Task-Specific Ionic Liquids Incorporating Novel Cations for the Coordination and Extraction of Hg²⁺ and Cd²⁺: Synthesis, Characterization, and Extraction Studies

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A series of hydrophobic task-specific ionic liquids designed to extract Hg²⁺ and Cd²⁺ from water were prepared by appending urea-, thiourea-, and thioether-substituted alkyl groups to imidazoles and combining the resulting cationic species with PF_6^-. The new ionic liquids were characterized and investigated for their metal ion extraction capabilities. When used in liquid/liquid extraction of Hg²⁺ and Cd²⁺ from aqueous solutions, the metal ion distribution ratios increased several orders of magnitude, regardless of whether the ionic liquids were used as the sole extracting phase or doped into a series of [1-alkyl-3-methylimidazolium][PF_6] (alkyl = n-C_4−C_8) ionic liquids to form a 1:1 solution. In the 1:1 mixtures, as the length of the alkyl chain increased from butyl to hexyl to octyl, the metal ion distribution ratios increased. Increasing the ratio TSIL/[C_4mim][PF_6] resulted in higher distribution ratios for both Hg²⁺ and Cd²⁺. Overall, the thiourea- and urea-derivatized cations yielded the highest distribution ratios, and those for Hg²⁺ were higher than those for Cd²⁺; however, a change in aqueous-phase pH does not promote the stripping of metal ions from the extracting phase. The combination of these imidazolium cations and PF_6^- produced ionic liquids with decreased thermal stability in comparison to [$C_n$mim]-[PF_6]. Gaussian98 restricted Hartree−Fock geometry optimizations for one of the thiourea-appended cations shows the charge delocalization around the ring and suggests that the thiourea group may aid in deprotonating the imidazolium ring and may be responsible for the lowered thermal stability of these cations.

Introduction

In contrast to high temperature melts that are commonly referred to as molten salts, ionic liquids (IL) are, as their name implies, ionic media resulting from combinations of organic cations and various anions that may be liquid at room temperature. (The adopted upper temperature limit for the classification "ionic liquid" is 100 °C and higher melting ionic systems are typically referred to as molten salts.) Common formulations of IL rely on pyridinium (*1, 2*) or imidazolium (*3, 4*) cations bearing simple alkyl appendages, as shown in Figure 1, to produce asymmetrical cations which lower the lattice energy, and hence the melting point, of the resulting ionic medium (*5*). The composition and associated properties of IL depend on the cation and anion combinations (estimated to be as high as 10¹⁸) (*6*). For example, using butyl ([C_4mim]⁺), hexyl ([C_6mim]⁺) or octyl ([C_8mim]⁺) derivatives of [1-alkyl-3-methylimidazolium][PF_6^-] increases both the hydrophobicity (*7*) and viscosity (*4*) and affects the melting points (*4*). IL formulation may also include cations composed of other heterocyclic aromatic molecules, quaternary ammonium and phosphonium salts, as well as ions with structurally and functionally complex side chains (*8−10*).

The introduction of different anions has become more popular as an increasing number of alternatives are being discovered that function as well as, or better than, the well-known anions such as $AlCl_4^-$ for applications in liquid/liquid separations, catalysis, or synthesis (*8, 9, 11−14*). The anion chemistry has a large influence on the properties of IL such that PF_6^- produces a water immiscible and air stable IL suitable for use in place of organic solvents in liquid/liquid extractions (*4, 15, 16*). However, other perfluorinated anions (*3*), such as bis(trifluoromethylsulfonyl)imide, may prove to be more stable anions for use in liquid/liquid separations in light of the PF_6^- degradation that has been reported (*17*).

The recent interest surrounding IL in regards to Green Chemistry and the associated development of new solvents and alternative technologies has largely been a result of the lack of a measurable vapor pressure for many IL. The principles of Green Chemistry encompass a new attitude toward industrial practices and chemical syntheses (*18*) where gaseous, liquid, or solid wastes are not treated as inevitable byproducts of the chemical manufacturing industry. Instead, the new approach involves steps to decrease or eliminate the hazards in the system and eliminate the waste before it is produced.

Thus, the potential of IL to provide a nonvolatile solvent system has become a practical target for reducing waste and hazards by eliminating traditional volatile organic solvents. Despite their widespread use, a majority of common solvents are flammable and are potential health hazards. For example, approximately half of the 189 hazardous air pollutants regulated by the Clean Air Act Amendment of 1990 are volatile organic compounds, including solvents such as dichloromethane and trichloromethane (*19*).

Despite the promise of IL to help eliminate solvent vapor loss, it is noteworthy to include that acute toxicity studies are reported for only one IL, [3-hexyloxymethyl-1-methylimidazolium][BF_4^-], and the experimental protocol is not reported (*20*). (The study reported an LD_{50} = 1400 mg/kg and 1370 mg/kg, for female and male rats, respectively (*20*).) Despite the lack of comprehensive toxicity data for all IL combinations, IL have demonstrated their use in place of organic solvents for synthesis, catalysis, and separations. IL are scientifically interesting and may prove to be less polluting with reduced exposure to health hazards. Certainly, even their study has led to an increased awareness of the goals of Green Chemistry.

The advent of moisture stable IL and their unique chemical and physical properties has brought about the

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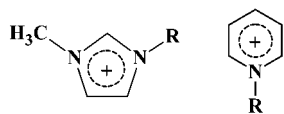‡ University of South Alabama.

FIGURE 1. Generic structure of 1-alkyl-3-methylimidazolium and alkylpyridinium cations.

widespread application of IL with significant contributions from their use as alternatives to traditional organic solvents (*7*, *21*, *22*) and unique reaction and as synthesis media (*23*). In most cases, the IL characteristic that has been exploited is their ability to dissolve a variety of solutes. For example, IL can be used in place of traditional organic solvents in liquid/liquid extractions where hydrophobic molecules such as simple benzene derivatives will partition to the IL phase (*4*, *7*, *16*, *21*). Ionizable organic solutes may display pH-dependent partitioning, as reported for the indicator dye thymol blue (*7*).

Conversely, for metal ions in $[C_n mim][PF_6]$/aqueous systems, the distribution ratios are below 1, indicating their hydrated nature and preference for the aqueous phase (e.g., the distribution ratios for Hg^{2+} and Cd^{2+} in $[C_4mim][PF_6]$/water systems are 0.84 and 0.03, respectively (*7*)). In traditional solvent extraction, increasing the metal ion partitioning to the more hydrophobic phase is accomplished by adding extractants that reside quantitatively in the extracting phase. The extractant molecules serve to dehydrate the metal ions and to offer a more hydrophobic environment that enables their transport to the extracting phase. To that end, we have used crown ethers to aid in the extraction of Sr^{2+} and Cs^+ from NO_3^- media (*17*), azo molecules for the extraction of transition metals (*15*), and both halides and pseudohalides for Hg^{2+} extraction (*15*) in liquid/liquid systems with $[C_n-mim][PF_6]$. Other literature reports highlight the use of crown ethers for Sr^{2+} extraction in liquid/liquid systems using IL composed of the bis(trifluoromethylsulfonyl)imide anion (*24*).

The drawbacks associated with this approach lie in finding extractant molecules that remain exclusively in the IL and also understanding the increased complexity of the system upon the addition of solutes, prompting our investigation of the task-specific ionic liquid (TSIL) concept for metal ion extraction in IL. Attaching a metal ion coordinating group directly to the imidazolium cation makes the extractant an integral part of the hydrophobic phase and greatly diminishes the chance for loss to the aqueous phase. Despite the added cost of TSIL, they can be used in a mixture with less expensive IL to achieve the same result (*25*).

Ligands employed in metal ion extraction have appended functional groups (e.g., carboxylic acids) or contain donor atoms (e.g., crown ethers) that interact to form complexes with metal ions. Ligands containing soft donor atoms (*26*) such as N or S have been explored in other systems for the extraction of heavy metals through the use of thioether (*27*), thiourea (*28*), and urea (*29*) functional groups. Other reports confirm that acidic conditions can be sufficient to induce Hg^{2+} and Cd^{2+} stripping from thiourea and thioether-based extractants (*30*, *31*). Hence, we have prepared IL with thioether, thiourea, and urea functional groups incorporated in the alkyl chains of the imidazolium cations (*16*). Here, we report the synthesis of a series of novel imidazolium PF_6^- TSIL, **1**–**6** (Figure 2) and their use in the specific task of extracting Hg^{2+} and Cd^{2+} from aqueous solutions.

Experimental Section

All chemicals except for HPF_6 were obtained from Aldrich (Milwaukee, WI) and were of reagent grade and used without further purification. HPF_6 was supplied by Ozark-Mahoning Co. (Tulsa, OK) and was used as received. $^{203}HgCl_2$ was
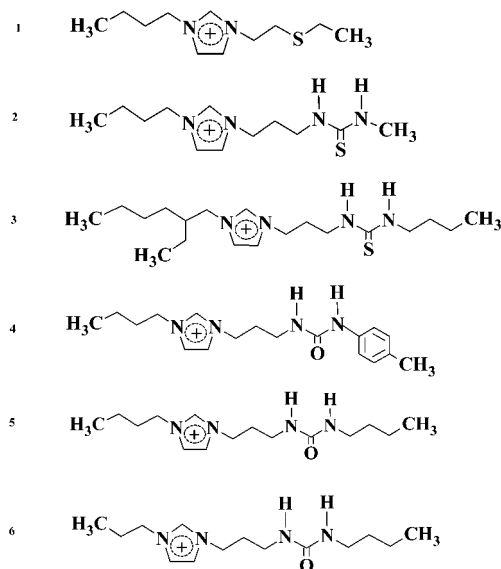

FIGURE 2. Structures of the TSIL cations utilized in these studies.

obtained from Isotope Products Laboratories (Burbank, CA) and $^{109}CdCl_2$ was obtained from Amersham Life Sciences (Arlington Heights, IL). $[C_4mim][PF_6]$, $[C_6mim][PF_6]$, and $[C_8-mim][PF_6]$ were synthesized and characterized as described elsewhere (*4*).

Synthesis of TSIL (2–6). The general synthesis of the thio- and urea-based IL **2**–**6** is described as follows. 1-(3′-Aminopropyl)imidazole (20.0 g, 0.160 mol) was mixed with 100 mL of acetonitrile under an atmosphere of dry nitrogen. To the stirred solution, 15.5 g (0.156 mol) of *n*-butylisocyanate dissolved in 25 mL of acetonitrile was added in a dropwise fashion. The combined solution was stirred overnight and the solvent stripped in vacuo. The residue was then dried overnight in vacuo. Proton NMR spectroscopy confirmed the structures of the product as being the desired urea-appended imidazole, and the crude material was used in the next step without further purification. Under a nitrogen atmosphere, the reaction residue was redissolved in aceto-nitrile (100 mL) and treated with 28.0 g (0.164 mol) of propyl iodide. The mixture was then heated gently without refluxing.

After stirring and heating overnight, the acetonitrile was removed in vacuo, leaving a sticky residue. The residue was dissolved/suspended in water and the aqueous layer washed with 2 × 100 mL of diethyl ether. A solution of 36.0 g (0.194 mol) of KPF_6 dissolved in 100 mL of water was added to the aqueous solution. The mixture was stirred overnight at 40 °C, during which time the product separated from the water as a separate liquid phase. An alternate route for exchanging I^- for PF_6^- could be accomplished using $AgPF_6$ in acetone. The water was decanted from the product, the latter being washed for four 2-h periods with 100 mL of water to remove any remaining KPF_6.

After the last water wash, the IL was dissolved in acetonitrile, toluene was added to aid in the azeotropic removal of water, and any solids were removed by filtration. The solution was then rotary evaporated. The isolated product was dried in vacuo for 24 h while being heated to 60 °C: unoptimized yield, 45.2 g (68%). The general procedure for the preparation of the urea-functionalized IL **5** and **6** and the thiourea-functionalized IL **2** and **3** is analogous, each being formed in similar yield. ^1H and ^{13}C NMR results are listed in Table 1.

Synthesis of TSIL (1). Under a nitrogen atmosphere, a solution of 10.0 g (0.122 mol) of 1-butylimidazole in 100 mL of toluene was treated with 16.0 g (0.130 mol) of 2-(chloroethyl)ethyl sulfide. The mixture was refluxed overnight,

TABLE 1. ¹H (300 MHz, CD₃CN, CD₃Cl, δ) and ¹³C NMR (75.57 MHz, proton decoupled, CD₃CN/CDCl₃, δ) Chemical Shifts

ionic liquid	¹H NMR	¹³C NMR
1	1.30 (t, 3H, CH₃), 2.50 (q, 2H, CH₂), 2.94 (m, 2H, CH₂), 3.95 (s, 3H, CH₃), 4.47 (t, 2H, CH₂), 7.38 (d, 1H, CH), 7.53 (d, 1H, CH), 10.22 (s, 1H, CH)	12.41, 24.67, 27.94, 39.83, 50.22, 122.32, 122.61, 137.02
2	1.01 (t, 3H, CH₃), 1.41 (m, 2H, CH₂), 1.80 (m, 2H, CH₂), 2.79 (broad d, 3H, CH₃), 2.90−3.05 (m, 4H, CH₂), 4.07 (m, 4H, CH₂), 5.11 (broad s, 1H, NH), 5.31 (broad s, 1H, NH), 7.13 (s, 1H, CH), 4.62 (d, 1H, CH), 8.26 (s, 1H, CH)	29.57, 30.70, 32.95, 34.14, 38.71, 40.97, 41.84, 42.96, 44.68, 119.31, 129.04, 137.11
3	0.93 (overlapping t, 9H, CH₃), 1.21−1.48 (complex m, 8H, CH₂), 1.74−1.99 (complex m, 7H, CH, CH₂), 3.15 (broad m, 4H, CH₂), 4.12 (t, 2H, CH₂), 4.18 (t, 2H, CH₂), 5.16 (broad s, 1H, NH), 5.25 (broad s, 1H, NH), 7.37 (d, 1H,CH), 7.46 (d, 1H, CH), 8.51 (s, 1H, CH)	13.20, 19.81, 27.88, 30.46, 30.52, 30.80, 30.98, 34.49, 38.64, 40.95, 41.08, 43.23, 43.48, 44.07, 44.16, 119.23, 128.57, 128.69, 137.35
4	1.02 (t, 3H, CH₃), 1.31 (m, 2H, CH₂), 1.86 (m, 2H, CH₂), 2.23 (s, 3H, CH₃), 2.88−3.36 (overlapping m, 6H, CH₂), 4.08 (m, 2H, CH₂), 6.21 (m, 2H, NH), 7.02 (d, 2H, CH), 7.21 (d, 2H, CH), 7.37 (d, 1H, CH), 7.46 (d, 1H, CH), 8.34 (s, 1H, CH)	11.02, 20.81, 31.64, 36.77, 44.29, 46.03, 50.00, 52.42, 119.38, 129.60, 132.37, 136.77, 137.25, 156.97
5	0.96 (overlapping t, 6H, CH₃), 1.18−1.44 (complex m, 6H, CH₂), 1.79−2.02 (complex m, 4H, CH₂), 3.00 (broad q, 4H, CH₂), 4.11 (t, 2H, CH₂), 4.19 (t, 2H, CH₂), 5.15 (broad s, 1H, NH), 7.41 (d, 1H, CH), 7.50 (d, 1H, CH), 8.52 (s, 1H, CH)	9.91, 12.99, 19.88, 21.02, 24.77, 31.09, 31.82, 35.73, 39.95, 46.89, 51.10, 120.02, 122.55, 136.50, 160.23
6	0.89 (overlapping t, 6H, CH₃), 1.23−1.43 (complex m, 4H, CH₂), 1.79−1.97 (complex m, 4H, CH₂), 3.05 (broad q, 4H, CH₂), 4.08 (t, 2H, CH₂), 5.26 (broad s, 1H, NH), 7.37 (d, 1H, CH), 7.46 (d, 1H, CH), 8.74 (s, 1H, CH)	9.88, 13.21, 18.31, 23.06, 30.87, 32.32, 35.84, 39.61, 47.09, 51.13, 122.26, 122.61, 136.10, 158.79

after which time the volatiles were removed in vacuo. The dark residue was washed with 3 × 100 mL portions of diethyl ether, then kept in vacuo overnight. The thick liquid was then dissolved in water to which was then added a solution of 26.9 g (0.146 mol) of KPF₆ in 150 mL of hot water. Stirring overnight resulted in the formation of a dark, dense phase that was isolated by decantation and washed with copious quantities of water. Drying in vacuo affords compound 1 (15.7 g, 0.050 mol, 41%) as a yellow liquid.

Characterization. The chemical data for ¹H and ¹³C NMR were obtained at 300 and 75.57 MHz, respectively, using a Bruker instrument (Houston, TX). The urea- and thiourea-appended imidazolium cations give rise to IL that are poorly soluble in most solvents. In each case, the NMR spectra of the products were obtained in a mixture (∼1:1) of CD₃CN and CDCl₃. It was noted that the chemical shift values, especially those associated with the imidazole rings, vary considerably depending upon the water content of materials, solvent composition, and on the counterion present.

Melting point and glass transition temperatures were determined by differential scanning calorimetry using a TA Instruments (New Castle, DE) model 2920 differential scanning calorimeter, using samples of approximately 10 mg, analyzed in hermetically sealed aluminum pans. For each experiment, an empty hermetically sealed aluminum pan was referenced as the blank. A temperature change of 5 °C/min was employed over the temperature range of −150 to 100 °C. Temperature calibration was performed on a sample of indium.

The range of thermal decomposition temperatures for each IL was determined by thermogravimetric analysis using a TA Instruments (New Castle, DE) model 2950 thermogravimetric analyzer. Each sample was analyzed in a platinum pan with nitrogen as the purge gas. In each experiment, the temperature was linearly increased at 10 °C/min over a temperature range of 30−600 °C.

The water content of each IL was determined using a volumetric Aquastar Karl Fischer titrator (EM Science, Gibbstown, NJ) with Composite 5 solution as the titrant and anhydrous methanol as the solvent. For each 1:1 mixture of [C₄mim][PF₆]/3−6, 2 mL of each mixture was contacted with deionized water, vortexed (2 min), centrifuged (2 min, 2000g), and allowed to equilibrate with the aqueous phase for 12 h. The samples were vortexed (2 min) and centrifuged (2 min, 2000g), and then the samples were removed from the IL phase. Each sample was at least 1 g, and duplicate measurements were performed on each sample. Repeated measurements agree to within 100 ppm.

The viscosity of each IL was measured with a Cole-Parmer (Vernon Hills, IL) 98936 series viscometer using 8 mL of sample. The temperature of the sample was maintained to ±0.1 °C via an external temperature controller. A correction factor for each of the experimentally determined values was determined by measuring the viscosity of a Cannon (State College, PA) certified viscosity standard (S200). Each sample was analyzed in duplicate, and the results agree to within 10 cP.

TSIL 4 Cation Leaching. UV−vis was used to detect the leaching, if any, of the TSIL cation 4 from a 2 M solution of 4 in [C₄mim][PF₆] contacted with water. All spectra were obtained on a Cary 3C spectrophotometer (Varian Optical Spectroscopy, Mulgrave, Victoria, Australia). Prior to recording any spectra, a baseline was obtained for DI water (and automatically subtracted for each experiment) using quartz cells, and the reference cell for all experiments contained DI water. For each experiment, 3 mL of IL and 3 mL of a specific aqueous phase were contacted, vortexed (2 min), centrifuged (2000g, 2 min) followed by another interval of vortexing (2 min) and centrifuging (2000g, 2 min) to ensure that the phases were fully separated. After contact, 2 mL of the aqueous phase were transferred to the quartz cell and the spectrum was collected from 200 to 500 nm at a scan rate of 100 nm/min.

Metal Ion Distribution Ratios. Mixtures of each TSIL were prepared at a specific ratio (by mass) in the appropriate [Cₙ-mim][PF₆] IL. Equal volumes of the IL and aqueous phase were contacted in the presence of either ²⁰³HgCl₂ or ¹⁰⁹CdCl₂

TABLE 2. Melting Points, Thermal Decomposition Data, and Viscosity

ionic liquid	melting point (°C)	freezing point (°C)	glass transition temperature (°C)	onset of thermal decomposition (°C)	viscosity (cP, 25 °C)	viscosity (cP, 90 °C)
1	−12.8	−55.2	−62.6	300	*a*	*a*
2	−18.7	−75.1	−52.4	300	*a*	*a*
3*c*	*b*	−49.3	−17.4	225	964	661
4*c*	*b*	17.7	−12.6	200	873	552
5*c*	46.2	*b*	−45.0	225	799	523
6*c*	64.5	*b*	−59.4	225	801	510

a Not measured. *b* Not observed. *c* 1:1 mixtures of **3**−**6** with [C$_4$mim][PF$_6$] (by mass).

to determine the distribution ratios between the aqueous phase (top) and the IL phase (bottom). Metal ion distribution ratios were determined by mixing 1 mL of IL and 1 mL of aqueous phase followed by vortexing (2 min) and centrifuging (2000*g*, 2 min) to equilibrate the phases. Addition of either ^{203}HgCl$_2$ or ^{109}CdCl$_2$ (0.005 μCi, ~5 μL in water) was followed by two intervals of vortexing (2 min) and centrifuging (2000*g*, 2 min) to ensure that the phases were fully separated. Both ^{203}HgCl$_2$ and ^{203}Hg(NO$_3$)$_2$ were used in selected experiments, and it was observed that the tracer anion does not affect the distribution ratios. The phases were separated and dispensed into shell vials from which 100 μL of each phase was removed for radiometric analysis. γ-ray emission analyses were carried out on a Packard Cobra II Auto-Gamma spectrometer (Packard Instrument Company, Downers Grove, IL).

Because equal volumes of both phases were removed for analysis, metal ion distribution ratios were calculated as follows:

$$D = \frac{\text{activity in the RTIL lower phase}}{\text{activity in the aqueous upper phase}}$$

Each experiment was done in duplicate, and the results agreed to within 5%.

Results and Discussion

Melting Points and Glass Transition Temperatures. Some IL exhibit thermotropic liquid crystalline behavior (*2*) in which the composite cations and anions spontaneously orient themselves in response to a thermal gradient. The IL studied here exhibit melting points, freezing points, and glass transitions, although not each sample has all characteristics, as summarized in Table 2. Thermal transitions for **1**−**6** occur over a wide temperature range, and the glass transition temperatures are between −10 and −65 °C. Because the anion in each sample is PF$_6^-$, as the overall cation size and bulk increases, the glass transition temperatures increase. For example, the phenyl group in **4** and the branched alkyl chain in **3** result in lower glass transition temperatures relative to the other cations which incorporate linear alkyl chains. Lower glass transition temperatures could be due to the higher temperatures necessary to orient the bulkier cations and anions in the glass phase.

Thermal properties for traditional imidazolium-based IL have been reported by McEwen et al. (*32*) and Ngo et al. (*33*) and show that the range of glass transition temperatures for short alkyl chain moieties is −80 to −100 °C. Our results for a series of 1-alkyl-3-methylimidazolium IL indicate that the anion has an effect on the glass transition temperature. In general, glass transition temperatures were less than −75 °C, although the bis(trifluoromethylsulfonyl)imide anion produced the lowest transition temperature of −104 °C (*4*). As compared to other alkylmethylimidazolium PF$_6^-$ or BF$_4^-$ IL in the literature (*2*, *5*), the TSIL described here have higher glass transition temperatures. Perhaps the bulkiness of the cations and anions in addition to the presence of the
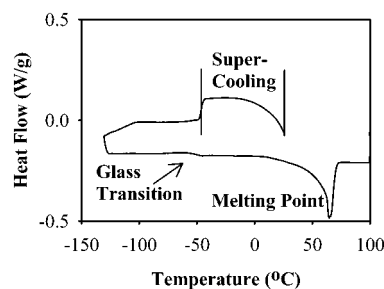

FIGURE 3. DSC trace for **6**.

thioether, urea, or thiourea functional groups significantly contribute toward higher glass transition temperatures.

The salts **5** and **6** are solids at room temperature and melt at 46.2 and 64.5 °C, respectively; the liquids **1** and **2** melt at −12.8 and −18.7 °C. Both **5** and **6** contain the urea functional group, whereas **1** and **2** contain sulfur-based functional groups with the associated tendency for weaker hydrogen bonding interactions resulting in lower melting points. It is interesting to note that **5** has a butyl substituent group and **6** has a propyl group, although the melting point of **6** is 18 °C higher. This trend has already been observed for [C$_n$mim]-[BF$_4$] IL and the results here may similarly reflect an odd−even phenomenon (*5*) where the melting points are greater for alkyl chains with odd numbers of carbons.

It is worth commenting that the absence of a melting point does not unambiguously indicate that compound has no melting point, only that crystallization under those experimental conditions was not observed. In fact, during thermal analysis experiments, some IL systems may remain in a supercooled state without crystallization (*34*) due to rapid cooling and a delayed thermodynamic response. The DSC trace of **6** is shown in Figure 3. Melting points are interpreted from the DSC traces as the first endothermic peak on the heating curve. The signature for a glass transition appears separate from the melting point and is easily distinguished for samples that undergo that phase change. The tendency for IL to supercool is observed in the cooling trace of Figure 3.

Thermal Stability. One of the marked characteristics of certain IL is their high thermal stability. The temperature at which decomposition begins is affected by the composite cations and anions, where, for example, [C$_2$mim][CF$_3$COO] begins to decompose at 150 °C and [C$_2$mim][Tf$_2$N] rapidly decomposes at 440 °C (*35*). The effect of composition on the properties is further detailed in a report by Huddleston et al. for a series of [C$_n$mim]$^+$ (*n* = 4, 6, or 8) with Cl$^-$, Br$^-$, I$^-$, PF$_6^-$, BF$_4^-$, or Tf$_2$N$^-$ (*4*).

Thermal stability studies on **1**−**6** indicate that the TSIL begin to decompose at temperatures approximately 100 °C lower than that for [C$_n$mim][PF$_6$] (*4*). Table 2 lists the thermal data and shows the onset for thermal decomposition for **4** to be the lowest, beginning at 200 °C. In general, the longer alkyl chains (**3**, **5**, and **6**) are less stable and the shortest alkyl appendages (**1** and **2**) have the highest temperatures for onset

TABLE 3. Distribution Ratios for Hg^{2+} and Cd^{2+} in Systems Incorporating IL 1 and 2

TSIL	cation	pH	*D* value TSIL only	*D* value 1:1 TSIL/[C$_4$mim][PF$_6$][a]
1	Hg^{2+}	1	198	174
	Hg^{2+}	7	208	210
2	Hg^{2+}	1	346	74
	Hg^{2+}	7	343	101
1	Cd^{2+}	1	330	307
	Cd^{2+}	7	376	360
2	Cd^{2+}	1	20	0.008
	Cd^{2+}	7	23	0.007

[a] 1:1 mixtures of **3**−**6** with [C$_4$mim][PF$_6$] (by mass).

of thermal decomposition. The type of functional group does not appear to have a large effect on this property.

Viscosity. The viscosities for 1:1 mixtures of **3**−**6** with [C$_4$mim][PF$_6$] have been measured at 25 and 90 °C and are listed in Table 2. Although the TSIL are mixed with [C$_4$mim]-[PF$_6$], the resulting mixtures are significantly more viscous than [C$_4$mim][PF$_6$] (*4*). This can be attributed to both the longer, bulkier alkyl chains incorporated in the TSIL and also to the presence of the heteroatom(s) in the side chains increasing the tendency for hydrogen bonding with the N, S, or O atoms. As can be expected, longer alkyl chains increase the viscosity due to increased van der Waals interactions. Thus, the viscosity for mixtures containing the branched-(**3**) or phenyl-substituted (**4**) cations are the highest of the TSIL, owing to van der Waals interactions and the reduced rotational freedom. The presence of heteroatoms also has an effect because, as shown by Bonhôte et al., the viscosity slightly increases when substituting [1-butyl-3-methyl-imidazolium][Tf$_2$N] with [1-methoxyethyl-3-methylimida-zolium][Tf$_2$N] (*35*).

Although **1**−**6** exhibit interesting properties akin to other IL systems, certain properties (e.g., high viscosity (**3** and **4**)) present a challenge for the exploration of TSIL in liquid/liquid separations. Instead, using those IL in a mixture with [C$_4$mim][PF$_6$] shows that they can function as both *solvent and extractant* without compromising the solvent characteristics.

Metal Ion Extraction. Table 3 shows the metal ion distribution ratios for **1** and **2** when used as the extracting phase and, for comparison, when used as 1:1 mixtures with [C$_4$mim][PF$_6$]. As metal ion extractants, **1** and **2** would be expected to interact with Hg^{2+} and Cd^{2+} through the S atoms in the alkyl chains. The distribution ratios shown in Table 3 at pH 7 indicate how the incorporation of a functional group can dramatically affect metal ion partitioning. In these systems, however, adjusting the pH to more acidic conditions does not facilitate stripping of these metal ions from the IL phase, although the distribution ratios decrease dramatically when **2** is doped into a traditional IL. When **1** and **2** are used as mixtures with [C$_4$mim][PF$_6$], the decrease in metal ion partitioning to the IL could be attributed to the methyl group at the end of the alkyl chain, which may leave the thioether group in **1** and the thiourea group in **2** exposed and subject to interactions with the [C$_4$mim]$^+$ cation or hydrophilic attack.

Although **1** and **2** are liquids at room temperature and have moderate viscosity, **3** and **4** are very viscous and sticky, warranting their investigation as metal ion extractants in a 1:1 ratio with [C$_4$mim][PF$_6$] to decrease the viscosity of the IL phase in the separation experiments. Similarly, **5** and **6** can be dissolved in [C$_4$mim][PF$_6$] at a 1:1 ratio to utilize those IL in liquid/liquid separations experiments. As Table 4 indicates, adding the TSIL decreases the water content of the IL phase in comparison to [C$_4$mim][PF$_6$] and this may play an important role toward increasing the metal ion distribution ratios.

TABLE 4. Water Content of Water-Equilibrated IL Containing 1:1 Mixtures of [C$_4$Mim][PF$_6$] and IL 3−6

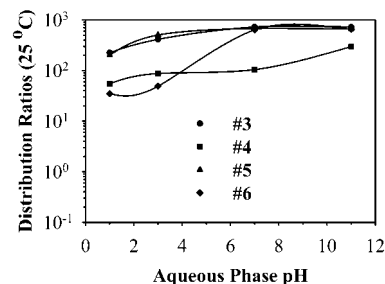| ionic liquid	water content (ppm)	ionic liquid	water content (ppm)
3/[C$_4$mim][PF$_6$]	224	**6**/[C$_4$mim][PF$_6$]	291
4/[C$_4$mim][PF$_6$]	238	[C$_4$mim][PF$_6$]	450
5/[C$_4$mim][PF$_6$]	270		

FIGURE 4. Distribution ratios for Hg^{2+} with IL **3**−**6** in a 1:1 weight ratio with [C$_4$mim][PF$_6$] as a function of aqueous-phase pH.
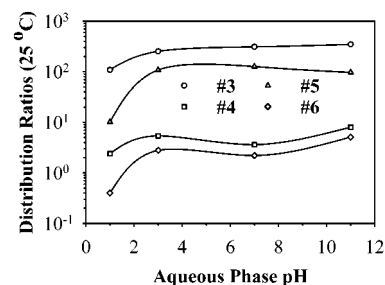

FIGURE 5. Distribution ratios for Cd^{2+} with IL **3**−**6** in a 1:1 weight ratio with [C$_4$mim][PF$_6$] as a function of aqueous-phase pH.
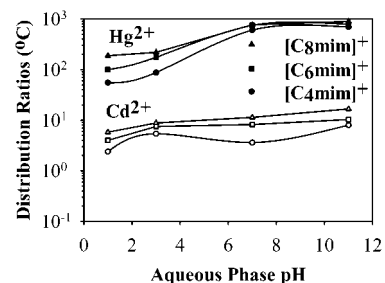

FIGURE 6. Distribution ratios for Hg^{2+} and Cd^{2+} with 4 in a 1:1 weight ratio with [C$_n$mim][PF$_6$] as a function of aqueous-phase pH.

The behavior of IL **3**−**6** is similar in that each IL extracts Hg^{2+} and Cd^{2+} from aqueous solutions (Figures 4 and 5) when utilized in a 1:1 mixture with [C$_4$mim][PF$_6$]. The metal ion distribution ratios in Figures 4 and 5 are the same order of magnitude as many of the results listed in Table 3. The pH study shows that acidic conditions are not sufficient to promote a significant change in the partitioning for Hg^{2+}, although Cd^{2+} distribution ratios with **6** are decreased to the point where stripping may be feasible with a pH change. Similarly, using 1:1 mixtures of **4** with [C$_6$mim][PF$_6$] or [C$_8$-mim][PF$_6$] produce slightly higher distribution ratios for both Hg^{2+} and Cd^{2+}, as shown in Figure 6. Previous reports (*4*) have shown that increasing the alkyl chain length from butyl to octyl increases the hydrophobicity of the IL, a fact that is also observed when TSIL are added to the IL. Thus, the perceived hydrophobicity suggests that longer alkyl chains provide a hydrophobic environment that may be less likely to undergo hydrolysis.
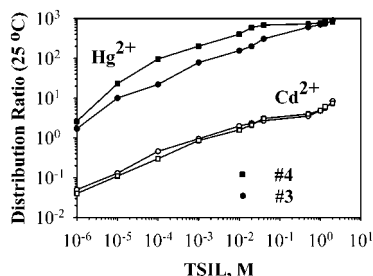
FIGURE 7. Distribution ratios for Hg^{2+} and Cd^{2+} with increasing concentration of 3 or 4 in [C_4mim][PF_6] at aqueous pH 7.

An extractant dependency study with TSIL **3** and **4** is illustrated in Figure 7. Slope analysis for Hg^{2+} extraction with **4** indicates the slope is approximately 0.5 and that two TSIL cations are involved in the partitioning. A clear understanding of the partitioning mechanism is more difficult for Hg^{2+} with **3** because the distribution ratios increase only slightly. For Cd^{2+} partitioning with **3** and **4**, the extraction appears to be similarly complex, as the slope analysis indicates that approximately two TSIL cations are involved in partitioning the metal cations.

A study of the partitioning of **4** indicated that the cation is not lost to the aqueous phase, even at a concentration of 2 M in [C_4mim][PF_6]. This is especially important in light of the increased cost of the TSIL and cross-contamination problems that can arise when the extractants are lost to the aqueous phase.

The type of functional group added to the cation may have an effect on the distribution ratios by creating a more hydrophobic environment around the metal–ligand coordination site. Comparing the D values for **2** and **3** shows that the extended alkyl "tail" near the thiourea group in **3** may be responsible for the significant increase in D values for both metals. Overall, the distribution ratios for Hg^{2+} and Cd^{2+} are the highest with **3** and **5**.

These results indicate that appending thioether, urea, and thiourea functional groups to imidazolium cations does produce TSIL cations that can be considered either a new class of IL or novel class of IL extractants. The TSIL cations, in combination with PF_6^- and used alone or in a mixture with [C_4mim][PF_6], result in significant distribution ratios for Hg^{2+} and Cd^{2+} in liquid/liquid separations while minimizing the reliance on traditional organic solvents for this process. The concept of TSIL illustrates how functional groups can be introduced into the scheme of IL synthesis with the inherent potential for achieving desirable properties tuned to specific applications. Although the extraction of Hg^{2+} and Cd^{2+} has been successfully demonstrated here, further work will be necessary to develop methods to strip the metal ions from the TSIL phase.

Geometry Optimization. Gaussian98 restricted Hartree–Fock geometry optimization calculations of the cation of **2**, using a 6-31+G(d) basis set (373 functions), revealed the ring to be the locus of positive charge accumulation, largely in the ring N–C–N vicinity. Indeed, the maximum of the positive charge density is on the C(2)–H, which has a Mullikan charge of +0.29. In turn, the maximal area of negative charge on the ion is on the thiourea sulfur, which bears a Mullikan charge of −0.32.

In the computed structure, the thiourea-containing appendage bends back over the imidazole ring, placing the thiourea sulfur only 3.8 Å from the nearest ring nitrogen atom, as shown in Figure 8. Given the apparent attraction between these regions of the molecule, it is conceivable that the relatively low decomposition temperature for IL comprised of these functionalized cations arises in part from a deprotonation of the imidazole ring by the Lewis basic
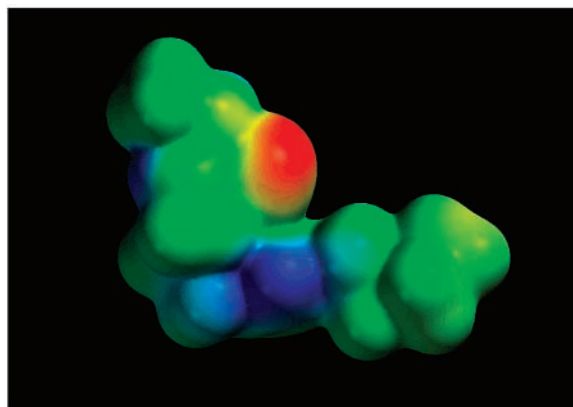

FIGURE 8. Computer-aided geometry optimization (Gaussian98) for the cation in 2.

appendage. Even so, the high partial negative charge manifested by the thiourea sulfur supports the categorization of it as an effective cation-tethered ligand for the binding of dissolved metal cations. Studying a series of IL with each functional group would better elucidate the trends in the structure of the cation and the effect on metal ion complexation, and we anticipate undertaking such an effort.

Acknowledgments

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