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Influence of Structural Variation in Room-Temperature Ionic Liquids on the Selectivity and Efficiency of Competitive Alkali Metal Salt Extraction by a Crown Ether

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An improved method for the preparation of 1-alkyl-3-methylimidazolium hexafluorophosphates provides a series of room-temperature ionic liquids (RTILs) in which the 1-alkyl group is varied systematically from butyl to nonyl. For competitive solvent extraction of aqueous solutions of alkali metal chlorides with solutions of dicyclohexano-18-crown-6 (DC18C6) in these RTILs, the extraction efficiency generally diminished as the length of the 1-alkyl group was increased. Under the same conditions, extraction of alkali metal chlorides into solutions of DC18C6 in chloroform, nitrobenzene, and 1-octanol was undetectable. The extraction selectivity order for DC18C6 in the RTILs was $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$. As the alkyl group in the RTIL was elongated, the K^+/Rb^+ and K^+/Cs^+ selectivities exhibited general increases with the larger enhancement for the latter. For DC18C6 in 1-octyl-3-methylimidazolium hexafluorophosphate, the alkali metal cation extraction selectivity and efficiency were unaffected by variation of the aqueous-phase anion from chloride to nitrate to sulfate.

Room-temperature ionic liquids (RTILs) are attracting ever-increasing attention as solvents and catalysts for a wide variety of organic reactions.[1,2] Applications of RTILs in separation processes have received much less attention.[3−9] When employed in solvent extraction processes, the negligible vapor pressure and low flammability of a RTIL are important advantages over conventional organic diluents. For metal ion separations, Dai and co-workers[6] found large distribution coefficient values for extraction of strontium nitrate from aqueous solutions into disubstituted imidazolium hexafluorophosphates and bis[(trifluoromethyl)sulfonyl]amides by dicyclohexano-18-crown-6 (DC18C6) (Figure 1). Subsequently, Rogers and co-workers[8] reported the extraction of sodium, cesium, and strontium nitrates from aqueous solutions into 1-butyl-, 1-hexyl-, and 1-octyl-3-methylimidazolium hexafluorophosphates by 18-crown-6, DC18C6, and 4,4′(5′)-di(*tert*-butylcyclohexano)-18-crown-6. Very recently, Rogers and co-workers[9] described “task specific” RTILs containing metal ion chelating units and their use in the solvent extraction of cadmium(II) and mercury(II) chlorides.

We now report an improved preparation of 1-alkyl-3-methylimidazolium hexafluorophosphates with alkyl = butyl → nonyl (Figure 1), their physical characterization, and an investigation of these RTILs as diluents for competitive solvent extractions of alkali metal salts by DC18C6.

EXPERIMENTAL SECTION

Reagents. Inorganic and organic compounds were reagent-grade commercial products and were used as received unless noted otherwise. Dicyclohexano-18-crown-6 (a mixture of the cis-syn-cis and cis-anti-cis isomers) was obtained from Aldrich. Deionized water was prepared by passing distilled water through three Barnstead D8922 combination cartidges in series. Before use in solvent extraction, chloroform was washed with deionized water to remove the ethanol stabilizer and saturate the chloroform with water. Nitrobenzene was distilled under reduced pressure and washed with deionized water. The 1-octanol was washed with distilled water.

Apparatus. The ^{1}H NMR spectra were taken in acetone-d_6 (∼0.1 M solutions) with a Bruker AF-200 NMR spectrometer. Proton chemical shifts are reported downfield from TMS. IR spectra were recorded as films between NaCl plates with a Perkin-Elmer model 1600 FT-IR spectrophotometer. UV−visible spectra were measured with a Shimadzu UV−visible spectrophotometer. Melting points and glass transition temperatures were determined with a Shimadzu DSC-50 differential scanning calorimeter and a LTC-50 low-temperature assembly. Alkali metal cation concentrations in aqueous solutions were determined with a Dionex DX-120 ion chromatograph using a Dionex CS12A column. For the solvent extraction studies, a Glas-Col multipulse vortex mixer and a Clay Adams Compact II centrifuge were used to mix and separate the organic and aqueous solutions, respectively. The extractions were performed in 15-mL, metal-free, polypropylene centrifuge tubes (Elkay), and samples were removed with Hamil-

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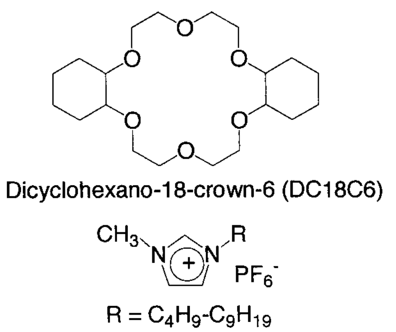

Figure 1. Structures of dicyclohexano-18-crown-6 and 1-alkyl-3-methylimidazolium hexafluorophosphates.

ton GasTight syringes. Elemental analysis was performed by Desert Analytics Laboratory of Tucson, AZ.

General Procedure for the Preparation of 1-Alkyl-3-methylimidazolium Bromides.[10] A flask containing 1-methylimidazole (60 mmol) and a primary alkyl bromide (60 mmol) was placed in a silicone oil bath. With magnetic stirring, the bath was heated to 140 °C during a 10-min period. In the latter stages of this heating, an exothermic reaction took place forming an emulsion that disappeared after a few minutes to form a transparent, golden, slightly viscous solution. When the emulsion disappeared, the flask was removed from the oil bath and the contents were allowed to stir and cool in the air for 10 min. The flask was returned to the 140 °C oil bath for 10−15 min. After cooling to room temperature, the hygroscopic 1-alkyl-3-methylimidazolium bromide was obtained in nearly quantitative yield and of sufficient purity for use directly in the preparation of the corresponding hexafluorophosphate salt.

General Procedure for the Preparation of 1-Alkyl-3-methylimidazolium Hexafluorophosphates. HPF_6 (22.2 mL of 60% solution in water, 0.15 mol) was added slowly to a magnetically stirred solution of the 1-alkyl-3-methylimidazolium bromide (0.15 mol) in 30 mL of water in a plastic bottle cooled in an ice bath. When the addition was completed, the mixture was stirred for 10 min in the ice bath and then for 10 min at room temperature. The mixture was poured into a separatory funnel containing Et_3N (20.9 mL, 0.15 mol) in 200 mL of deionized water. The mixture was shaken repeatedly, and the layers were separated. The organic layer was washed with 200 mL of warm, deionized water. (As determined by ion chromatographic analysis of the contacting aqueous phase, the 1-alkyl-3-methylimidazolium hexafluorophosphate was usually contaminated at this stage by significant levels of alkali metal salts from the HPF_6.) The organic layer was dissolved in dichloromethane (100 mL), and deionized water (200 mL) was added. After vigorous, magnetic stirring of the mixture for 30 min, the water layer was replaced with 200 mL of fresh deionized water and the mixture was vigorously stirred for 30 min. The organic layer was separated, and the dichloromethane was evaporated in vacuo. Residual water in the 1-alkyl-3-methylimidazolium hexafluorophosphate was removed by azeotropic distillation with benzene using a Dean−Stark trap. The benzene was evaporated in vacuo and the oil was dried in vacuo (oil pump) at 110−130 °C for 4−8 h.

1-Butyl-3-methylimidazolium hexafluorophosphate:[3] 64% yield; ^1H NMR δ 0.93 (3H, t, $J = 7.2$ Hz), 1.36 (2H, sept, $J = 7.5$ Hz), 1.89 (2H, pen, $J = 7.6$ Hz), 3.98 (3H, s), 4.28 (2H, t, $J = 4.0$ Hz), 7.58 (1H, t, $J = 1.8$ Hz), 7.63 (1H, t, $J = 1.8$ Hz), 8.76 (1H, s); IR 3160, 2965, 1467, 836 cm^{-1}.

3-Methyl-1-pentylimidazolium hexafluorophosphate: 66% yield; ^1H NMR δ 0.89 (3H, m), 1.37 (4H, m), 1.96 (2H, m), 4.04 (3H, s), 4.34 (2H, t, $J = 7.2$ Hz), 7.68 (1H, t, $J = 1.8$ Hz), 7.74 (1H, t, $J = 1.8$ Hz), 8.94 (1H, s); IR 3170, 2961, 1576, 1458, 835 cm^{-1}. Anal. Calcd for $C_9H_{17}F_6N_2P$: C, 36.25; H, 5.75; N, 9.39. Found: C, 36.24; H, 6.04; N, 9.48.

1-Hexyl-3-methylimidazolium hexafluorophosphate: 70% yield; ^1H NMR δ 0.84 (3H, m), 1.39 (6H, m), 1.96 (2H, m), 4.02 (3H, s), 4.32 (2H, t, $J = 7.2$ Hz), 7.64 (1H, t, $J = 1.8$ Hz), 7.70 (1H, t, $J = 1.8$ Hz), 8.87 (1H, s); IR 3169, 2933, 1576, 1458, 836 cm^{-1}. Anal. Calcd for $C_{10}H_{19}F_6N_2P$: C, 38.46; H, 6.13; N, 8.97. Found: C, 38.60; H, 6.28; N, 8.97.

1-Heptyl-3-methylimidazolium hexafluorophosphate: 78% yield; ^1H NMR δ 0.87 (3H, m), 1.35 (8H, m), 1.97 (2H, m), 4.03 (3H, s), 4.33 (2H, t, $J = 7.2$ Hz), 7.65 (1H, t, $J = 1.8$ Hz), 7.72 (1H, t, $J = 1.8$ Hz), 8.90 (1H, s); IR 3166, 2929, 1574, 1463, 834 cm^{-1}. Anal. Calcd for $C_{11}H_{21}F_6N_2P$: C, 40.49; H, 6.49; N, 8.59. Found: C, 40.63; H, 6.63; N, 8.59.

3-Methyl-1-octylimidazolium hexafluorophosphate: 85% yield; ^1H NMR δ 0.87 (3H, m), 1.33 (10H, m), 1.95 (2H, m), 4.04 (3H, s), 4.35 (2H, t, $J = 7.4$ Hz), 7.69 (1H, t, $J = 1.8$ Hz), 7.75 (1H, t, $J = 1.8$ Hz), 8.99 (1H, s); IR 3168, 2928, 1575, 1460, 835 cm^{-1}. Anal. Calcd for $C_{12}H_{23}F_6N_2P$: C, 42.35; H, 6.81; N, 8.23. Found: C, 42.59; H, 6.57; N, 8.26.

3-Methyl-1-nonylimidazolium hexafluorophosphate: 87% yield; ^1H NMR δ 0.87 (3H, m), 1.36 (12H, m), 1.99 (2H, m), 4.05 (3H, s), 4.36 (2H, t, $J = 7.2$ Hz), 7.70 (1H, t, $J = 1.8$ Hz), 7.76 (1H, t, $J = 1.8$ Hz), 8.98 (1H, s); IR 3170, 2926, 1575, 1466, 832 cm^{-1}. Anal. Calcd for $C_{13}H_{25}F_6N_2P$: C, 44.07; H, 7.11; N, 7.91. Found: C, 44.38; H, 7.32; N, 7.94.

Phase-Transition Temperature Determination. A weighed amount of the 1-alkyl-3-methylimidazolium hexafluorophosphate (2−16 mg) was sealed under air in an aluminum crucible. The temperature in the DSC instrument was lowered to −130 to −140 °C by pouring liquid nitrogen into the low-temperature assembly. After all of the liquid nitrogen had evaporated from the cooling unit and the temperature started to rise, heating at 30 °C/min was initiated.

Density Measurements. A 1.0-mL volumetric flask was filled to the mark with the 1-alkyl-3-methylimidazolium hexafluorophosphate at room temperature and weighed. A heat gun was used to remove air bubbles in the sample.

Solubility in Water. In a 15-mL polypropylene centrifuge tube, 1.00 g of the RTIL and 2.5 mL of deionized water were shaken on a vortex mixer for 30 min and centrifuged for 10 min. A 10-μL aliquot of the aqueous phase was removed with a microsyringe and diluted to 2.5 mL with deionized water. The absorbance of this solution at 211 nm was measured and compared with that obtained from dissolving a weighed amount (1−9 mg) of the RTIL in 2.5 mL of deionized water.

Competitive Solvent Extraction of Alkali Metal Salts from Water by DC18C6 in Chloroform, Nitrobenzene, and 1-Octanol. A mixture of 2.0 mL of 20 mM DC18C6 in chloroform, nitrobenzene, or 1-octanol and 5.0 mL of a 2.0 mM (in each) aqueous solution of five alkali metal chlorides in a 15-mL

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polypropylene centrifuge tube was shaken on a vortex mixer for 5 min (10 min with nitrobenzene). The tube was centrifuged for 5 min (10 min with nitrobenzene) to promote phase separation. A 1.5-mL portion of the organic phase was removed with a syringe and added to 3.0 mL of deionized water in a new centrifuge tube. The tube was shaken on a vortex mixer for 5 min (10 min with nitrobenzene) and centrifuged for 5 min (10 min with nitrobenzene). A 1.0-mL portion of the aqueous phase was removed with a syringe and transferred to a 10-mL volumetric flask. The flask was filled to the mark with deionized water, and the alkali metal cation concentrations were determined by ion chromatography.

Competitive Solvent Extraction of Alkali Metal Salts from Water into RTIL Solutions of DC18C6. For each RTIL, the competitive solvent extraction experiment was performed in triplicate. A mixture of 1.00 g of a 20 mM solution of DC18C6 in the RTIL and 2.5 mL of a 2.0 mM (in each) aqueous solution of the alkali metal salts in a 15-mL polypropylene centrifuge tube was shaken on a vortex mixer for 30 min, centrifuged for 10 min, shaken on a vortex mixer for 30 min, and centrifuged for 10 min. A 1.0-mL portion of the aqueous phase was removed with a syringe and transferred to a 10-mL volumetric flask. The flask was filled to the mark with deionized water, and the alkali metal cation concentrations were determined by ion chromatography. Control experiments were conducted in the absence of DC18C6 to correct for alkali metal salt extraction by the RTIL itself.

RESULTS AND DISCUSSION

Synthesis of 1-Alkyl-3-methylimidazolium Hexafluorophosphates. Although hexafluorophosphate-based RTILs have been utilized as solvents in many processes,[1,2] no convenient method has been reported for the preparation of such solvents in large quantities and with sufficient purity for analytical studies.

Preparation of 1-butyl-3-methylimidazolium hexafluorophosphate by treatment of 1-butyl-3-methylimidazolium chloride with HPF_6 using a published procedure[3] followed by washing several times with deionized water to remove contaminating HCl afforded only 35−40% yields of the pure RTIL (free from alkali metal cation contaminants by ion chromatography). Since this RTIL has some water solubility, the low yield is attributed to losses during the washing steps. Replacing the HPF_6 with KPF_6 gave the crude RTIL in 90−95% yield. However, repeated washings with deionized water to remove contaminating potassium chloride reduced the yield of the pure RTIL to approximately 50%. In view of such difficulties, a new procedure was developed for the synthesis of 1-alkyl-3-methylimidazolium hexafluorophosphates.

An aqueous solution of the 1-alkyl-3-methylimidazolium bromide, formed by the neat reaction of 1-methylimidazole with equimolar 1-bromoalkane at 140 °C,[10] in a plastic bottle was stirred magnetically in an ice bath and 1 equiv of HPF_6 (60% aqueous solution) was added slowly. After stirring in the ice bath and then at room temperature, the contents were transferred to a separatory funnel containing water and 1 equiv of Et_3N. The 1-alkyl-3-methylimidazolium hexafluorophosphate was separated, washed with water, and dissolved in dichloromethane. The solution was washed with water, and the dichloromethane was evaporated in vacuo. Traces of water were removed from the residue by azeotropic distillation with benzene using a Dean−Stark trap. The benzene was evaporated in vacuo, and the resultant oil was dried at elevated temperature in vacuo. Yields of 1-alkyl-3-methylimidazolium hexafluorophosphates based upon two-step reactions from 1-methylimidazole were 64−87% and increased as the alkyl group of the 1-alkyl group was elongated.

Table 1. Densities, Solubilities in Water, and Phase Transitions of 1-Alkyl-3-methylimidazolium Hexafluorophosphates

1-alkyl group	density (g/mL)	water solub (g/100 mL)	midpoint of glass transition (°C)[a]	ΔC_p (mJ/s·K)
butyl	1.363	1.88	−77	0.18
pentyl	1.333	1.23	−80	0.16
hexyl	1.307	0.75	−80	0.13
heptyl	1.274	0.37	−84	0.23
octyl	1.237	∼0.20	−71	0.07
nonyl	1.202	∼0.15	−66	0.02
			14[b]	5.8[c]

[a] Heating rate of 30 °C/min. [b] Melting point. [c] Units are ΔH (kJ/mol).

Physical Properties of 1-Alkyl-3-methylimidazolium Hexafluorophosphates. The data in Table 1 show that the densities and water solubilities of the 1-alkyl-3-methylimidazolium hexafluorophosphates decrease monotonically as the 1-alkyl group is lengthened.

Melting points and/or glass transition temperatures for the 1-alkyl-3-methylimidazolium hexafluorophosphates with 1-alkyl groups of butyl → nonyl were determined by DSC and are presented in Table 1. Although a glass transition temperature of 6 °C has been reported for 1-butyl-3-methylimidazolium hexafluorophosphate,[11] we were unable to observe any phase transition in the region of 0−10 °C for several measurements made with different samples of this RTIL.

Competitive Solvent Extraction of Alkali Metal Chlorides by DC18C6 in Chloroform, Nitrobenzene, and 1-Octanol. For comparison with solvent extraction results obtained with the RTILs, competitive solvent extractions of alkali metal chlorides by DC18C6 were performed in the freqently encountered organic diluents of chloroform, nitrobenzene, and 1-octanol. From contact of 2.0 mM (in each) aqueous solutions of the five alkali metal chlorides with a 20 mM solutions of DC18C6 in chloroform, nitrobenzene, and 1-octanol, transfer of alkali metal chlorides into the organic phase was undetectable. This low extraction efficiency is attributed to the high hydration energy of chloride ion.[12]

Competitive Solvent Extraction of Alkali Metal Chlorides by DC18C6 in 1-Alkyl-3-methylimidazolium Hexafluorophosphates. To assess the levels of alkali metal chloride extractions by the RTIL alone, solvent extractions of aqueous solutions containing 2.0 mM concentrations of each of the five alkali metal chlorides were conducted with no DC18C6 in the organic phase. For ease of comparison, the alkali metal cation concentrations in the RTILs shown in Figure 2 are given as percent metal salt loadings of the crown ether if it had been present in the diluent. As can be seen, the levels of alkali metal chloride transfer into the RTIL are appreciable for 1-butyl-3-methylimidazolium hexafluorophosphate and diminish rapidly as the 1-alkyl group in the RTIL is elongated. For all six RTILs, the extraction selectivity is $Cs^+ > Rb^+ > K^+ > Li^+ \sim Na^+$. This is consistent with the relative hydrophobicities of the alkali metal cations.

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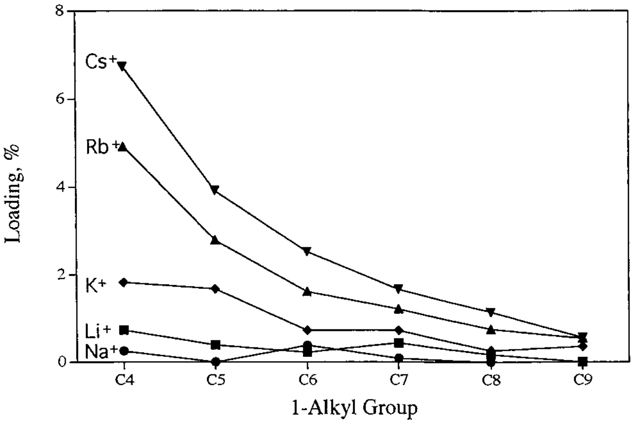

Figure 2. Influence of 1-alkyl group variation on efficiency of competitive alkali metal cation extraction from aqueous solutions into 1-alkyl-3-methylimidazolium hexafluorophosphates in the absence of dicyclohexano-18-crown-6.

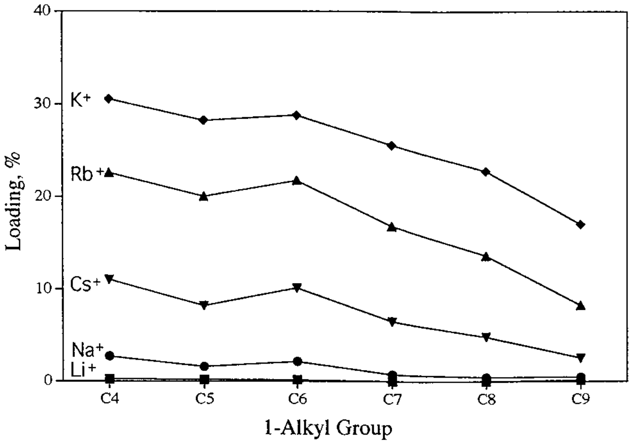

Figure 3. Influence of 1-alkyl group variation on efficiency of competitive alkali metal cation extraction from aqueous solutions by dicyclohexano-18-crown-6 in 1-alkyl-3-methylimidazolium hexafluorophosphates.

Results from competitive solvent extraction of 2.0 mM (in each) aqueous solutions of the alkali metal chlorides with 20 mM solutions of DC18C6 in the six RTILs are shown in Figure 3. (The data are corrected for the levels of alkali metal cations that are extracted by the RTIL alone.) Immediately apparent is the change in extraction selectivity from that observed in the absence of DC18C6 (Figure 2). The observed extraction selectivity of $K^+ > Rb^+ > Cs^+ > Na^+ \geq Li^+$ reflects the relative complexing abilities of 18-crown-6 ligands for the alkali metal cations.[13]

With the exception of 1-hexyl-3-methylimidazolium hexafluorophosphate, there is a smooth decrease in the extraction efficiency for each alkali metal cation species as the 1-alkyl group in the RTIL is elongated (Figure 3). Thus, increasing the lipophilicity of the RTIL is found to diminish the propensity for alkali metal cation extraction by DC18C6. The somewhat greater alkali metal extraction efficiencies with 1-hexyl-3-methylimidazolium hexafluorophosphate as the diluent than those expected from the correlation established by the other 1-alkyl-3-methylimidazolium hexafluorophosphates were reproducible for different batches of this RTIL. The reason for the slightly anomalous behavior of 1-hexyl-3-methylimidazolium hexafluorophosphate as a solvent for the competitive solvent extraction of alkali metal cations by DC18C8 is not apparent at this stage. (Unusual behavior of 1-hexyl-3-methylimidazolium ion has been noted earlier by others.[14])

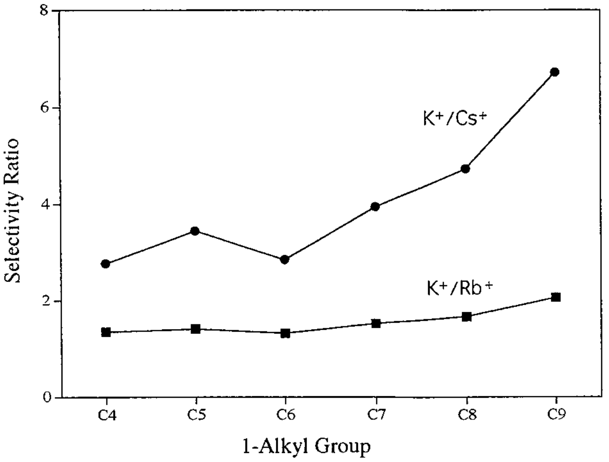

Figure 4. Influence of the 1-alkyl group variation on the K^+/Cs^+ and K^+/Rb^+ selectivies in competitive alkali metal cation extraction from aqueous solutions by dicyclohexano-18-crown-6 in 1-alkyl-3-methylimidazolium hexafluorophosphates.

The influence of varying the 1-alkyl group of the 1-alkyl-3-methylimidazolium hexafluorophosphate diluent on the K^+/Cs^+ and K^+/Rb^+ selectivities for competitive alkali metal cation extractions by DC18C6 is depicted in Figure 4. With the exception of 1-hexyl-3-methylimidazolium hexafluorophosphate, the K^+/Cs^+ selectivity and, to a lesser extent, the K^+/Rb^+ selectivity increase as the 1-alkyl group of the RTIL is elongated. Thus, the decrease in extraction efficiency (Figure 3) as the 1-alkyl group of the 1-alkyl-3-methylimidazolium hexafluorophosphate is lengthened is coupled with an increase in extraction selectivity.

Competitive Solvent Extraction of Alkali Metal Salts by DC18C6 in 1-Octyl-3-methylimidazolium Hexafluorophosphate. For competitive solvent extractions of alkali metal salts from aqueous solution into common organic solvents by crown ethers, the identity of the anion influences both the extraction efficiency and selectivity.[15–17] To probe the counteranion influence in extractions involving RTIL diluents, competitive extractions of alkali metal nitrates and alkali metal sulfates from aqueous solutions by DC18C6 in 1-octyl-3-methylimidizolium hexafluorophosphate were performed. A comparison of the percent crown ether loadings for the five alkali metal cations as the anion was varied from chloride to nitrate to sulfate is presented in Table 2. It is immediately apparent that the efficiencies and selectivities of alkali metal cation extraction are unaffected by this variation in the aqueous-phase anion. This differs markedly from results reported for competitive alkali metal salt extractions by DC18C6 in chloroform and 1-octanol.[16,17] For these molecular solvents, the metal ion loading was strongly affected by anion variation. This

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Table 2. Effect of Anion on Percent Loading for Competitive Solvent Extraction of Alkali Metal Salts from Aqueous Solutions by Dicyclohexano-18-crown-6 in 1-Octyl-3-methylimidazolium Hexafluorophosphate

	loading (%)[a,b]				
	Li^+	Na^+	K^+	Rb^+	Cs^+
chloride	0.2	0.4	22.8	13.6	4.8
nitrate	0.2	0.4	22.3	13.2	4.6
sulfate	0.2	1.0	22.7	13.6	5.0

[a] Each extraction was conducted in triplicate. [b] Standard deviation from the average was ±0.3%.

further underscores the uniqueness of RTILs as diluents in solvent extraction.

SUMMARY

A convenient method for the preparation of high-purity 1-alkyl-3-methylimidazolium hexafluorophosphates in two steps using commercially available reagents is reported. Solutions of DC18C6 in these RTILs provide efficient extractions of alkali metal chlorides from aqueous solutions under conditions that gave negligible extraction with customary organic diluents of chloroform, nitrobenzene, and 1-octanol. As the lipophilicity of the RTIL is enhanced by lengthening the 1-alkyl group, the extraction efficiency decreases, but the extraction selectivity increases. In contrast to customary organic diluents, the efficiency and selectivity of alkali metal salt extraction from aqueous solutions into RTIL solutions of DC18C6 is unaffected by variation of the counteranion from chloride to nitrate to sulfate. Further exploration of the intriguing features of ionic liquids in separation processes is underway in our laboratories.

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