTf$_2$] containing *N*-alkyl aza-18-crown-6 (0.1M).

started with the alkylamine followed by several steps to reach the desired monoaza crown ethers. The reaction used for synthesizing recyclable monoaza crown ethers in this study is illustrated in Scheme 1. Eight monoaza crown ethers were successfully synthesized in good yield except for the fluorinated alkyl crown ether **7**. The basic reaction involves the alkylation of the monoaza group of 1-aza-18-crown-6. The hydrophobicity of the longer chain alkyl group substituents should significantly reduce the solubilities of the aza-substituted crown ethers in water.

Extraction Results of [C$_4$min][NTf$_2$] Containing Recyclable Extractants. The extraction results with eight monoaza-substituted crown ethers for Sr^{2+} and Cs^{+} are listed in Table 2. Figure 2 shows the variation of D_{Sr} as a function of the alkyl chain length on the aza group of crown ethers. As seen from Table 2 and Figure 2, the value of D_{Sr} increases as the alkyl chain length on the aza group of crown ethers increases, peaking with octyl substitution. This observation can be rationalized according to the hydrophobicity of the different alkyl-substituted crown ethers. The longer the alkyl chain, the less partitioning of the crown ethers to the aqueous phases. Therefore, the enhanced D_{Sr} values could be expected for the crown ethers with longer alkyl chains. D_{Sr} values as high as 1000 can be achieved with a concentration of 0.1 M *N*-octyl aza 18-crown-6 in [C$_4$mim][NTf$_2$], which is comparable to the extraction efficiency of DCH18C6 at the same condition.[10,11] However, the D_{Sr} values decrease slightly as the alkyl chain length on the aza group of crown ethers increases from C$_8$ to C$_{12}$ and C$_{16}$. This may be due to solubility problems associated with the latter compounds. We noticed that some cloudiness occurred when both *N*-dodecyl aza-18-crown-6 and *N*-hexadecyl aza-18-crown-6 were dissolved in [C$_4$mim][NTf$_2$]. Also, the extraction results for the anthracenyl-substituted crown (**8** in Scheme 1) and the fluorinated substituted crown (**7** in Scheme 1) gave relative lower distribution coefficients despite the high hydrophobicity of both substituents. This observation indicates that both aromatic and fluorinated substituents may significantly influence the binding capability of the monoaza-substituted crown ethers. Another point that can be seen from Table 2 is that the counteranions of metal cations have little influence on the values of both D_{Sr} and D_{Cs}. This weak dependence on the counteranions is reminiscent of the observation with DCH18C6-based IL systems[9] and can be rationalized with the ion-exchange model.[10] As seen from Table 2, D_{Cs} values are in the range of 2−30, whereas DCH18C6 gave a D_{Cs} value around 400 at the same conditions. Therefore, these monoaza-substituted crown ethers have lower extraction efficiency for Cs^{+} than DCH18C6.

Recycling Experimental Results. The cation-binding capabilities of monoaza-substituted crown ethers are extremely pH sensitive.[14] At low pH, the aza crown will be protonated, and the binding constant for metal cations will be severely reduced, relative to that of the neutral aza crown, due to charge repulsion. The binding affinity can accordingly be switched by varying the pH, with metal ion binding taking place at neutral or high pH, and metal ion release taking place at low pH. This switchable binding property forms the main rationale for us to develop IL-based separation processes using monoaza-substituted crown ethers. The basic recycling strategy for the monoaza-substituted crown ethers is summarized in Scheme 2. The recycling experiments with *N*-octyl aza-18-crown-6 (**4**) or *N*-(9-anthracenylmethyl) aza-18-crown-6 (**8**) in [C$_4$mim][NTf$_2$] for extraction of metal ions from the aqueous solution containing CsNO$_3$ or Sr(NO$_3$)$_2$ were conducted. The experimental results are listed in Table 3. It is clear from the table that more than 98% Cs or Sr cations were recovered in each case. The IL phases containing *N*-alkyl aza crown ethers could be reused for solvent extractions after deprotonation with a base. No significant changes of extraction efficiencies were observed, indicating that a stripping process based on monoaza crown ethers and ionic liquids is feasible. In addition, the NMR spectral results (see Supporting Information) indicated that the IL's NMR peaks did not change even after three cycles, though the aza crown ether's NMR peaks shifted to higher

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Scheme 2

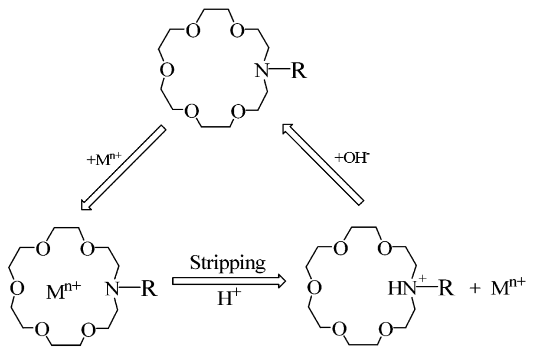

Table 3. Recycling Experimental Results of $[C_4mim][NTf_2]$ Containing Recyclable *N*-Alkyl Aza-18-crown-6 (0.1 M)

	D_M in different aqueous phases (1.5 mM)			
R substituents in *N*-alkyl aza-18-C6	$CsNO_3$	$+ 6$ N HNO_3 (recovery)[a]	$Sr(NO_3)_2$	$+ 6$ N HNO_3 (recovery)
octyl, C_8	24.0	0.096 (99.1%)	919	0.078 (99.2%)
9-anthracenylmethyl	14.9	0.115 (98.9%)	3.77	0.127 (98.7%)

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

Table 4. Effects of Different ILs on Extraction Efficiency of *N*-Alkyl Aza-18-crown-6 and Comparison with DCH18C6[a]

		D_M as a function of C_n in $[C_nmim][NTf_2]$			
concn of crown ethers in ILs	aqueous phase (1.5 mM)	ethyl, C_2	butyl, C_4	hexyl, C_6	octyl, C_8
0.02 M DCH18C6	CsCl	33.1	16.8	12.1	2.69
	$SrCl_2$	465	74.1	15.1	2.06
0.10 M DCH18C6	CsCl	589	380	66.0	8.35
	$SrCl_2$	10700[b]	935	82.2	3.95
0.10 M *N*-dodecyl	CsCl	45.5	30.5	19.4	6.66
aza-18-crown-6	$SrCl_2$	3840[b]	982	209	17.5
0.10 M N−octyl	CsCl	25.2	25.7	14.3	3.22
aza-18-crown-6	$SrCl_2$	8430[b]	1070	169	5.29
0.10 M N−hexyl	CsCl	24.4	22.0	14.3	4.31
aza-18-crown-6	$SrCl_2$	2900	518	135	4.47
0.10 M N−butyl	CsCl	17.4	13.7	6.59	2.74
aza-18-crown-6	$SrCl_2$	1000	381	26.0	2.47
0.10 M *N*-ethyl	CsCl	6.02	2.48	3.10	1.74
aza-18-crown-6	$SrCl_2$	799	55.8	5.62	0.38

[a] Single species extraction. [b] Determined by ICP-AE.

field because of protonation, implying that ILs are stable under these experimental conditions.

Effects of 1-Alkyl Group of ILs on Extraction Efficiency of *N*-Alkyl Aza-18-crown-6 and Their Comparison with DCH18C6. Table 4 shows the comparison of D_{Sr} and D_{Cs} for DCH18C6 and five *N*-alkyl aza-18-crown-6 in four different ILs. Experiments were performed with single-species extractions, using either $SrCl_2$ or CsCl solution. The distribution coefficients for both Sr and Cs increase with the decrease of the alkyl chain length in ILs. Such dependence can be attributed to the ion-exchange capability of the corresponding cations of a specific IL. It is also clear from Table 4 that both D_{Sr} and D_{Cs} greatly increase with the concentration of DCH18C6 in the ILs, reflecting the important role played by the extractant. The D_{Sr} values obtained using *N*-alkyl aza-18-crown-6 in different ILs exhibit the same trend. In fact, the extraction efficiencies for Sr^{2+} for the IL systems containing DCH18C6 and *N*-alkyl aza-18-crown-6 are very similar. For instance, as can be seen from Table 4, *N*-octyl aza-18-crown-6 gave D_{Sr} values of 8430 in $[C_2mim\text{-}][NTf_2]$ and 1070 in $[C_4mim]\text{-}[NTf_2]$, which are comparable to 10 700 in $[C_2mim][NTf_2]$ and 935 in $[C_4mim][NTf_2]$ for the corresponding DCH18C6-based system. Accordingly, the extractive strength of *N*-octyl aza-18-crown-6 for Sr^{2+} in ILs is very similar to that of DCH18C6.

Table 5. Extraction Results of $[C_nmim][NTf_2]$ Containing No Crown Ethers[a]

	D_M as a function of C_n in $[C_nmim][NTf_2]$			
distribution coefficient	ethyl, C_2	butyl, C_4	hexyl, C_6	octyl, C_8
D_{Na}	0.66	0.14	ne[b]	ne
D_K	1.30	0.48	0.58	ne
D_{Cs}	2.08	0.065	0.098	ne
D_{Sr}	ne	0.45	0.24	ne

[a] Competitive extractions for four metal cations. [b] ne, no extraction.

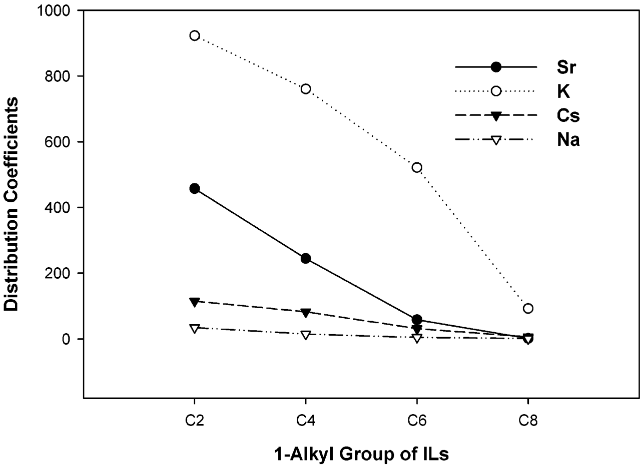

Figure 3. Effect of 1-alkyl group variation of ILs on efficiency of competitive metal cation extraction from aqueous solutions by DCH18C6 (0.1 M) in $[C_nmim][NTf_2]$.

Competitive Solvent Extraction of Four Metal Chlorides by *N*-Alkyl Aza-18-crown-6 and Their Comparison with DCH18C6. Bartsch and co-workers reported very interesting results[9] in which the effect of varying the alkyl group in $[C_nmim]\text{-}[PF_6]$ on the efficiency and selectivity of competitive extraction of five alkali metal cations by DCH18C6 was reported. The reason we chose $[C_nmim][NTf_2]$ instead of $[C_nmim][PF_6]$ in our study is that the water solubilities of $[C_nmim][NTf_2]$ are significantly lower than those of $[C_nmim][PF_6]$ and the former IL system is more stable than the latter IL system.[1] In a similar vein, we wanted to understand the extraction efficiency of four metal chlorides by ionic liquids alone, and thus, solvent extraction experiments using aqueous solutions containing 2.5 mM of Na^+ and K^+ and 0.5 mM of Cs^+ and Sr^{2+} were performed with no crown ethers in ILs. As can be seen from the results listed in Table 5, the extraction efficiency with ILs alone is very limited and most distribution

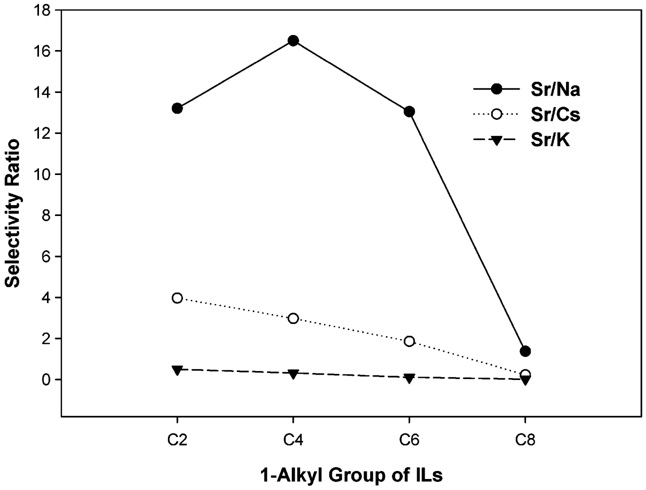

Figure 4. Effect of 1-alkyl group variation of ILs on Sr^{2+}/Na^+, Sr^{2+}/Cs^+, and Sr^{2+}/K^+ selectivities in competitive metal cation extraction from aqueous solutions by DCH18C6 (0.1 M) in $[C_n mim][NTf_2]$.

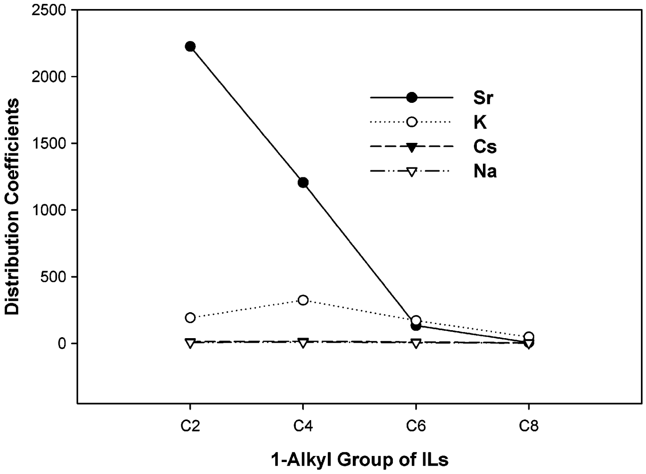

Figure 5. Effect of 1-alkyl group variation of ILs on efficiency of competitive metal cation extraction from aqueous solutions by *N*-octyl aza-18-crown-6 (0.1M) in $[C_n mim][NTf_2]$.

coefficients are less than 1. Such partitions are mainly induced by the ion-exchange process. This observation indicates that the enhanced extraction of the target metal ions is mainly through the complexation reactions of the macrocyclic ligands.

The extraction results for the competitive solvent extraction of the aqueous solution with DCH18C6 in four ILs are illustrated in Figure 3. (The data are corrected for the levels of metal cations that are extracted by the ILs alone). As can be seen from Figure 3, there is a smooth decrease in the extraction efficiency for each metal cation as the carbon chain length in ILs increases. Figure 4 shows the influence of varying the carbon chain length of ILs on the selectivities of Sr^{2+}/Na^+, Sr^{2+}/Cs^+, and Sr^{2+}/K^+ for competitive extraction by DCH18C6 based in Figure 3. With the exception of Sr^{2+}/Na^+ in $[C_2mim][NTf_2]$, the Sr^{2+}/Na^+, Sr^{2+}/Cs^+, and Sr^{2+}/K^+ selectivities decrease as the 1-alkyl group of ILs is lengthened. The order of extraction efficiency is $K^+ \gg Sr^{2+} > Cs^+ > Na^+$ in all four ionic liquids. This observation is consistent with the reported results[9] for $[C_n mim][PF_6]$. The high extraction efficiency for K^+ significantly hampers the applications of these systems for extraction of Sr^{2+} in the presence of K^+.

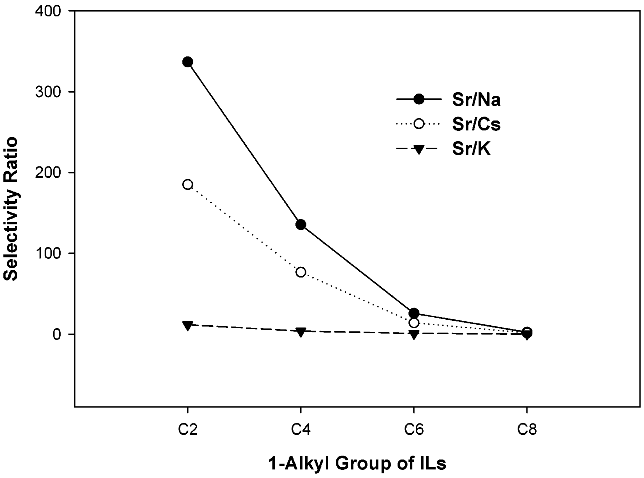

Figure 6. Effect of 1-alkyl group variation of ILs on Sr^{2+}/Na^+, Sr^{2+}/Cs^+, and Sr^{2+}/K^+ selectivities in competitive metal cation extraction from aqueous solutions by *N*-octyl aza-18-crown-6 (0.1M) in $[C_n mim][NTf_2]$.

Table 6. Selectivity Results of $[C_n mim][NTf_2]$ Containing *N*-Dodecyl Aza-18-crown-6 (0.1 M)[a]

	D_M as a function of C_n in $[C_n mim][NTf_2]$			
distribution coefficient or selectivity ratio	ethyl, C_2	butyl, C_4	hexyl, C_6	octyl, C_8
D_{Na}	11.01	7.74	3.84	1.66
D_K	849	282	126	57.1
D_{Cs}	17.6	14.3	8.01	4.09
D_{Sr}	7446[b]	2600[b]	129	12.3
D_{Sr}/D_{Na}	673	336	33.5	7.40
D_{Sr}/D_K	8.76	9.21	1.02	0.215
D_{Sr}/D_{Cs}	424	182	16.1	3.00

[a] Competitive extractions for four metal cations. [b] Determined by ICP-AES.

Table 7. Selectivity Results of $[C_n mim][NTf_2]$ Containing *N*-Hexyl Aza-18-crown-6 (0.1 M)[a]

	D_M as a function of C_n in $[C_n mim][NTf_2]$			
distribution coefficient or selectivity ratio	ethyl, C_2	butyl, C_4	hexyl, C_6	octyl, C_8
D_{Na}	8.74	9.64	3.95	1.38
D_K	273	396	187	45.2
D_{Cs}	17.4	13.5	8.46	3.64
D_{Sr}	1985	852	90.9	4.13
D_{Sr}/D_{Na}	227	88.4	23.0	2.99
D_{Sr}/D_K	7.27	2.15	0.487	0.091
D_{Sr}/D_{Cs}	114	63.2	10.8	1.13

[a] Competitive extractions for four metal cations.

The results for competitive extraction of the same aqueous solutions with *N*-octyl aza-18-crown-6 in the same four ILs are shown in Figure 5. With the exception of D_K value for $[C_4mim][NTf_2]$, extraction efficiency for each metal cation decreases as the carbon chain length in ILs increases. The key change from the selectivity order of the DCH18C6 system is that the order of extraction efficiency is $Sr^{2+} \gg K^+ > Cs^+ > Na^+$ for the *N*-octyl aza-18-crown-6 extraction systems based on $[C_2mim][NTf_2]$ and $[C_4mim][NTf_2]$. This observation clearly demonstrates the advan-

Table 8. Selectivity Results of $[C_n\mathrm{mim}][\mathrm{NTf}_2]$ Containing *N*-Butyl Aza-18-crown-6 (0.1 M)[a]

distribution coefficient or selectivity ratio	D_M as a function of C_n in $[C_n\mathrm{mim}][\mathrm{NTf}_2]$			
	ethyl, C_2	butyl, C_4	hexyl, C_6	octyl, C_8
D_{Na}	7.04	2.34	1.42	ne[b]
D_K	184	87.8	72.0	23.4
D_{Cs}	13.2	7.09	4.84	1.50
D_{Sr}	1510	157	23.8	3.19
D_{Sr}/D_{Na}	214	67.1	16.8	n/a[c]
D_{Sr}/D_K	8.17	1.79	0.33	0.136
D_{Sr}/D_{Cs}	115	22.1	4.91	2.13

[a] Competitive extractions for four metal cations. [b] ne, no extraction. [c] n/a, not applicable.

Table 9. Selectivity Results of $[C_n\mathrm{mim}][\mathrm{NTf}_2]$ Containing *N*-Ethyl Aza-18-crown-6 (0.1 M)[a]

distribution coefficient or selectivity ratio	D_M as a function of C_n in $[C_n\mathrm{mim}][\mathrm{NTf}_2]$			
	ethyl, C_2	butyl, C_4	hexyl, C_6	octyl, C_8
D_{Na}	1.15	0.271	ne[b]	0.932
D_K	42.5	24.2	11.0	7.20
D_{Cs}	2.10	0.124	0.28	ne
D_{Sr}	271	46.5	3.99	1.20
D_{Sr}/D_{Na}	235	172	n/a[c]	1.28
D_{Sr}/D_K	6.38	1.92	0.363	0.166
D_{Sr}/D_{Cs}	129	376	14.3	n/a

[a] Competitive extractions for four metal cations. [b] ne, no extraction. [c] n/a, not applicable.

tage of using *N*-alkyl aza-18-crown-6 for extraction of Sr^{2+} based on ILs on the presence of other competitive cations. Interestingly, the order of extraction efficiency is the same as that ($K^+ > Sr^{2+} > Cs^+ > Na^+$) of DCH18C6 for the *N*-octyl aza-18-crown-6 extraction systems based on $[C_6\mathrm{mim}][\mathrm{NTf}_2]$ and $[C_8\mathrm{mim}][\mathrm{NTf}_2]$. The reversal of the extraction efficiency for Sr^{2+} and K^+ induced by the variation of the IL cations further demonstrates the strong role played by ILs in determining not only distribution coefficients but also orders of the selectivities. Such an effect is unusual in solvent extractions based on conventional solvents. Figure 6 shows the influence of varying the carbon chain length of ILs on the Sr^{2+}/Na^+, Sr^{2+}/Cs^+, and Sr^{2+}/K^+ for competitive metal cation extraction by *N*-octyl aza-18-crown-6. The Sr^{2+}/Na^+, Sr^{2+}/Cs^+, and Sr^{2+}/K^+ selectivities increase as the carbon chain length in ILs decreases. For $[C_2\mathrm{mim}][\mathrm{NTf}_2]$, a Sr^{2+}/Na^+ selectivity of more than 300 can be achieved. Similar trends were observed for other four *N*-alkyl aza-18-crown-6, where the alkyl groups are *n*-dodecyl, *n*-hexyl, *n*-butyl, and ethyl. The results are summarized in Tables 6−9. For the most part, D_{Sr}/D_K is relatively constant in a given IL as the alkyl chain on the aza crown is varied.

CONCLUSION

The synthesis and characterization of eight *N*-alkyl aza-18-crown-6 ethers were reported. The extraction efficiency and selectivity of these monoaza-substituted crown ethers in ionic liquids have been studied with comparison to DCH18C6. These monoaza-substituted crown ethers have lower extraction efficiency for Cs than DCH18C6. However, *N*-octyl aza-18-crown-6 has a comparable extraction efficiency for Sr by DCH18C6. The extraction selectivity order for DCH18C6 in all four ILs was $K^+ \gg Sr^{2+} > Cs^+ > Na^+$. The extraction selectivity order for *N*-octyl aza-18-crown-6 was $Sr^{2+} \gg K^+ > Cs^+ > Na^+$ in $[C_2\mathrm{mim}][\mathrm{NTf}_2]$ and $[C_4\mathrm{mim}][\mathrm{NTf}_2]$. Our recycling experiments clearly indicated that a stripping process based on monoaza crown ethers and ionic liquids is feasible. These observations demonstrated that the extraction systems based on *N*-alkyl aza-18-crown-6 in ILs offer not only easier recycling strategy but also better selectivity toward Sr^{2+}.

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