Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Solvent Extraction of Sr^{2+} and Cs^{+} using Protic Amide-Based Ionic Liquids

Huimin Luo[a]; Jing-Fang Huang[b]; Sheng Dai[b]
[a] Nuclear Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA [b] Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA

Online publication date: 30 August 2010

To cite this Article Luo, Huimin , Huang, Jing-Fang and Dai, Sheng(2010) 'Solvent Extraction of Sr^{2+} and Cs^{+} using Protic Amide-Based Ionic Liquids', Separation Science and Technology, 45: 12, 1679 — 1688
To link to this Article: DOI: 10.1080/01496395.2010.493798
URL: http://dx.doi.org/10.1080/01496395.2010.493798

Separation Science and Technology, 45: 1679–1688, 2010

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496395.2010.493798

Taylor & Francis
Taylor & Francis Group

Solvent Extraction of Sr^{2+} and Cs^{+} using Protic Amide-Based Ionic Liquids

Huimin Luo,[1] Jing-Fang Huang,[2] and Sheng Dai[2]
[1]*Nuclear Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA*
[2]*Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA*

Sixteen protic amide-based ionic liquids (ILs) derived from N,N-dimethylformamide and other protophilic amide derivatives with bis(trifluoromethanesulfonyl)imide or bis(perfluoroethylsulfonyl)-imide as conjugated anions were synthesized in a one-pot reaction with very high yields. All sixteen of these protic ionic liquids (PILs) were characterized by NMR spectra, thermogravimetric analysis, and differential scanning calorimetry. These protic amide-based ionic liquids were tested as extraction solvents using dicyclohexano-18--crown-6 (DCH18C6) as an extractant for separation of Sr^{2+} and Cs^{+} from aqueous solutions. The extraction efficiencies were studied in comparison with those derived from both imidazolium-based and ammonium-based IL extraction systems. Excellent extraction efficiencies were found for a number of these ILs using DCH18C6 as an extractant. Unlike findings for imidazolium-based and ammonium-based ILs, the observed enhancement trend for the extraction efficiency associated with our amide-based ILs is not directly correlated with the enhanced hydrophilicity of the corresponding cations of the PIL system. The effects on extraction efficiencies of solution acidities, anions, and alkyl chain lengths in the cations of ILs were also investigated and reported.

Keywords Ionic liquids; protic amide-based ionic liquids; solvent extraction

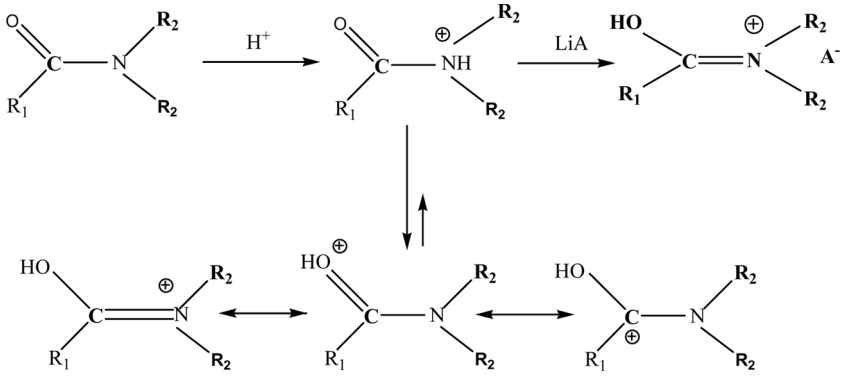
INTRODUCTION

Ionic liquids (ILs) exhibit great promise as new diluents for solvent extraction of metal ions from aqueous solutions (1–5). The general extraction mechanism associated with these hydrophobic ionic solvents can be considered to involve the conventional complexation of metal ions via an extractant that is coupled to an ion-exchange process (4). This synergistic interplay of the two separation processes is the key to the high extraction efficiencies observed for a number of IL extraction systems containing extractants (1,6,4). It has been demonstrated that the ion-exchange process associated with IL diluents is dependent on the hydrophilicity of the corresponding IL cation. The high hydrophilicity of the cations of a hydrophobic IL can lead to enhanced extraction efficiency (1,6,4). This assertion regarding the relationship of the extraction efficiency to the hydrophilicity of the IL cation has prompted our recent investigation of protic ionic liquids (PILs) as potential diluents for extraction of metal ions (7). Currently, ILs can be categorized into three classes (aprotic, protic, and metal ion) based on the specific cation-transfer mechanisms for their cation formation. The cations of aprotic ionic liquids (AILs) can be readily formed via transfer of alkyl cations (8), while the cations of metal-ion ionic liquids (MILs) are derived from transfer of cationic metal ions to neutral ligands (9–11). The cations of PILs are formed through transfer of protons to neutral bases (12). The key property of PILs is the hydrophilicity of their cations. In general, the hydrophilicity of ILs is correlated with structures of ILs. The shorter the carbon chain length on cations of ILs is the higher the hydrophilicity of ILs is. Our prior results show that the extraction efficiency of crown ethers can be further enhanced through these PILs because of the enhanced hydropholicity of PIL cations (7). In support of our continuing interest in the development of new solvent-extraction methods based on ILs for separation of fission products from high-level wastes (1,13,14), we describe herein the application of another class of PILs in the solvent extraction of metal ions with crown ethers. Our research objectives are twofold:

1. to further explore the applications of PILs in extraction of metal ions in aqueous phases and
2. to probe the structural dependence of extraction efficiencies on IL cations.

The PILs used in our study are based on amide-based hydrophobic ILs. We have recently reported a convenient and efficient one-pot synthesis route to this new family of room-temperature ionic liquids (RTILs) based on N,N-dimethylformamide and other amide derivatives (15). A total of 16 ILs with a broad structural diversity were synthesized in a one-pot reaction with a high yield. Unlike the PILs used in our previous investigation, this class of the PILs is not based on traditional ammonium or imidazolium cations; instead, proton ions are attached to the oxygen group in amide structures to form the cations of the PILs (Scheme 1).

Received 19 November 2009; accepted 18 April 2010.
Address correspondence to Huimin Luo, Nuclear Science and Technology Divison, Oak Ridge National Laboratory, Oak Ridge, TN 37831. E-mail: luoh@ornl.gov



1. $R_1 = H$, $R_2 = CH_3$, $A = NTf_2$
2. $R_1 = H$, $R_2 = CH_3$, $A = BETI$
3. $R_1 = H$, $R_2 = C_2H_5$, $A = NTf_2$
4. $R_1 = H$, $R_2 = C_2H_5$, $A = BETI$
5. $R_1 = H$, $R_2 = i\text{-}C_3H_7$, $A = NTf_2$
6. $R_1 = H$, $R_2 = i\text{-}C_3H_7$, $A = BETI$
7. $R_1 = H$, $R_2 = n\text{-}C_4H_9$, $A = NTf_2$
8. $R_1 = H$, $R_2 = n\text{-}C_4H_9$, $A = BETI$
9. $R_1 = CH_3$, $R_2 = CH_3$, $A = NTf_2$
10. $R_1 = CH_3$, $R_2 = CH_3$, $A = BETI$
11. $R_1 = CH_3$, $R_2 = C_2H_5$, $A = NTf_2$
12. $R_1 = CH_3$, $R_2 = C_2H_5$, $A = BETI$
13. $R_1 = C_2H_5$, $R_2 = CH_3$, $A = NTf_2$
14. $R_1 = C_2H_5$, $R_2 = CH_3$, $A = BETI$
15. $R_1 = Ph$, $R_2 = CH_3$, $A = NTf_2$
16. $R_1 = Ph$, $R_2 = CH3$, $A = BETI$

SCH. 1. Synthesis scheme of amide-based ionic liquids.

EXPERIMENTAL

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. The density of ILs was measured by filling a 1.0 mL volumetric flask to the mark with each IL and then weighing (14). The water content of the ILs was measured using a Metrohm 652 KF coulometer. The synthesis yields of these PILs and their physical properties are summarized in Table 1. Aqueous solutions were prepared using deionized (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. Proton and carbon chemical shifts are reported relative to tetramethylsilane (TMS). Viscosities were measured using a Minivis II microviscometer (Grabner Instruments^{TM}). Thermogravimetric analysis (TGA) curves were measured in nitrogen at a scan rate of 10°C/min with a TA Instruments TGA 2950. Differential scanning calorimetry (DSC) curves were performed with a TA Instruments DSC Q100. The scanning sequence is first freezing the sample to −90°C, next retaining this temperature for 20 min, and then heating the sample to 150°C at 10°C/min. 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 strontium concentrations using inductively coupled plasma–atomic emission spectroscopy (ICP-AES).

Extraction Experiments

The extraction experiments were performed in duplicate for each IL by contacting 1 mL of IL containing 0.10 M of DCH18C6 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 the cations were determined by ion chromatography or ICP-AES.

The distribution coefficients (D_M) for extraction of M^{n+} are defined in Eq. (1) as (13,14)

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

where C_i and C_f represent the initial and final concentrations of M^{n+} in the aqueous phase, respectively. 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 the 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+} for the

TABLE 1
Physical properties of amide-based ionic liquids

ILs	Molecular formula	Density (g/mL)	Viscosity (cP) 23°C	40°C	100°C	Water content (ppm)	T_{onset}[a] (°C) Free amide	T_{onset}[a] (°C) Cation	T_{onset}[a] (°C) Anion
1	[DMFH] [NTf_2]	1.55	238.8	86.06	11.04	2690	78	185	350
2	[DMFH] [BETI]	1.59	NM[b]	NM[b]	NM[b]	NM[b]		181	343
3	[DEFH] [NTf_2]	1.43	130.2	52.91	8.020	2400	90	188	347
4	[DEFH] [BETI]	1.46	89.95	38.12	6.221	2710		201	331
5	[Di-PrFH] [NTf_2]	1.33	202.1	73.49	8.713	2570	84	194	314
6	[Di-PrFH] [BETI]	1.39	406.7	125.6	10.69	2590		196	313
7	[Dn-BuFH] [NTf_2]	1.16	101.2	43.52	6.343	1250	126	184	335
8	[Dn-BuFH] [BETI]	1.23	138.4	55.46	7.009	1230		192	326
9	[DMAH] [NTf_2]	1.51	162.4	66.74	9.837	1700	77	229	364
10	[DMAH] [BETI]	1.53	NM[b]	NM[b]	NM[b]	1200		224	328
11	[DEAH] [NTf_2]	1.42	138.6	58.25	8.670	1630	75	223	337
12	[DEAH] [BETI]	1.43	174.2	67.92	8.642	1650		232	335
13	[DMPAH] [NTf_2]	1.47	132.5	58.19	9.177	1650	92	228	382
14	[DMPAH] [BETI]	1.48	188.1	75.88	9.950	1760		223	328
15	[DMBAH] [NTf_2]	1.41	598.6	168.3	14.10	3170	139	223	339
16	[DMBAH] [BETI]	1.39	684.4	174.9	13.10	1350		225	324

[a]T_{onset}: Onset decomposition temperature based on TGA measurement. The estimated errors are ±5°C.
[b]NM: not measured.

IL phase. The values of D_M were measured in duplicate with uncertainty within 5%.

General Procedure for Synthesis of Amide-Based Ionic Liquids

The method for synthesizing these ILs is based on a combination of neutralization and the metathesis methodology (16,17). Briefly, organic amides and a slightly excess amount of concentrated HCl aqueous solution were mixed at room temperature. To this mixture, either lithiumbis(trifluoromethanesulfonyl)imide ($LiNTf_2$) or lithium bis(perfluoroethylsulfonyl)imide (LiBETI) predissolved in D.I. water was added in equal molar ratios in flasks. In each of these mixtures, the IL phase formed readily following the addition of aqueous solution of $LiNTf_2$ or LiBETI and the reaction is quite exothermic. The lower layers (IL) were separated from the aqueous phase and washed with D.I. water 4 times to ensure the removal of LiCl. The final products in the form of nearly colorless free-flowing liquids were dried under vacuum at 70°C for 4 h.

N,N-Dimethylformamidium bis(trifluoromethylsulfonyl)-imide (1). From N,N-dimethylformamide (4.27 g, 0.058 mol), concentrated HCl, and $LiNTf_2$ (predissolved in D.I. water), 18.45 g (0.053 mol) of [DMFH] [NTf_2] was obtained as a colorless liquid (yield of 90%). ^{1}H-NMR data: δ, 13.10 (broad peak, 1H), 8.27 (s, 1H), and 3.27 (d, 6H, J = 49.5 Hz). ^{13}C-NMR: δ, 165.36 (CHOH), 119.45 (CF_3, q, $J_{C\text{-}F}$ = 319.2 Hz), 40.99 (CH_3), and 35.53 (CH_3).

N,N-Dimethylformamidium bis(perfluoroethylsulfonyl)imide (2). From N,N-dimethylformamide (3.07 g, 0.042 mol), concentrated HCl, and LiBETI (predissolved in D.I. water), 17.86 g (0.098 mol) of [DMFH] [BETI] was obtained as a colorless liquid (yield of 93%). ^{1}H-NMR data: δ, 11.24 (broad peak, 1H), 8.31 (s, 1H), 3.24 (d, 6H, J = 49.7 Hz). ^{13}C-NMR: δ, 164.05 (CHOH), 117.70 (CF_3, qt, $J_{C\text{-}F}$ = 287.2 Hz, $J_{C\text{-}C\text{-}F}$ = 33.0 Hz), 111.57 (CF_2, tq, $J_{C\text{-}F}$ = 293.9 Hz, $J_{C\text{-}C\text{-}F}$ = 39.0 Hz), 40.37 (CH_3), and 34.58 (CH_3).

N,N-Diethylformamidium bis(trifluoromethylsulfonyl)imide (3). From N,N-diethylformamide (6.07 g, 0.060 mol), concentrated HCl, and $LiNTf_2$ (predissolved in D.I. water), 21.10 g (0.055 mol) of [DEFH] [NTf_2] was obtained as a colorless liquid (yield of 92%). ^{1}H-NMR data: δ, 11.87 (broad peak, 1H), 8.36 (s, 1H), 3.65 (m, 4H, J = 7.1 Hz), 1.48 (t, 3H, J = 7.28 Hz) and 1.32 (t, 3H, J = 7.30 Hz). ^{13}C-NMR: δ, 163.86 (CHOH), 119.36 (CF_3, q, $J_{C\text{-}F}$ = 320.2 Hz), 46.70 (CH_2), 41.17 (CH_2), 13.02 (CH_3), and 11.45 (CH_3).

N,N-Diethylformamidium bis(perfluoroethylsulfonyl)imide (4). From N,N-diethylformamide (5.57 g, 0.055 mol), concentrated HCl, and LiBETI (predissolved in D.I. water), 25.00 g (0.052 mol) of [DEFH] [BETI] was obtained as a colorless liquid (yield of 95%). ^{1}H-NMR data: δ, 11.20 (broad peak, 1H), 8.28 (s,

1H), 3.58 (m, 4H), 1.35 (t, 3H, J = 7.24 Hz) and 1.28 (t, 3H, J = 7.25 Hz). ^{13}C-NMR: δ, 164.20 (CHOH), 117.79 (CF_3, qt, $J_{C-F} = 287.6$ 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), 46.16 (CH_2), 40.60 (CH_2), 13.10 (CH_3), and 11.45 (CH_3).

N,N-Diisopropylformamidium bis(trifluoromethylsulfonyl)-imide (5). From N,N-diisopropylformamide (7.23 g, 0.056 mol), concentrated HCl, and $LiNTf_2$ (predissolved in D.I. water), 21.63 g (0.064 mol) of [(Di-PrFH] [NTf_2] was obtained (yield of 94%). ^{1}H-NMR data: δ, 11.66 (broad peak, 1H), 8.24 (s, 1H), 4.04 (m, 1H, J = 6.87 Hz), 3.97 (m, 1H, J = 6.76 Hz), 1.44 (d, 6H, J = 6.89 Hz), and 1.39 (d, H, J = 6.81 Hz). ^{13}C-NMR: δ, 164.04 (CHOH), 119.53 (CF_3, q, $J_{C-F} = 320.9$ Hz), 52.52 (CH), 48.22 (CH), 22.87 (CH_3), and 18.96 (CH_3).

N,N-Diisopropylformamidium bis(perfluoroethylsulfonyl)-imide (6). From N,N-diisopropylformamide (4.09 g, 0.032 mol), concentrated HCl, and LiBETI (predissolved in D.I. water), 15.32 g (0.030 mol) of [(Di-PrFH] [NTf_2] was obtained (yield of 94%). ^{1}H-NMR data: δ, 10.46 (broad peak, 1H), 8.24 (s, 1H), 4.10 (m, 1H, J = 6.88 Hz), 3.96 (m, 1H, J = 6.75 Hz), 1.40 (d, 6H, J = 6.89 Hz), and 1.37 (d, H, J = 6.80 Hz). ^{13}C-NMR: δ, 164.00 (CHOH), 117.64 (CF_3, qt, $J_{C-F} = 287.5$ Hz, $J_{C-C-F} = 33.3$ Hz), 111.55 (CF_2, tq, $J_{C-F} = 294.3$ Hz, $J_{C-C-F} = 38.8$ Hz), 53.18 (CH), 48.95 (CH), 21.23 (CH_3), and 18.94 (CH_3).

N,N-Dibutylformamidium bis(trifluoromethylsulfonyl)imide (7). From N,N-dibutylformamide (5.51 g, 0.035 mol), concentrated HCl, and $LiNTf_2$ (predissolved in D.I. water), 14.12 g (0.032 mol) of [(Dn-BuFH] [NTf_2] was obtained (yield of 92%). ^{1}H-NMR data: δ, 12.20 (broad peak, 1H), 8.26 (s, 1H), 3.44 (m, 4H), 1.63 (m, 4H), 1.37 (m, 4H), and 0.95 (t, 6H, $J = 7.35$ Hz). ^{13}C-NMR: δ, 165.05 (CHOH), 119.66 (CF_3, q, $J_{C-F} = 321.3$ Hz), 50.35 (CH_2), 44.64 (CH_2), 29.84 (CH_2), 28.44 (CH_2), 19.77 (CH_2), 19.31 (CH_2), 13.33 (CH_3), and 13.26 (CH_3).

N,N-Dibutylformamidium bis(perfluoroethylsulfonyl)imide (8). From N,N-dibutylformamide (5.06 g, 0.032 mol), concentrated HCl, and LiBETI (predissolved in D.I. water), 16.55 g (0.031 mol) of [(Dn-BuFH] [BETI] was obtained (yield of 96%). ^{1}H-NMR data: δ, 12.94 (broad peak, 1H), 8.25 (s, 1H), 3.44 (m, 4H), 1.61 (m, 4H), 1.33 (m, 4H), and 0.95 (t, 6H, $J = 7.34$ Hz). ^{13}C-NMR: δ, 165.07 (CHOH), 117.93 (CF_3, qt, $J_{C-F} = 287.4$ Hz, $J_{C-C-F} = 33.3$ Hz), 111.59 (CF_2, tq, $J_{C-F} = 294.1$ Hz, $J_{C-C-F} = 38.5$ Hz), 50.31 (CH_2), 44.61 (CH_2), 29.86 (CH_2), 28.46 (CH_2), 19.78 (CH_2), 19.31 (CH_2), 13.31 (CH_3), and 13.22 (CH_3).

N,N-Dimethylacetamidium bis(trifluoromethylsulfonyl)imide (9). From N,N-dimethylacetamide (4.03 g, 0.046 mol), concentrated HCl, and $LiNTf_2$ (predissolved in D.I. water), 15.88 g (0.043 mol) of [DMAH] [NTf_2] was obtained as a colorless liquid (yield of 94%). ^{1}H-NMR data: δ, 8.07 (broad peak, 1H), 3.33 (s, 3H), 3.26 (s, 3H), and 2.48 (s, 3H). ^{13}C-NMR: δ, 174.45 (C), 119.57 (CF_3, q, $J_{C-F} = 320.1$ Hz), 39.69 (CH_3), 37.68 (CH_3), and 17.84 (CH_3).

N,N-Dimethylacetamidium bis(perfluoroethylsulfonyl)imide (10). From N,N-dimethylacetamide (3.52 g, 0.040 mol), concentrated HCl, and LiBETI (predissolved in D.I. water), 17.0 g (0.036 mol) of [DMAH] [BETI] was obtained as a colorless liquid (yield of 91%). ^{1}H-NMR data: δ, 11.35 (broad peak, 1H), 3.15 (s, 3H), 3.07 (s, 3H), and 2.29 (s, 3H). ^{13}C-NMR: δ, 174.18 (C), 117.64 (CF_3, qt, $J_{C-F} = 287.3$ Hz, $J_{C-C-F} = 33.1$ Hz), 111.41 (CF_2, tq, $J_{C-F} = 293.7$ Hz, $J_{C-C-F} = 38.8$ Hz), 39.41 (CH_3), 37.31 (CH_3), and 17.81 (CH_3).

N,N-Diethylacetamidium bis(trifluoromethylsulfonyl)imide (11). From N,N-diethylacetamide (5.56 g, 0.048 mol), concentrated HCl, and $LiNTf_2$ (predissolved in D.I. water), 17.62 g (0.044 mol) of [DEAH] [NTf_2] was obtained as a colorless liquid (yield of 93%). ^{1}H-NMR data: δ, 11.80 (broad peak, 1H), 3.63 (q, 4H, J = 7.15 Hz), 2.53 (m, 3H), 1.36 (t, 3H, J = 7.30 Hz) and 1.33 (t, 3H, J = 7.20 Hz). ^{13}C-NMR: δ, 173.86 (C), 119.54 (CF_3, q, $J_{C-F} = 320.8$ Hz), 46.45 (CH_2), 44.45 (CH_2), 18.13 (CH_3), 12.61 (CH_3), and 11.84 (CH_3).

N,N-Diethylacetamidium bis(perfluoroethylsulfonyl)imide (12). From N,N-diethylacetamide (5.10 g, 0.044 mol), concentrated HCl, and LiBETI (predissolved in D.I. water), 20.60 g (0.042 mol) of [DEAH] [BETI] was obtained as a colorless liquid (yield of 95%). ^{1}H-NMR data: δ, 9.53 (broad peak, 1H), 3.55 (q, 4H, J = 7.22 H), 2.40 (s, 3H), 1.37 (t, 3H, J = 7.30 Hz) and 1.26 (t, 3H, J = 7.22 Hz). ^{13}C-NMR: δ, 173.80 (C), 117.86 (CF_3, qt, $J_{C-F} = 287.5$ Hz, $J_{C-C-F} = 33.2$ Hz), 111.57 (CF_2, tq, $J_{C-F} = 294.1$ Hz, $J_{C-C-F} = 38.7$ Hz), 45.36 (CH_2), 43.59 (CH_2), 17.96 (CH_3), 12.55 (CH_3), and 11.73 (CH_3).

N,N-Dimethylpropylamidium bis(trifluoromethylsulfonyl)-imide (13). From N,N-dimethylpropylamide (6.24 g, 0.062 mol), concentrated HCl, and $LiNTf_2$ (predissolved in D.I. water), 21.85 g (0.057 mol) of [DMPAH] [NTf_2] was obtained as a colorless liquid (yield of 92%). ^{1}H-NMR data: δ, 9.33 (broad peak, 1H), 3.31 (s, 3H), 3.26 (s, 3H), 2.75 (q, 2H, J = 7.32 Hz), and 1.30 (t, 3H, J = 7.20 Hz). ^{13}C-NMR: δ, 178.07 (C), 119.67 (CF_3, q, $J_{C-F} = 319.6$ Hz), 41.16 (CH_3), 39.72 (CH_3), 25.01 (CH_2), and 8.90 (CH_3).

N,N-Dimethylpropylamidium bis(perfluoroethylsulfonyl)-imide (14). From N,N-diisopropylethylamine (5.62 g, 0.056 mol), concentrated HCl, and LiBETI (predissolved in D.I. water), 24.22 g (0.050 mol) of [DMPAH] [BETI] was obtained as a colorless liquid (yield of 91%). ^{1}H-NMR data: δ, 10.34 (broad peak, 1H), 3.32 (s, 3H), 3.21 (s, 3H), 2.72 (q, 2H,

J = 7.69 Hz), and 1.28 (t, 3H, J = 7.71 Hz). ^{13}C-NMR: δ, 177.76 (C), 117.66 (CF_3, qt, $J_{C\text{-}F} = 287.4$ Hz, $J_{C\text{-}C\text{-}F} = 33.1$ Hz), 111.42 (CF_2, tq, $J_{C\text{-}F} = 293.9$ Hz, $J_{C\text{-}C\text{-}F} = 38.9$ Hz), 39.11 (CH_3), 38.13 (CH_3), 24.67 (CH_2), and 8.70 (CH_3).

N,N-Dimethylbenzamidium bis(trifluoromethylsulfonyl)imide (15). From N,N-dimethylbenzamide (4.28 g, 0.029 mol), concentrated HCl, and $LiNTf_2$ (predissolved in D.I. water), 11.50 g (0.027 mol) of [DMBAH] [NTf_2] was obtained as a colorless liquid (yield of 92%). ^{1}H-NMR data: δ, 9.57 (broad peak, 1H), 7.94 (m, 1H), 7.61 (m, 2H), 7.33 (m, 2H), 3.26 (s, 3H), and 3.16 (s, 3H). ^{13}C-NMR: δ, 173.43 (C), 133.93 (C), 132.98 (CH), 129.23 (CH), 127.58 (CH), 119.55 (CF_3, q, $J_{C\text{-}F} = 321.1$ Hz), 41.30 (CH_3), and 37.95 (CH_3).

N,N-Dimethylbenzamidium bis(trifluoroethylsulfonyl)imide (16). From N,N-dimethylbenzamide (3.48 g, 0.023 mol), concentrated HCl, and LiBETI (predissolved in D.I. water), 11.52 g (0.022 mol) of [DMBAH] [BETI] was obtained as a colorless liquid (yield of 93%). ^{1}H-NMR data: δ, 9.98 (broad peak, 1H), 7.59 (m, 1H), 7.50 (m, 2H), 7.29 (m, 2H), 3.16 (s, 3H), and 3.09 (s, 3H). ^{13}C-NMR: δ, 173.40 (C), 132.32 (C), 128.97 (CH), 128.37 (CH), 127.25 (CH), 117.87 (CF_3, qt, $J_{C\text{-}F} = 287.8$ Hz, $J_{C\text{-}C\text{-}F} = 33.3$ Hz), 111.53 (CF_2, tq, $J_{C\text{-}F} = 294.1$ Hz, $J_{C\text{-}C\text{-}F} = 38.6$ Hz), 40.71 (CH_3), and 37.22 (CH_3).

RESULTS AND DISCUSSION

Synthesis and Physical Properties

The reaction developed for synthesizing the amide-based ILs used in our current study is illustrated in Scheme 1 and has been previously reported (15). The essence of this synthesis method involves first the neutralization of a given amide with a strong acid, followed by metathesis with a desired anion donor, all in aqueous phase (16,17). This method avoids the use of more-expensive superacid reagents (e.g., HTFSI). For the metathesis reaction, we selected the lithium salt of either bis(trifluoromethanesulfonyl)imide ($LiNTf_2$) or bis(perfluoroethylsulfonyl)imide (LiBETI). Using this methodology, 16 amide-based ILs were successfully synthesized in high yields.

The thermal properties of some of these PILs have been investigated before by TGA and DSC (18). The TGA curves measured for all 16 amide-based ILs reveal a two-step weight-loss process as summarized in Table 1. The calculations of weight balances indicate that the first step is consistent with the loss of the amide of the ILs and the second step is correlated with the loss of the anion. The first-step thermal decomposition temperature (T_{onset}) for protonated amide cations is in the range of 180 to 230°C, about 100°C higher than those of the corresponding free amides. Interestingly, the second-step thermal decomposition temperature (T_{onset}) depends somewhat on the choice of amide cations and lies roughly within a 50°C window centered at 350°C. For the same cation, the ILs with NTf_2^- as the conjugate anion have slightly higher thermal stabilities than those with $BETI^-$ as the conjugate anion. The difference in T_{onset} is closely related to the choice of cations. Generally, the larger the substituents on cations are, the greater the differences in T_{onset}.

After they are subjected to drying, these PILs have higher water contents than those of aprotic imidazolium-based ILs (13,14). This observation is consistent with the enhanced hydrophilicity of the IL cations. The viscosities of the PILs were measured at three different temperatures and summarized in Table 1. 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 PILs and the measured viscosities. As expected, the ILs with $BETI^-$ are more viscous than those with NTf_2^- for the same cations.

In our previous work (15), the Fourier transform infrared (FTIR) spectra of these ILs indicated a band at 1721 cm^{-1}, which was assigned to a C=N stretch mode. This result suggests that the left-most resonance structure of the bottom tautomer in Scheme 1 is a dominant structure. Further support for this premise is found in our NMR investigation as shown in Fig. 1. The case is best illustrated using IL 4, based on N,N-diethylformamide (DEF). The NMR clearly shows that the asymmetry imposed by the C=N bond results in

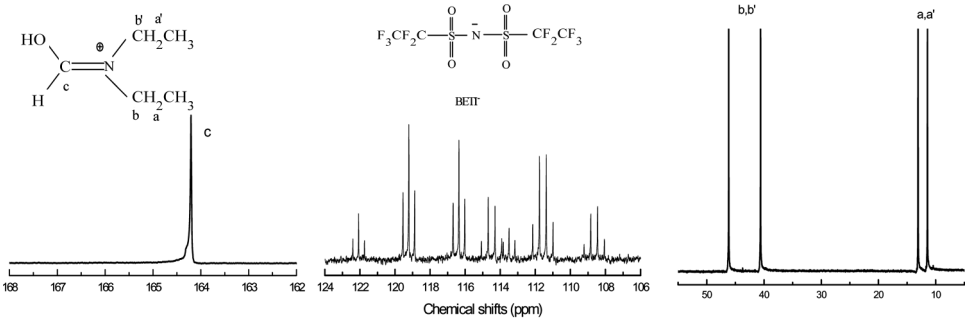


FIG. 1. Expanded regions of ^{13}NMR spectrum of IL4.

different chemical shifts being assigned to the carbons of the two ethyl groups.

Extraction Results

All 16 amide-based ILs were investigated as new extraction media in our current study. Strontium and cesium ions were selected as targeted metal cations of interest because they are model-divalent and univalent metal ions well investigated in the context of crown ethers and in our earlier studies (13,14). 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. Because it is abundant in contaminated radioactive waste sites, chloride ion was chosen as a typical hydrophilic aqueous anion. The crown ether chosen for extraction of Sr^{2+} and Cs^{+} in this study was DCH18C6, which is known to form strong coordination complexes with the corresponding targeted metal ions (19,20).

Cs-Extraction Results of Amide-Based ILs Containing DCH18C6

The solubilities of DCH18C6 in amide-based ILs are reasonably high, and a concentration of 0.1 M can be readily achieved. The Cs-extraction results with these amide-based ILs containing DCH18C6 are summarized in Table 2. The extractions were performed as single-species (i.e., noncompetitive) extractions from a CsCl aqueous solution at two different acidities. One extraction was conducted under a neutral pH condition and another in 0.1 N HCl.

TABLE 2
Cs extraction efficiency of ionic liquids containing 0.10 M DCH18C6

		D_{Cs} at different pH conditions	
		100 mM DCH18C6, 1.5 mM CsCl	
ILs	Molecular formula	D.I. H_2O	0.1 N HCl
1	[DMFH] [NTf_2]	NM[a]	NM[a]
2	[DMFH] [BETI]	55.4	26.8
3	[DEFH] [NTf_2]	133	44.7
4	[DEFH] [BETI]	70.8	122
5	[Di-PrFH] [NTf_2]	33.1	21.8
6	[Di-PrFH] [BETI]	67.9	34.5
7	[Dn-BuFH] [NTf_2]	37.4	14.1
8	[Dn-BuFH] [BETI]	118	24.0
9	[DMAH] [NTf_2]	NM[a]	NM[a]
10	[DMAH] [BETI]	62.0	30.6
11	[DEAH] [NTf_2]	208	16.7
12	[DEAH] [BETI]	NM[a]	NM[a]
13	[DMPAH] [NTf_2]	30.3	32.3
14	[DMPAH] [BETI]	126	7.35
15	[DMBAH] [NTf_2]	119	12.8
16	[DMBAH] [BETI]	108	37.7

[a]NM: not measured.

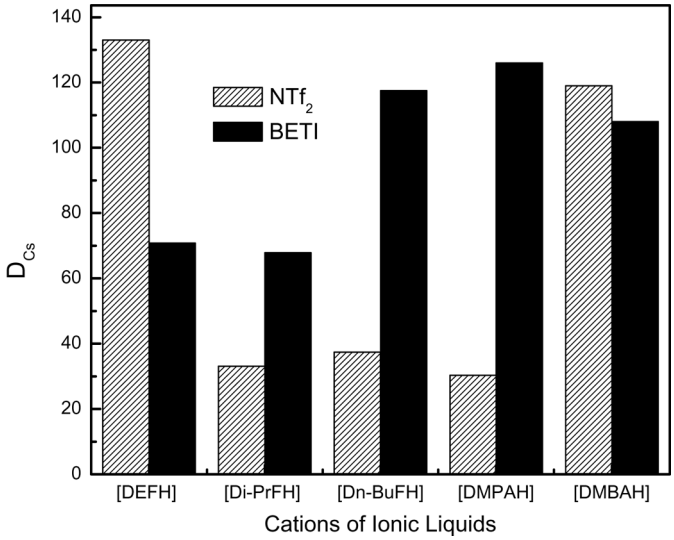


FIG. 2. Dependence of D_{Cs} on anions and cations of ILs.

Effect of Acidity on Cs-Extraction Efficiencies

As shown in Table 2, the D_{Cs} values of this extraction system decrease for all ILs listed, with the exception of [DEFH] [BETI] (4), as the aqueous solution changes from neutral to acidic conditions. This variation in the extraction efficiency with pH indicates that a 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

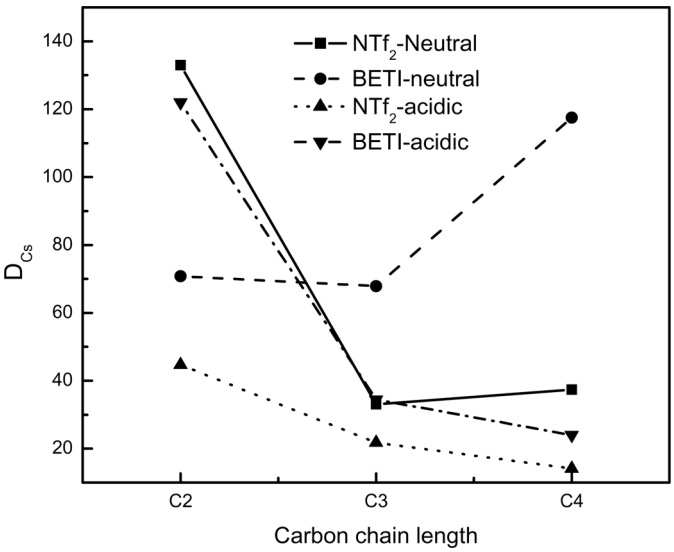


FIG. 3. Dependence of D_{Cs} on carbon chain length on cations of ILs.

TABLE 3
Sr-extraction efficiency of ionic liquids containing 0.10 M DCH18C6

		D_{Sr} at different pH conditions				
		1.5 mM $SrCl_2$				
Ils	Molecular formula	D.I. H_2O	0.1 N HCl	0.2 N HCl	0.5 N HCl	1.0 N HCl
1	[DMFH] [NTf_2]	729	466	356	205	126
2	[DMFH] [BETI]	2520	1080	367	53.8	17.0
3	[DEFH] [NTf_2]	6880	3660	2530	1100	410
4	[DEFH] [BETI]	51600	15200	4090	1270	347
5	[Di-PrFH] [NTf_2]	34700	6320	1920	369	102
6	[Di-PrFH] [BETI]	41400	6660	2180	434	121
7	[Dn-BuFH] [NTf_2]	41400	16100	5930	997	267
8	[Dn-BuFH] [BETI]	381000	29400	8000	1040	232
9	[DMAH] [NTf_2]	1090	631	459	260	131
10	[DMAH] [BETI]	4550	3010	588	85.7	32.6
11	[DEAH] [NTf_2]	2800	882	455	144	64.0
12	[DEAH] [BETI]	10500	1960	710	170	59.8
13	[DMPAH] [NTf_2]	1020	810	638	270	122
14	[DMPAH] [BETI]	13500	3680	1630	441	151
15	[DMBAH] [NTf_2]	4630	1880	926	273	75.2
16	[DMBAH] [BETI]	81600	7050	2960	674	219

competition for the binding of DCH18C6 from oxonium ions under the acidic condition.

Effect of Anion on Cs-Extraction Efficiencies

As seen in Fig. 2, there does not appear to be a systematic correlation between the anions and the D_{Cs} values for this extraction system. Three ILs with $BETI^{-}$ as anion had greater D_{Cs} values than the ILs with NTf_2^{-} as anion; however, the other two ILs with NTf_2^{-} as anion had higher D_{Cs} values. The enhancement of the D_{Cs} values through hydrophobic conjugate anions can be attributed to the "latent" ion-exchange properties of ILs, which we have recently explored (21).

Effect of Carbon Chain Length of Amide on Cs-Extraction Efficiencies

The previous investigations by Chun et al., (6) Dietz et al., (4) Visser et al., (2) and our team (1) revealed that

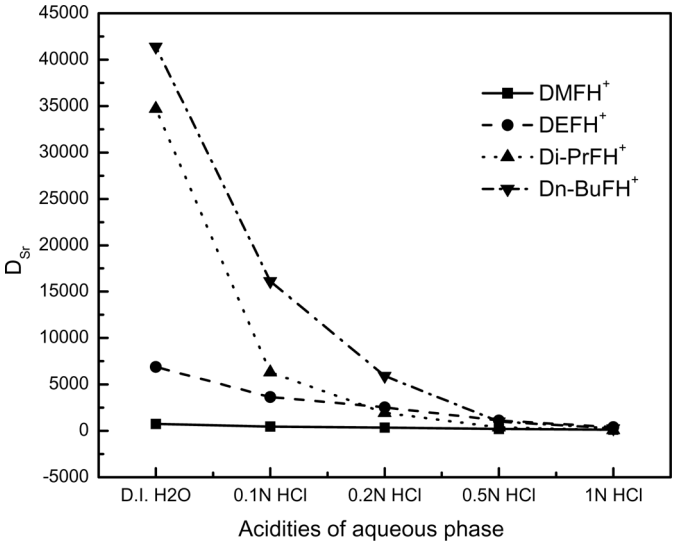


FIG. 4. Dependence of D_{Sr} on acidities of aqueous for [DXFH] [NTf_2].

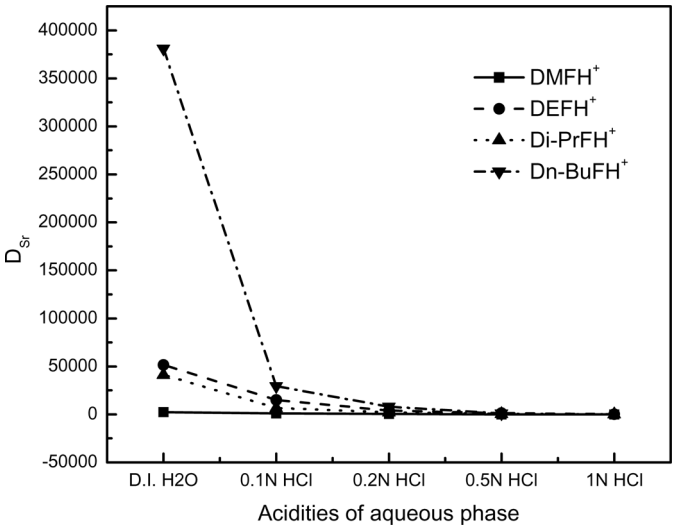


FIG. 5. Dependence of D_{Sr} on acidities of aqueous phase for [DXFH] [BETI].

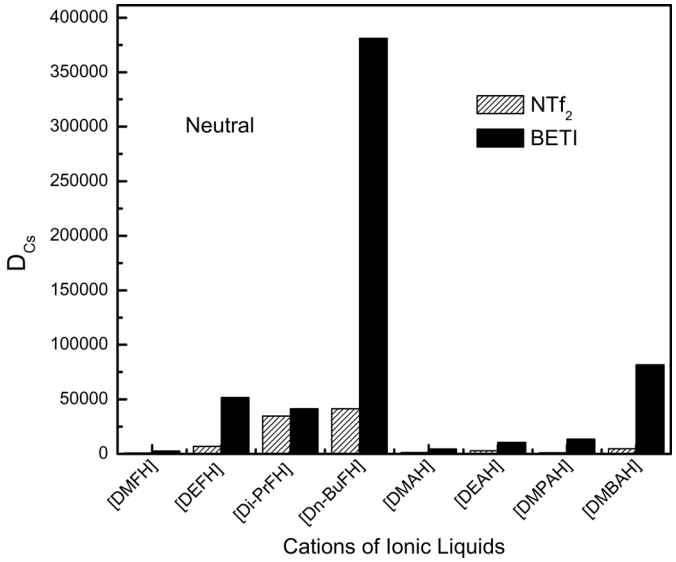


FIG. 6. Dependence of D_{Sr} on anions and cations of ILs.

for the same anions, the more hydrophilic the cations of an IL are, 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 PILs containing DCH18C6 relative to those of the AILs 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. However, as seen in Fig. 3, the correlation between D_{Cs} values and the carbon chain length is not clear for Cs extraction under neutral conditions. Under neutral conditions, the D_{Cs} values decrease from C2 to C3 and then increase from C3 to C4. Under acidic conditions, the D_{Cs} values decrease as the length of the carbon chain on the amide increases.

Sr-Extraction Results of Amide-Based ILs Containing DCH18C6

The Sr-extraction experiments based on the PILs were also performed as single-species (i.e., noncompetitive) extractions from $SrCl_2$ aqueous solutions at five different acidities. Table 3 summarizes the Sr-extraction results under these five different conditions.

Effect of Acidity on Sr-Extraction Efficiencies

As seen in Figs. 4 and 5, the D_{Sr} values decrease sharply with the acidity of aqueous solutions. For example, the D_{Sr} value of the extraction system based on IL 8 is reduced from 381,000 under the neutral condition to 232 under the acidic condition (1 N HCl). This change in D_{Sr} with pH value levels off under highly acidic conditions. The pronounced

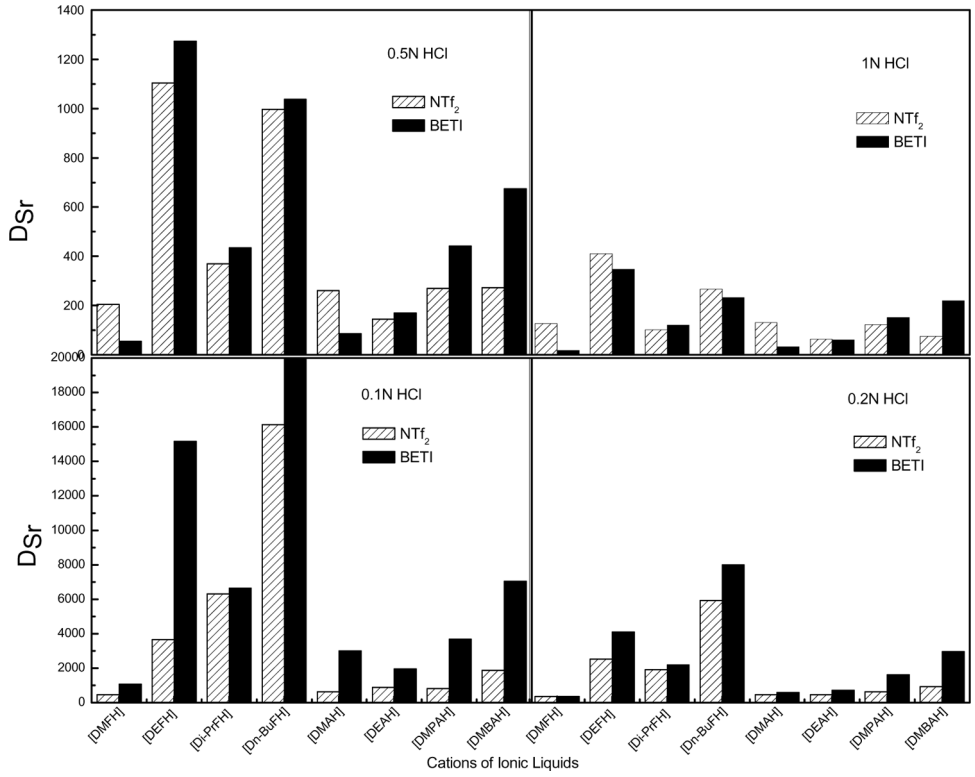


FIG. 7. Dependence of D_{Sr} on anions and cations of ILs at different acidity.

dependence of D_{Sr} on pH is also correlated with the strong complex formation of DCH18C6 with oxonium cations, which compete with Sr^{2+} during solvent extractions. The D_{Sr} values for ILs with BETI as anion decrease more drastically than those for ILs with NTf_2 as anion.

Effect of Anion on Sr-Extraction Efficiencies

As seen in Figs. 6 and 7, the correlations between IL anions and D_{Sr} values are obvious under neutral and mild acidic (0.1 N and 0.2 N HCl, respectively) conditions and the ILs with $BETI^-$ as anions give rise to much higher D_{Sr} values than the ILs with NTf_2^- as anions 21. The correlations between IL anions and D_{Sr} values become less obvious as the acidities of the aqueous phase increase. At 0.5 N HCl, two sets of ILs with NTf_2^- as anions yielded higher D_{Sr} values than the ILs with $BETI^-$ as anions. At the strongest acidic conditions, four sets of ILs with NTf_2^- as anions yielded higher D_{Sr} values than the ILs with $BETI^-$ as anions.

Effect of Carbon Chain Length of Amide on Sr-Extraction Efficiencies

As seen in Fig. 8, under both neutral and acidic conditions, the D_{Sr} values increase as the carbon chain length on the corresponding amide cations increases. For example, the D_{Sr} value (729) of the [DMFH] $[NTf_2]$-C1–based extraction system is significantly less than that (41,400) of the [Dn-BuFH] $[NTf_2]$-C4–based extraction system under neutral conditions. This observation is not consistent with the results concerning the imidazolium-based IL and ammonium-based IL extraction systems reported previously (7,4). This trend cannot be attributed to the synergistic effect of the ion-exchange capability of the IL cations and the unique ionic solvation environment of the ILs for the charged macrocyclic complexes. The amide cations with long alkyl chains are more hydrophobic than those with short alkyl chains. Accordingly, both ion-exchange and solvation capabilities decrease with the alkyl chain length.

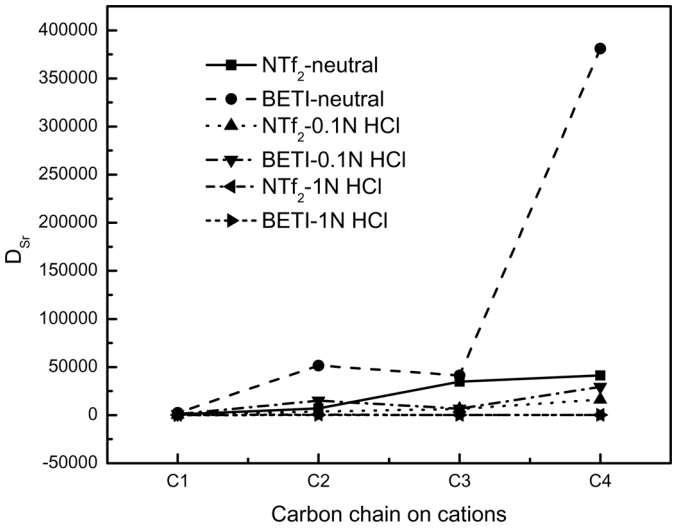


FIG. 8. Dependence of D_{Sr} values on carbon chain length on cations of ILs.

CONCLUSIONS

Sixteen amide-based ionic liquids have been synthesized and characterized by NMR, TGA, and DSC. The extraction efficiencies of the amide-based IL extraction systems using DCH18C6 as an extractant have been studied in comparison with the imidazolium-based and ammonium-based extraction systems. The dependence of the extraction efficiencies on the acidities of the extraction media, the carbon chain length on cations, and anions has also been studied and discussed.

ACKNOWLEDGEMENTS

This research was supported by the Basic Energy Science Program of the Office of Science, U.S. Department of Energy, under Contract DE-AC05-0096OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC.

REFERENCES

1. Dai, S.; Ju, Y.H.; Barnes, C.E. (1999) Solvent extraction of strontium nitrate by a crown ether using room-temperature ionic liquids. *J. Chem. Soc. Dalton Trans.*, 1201–1202.
2. Visser, A.E.; Swatloski, R.P.; Reichert, W.M.; Griffin, S.T.; Rogers, R.D. (2000) Metal ion distribution ratios in $[C_4mim][PF_6]$/water with crown ethers. *Ind. Eng. Chem. Res.*, 39: 3596–3604.
3. Visser, A.E.; Swatloski, R.P.; Griffin, S.T.; Hartman, D.H.; Rogers, R.D. (2001) Liquid/liquid extraction of metal ions in room temperature ionic liquids. *Sep. Sci. Tech.*, 36: 785–804.
4. Dietz, M.L.; Dzielawa, J.A. (2001) Ion-exchange as a mode of cation transfer into room-temperature ionic liquids containing crown ethers: Implications for the 'greenness' of ionic liquids as diluents in liquid-liquid extraction. *Chem. Commun.*, 2124–2125.
5. Dietz, M.L.; Stepinski, D.C. (2005) A ternary mechanism for the facilitated transfer of metal ions into room-temperature ionic liquids (RTILs): Implications for the "greenness" of RTILs as extraction solvents. *Green Chem.*, 7: 747–750.
6. Chun, S.; Dzyuba, S.V.; Bartsch, R.A. (2001) Influence of structural variation in room-temperature ionic liquids on the selectivity and efficiency of competitive alkali metal salt extraction by a crown ether. *Anal. Chem.*, 73: 3737–3741.
7. Luo, H.M.; Yu, M.; Dai, S. (2007) Solvent extraction of Sr^{2+} and Cs^{+} based on hydrophobic protic ionic liquids. *Z. Naturfors. Sect. A-J. Phys. Sci.*, 62: 281–291.
8. Welton, T. (1999) Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chem. Rev.*, 99: 2071–2083.
9. Huang, J.F.; Luo, H.M.; Liang, C.D.; Jiang, D.E.; Dai, S. (2008) Advanced liquid membranes based on novel ionic liquids for selective separation of olefin/parafrin via olefin-facilitated transport. *Ind. Eng. Chem. Res.*, 47: 881–888.
10. Zhu, H.G.; Huang, J.F.; Pan, Z.W.; Dai, S. (2006) Ionothermal synthesis of hierarchical ZnO nanostructures from ionic-liquid precursors. *Chem. Mat.*, 18: 4473–4477.
11. Huang, J.F.; Luo, H.M.; Dai, S. (2006) A new strategy for synthesis of novel classes of room-temperature ionic liquids based on complexation reaction of cations. *J. Electrochem. Soc.*, 153: J9–J13.

12. Greaves, T.L.; Drummond, C.J. (2008) Protic ionic liquids: Properties and applications. *Chem. Rev.*, 108: 206–237.
13. Luo, H.M.; Dai, S.; Bonnesen, P.V. (2004) Solvent extraction of Sr^{2+} and Cs^{+} based on room-temperature ionic liquids containing monoaza-substituted crown ethers. *Anal. Chem.*, 76: 2773–2779.
14. Luo, H.M.; Dai, S.; Bonnesen, P.V.; Buchanan, A.C.; Holbrey, J.D.; Bridges, N.J.; Rogers, R.D. (2004) Extraction of cesium ions from aqueous solutions using calix[4]arene-bis(tert-octylbenzo-crown-6) in ionic liquids. *Anal. Chem.*, 76: 3078–3083.
15. Huang, J.F.; Baker, G.A.; Luo, H.M.; Hong, K.L.; Li, Q.F.; Bjerrum, N.J.; Dai, S. (2006) Bronsted acidic room temperature ionic liquids derived from N,N-dimethylformamide and similar protophilic amides. *Green Chem.*, 8: 599–602.
16. Bonhote, P.; Dias, A.P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. (1996) Hydrophobic, highly conductive ambient-temperature molten salts. *Inorg. Chem.*, 35: 1168–1178.
17. Huang, J.F.; Luo, H.M.; Liang, C.D.; Sun, I.W.; Baker, G.A.; Dai, S. (2005) Hydrophobic bronsted acid-base ionic liquids based on PAMAM dendrimers with high proton conductivity and blue photo-luminescence. *J. Am. Chem. Soc.*, 127: 12784–12785.
18. Luo, H.M.; Huang, J.F.; Dai, S. (2008) Studies on thermal properties of selected aprotic and protic ionic liquids. *Sep. Sci. Technol.*, 43: 2473–2488.
19. Pedersen, C.J. (1988) The discovery of crown ethers (Noble Lecture). *Angew. Chem.-Int. Edit.*, 27: 1021–1027.
20. Haverlock, T.J.; Bonnesen, P.V.; Sachleben, R.A.; Moyer, B.A. (1997) Applicability of a calixarene-crown compound for the removal of cesium from alkaline tank waste. *Radiochim. Acta.*, 76: 103–108.
21. Lee, B.; Im, H.-J.; Luo, H.; Hagaman, E.W.; Dai, S. (2005) Synthesis and characterization of periodic mesoporous organosilicas as anion exchange resins for perrhenate adsorption. *Langmuir*, 21: 5372–5376.