Solvent Extraction of Sr^{2+} and Cs^{+} Based on Hydrophobic Protic Ionic Liquids

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A series of new hydrophobic and protic alkylammonium ionic liquids with bis(trifluoromethylsulfonyl)imide or bis(perfluoroethylsulfonyl)imide as conjugated anions was synthesized in a one-pot reaction with a high yield. In essence our synthesis method involves the combination of neutralization and metathesis reactions. Some of these hydrophobic and protic ionic liquids were liquids at room temperature and therefore investigated as new extraction media for separation of Sr^{2+} and Cs^{+} from aqueous solutions. An excellent extraction efficiency was found for some 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 new solvent systems for solvent extraction opens up a new avenue in searching for simple and efficient ionic liquids for tailored separation processes.

Key words: Protic Ionic Liquids; Solvent Extraction; Crown Ethers.

1. Introduction

Ionic liquids (ILs) have recently been demonstrated to be highly effective solvents for solvent extraction of metal ions based on macrocyclic extractants [1 – 16]. In comparison with conventional molecular solvents, ILs exhibit enhanced distribution ratios (D_M values) when using certain complexing neutral ligands as extractants for metal ions from aqueous solutions [1, 17]. Such enhancements can be attributed to three major fundamental factors: 1.) ion-recognition capabilities of complexing ligands [1], 2.) unique ionic solvation environments provided by ILs for ionic species [1, 10, 18], and 3.) ion-exchange abilities of ILs [4, 6]. The most commonly studied class of ILs for separation applications is based on dialkylimidazolium cations, which are aprotic in nature and formed by transfer of an alkyl (or equivalent) group, usually through an S_N2 reaction [19, 20]. Another type of ILs, which gains popularity in the applications related to fuel cells, is protic in nature [21 – 25]. These protic ILs are formed by proton transfer between Brønsted acids and bases.

For our continuing interest in the development of new solvent extraction methods based on ILs for separation of fission products from high level wastes [1, 26, 27], we describe herein the application of protic ILs in the solvent extraction of metal ions with crown ethers. Some new alkylammonium ILs were synthesized in a one-pot reaction with a high yield. Watanabe and coworkers [21, 22] have recently reported a straightforward synthesis of protic ILs by a neutralization reaction of a wide variety of organic amines with superacids [e. g. hydrogen bis(trifluoromethylsulfonyl)amide (HTFSI)] under solvent-free conditions. The one-pot synthesis we have developed involves the neutralization of an alkylamine with a common acid (e. g. HCl), which is followed by a metathesis reaction of the resulting ammonium salt with lithium bis(trifluoromethylsulfonyl)imide or lithium bis(perfluoroethylsulfonyl)imide in an aqueous solution [28, 29]. Accordingly, the more expensive acid precursor (e. g. HTFSI) can be avoided.

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2. Experimental

2.1. 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. Calix[4]arene-bis(*tert*-octylbenzo-crown-6) (BOBCalixC6) was obtained from IBC Advanced Technologies (American Fork, UT) and used as received (97% stated purity). The loss of ILs in water was determined by combining 1 mL of IL and 10 mL deionized (D. I.) water and shaking for 60 min in a vibrating mixer. The solubility of each IL in water was calculated by measuring the concentration of the corresponding IL cations in the aqueous phase with NMR spectroscopy. The density of ILs was measured by filling a 1.0 mL volumetric flask to the mark with each IL and weighing [27]. The water content of the ILs was measured using a Metrohm 652 KF coulometer. The synthesis yields of these ILs and their physical properties are summarized in Table 1. Aqueous solutions were prepared using D. I. water with a specific resistance of 18 MΩ cm or greater. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ with a Bruker MSL-400 NMR spectrometer operating at 400.13 MHz for proton and 100.61 MHz for carbon. The proton and carbon chemical shifts are reported relative to tetramethylsilane (TMS). The molecular weights of some ILs were confirmed using electrospray mass spectra, which were obtained with a Thermo-Finnigan PolarisQ® Ion-Trap mass spectrometer (Austin, TX) modified with the addition of a Thermo-Finnigan Deca® electrospray ion source. The concentrations of Cs^+ and Sr^{2+} were determined using a Dionex LC20 ion chromatograph equipped with an IonPac CS-12 analytical column. In some cases, the distribution coefficients for Sr^{2+} were also verified by measuring the strontium concentrations using inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

2.2. 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.

The distribution coefficients (D_M) for extraction of M^{n+} are defined as [26, 27]

$$D_M = \left\{ \frac{(C_i - C_f)}{(C_f)} \right\} \times \frac{V_{AS}}{V_{IL}}, \qquad (1)$$

where C_i and C_f represent the initial and final concentrations of M^{n+} in the aqueous phase, and V_{AS} is the volume of the aqueous solution and V_{IL} the volume of the IL. Although 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 the calculation of distribution coefficients in (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%.

2.3. General Procedure for the Synthesis of Quaternary Tri-, Di-, and Monoalkylammonium Ionic Liquids

The protocol for synthesizing these ILs is based on the combination of neutralization and the metathesis methodology [28, 29]. Briefly, organic amines and either lithium bis(trifluoromethylsulfonyl)imide ($LiNTf_2$) or lithium bis(perfluoroethylsulfonyl)imide (LiBETI) dissolved in D. I. water were mixed in equal molar ratios in flasks at room temperature. To each of these mixtures, a slight excess amount of conc. HCl was added. The resulting IL layers formed immediately following the addition of acid. The reaction is quite exothermic. The lower layers (IL) were separated from the aqueous phase and washed with D. I. H_2O four times to ensure the removal of LiCl. The final products were dried under vacuum at 70 °C for 4 h.

N,N-Dimethylisopropylammonium bis(trifluoromethylsulfonyl)imide ***(1)***. From *N,N*-dimethylisopropylamine (5.94 g, 0.068 mol), $LiNTf_2$ (19.57 g, 0.068 mol) in D. I. H_2O (10 mL), and conc. HCl (37%, 7.5 g, 0.076 mol), 23.4 g (0.064 mol) of $[(CH_3)_2(i\text{-}C_3H_7)NH][NTf_2]$ were obtained as a colorless liquid (yield 94%). – ^{1}H NMR: $\delta = 7.16$ (broad peak, 1H), 3.52 (m, 1H), 2.82 (d, 6H, $J = 5.05$ Hz), 1.36 (d, 6H, $J = 6.54$ Hz). – ^{13}C NMR: $\delta = 119.51$ (CF_3, q,

J_{C-F} = 320.6 Hz), 59.23 (CH), 39.64 (CH_3), 16.13 (CH_3). – MS: *m/z* = calcd. 368.23, found 368.04 [M^+].

*N,N-Dimethylisopropylammonium bis(perfluoroethylsulfonyl)imide (**2**).* From *N,N*-dimethylisopropylamine (3.48 g, 0.040 mol), LiBETI (15.45 g, 0.040 mol) in D. I. H_2O (8 mL), and conc. HCl (37%, 4.84 g, 0.049 mol), 17.66 g (0.038 mol) of [$(CH_3)_2$(*i*-C_3H_7)NH][BETI] were obtained as a colorless liquid (yield 95%). – ^{1}H NMR: δ = 7.04 (broad peak, 1H), 3.46 (m, 1H), 2.76 (d, 6H, J = 5.05 Hz), 1.29 (d, 6H, J = 6.54 Hz). – ^{13}C NMR: δ = 117.71 (CF_3, qt, J_{C-F} = 287.4 Hz, J_{C-C-F} = 33.2 Hz), 111.16 (CF_2, tq, J_{C-F} = 293.8 Hz, J_{C-C-F} = 38.9 Hz), 59.25 (CH_2), 39.50 (CH_3), 15.88 (CH_3). – MS: *m/z* = calcd. 468.23, found 467.84 [M^+].

*N,N-Diethylmethylammonium bis(trifluoromethylsulfonyl)imide (**3**).* From *N,N*-diethylmethylamine (4.46 g, 0.051 mol), $LiNTf_2$ (14.68 g, 0.051 mol) in D. I. H_2O (7 mL), and conc. HCl (37%, 6.17 g, 0.063 mol), 17.41 g (0.047 mol) of [$(CH_3)(C_2H_5)_2$NH][NTf_2] were obtained as a colorless liquid (yield 93%). – ^{1}H NMR: δ = 7.07 (broad peak, 1H), 3.23 (m, 4H), 2.84 (d, 3H, J = 5.3 Hz), 1.37 (t, 3H, J = 7.30 Hz). – ^{13}C NMR: δ = 119.55 (CF_3, q, J_{C-F} = 320.6 Hz), 51.34 (CH_2), 39.18 (CH_3), 8.87 (CH_3). – MS: *m/z* = calcd. 368.23, found 367.93 [M^+].

*N,N-Diethylmethylammonium bis(perfluoroethylsulfonyl)imide (**4**).* From *N,N*-diethylmethylamine (3.65 g, 0.042 mol), LiBETI (16.22 g, 0.042 mol) in D. I. H_2O (8 mL), and conc. HCl (37%, 5.0 g, 0.051 mol), 18.88 g (0.040 mol) of [$(CH_3)(C_2H_5)_2$NH][BETI] were obtained as a colorless liquid (yield 96%). – ^{1}H NMR: δ = 6.93 (broad peak, 1H), 3.16 (m, 4H), 2.78 (s, 3H), 1.32 (t, 3H, J = 7.34 Hz). – ^{13}C NMR: δ = 117.56 (CF_3, qt, J_{C-F} = 287.4 Hz, J_{C-C-F} = 33.3 Hz), 111.55 (CF_2, tq, J_{C-F} = 293.8 Hz, J_{C-C-F} = 39.0 Hz), 58.62 (CH_2), 43.49 (CH_3), 26.21 (CH_2), 19.33 (CH_2), 13.12 (CH_3). – MS: *m/z* = calcd. 468.23, found 468.03 [M^+].

*N,N-Dimethylbutylammonium bis(trifluoromethylsulfonyl)imide (**5**).* From *N,N*-dimethylbutylamine (6.67 g, 0.066 mol), $LiNTf_2$ (18.92 g, 0.066 mol) in D. I. H_2O (10 mL), and conc. HCl (37%, 7.52 g, 0.076 mol), 24.52 g (0.064 mol) of [$(CH_3)_2$(*n*-C_4H_9)NH][NTf_2] were obtained as a colorless liquid (yield 97%). – ^{1}H NMR: δ = 7.24 (broad peak, 1H), 3.12 (m, 2H), 2.91 (s, 6H), 1.70 (m, 2H), 1.42 (m, 2H), 0.98 (t, 3H, J = 7.34 Hz). – ^{13}C NMR: δ = 119.60 (CF_3, q, J_{C-F} = 320.6 Hz), 58.52 (CH_2), 43.45 (CH_3), 26.20 (CH_2), 19.19 (CH_2), 12.99 (CH_3). – MS: *m/z* = calcd. 382.23, found 382.02 [M^+].

*N,N-Dimethylbutylammonium bis(perfluoroethylsulfonyl)imide (**6**).* From *N,N*-dimethylbutylamine (4.53 g, 0.045 mol), LiBETI (17.34 g, 0.045 mol) in D. I. H_2O (8 mL), and conc. HCl (37%, 4.80 g, 0.049 mol), 20.25 g (0.042 mol) of [$(CH_3)_2$(*n*-C_4H_9)NH][BETI] were obtained as a white solid (yield 94%). – ^{1}H NMR: δ = 7.56 (broad peak, 1H), 3.06 (m, 2H), 2.87 (s, 6H), 1.68 (m, 2H), 1.38 (m, 2H), 0.96 (t, 3H, J = 7.34 Hz). – ^{13}C NMR: δ = 117.79 (CF_3, qt, J_{C-F} = 287.7 Hz, J_{C-C-F} = 33.3 Hz), 111.64 (CF_2, tq, J_{C-F} = 294.2 Hz, J_{C-C-F} = 39.1 Hz), 58.62 (CH_2), 43.49 (CH_3), 26.21 (CH_2), 19.33 (CH_2), 13.12 (CH_3). – MS: *m/z* = calcd. 482.23, found 482.33 [M^+].

*Triethylammonium bis(trifluoromethylsulfonyl)imide (**7**).* From triethylamine (3.75 g, 0.037 mol), $LiNTf_2$ (10.6 g, 0.037 mol) in D. I. H_2O (5 mL), and conc. HCl (37%, 3.94 g, 0.040 mol), 13.73 g (0.036 mol) of [$(C_2H_5)_3$NH][NTf_2] were obtained as a colorless liquid (yield 97%). – ^{1}H NMR: δ = 6.92 (broad peak, 1H), 3.21 (m, 6H), 1.41 (t, 9H, J = 7.33 Hz). – ^{13}C NMR: δ = 119.66 (CF_3, q, J_{C-F} = 320.7 Hz), 47.22 (CH_2), 8.437 (CH_3). – MS: *m/z* = calcd. 382.23, found 382.20 [M^+].

*Triethylammonium bis(perfluoroethylsulfonyl)imide (**8**).* From triethylamine (5.15 g, 0.051 mol), LiBETI (19.7 g, 0.051 mol) in D. I. H_2O (10 mL), and conc. HCl (37%, 5.42 g, 0.055 mol), 23.97 g (0.050 mol) of [$(C_2H_5)_3$NH][BETI] were obtained as a colorless liquid (yield 97%). – ^{1}H NMR: δ = 7.14 (broad peak, 1H), 3.17 (m, 6H), 1.32 (t, 9H, J = 7.23 Hz). – ^{13}C NMR: δ = 116.66 (CF_3, qt, J_{C-F} = 287.5 Hz, J_{C-C-F} = 32.9 Hz), 115.66 (CF_2, tq, J_{C-F} = 293.7 Hz, J_{C-C-F} = 38.9 Hz), 47.17 (CH_2), 8.381 (CH_3). – MS: *m/z* = calcd. 482.23, found 482.40 [M^+].

*N-Methyldipropylammonium bis(trifluoromethylsulfonyl)imide (**9**).* From *N*-methyldipropylamine (4.11 g, 0.036 mol), $LiNTf_2$ (10.23 g, 0.036 mol) in D. I. H_2O (5 mL), and conc. HCl (37%, 4.10 g, 0.042 mol), 13.48 g (0.034 mol) of [(CH_3)(*n*-$C_3H_7)_2$NH][NTf_2] were obtained as a colorless liquid (yield 96%). – ^{1}H NMR: δ = 6.18 (broad peak, 1H), 3.07 (m, 4H), 2.86 (s, 3H), 1.76 (m, 4H), 1.06 (t, 6H, J = 7.33 Hz). – ^{13}C NMR: δ = 119.55 (CF_3, q, J_{C-F} = 320.7 Hz), 58.22 (CH_2), 40.27 (CH_3), 17.38 (CH_2), 10.29 (CH_3). – MS: *m/z* = calcd. 396.28, found 395.85 [M^+].

*N-Methyldipropylammonium bis(perfluoroethylsulfonyl)imide (**10**).* From *N*-methyldipropylamine

(3.21 g, 0.028 mol), LiBETI (10.78 g, 0.028 mol) in D. I. H_2O (5 mL), and conc. HCl (37%, 3.05 g, 0.031 mol), 13.47 g (0.040 mol) of $[(CH_3)(n\text{-}C_3H_7)_2NH][BETI]$ were obtained as a white solid (yield 98%). – ^1H NMR: $\delta = 7.14$ (broad peak, 1H), 3.08 (m, 4H), 2.84 (s, 3H), 1.76 (m, 4H), 1.00 (t, 6H, $J = 7.35$ Hz). – ^{13}C NMR: $\delta = 117.82$ (CF_3, qt, $J_{C-F} = 287.8$ Hz, $J_{C-C-F} = 33.3$ Hz), 111.64 (CF_2, tq, $J_{C-F} = 294.2$ Hz, $J_{C-C-F} = 39.0$ Hz), 58.26 (CH_2), 40.38 (CH_3), 17.34 (CH_2), 10.36 (CH_3). – MS: *m/z* = calcd. 496.28, found 496.40 $[M^+]$.

*N,N-Diethylbutylammonium bis(trifluoromethylsulfonyl)imide (**11**).* From *N,N*-diethylbutylamine (7.82 g, 0.061 mol), $LiNTf_2$ (17.37 g, 0.061 mol) in D. I. H_2O (8 mL), and conc. HCl (37%, 6.78 g, 0.069 mol), 23.39 g (0.057 mol) of $[(C_2H_5)_2(n\text{-}C_4H_9)NH][NTf_2]$ were obtained as a yellow liquid (yield 94%). – ^1H NMR: $\delta = 7.24$ (broad peak, 1H), 3.22 (m, 4H), 3.05 (m, 2H), 1.68 (m, 2H), 1.44 (m, 2H), 1.38 (m, 6H), 0.97 (t, 3H, $J = 7.33$ Hz). – ^{13}C NMR: $\delta = 119.60$ (CF_3, q, $J_{C-F} = 320.8$ Hz), 52.10 (CH), 47.53 (CH_2), 25.37 (CH_2), 19.65 (CH_2), 13.25 (CH_3), 8.479 (CH_3). – MS: *m/z* = calcd. 410.31, found 409.74 $[M^+]$.

*N,N-Diethylbutylammonium bis(perfluoroethylsulfonyl)imide (**12**).* From *N,N*-diethylbutylamine (3.92 g, 0.030 mol), LiBETI (11.75 g, 0.030 mol) in D. I. H_2O (6 mL), and conc. HCl (37%, 3.35 g, 0.034 mol), 14.88 g (0.029 mol) of $[(C_2H_5)_2(n\text{-}C_4H_9)NH][BETI]$ were obtained as a yellow liquid (yield 96%). – ^1H NMR: $\delta = 6.78$ (broad peak, 1H), 3.22 (m, 4H), 3.06 (m, 2H), 1.67 (m, 2H), 1.42 (m, 2H), 1.36 (m, 6H), 0.97 (t, 3H, $J = 7.31$ Hz). – ^{13}C NMR: $\delta = 117.79$ (CF_3, qt, $J_{C-F} = 287.5$ Hz, $J_{C-C-F} = 33.3$ Hz), 111.57 (CF_2, tq, $J_{C-F} = 294.0$ Hz, $J_{C-C-F} = 38.9$ Hz), 53.16 (CH_2), 47.78 (CH_2), 25.34 (CH_2), 19.47 (CH_2), 12.97 (CH_3), 8.301 (CH_3). – MS: *m/z* = calcd. 510.31, found 509.93 $[M^+]$.

*N,N-Diisopropylethylammonium bis(trifluoromethylsulfonyl)imide (**13**).* From *N,N*-diisopropylethylamine (5.75 g, 0.044 mol), $LiNTf_2$ (12.78 g, 0.044 mol) in D. I. H_2O (6 mL), and conc. HCl (37%, 4.72 g, 0.048 mol), 16.6 g (0.040 mol) of $[(i\text{-}C_3H_7)_2(C_2H_5)NH][NTf_2]$ were obtained as a colorless liquid (yield 91%). – ^1H NMR: $\delta = 6.61$ (broad peak, 1H), 3.68 (m, 2H), 3.18 (m, 2H), 1.41 (m, 15H). – ^{13}C NMR: $\delta = 119.63$ (CF_3, q, $J_{C-F} = 320.8$ Hz), 55.42 (CH), 43.45 (CH_2), 18.37 (CH_3), 16.87 (CH_3), 12.59 (CH_3). – MS: *m/z* = calcd. 410.31, found 410.02 $[M^+]$.

*N,N-Diisopropylethylammonium bis(perfluoroethylsulfonyl)imide (**14**).* From *N,N*-diisopropylethylamine (6.54 g, 0.051 mol), LiBETI (19.59 g, 0.051 mol) in D. I. H_2O (10 mL), and conc. HCl (37%, 5.52 g, 0.056 mol), 24.77 g (0.049 mol) of $[(i\text{-}C_3H_7)_2(C_2H_5)NH][BETI]$ were obtained as a white solid (yield 96%). – ^1H NMR: $\delta = 6.56$ (broad peak, 1H), 3.66 (m, 2H), 3.18 (m, 2H), 1.48 (m, 15H). – ^{13}C NMR: $\delta = 117.71$ (CF_3, qt, $J_{C-F} = 287.5$ Hz, $J_{C-C-F} = 33.3$ Hz), 115.66 (CF_2, tq, $J_{C-F} = 294.2$ Hz, $J_{C-C-F} = 39.0$ Hz), 55.46 (CH), 43.47 (CH_2), 18.36 (CH_3), 16.87 (CH_3), 12.51 (CH_3). – MS: *m/z* = calcd. 510.31 $[M^+]$, not measured.

*Tripropylammonium bis(trifluoromethylsulfonyl)imide (**15**).* From tripropylamine (5.09 g, 0.035 mol), $LiNTf_2$ (10.19 g, 0.035 mol) in D. I. H_2O (5 mL), and conc. HCl (37%, 3.74 g, 0.038 mol), 14.0 g (0.033 mol) of $[(n\text{-}C_3H_7)_3NH][NTf_2]$ were obtained (yield 93%). – ^1H NMR: $\delta = 6.88$ (broad peak, 1H), 3.08 (m, 6H), 1.76 (m, 6H), 1.01 (t, 9H, $J = 7.34$ Hz). – ^{13}C NMR: $\delta = 119.55$ (CF_3, q, $J_{C-F} = 320.8$ Hz), 54.93 (CH_2), 16.99 (CH_2), 10.40 (CH_3). – MS: *m/z* = calcd. 424.33, found 424.22 $[M^+]$.

*Tributylammonium bis(trifluoromethylsulfonyl)imide (**16**).* From tributylamine (6.47 g, 0.035 mol), $LiNTf_2$ (10.1 g, 0.035 mol) in D. I. H_2O (5 mL), and conc. HCl (37%, 3.74 g, 0.038 mol), 15.2 g (0.033 mol) of $[(n\text{-}C_4H_9)_3NH][NTf_2]$ were obtained (yield 93%). – ^1H NMR: $\delta = 6.89$ (broad peak, 1H), 3.09 (m, 6H), 1.68 (m, 6H), 1.39 (m, 6H), 0.98 (t, 9H, $J = 7.30$ Hz). – ^{13}C NMR: $\delta = 119.57$ (CF_3, q, $J_{C-F} = 320.9$ Hz), 53.17 (CH_2), 25.35 (CH_2), 19.58 (CH_2), 13.20 (CH_3). – MS: *m/z* = calcd. 466.42 $[M^+]$, not measured.

*Triisobutylammonium bis(trifluoromethylsulfonyl)imide (**17**).* From triisobutylamine (8.91 g, 0.048 mol), $LiNTf_2$ (13.79 g, 0.048 mol) in D. I. H_2O (7 mL), and conc. HCl (37%, 5.22 g, 0.053 mol), 21.23 g (0.045 mol) of $[(i\text{-}C_4H_9)_3NH][NTf_2]$ were obtained (yield 95%). – ^1H NMR: $\delta = 5.80$ (broad peak, 1H), 3.07 (m, 6H), 2.14 (m, 3H), 1.07 (d, 18H, $J = 6.64$ Hz). – ^{13}C NMR: $\delta = 119.68$ (CF_3, q, $J_{C-F} = 320.8$ Hz), 62.31 (CH), 23.93 (CH_2), 20.10 (CH_3). – MS: *m/z* = calcd. 466.42, found 466.13 $[M^+]$.

*Trihexylammonium bis(trifluoromethylsulfonyl)imide (**18**).* From trihexylamine (6.86 g, 0.025 mol), $LiNTf_2$ (7.31 g, 0.025 mol) in D. I. H_2O (4 mL), and conc. HCl (37%, 3.17 g, 0.032 mol), 13.0 g (0.023 mol) of $[(n\text{-}C_6H_{13})_3NH][NTf_2]$ were obtained (yield 93%). – ^1H NMR: $\delta = 6.28$ (broad peak, 1H), 3.09 (m, 6H), 1.68 (m, 6H), 1.34 (m, 18H), 0.90 (t, 9H, $J = 6.53$ Hz). – ^{13}C NMR: $\delta = 119.58$ (CF_3, q, $J_{C-F} = 321.0$ Hz), 53.48 (CH_2), 30.86 (CH_2), 25.87 (CH_2), 23.43 (CH_2), 22.12 (CH_2), 13.57 (CH_3). – MS: *m/z* = calcd. 550.57 [M^+], not measured.

*Trioctylammonium bis(trifluoromethylsulfonyl)imide (**19**).* From trioctylamine (7.91 g, 0.022 mol), $LiNTf_2$ (6.31 g, 0.022 mol) in D.I. H_2O (3 mL), and conc. HCl (37%, 2.36 g, 0.024 mol), 13.21 g (0.021 mol) of $[(n\text{-}C_8H_{17})_3NH][NTf_2]$ were obtained (yield 99%). – ^{1}H NMR: $\delta = 5.80$ (broad peak, 1H), 3.05 (m, 6H), 1.67 (m, 6H), 1.29 (m, 30H), 0.89 (t, 9H, $J = 6.84$ Hz). – ^{13}C NMR: $\delta = 119.63$ (CF_3, q, $J_{C-F} = 320.8$ Hz), 53.20 (CH_2), 31.57 (CH_2), 29.25 (CH_2), 28.89 (CH_2), 26.41 (CH_2), 23.35 (CH_2), 22.52 (CH_2), 13.99 (CH_3). – MS: *m/z* = calcd. 634.74, found 634.24 [M^+].

*N,N-Dimethyldodecylammonium bis(trifluoromethylsulfonyl)imide (**20**).* From *N,N*-dimethyldodecylamine (6.70 g, 0.031 mol), $LiNTf_2$ (9.01 g, 0.031 mol) in D.I. H_2O (5 mL), and conc. HCl (37%, 5.13 g, 0.052 mol), 15.22 g (0.0308 mol) of $[(CH_3)_2(n\text{-}C_{12}H_{25})NH][NTf_2]$ were obtained (yield 98%). – ^{1}H NMR: $\delta = 5.80$ (broad peak, 1H), 3.09 (m, 3H), 2.89 (s, 6H), 1.69 (m, 2H), 1.26 (m, 18H), and 0.88 (t, 9H, $J = 6.76$ Hz). – ^{13}C NMR: $\delta = 119.57$ (CF_3, q, $J_{C-F} = 320.8$ Hz), 58.78 (CH_2), 43.47 (CH_3), 31.79 (CH_2), 29.46 (CH_2), 29.31 (CH_2), 29.21 (CH_2), 29.12 (CH_2), 28.83 (CH_2), 25.99 (CH_2), 25.61 (CH_2), 24.42 (CH_2), 22.56 (CH_2), 13.96 (CH_3). – MS: *m/z* = calcd. 494.47 [M^+], not measured.

*Dibutylammonium bis(trifluoromethylsulfonyl)imide (**21**).* From dibutylamine (5.59 g, 0.043 mol), $LiNTf_2$ (12.41 g, 0.043 mol) in D.I. H_2O (6 mL), and conc. HCl (37%, 5.0 g, 0.051 mol), 16.3 g (0.040 mol) of $[(n\text{-}C_4H_9)_2NH_2][NTf_2]$ were obtained (yield 92%). – ^{1}H NMR: $\delta = 6.55$ (broad peak, 2H), 3.05 (m, 4H), 1.70 (m, 4H), 1.40 (m, 4H), 0.94 (t, 6H, $J = 7.35$ Hz). – ^{13}C NMR: $\delta = 119.50$ (CF_3, q, $J_{C-F} = 320.4$ Hz), 48.82 (CH_2), 27.69 (CH_2), 19.40 (CH_2), 13.11 (CH_3). – MS: *m/z* = calcd. 410.41 [M^+], not measured.

*Dihexylammonium bis(trifluoromethylsulfonyl)imide (**22**).* From dihexylamine (2.42 g, 0.013 mol), $LiNTf_2$ (3.75 g, 0.013 mol) in D.I. H_2O (2 mL), and conc. HCl (37%, 2.8 g, 0.028 mol), 5.6 g (0.012 mol) of $[(n\text{-}C_6H_{13})_2NH_2][NTf_2]$ were obtained (yield 92%). – ^{1}H NMR: $\delta = 6.70$ (broad peak, 2H), 3.01 (m, 4H), 1.70 (m, 4H), 1.30 (m, 12H), 0.89 (t, 6H, $J = 6.56$ Hz). – ^{13}C NMR: $\delta = 119.52$ (CF_3, q, $J_{C-F} = 320.5$ Hz), 48.92 (CH_2), 30.96 (CH_2), 25.85 (CH_2), 25.74 (CH_2), 22.18 (CH_2), 13.70 (CH_3). – MS: *m/z* = calcd. 466.42, found 466.53 [M^+].

*Octylammonium bis(trifluoromethylsulfonyl)imide (**23**).* From octylamine (1.05 g, 0.0081 mol), $LiNTf_2$ (2.32 g, 0.0081 mol) in D.I. H_2O (1 mL), and conc. HCl (37%, 1.4 g, 0.014 mol), 3.15 g (0.0077 mol) of $[(n\text{-}C_8H_{17})NH_3][NTf_2]$ were obtained (yield 95%). – ^{1}H NMR: $\delta = 5.30$ (broad peak, 3H), 3.03 (m, 2H), 1.67 (m, 2H), 1.28 (m, 10H), 0.88 (t, 3H, $J = 6.81$ Hz). – ^{13}C NMR: $\delta = 119.40$ (CF_3, q, $J_{C-F} = 320.2$ Hz), 41.15 (CH_2), 31.57 (CH_2), 28.83 (CH_2), 28.76 (CH_2), 27.10 (CH_2), 25.95 (CH_2), 22.50 (CH_2), 13.92 (CH_3). – MS: *m/z* = calcd. 410.31 [M^+], not measured.

*Octylammonium bis(perfluoroethylsulfonyl)imide (**24**).* From octylamine (8.68 g, 0.067 mol), LiBETI (26.01 g, 0.067 mol) in D.I. H_2O (13 mL), and conc. HCl (37%, 7.2 g, 0.073 mol), 33.1 g (0.065 mol) of $[(n\text{-}C_8H_{17})NH_3][BETI]$ were obtained (yield 96%). – ^{1}H NMR: $\delta = 6.52$ (broad peak, 3H), 3.04 (m, 2H), 1.65 (m, 2H), 1.30 (m, 10H), 0.89 (t, 3H, $J = 6.81$ Hz). – ^{13}C NMR: $\delta = 117.67$ (CF_3, qt, $J_{C-F} = 287.5$ Hz, $J_{C-C-F} = 33.3$ Hz), 111.64 (CF_2, tq, $J_{C-F} = 294.4$ Hz, $J_{C-C-F} = 39.4$ Hz), 41.23 (CH_2), 31.57 (CH_2), 28.84 (CH_2), 28.75 (CH_2), 27.03 (CH_2), 25.96 (CH_2), 22.45 (CH_2), and 13.71 (CH_3). – MS: *m/z* = calcd. 510.31 [M^+], not measured.

3. Results and Discussion

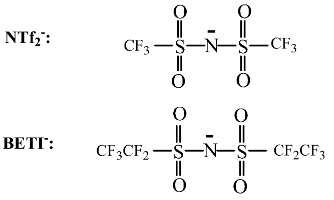
3.1. Synthesis and Physical Properties

Though a large number of quaternary tetraalkylammonium compounds (R_4N^+) has been investigated as media for various applications ranging from electrochemistry to catalysis [11,19,30] few trialkylammonium, dialkylammonium, and monoalkylammonium salts have been explored for similar purposes

$$R^1R^2R^3N(aq) + \text{conc. HCl} + LiA(aq) \xrightarrow{RT} [R^1R^2R^3NH][A] \downarrow + LiCl(aq)$$

R^n = alkyl groups ranging from C_1 to C_{12}

A = NTf_2^- or $BETI^-$



NTf_2^-: $CF_3-S(=O)_2-N^--S(=O)_2-CF_3$

$BETI^-$: $CF_3CF_2-S(=O)_2-N^--S(=O)_2-CF_2CF_3$

Scheme 1.

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

IL	Yield (%)	M.p. (°C)	T_{onset}[a] (°C)	Solubility in H_2O (mM)	Water content (ppm) Dried	Wet[b]
$[(CH_3)_2(i\text{-}C_3H_7)NH][NTf_2]$ (**1**)	94	Liq. at r.t.[c]	360	153	219	31900
$[(CH_3)_2(i\text{-}C_3H_7)NH][BETI]$ (**2**)	95	Liq. at r.t.	340	31.2	193	24100
$[(CH_3)(C_2H_5)_2NH][NTf_2]$ (**3**)	93	Liq. at r.t.	360	117	634	38400
$[(CH_3)(C_2H_5)_2NH][BETI]$ (**4**)	97	Liq. at r.t.	340	25.1	448	19700
$[(CH_3)_2(n\text{-}C_4H_9)NH][NTf_2]$ (**5**)	97	Liq. at r.t.	360	87.3	284	34600
$[(CH_3)_2(n\text{-}C_4H_9)NH][BETI]$ (**6**)	94	36	300	NM[d]	NM	NM
$[(C_2H_5)_3NH][NTf_2]$ (**7**)	97	Liq. at r.t.	360	95.7	453	27800
$[(C_2H_5)_3NH][BETI]$ (**8**)	97	Liq. at r.t.	340	14.1	131	22700
$[(CH_3)(n\text{-}C_3H_7)_2NH][NTf_2]$ (**9**)	96	Liq. at r.t.	350	20.6	530	13600
$[(CH_3)(n\text{-}C_3H_7)_2NH][BETI]$ (**10**)	98	64	300	NM	NM	NM
$[(C_2H_5)_2(n\text{-}C_4H_9)NH][NTf_2]$ (**11**)	94	Liq. at r.t.	335	35.4	299	35600
$[(C_2H_5)_2(n\text{-}C_4H_9)NH][BETI]$ (**12**)	96	Liq. at r.t.	310	27.6	220	17100
$[(i\text{-}C_3H_7)_2(C_2H_5)NH][NTf_2]$ (**13**)	91	Liq. at r.t.	350	52.9	220	21700
$[(i\text{-}C_3H_7)_2(C_2H_5)NH][BETI]$ (**14**)	96	36	330	NM	NM	NM
$[(n\text{-}C_3H_7)_3NH][NTf_2]$ (**15**)	93	49	350	NM	NM	NM
$[(n\text{-}C_4H_9)_3NH][NTf_2]$ (**16**)	93	37	335	NM	NM	NM
$[(i\text{-}C_4H_9)_3NH][NTf_2]$ (**17**)	95	62	315	NM	NM	NM
$[(n\text{-}C_6H_{13})_3NH][NTf_2]$ (**18**)	93	Liq. at r.t.	345	37.0	429	13000
$[(n\text{-}C_8H_{17})_3NH][NTf_2]$ (**19**)	99	Liq. at r.t.	360	19.6	232	11600
$[(CH_3)_2(n\text{-}C_{12}H_{25})NH][NTf_2]$ (**20**)	98	Liq. at r.t.	378	6.55	1396	19100
$[(n\text{-}C_4H_9)_2NH_2][NTf_2]$ (**21**)	92	62	310	NM	NM	NM
$[(n\text{-}C_6H_{13})_2NH_2][NTf_2]$ (**22**)	92	87	320	NM	NM	NM
$[(n\text{-}C_8H_{17})NH_3][NTf_2]$ (**23**)	95	Liq. at r.t.	350	96.0	2285	63100
$[(n\text{-}C_8H_{17})NH_3][BETI]$ (**24**)	96	Liq. at r.t.	325	17.9	608	17300

[a] T_{onset}, onset decomposition temperature based on TGA measurement. The estimated errors are ±5 °C.

[b] The water partition experiments were conducted by contacting 1 mL of ionic liquid with 10 mL of deionized H_2O for one hour.

[c] Liquid at room temperature; so melting points were not measured.

[d] NM, not measured.

[21 – 25, 31]. The reaction used for synthesizing trialkylammonium compounds (R_3NH^+) in our current study is illustrated in Scheme 1. The essence of this synthesis method is the combination of neutralization and metathesis reactions [28, 29] and thereby avoiding the use of more expensive reagents (e. g. HTFSI). Similar combinational reactions were also employed to synthesize protic ILs based on dialkylammonium and monoalkylammonium compounds.

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 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 the alkyl groups at the ammonium ions. However, there does appear to be a systematic correlation between the anion and the onset of the decomposition temperature of a specific IL. For the same cation, the ILs with $BETI^-$ as the conjugate anion have slightly lower thermal stability (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 $NTf_2{}^-$ [24].

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 [3, 4]. Accordingly, the hydrophobicity of the longer alkyl chain 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 the 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 [26, 27]. However, the water contents of the wet protic ILs (equilibrated with water for 1 h) 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

Table 2. Density and viscosity of ionic liquids.

IL	Molecular weight (g/mol)	Density (g/mL)	Viscosity (cP)[a] 23 °C	40 °C	100 °C
1	368.3	1.42	67.72	29.93	6.194
2	468.3	1.53	216.7	81.19	9.967
3	368.3	1.43	46.42	23.31	5.328
4	468.3	1.51	159.4	64.66	8.924
5	382.3	1.39	55.69	25.97	5.246
7	382.3	1.36	49.20	25.21	5.862
8	482.3	1.48	163.4	67.09	9.281
9	396.3	1.34	61.40	27.95	5.434
11	410.3	1.33	67.12	31.34	6.090
12	510.3	1.42	158.4	64.28	8.773
13	410.3	1.32	191.7	77.82	10.88
18	550.6	1.12	170.4	71.60	9.690
19	634.7	1.06	219.3	89.43	11.74
20	494.5	1.17	158.6	63.87	8.767
23	410.3	1.32	331.4	125.0	14.20
24	510.3	1.38	763.2	265.4	26.77
[C_4mim][NTf_2]	419.38	1.42	50.72	25.30	5.849
[C_4mim][BETI]	519.38	1.46	117.6	51.25	8.264
[C_6mim][NTf_2]	446.35	1.33	68.98	34.42	6.818
[C_6mim][BETI]	546.35	1.46	141.5	60.08	8.775

[a] The estimated errors are ±0.005 cP.

shorter carbon chain length, they have comparable viscosities with those of aprotic imidazolium-based ILs. As expected, the ILs with $BETI^-$ are more viscous than the ILs with $NTf_2{}^-$ for the same cations.

3.2. Extraction Results

In this study, only trialkylammonium-based ILs were investigated as new extraction media because monoalkyl- or dialkylammonium salts can form coordination complexes with crown ethers [32]. The syntheses of both mono- and dialkylammonium ILs were conducted for validating the generality of our metathesis-based synthesis method. Strontium and caesium ions were selected as target metal cations of interest, because they are divalent and univalent metal ions well studied in the context of crown ethers and our earlier studies [26,27]. In addition, both ^{90}Sr and ^{137}Cs are fission products that are ubiquitous in nuclear wastes and contaminated nuclear sites. Consequently, the development of efficient extraction methodologies is important for their detection and removal. Chloride ion was chosen as a typical hydrophilic aqueous anion, because it is abundant in contaminated radioactive waste sites. The crown ethers chosen for extraction of Sr^{2+} and Cs^{+} in this study were DCH18C6 and BOBCalixC6, which are known to form strong coordination complexes with the corresponding targeted metal ions [33,34].

Table 3. Effects of different pH conditions on the Cs extraction efficiency of ionic liquids containing 7.6 mM BOBCalixC6 or 100 mM DCH18C6.

IL	D_{Cs} at different pH conditions 7.6 mM BOBCalixC6 1.5 mM CsCl D.I. H_2O	 0.1 M HCl	 100 mM DCH18C6 1.5 mM CsCl D.I. H_2O	 0.1 M HCl
1	NA[a]	NA	154	13.8
2	NA	NA	2610	18.8
3	NA	NA	709	18.2
4	NA	NA	1330	23.4
5	NA	NA	82.9	19.9
7	NA	NA	80.3	20.0
8	NA	NA	2340	22.8
9	NA	NA	97.4	16.4
11	NA	NA	122	15.1
12	NA	NA	177	10.6
13	NA	NA	140	19.6
18	13.9	17.9	1.49	2.65
19	9.78	22.9	0.62	3.13
20	10.3	14.9	1.37	2.90

[a] NA, limited solubility of BOBCalixC6.

Cs-Extraction Results of [$R^1R^2R^3$NH][NTf_2] and [$R^1R^2R^3$NH][BETI] Containing DCH18C6 or BOBCalixC6

The solubility of BOBCalixC6 in the trialkylammonium ILs is very limited. This observation can be attributed to the enhanced hydrophilicity of the corresponding cations in these ILs. The lack of any aromatic group in the trialkylammonium ILs for solubilizing BOBCalixC6, which contains phenyl groups, is another potential reason for the low solubility. Appreciable solubility of BOBCalixC6 was found only for three ionic liquids: [(n-C_6H_{13})$_3$NH][NTf_2] (**18**), [(n-C_8H_{17})$_3$NH][NTf_2] (**19**), and [$(CH_3)_2$(n-$C_{12}H_{25}$)NH][NTf_2] (**20**) (see Table 3). These three ILs are the most hydrophobic among the trialkylammonium ILs listed in Table 3. However, the solubility of DCH18C6 in the same trialkylammonium ILs is quite high, and a concentration of 0.1 M can be readily achieved. The Cs extraction results with the three ILs based on the trialkylammonium ILs containing BOBCalixC6 and the fourteen ILs based on the trialkylammonium ILs containing DCH18C6 are summarized in Table 3. The extractions were performed as single-species (i. e., noncompetitive) extractions from a CsCl aqueous solution at two different acidities. One is under neutral condition and another in 0.1 M HCl.

As seen from Table 3, the D_{Cs} values of the DCH18C6 extraction system decrease drastically for all ILs listed in Table 3 with exception of [(n-C_6H_{13})$_3$NH][NTf_2] (**18**), [(n-C_8H_{17})$_3$NH][NTf_2] (**19**), and $[(CH_3)_2(n\text{-}C_{12}H_{25})NH][NTf_2]$ (**20**) as the aqueous solution changes from neutral to acidic conditions. This sharp variation of the extraction efficiency with the pH value indicates that the potential stripping method based on the pH swing can be developed for this new extraction system. The decrease of the D_{Cs} values with the acidity of aqueous solutions can be attributed to the competition for the binding of DCH18C6 from oxonium ions under the acidic condition. There does appear to be a systematic correlation between the anions and the D_{Cs} values for the DCH18C6 extraction system. As expected, the protic ILs with $BETI^-$ gave much greater D_{Cs} values than the protic ILs with NTf_2^-. The enhancement of the D_{Cs} values through hydrophobic conjugate anions can be attributed to the "latent" ion-exchange properties of ILs, which have been recently explored by us [35]. Under a neutral condition, a D_{Cs} value as high as 2610 can be achieved for $[(CH_3)_2(i\text{-}C_3H_7)NH][BETI]$. This D_{Cs} value is considerably greater than those of the DCH18C6 extraction system based on imidazolium-based ILs [26, 35]. The previous investigations by Chun et al. [3], Dietz et al. [4], Visser et al. [2], and us [1] revealed that, with the same anions, the more hydrophilic the cations of an IL the greater the extraction efficiency for DCH18C6. This dependence of the extraction efficiency on the hydrophilicity of IL cations is one of the key evidences for the ion-exchange model proposed by Dietz et al. [4]. Accordingly, the higher extraction efficiency achieved by the protic ILs containing DCH18C6 relative to that of the aprotic ILs containing the same extractant can be attributed to the enhanced hydrophilicity of the corresponding IL cations for facilitating ion-exchange processes and solvating hydrated crown ether complexes.

Interestingly, the change from neutral to acidic conditions for aqueous solutions slightly increases the extraction efficiency of the extraction systems based on ILs **18**, **19**, and **20**. These three protic ILs have considerably smaller D_{Cs} values, which can be attributed to their more hydrophobic cations and their limited ion-exchange and solvation capabilities. A similar phenomenon was observed for the BOBCalixC6 extraction system based on these three ILs, in further support of the different extraction mechanisms for ILs **18**, **19** and **20**. As seen in Table 4, the D_{Cs} values for the ILs in the absence of the extractants are very small in comparison to those in the presence of the extractants with exception of ILs **18**, **19**, and **20**. This observation is consistent with the important role played by the extractants in the protic extraction system. The amount of Cs^+, which partitions into the ILs via the direct ion-exchange process, correlates with the observed hydrophobicities of the IL organic cations. The hydrophobicity is also inversely related to the solubility of the corresponding ammonium cation ($[HNR^1R^2R^3]^+$) in the aqueous phase and, thus, its ion-exchange capability. The D_{Cs} values exhibit less dramatic changes for ILs **18**, **19**, and **20** with and without the extractants, indicating that the solvation properties of ILs **18**, **19**, and **20** for the extractant complexes are limited.

Table 4. Extraction results of ionic liquids containing no extractants.

IL	D_M at different pH conditions			
	1.5 mM CsCl		1.5 mM $SrCl_2$	
	D.I. H_2O	0.1 M HCl	D.I. H_2O	0.1 M HCl
1	4.95	5.57	0.247	0.661
2	3.99	3.73	NM[a]	0.149
3	7.28	4.84	NM	NM
4	8.20	6.11	0.153	0.036
5	3.58	2.87	NM	0.639
7	4.84	4.47	NM	NM
8	4.66	3.41	0.257	0.140
9	2.74	1.66	0.169	NM
11	2.62	0.748	NM	0.253
12	3.64	1.60	NM	0.349
13	2.98	0.753	NM	0.356
18	1.97	0.669	0.426	0.015
19	0.774	0.358	0.582	NM
20	0.052	0.201	NM	NM

[a] NM, no measurable partition of Sr^{2+} via a direct ion-exchange process.

Sr-Extraction Results of $[R^1R^2R^3NH][NTf_2]$ and $[R^1R^2R^3NH][BETI]$ Containing DCHC18C6

The Sr extraction experiments based on the protic ILs were also performed as single-species (i. e., non-competitive) extractions from $SrCl_2$ aqueous solutions at five different acidities. Table 5 summarizes the Sr extraction results under these five different conditions. As seen in Table 5, the D_{Sr} values are inversely proportional to the alkyl (R^1, R^2, R^3) chain length of the corresponding ammonium cations. For example, the D_{Sr} value (0.571) of the $[(n\text{-}C_8H_{17})_3NH][NTf_2]$-based extraction system is significantly smaller than that (12300) of the $[(CH_3)(C_2H_5)_2NH][NTf_2]$-based extraction system under neutral conditions. This observation is again consistent with the previous results concerning the imidazolium-based IL extraction system reported previously [3, 4]. This trend can again be attributed to the synergistic effect of the ion-exchange

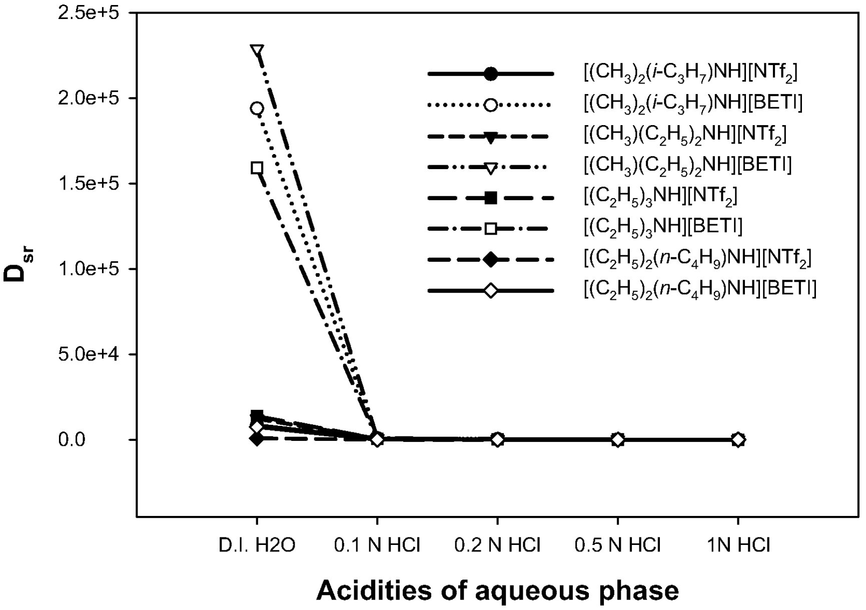


Fig. 1. Dependence of extraction efficiencies for Sr^{2+} on acidities of aqueous phases.

Table 5. Effects of acidities of aqueous solutions on the Sr extraction efficiency of ionic liquids containing 0.10 M DCH18C6.

IL	D_{Sr} at different pH conditions 1.5 mM $CrCl_2$				
	D.I. H_2O	0.1 M HCl	0.2 M HCl	0.5 M HCl	1.0 M HCl
1	8460	613	282	106	55.7
2	194000	911	369	129	66.9
3	12300	655	287	107	54.6
4	229000	904	363	126	64.5
5	2520	193	90.2	35.5	20.0
7	13800	571	270	104	53.9
8	159000	604	256	94.9	50.8
9	1750	128	62.1	25.1	14.7
11	870	82.3	34.4	17.6	10.6
12	7520	107	49.6	21.3	13.4
13	2680	218	94.2	40.2	25.1
18	0.810	0.268	0.280	0.313	0.398
19	0.571	0.329	0.222	0.161	0.235
20	0.341	0.448	0.442	0.310	0.483

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 the 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 anion give rise to much higher D_{Sr} values than the ILs with NTf_2^- as anion [35].

As seen from Tables 3 and 5, the variation of the alkyl chain length has a greater effect on D_{Sr} than on D_{Cs} values. This observation is also consistent with the ion-exchange extraction model for the IL-based extraction systems [35]. Because the number of IL cations involved in each ion-exchange reaction is equal to the metal cation charge q, the decrease in D_{Sr} with the alkyl chain length is much faster than the decrease in D_{Cs}. As seen from Fig. 1, the D_{Sr} values also decrease sharply with the acidity of aqueous solutions. For example, the D_{Sr} value of the extraction system based on IL **4** is reduced from 229 000 under neutral condition to 64.5 under acidic condition (1 M HCl). The change of the D_{Sr} values with pH is leveled off under highly acidic conditions. The sharp dependence of the D_{Sr} values on the pH value is also correlated to the strong complex formation of DCH18C6 with oxonium cations, which competes with Sr^{2+} during solvent extractions. Figure 2 shows the comparison of the extraction efficiencies between the imidazolium-based and protic IL extraction systems under similar conditions. The highest extraction efficiency achieved with the new protic IL system containing DCH18C6 is ~ 229 000, which is about three times better than that achieved with the imidazolium-based IL system under similar extraction conditions [35]. This enhancement clearly demonstrates the potential to increase the extraction efficiency with increased hydrophilicity of the IL cations.

As seen from Table 4, the extraction efficiencies for Sr^{2+} are smaller than those for Cs^{+} based on the di-

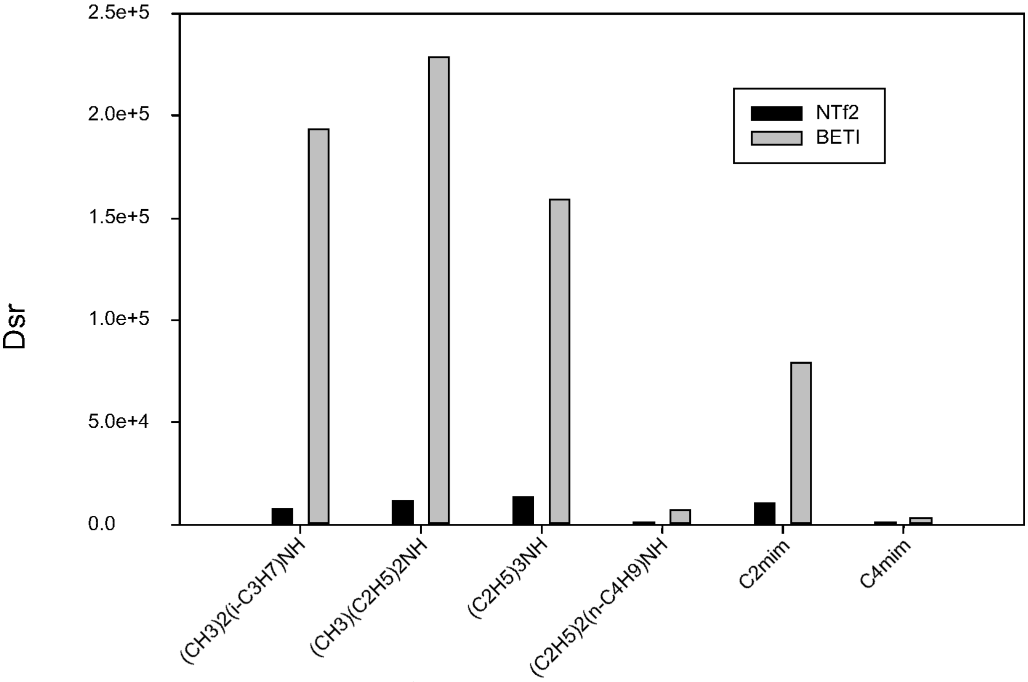


Fig. 2. Dependence of extraction efficiencies for Sr^{2+} by DCH18C6 on cations and anions of ILs.

rect ion-exchange process in the absence of the extractants. The selectivity of the ILs is dominated by the hydrophobicity of the metal ions extracted (i. e., their Hofmeister selectivity) in this direct ion-exchange process. The very limited extraction efficiencies observed for Sr^{2+} via the direct ion-exchange process again underscore the key role played by the extractants. The high extraction efficiencies observed for the new IL extraction systems with the crown ether extractants can be attributed to the synergism of the ion-exchange process and the extractant complexation.

4. Conclusions

The synthesis and characterization of new hydrophobic and protic alkylammonium ionic liquids with bis(trifluoromethylsulfonyl)imide or bis-(perfluoroethylsulfonyl)imide as conjugated anions were reported. The extraction efficiencies of the trialkylammonium-based IL extraction systems using BOBCalixC6 and DCH18C6 as extractants have been studied with comparison to the imidazolium-based extraction systems. These new protic extraction systems exhibit the enhanced extraction efficiencies resulted from the increased hydrophilicity of the corresponding IL cations. A strong dependence of the extraction efficiencies on the pH value has been observed, indicating the possibility for the development of stripping strategies based on pH swing.

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