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LIQUID/LIQUID EXTRACTION OF METAL IONS IN ROOM TEMPERATURE IONIC LIQUIDS

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ABSTRACT

The search for more environmentally-friendly reaction media has prompted the development of a wide array of alternative systems that will sustain biphasic separations with aqueous solutions without the use of volatile organic compounds (VOCs). We have begun to employ *R*oom *T*emperature *I*onic *L*iquids (RTIL), specifically 1-alkyl-3-methylimidazolium hexafluorophosphate ([$C_n$mim][PF_6]), as VOC replacements in liquid/liquid separations of metal ions from aqueous solutions. Here we show that the partitioning of metal ions in these novel biphasic systems is consistent with traditional liquid/liquid separations: the metal ion affinity for the hydrophobic phase necessitates the presence of an extractant. In this report we explore the application of well-known organic (1-(pyridylazo)-2-napthol, PAN, and (1-thiazolylazo)-2-napthol, TAN) and inorganic (CN^-, OCN^-, SCN^-, and halides) extractants for partitioning a variety of metal cations be-

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tween $[C_4mim][PF_6]$ or $[C_6mim][PF_6]$ and an aqueous phase. PAN and TAN show pH dependent extraction of Cd^{2+}, Co^{2+}, Ni^{2+}, and Fe^{3+} where their partitioning to the RTIL increases at least 2 orders of magnitude from pH 1 to 13. The effect of the halides on the partitioning of Hg^{2+} complexes increases $F^- < Cl^- < Br^- < I^-$. Pseudohalides, especially SCN^-, had the greatest effect on enhancing the partitioning of Hg^{2+} to the RTIL, whereas CN^- and OCN^- provided little benefit for the extraction of any of the metal ions examined.

INTRODUCTION

In many manufacturing processes, syntheses, and nuclear waste processing there is common ground; a separation must take place to partition a specific product from the mixture. To accommodate the requirements for each unique process, conditions for separation are tailored to make them as efficient as possible. Complicated mixtures often require several stages and employ various chemicals to fine-tune each step. A widely recognized method for separations is liquid/liquid extraction that is traditionally accepted as the partitioning of solutes between an aqueous phase and an organic solvent (1). These systems can effect the removal of organic molecules from aqueous streams due to the hydrophobic nature of the organic solvent selected, or, with the addition of a metal ion extractant that remains in the hydrophobic phase, metal ion separations can be induced.

Finding sustainable alternatives to the volatile organic compounds (VOCs) used in traditional solvent extraction is a direct result of inherent problems with commonly used solvents, many of which are known laboratory and workplace hazards. New technologies to reduce the polluting nature of traditional separations have led to solvent alternatives that intend to maintain the mechanics of liquid/liquid separations while imparting more environmentally-friendly characteristics to the components involved (2,3). Although other separation methods have been proven (2,4) liquid/liquid two-phase systems continue to be favored for the development of many separation processes (1,5).

The hydrated nature of most metal ions lowers their affinity for the hydrophobic phase, thus, it is necessary to change the hydration environment of the metal ion by either using organic ligands which provide a more hydrophobic region around the metal, or with inorganic anions that form softer more extractable anionic complexes with the metal (6-12). Ideally, in a biphasic system, the extractant would remain in the hydrophobic phase to ensure the complete removal of the metal ions from the aqueous phase. Thus, the challenges in adapting new classes of solvents to traditional separations include finding extractants which are quantitatively partitioned to the solvent phase and can still readily complex target metal ions; or finding conditions under which specific metal ion species can be selectively extracted from aqueous streams containing inorganic complexing ions.

Alternative Separations Media

*R*oom *T*emperature *I*onic *L*iquids (RTIL) represent a novel medium that is composed entirely of ions and, in certain ways, are akin to molten metallic ionic melts such as NaCl at 800 ºC. In contrast to high temperature melts, certain RTIL exhibit characteristics (e.g., water immiscibility, moisture stability, miniscule volatility, and non-flammability (13-17)) which warrant their consideration as the receiving phase in biphasic liquid/liquid extraction. As solvents they are highly solvating and non-coordinating which makes them suitable media for catalysis and synthesis (18-21). The most widely studied RTIL cations include 1-alkyl-3-methylimidazolium ($[C_n\text{mim}]^+$) and *N*-alkylpyridinium ($[C_n\text{py}]^+$), as shown in Fig. 1, where the alkyl group is typically an alkane and its length or branching allows for moderate adjustment of the resulting properties such as hydrophobicity, melting point, or viscosity (22,23). Anions such as PF_6^-, BF_4^-, and a series of fluorinated anions have been used to produce hydrophobic RTIL (17,24).

The study of metal ion complexes in RTIL has also been rewarding since their role as ionic solvents limits dissociation, disproportionation, and degradation reactions, typical of anionic metal complexes in aqueous solutions, thus increasing the stability of otherwise transient species (18-20,25). The electronic spectra of $[CrCl_6]^{3-}$ and $[VCl_6]^{3-}$ have been obtained in basic $[C_4\text{py}]Cl\text{-}AlCl_3$ ionic liquids, whereas traditional organic solvents left the species prone to solvation and solvolysis (20). In addition, other work has shown that the use of catalysts in biphasic systems with certain RTIL may promote facilitated product separation simply via decanting the organic phase (21).

For the current study, we have chosen to use alkyl derivatives of the 1-methylimidazolium cation with the hexafluorophosphate anion since these RTIL form a stable two phase system when contacted with water and are not too viscous, thus allowing facilitated handling in the experiments. Here, we report our preliminary assessment of the performance of both organic extractants (1-(2-pyridylazo)-2-napthol, PAN and 1-(2-thiazolylazo)-2-napthol, TAN), and inorganic anionic extractants (halides and pseudohalides) for the transfer of Hg^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, and Fe^{3+} from aqueous to RTIL phases.

EXPERIMENTAL METHODS

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 obtained from Isotope Products Laboratories (Burbank, CA) and $^{60}CoCl_2$ was purchased from New England Nuclear (Boston, MA). The remaining tracers ($^{59}FeCl_3$, $^{152}EuCl_3$, $^{63}NiCl_2$, and $^{109}CdCl_2$) were obtained from Amersham Life Sciences (Arlington Heights, IL).

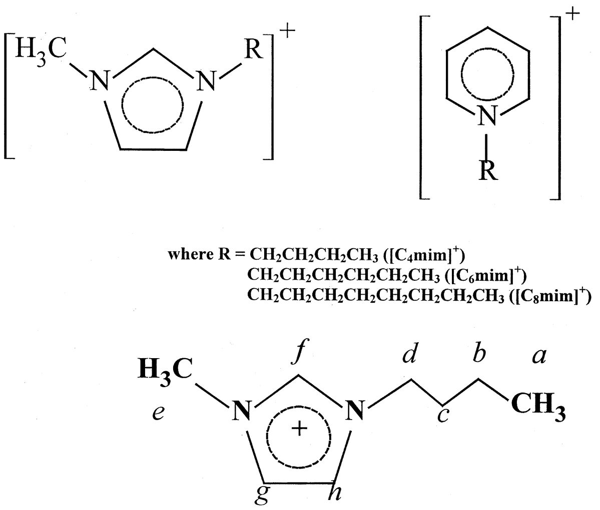
Liquid scintillation analyses were performed for analysis of ^{63}Ni using Ultima Gold scintillation cocktail (Packard Instrument, Downers Grove, IL) and a Packard Tri-Carb 1900 TR Liquid Scintillation Analyzer (Packard Instrument Company, Downers Grove, IL). Gamma ray emission analyses were used to study the remaining isotopes and carried out on a Packard Cobra II Auto-Gamma Spectrometer (Packard Instrument Company, Downers Grove, IL).

All aqueous solutions were prepared with deionized water that was purified with a Barnsted deionization system (Dubuque, IA) and polished to 18.3 MΩ(cm. Salt solutions of KSCN, NaOCN, NaCN, and NaX (where X = halide) were prepared as molar concentrations by weighing out a known amount of salt and adding it to a volumetric flask and diluting to the specified volume with water (or 2 M H_2SO_4 from a stock solution, where appropriate). After contact with the RTIL phase, the pH of the aqueous solutions was 5.1. All pH measurement were made with a Corning pH meter 220 (Corning Incorporated Science Products Division, Corning, NY). PAN and TAN were prepared in molar concentrations by weighing out a known amount of material and transferring it to a volumetric flask and diluting to the specific volume with the appropriate ionic liquid.

The ionic liquids were synthesized using the methods described in previously published material (26,27) and stored in contact with DI water to equilibrate the water content of that phase. However, before NMR analysis, the majority of water was removed from the RTIL by heating to 70°C while on a vacuum line. NMR (H at 360.13 MHz and ^{19}F at 470.56 MHz) spectroscopy was used to determine the purity of each ionic liquid and ensure complete reaction. Each H-NMR spectrum contained peaks corresponding to 1-alkyl-3-methylimidazolium cation and indicated no residual reactants.

The chemical shifts (ppm, *d*-acetone) for the H-NMR of [C_4mim][PF_6] were assigned as follows (Fig. 1): 0.72 (triplet, H_A), 1.15 (sextet, H_B), 1.68 (quintet, H_C), 2.25 (singlet, broad, water), 3.73 (singlet, H_E), 4.05 (triplet, H_D), 7.22 (singlet, H_G), 7.30 (singlet, H_H), and 8.26 (singlet, H_F). The ^{19}F-NMR spectra consists of two peaks, one at –74 ppm and the other at –72.5 ppm, corresponding to the splitting of ^{19}F(I = 1/2) by ^{31}P(I = 1//2). The H-NMR analyses were performed on a Bruker AM 360 instrument (Houston, TX) while ^{19}F-NMR analyses used a Bruker AM 500 instrument.

Metal ion distribution ratios were determined by mixing 1 mL of RTIL and 1 mL of aqueous phase followed by vortexing (2 min) and centrifuging (2000 *g*, 2 min) to equilibrate the phases. Addition of the metal ion tracer (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. The phases were separated and dispensed into shell vials from which 100 μL of each phase was removed for radiometric analysis. Since equal volumes of both phases were re-



where R = $CH_2CH_2CH_2CH_3$ **([C$_4$mim]$^+$)**
$CH_2CH_2CH_2CH_2CH_2CH_3$ **([C$_6$mim]$^+$)**
$CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ **([C$_8$mim]$^+$)**

Labels for H-NMR peak assignment.

Figure 1. Typical cations for RTIL; 1-alkyl-3-methylimidazolium ([C$_4$mim]$^+$) and 1-alkylpyridinium ([C$_n$py]$^+$) and labels for H-NMR peak assignments.

moved for analysis, the distribution ratio for the metal ions was calculated as in Eq. 1.

$$D = \frac{\text{Activity (cpm) in the RTIL lower phase}}{\text{Activity (cpm) in the aqueous upper phase}} \qquad (1)$$

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

Distribution ratios of 0.1 mM PAN and TAN were determined for [C$_4$mim][PF$_6$] and [C$_6$mim][PF$_6$] systems in contact with an aqueous phase at pH 1.9, 3.8, 7.9, 9.2, and 12 using 1 M H_2SO_4 or 1 M NaOH to adjust pH of the aqueous stock solutions where appropriate. The partitioning was monitored with a Cary 3C UV-visible Spectrophotometer (Varian Optical Spectroscopy, Mulgrave, Victoria, Australia) at 468 nm for PAN and 485 nm for TAN. Once the Beer's Law plots for PAN and TAN were determined in each of the RTIL used in this study, the quantitative partitioning of the solutes was determined by the following example with [C$_4$mim][PF$_6$]. A 2 mL aliquot of 0.1 mM PAN in [C$_4$mim][PF$_6$] was contacted with 2 mL of a pH-adjusted aqueous phase. Each system was vortexed (2 min) and centrifuged (2000 *g*, 2 min) twice to fully separate the phases. One mL aliquots were removed from each phase and placed into 1 mL quartz cells for UV/VIS analysis. The concentration of the molecules in each phase was determined from the Beer's Law plot and expressed as distribution ratios according to Eq. 2.

$$D = \frac{\text{Concentration in the RTIL lower phase}}{\text{Concentration in the acqueous upper phase}} \qquad (2)$$

Mass balance in each system was maintained.

RESULTS AND DISCUSSION

We have previously demonstrated that [C_4mim][PF_6] in contact with an aqueous phase forms a biphasic system and promotes the partitioning of simple, substituted benzene derivatives to the RTIL phase in correlation with the solutes' 1-octanol/water partition coefficients (log P) (26). When the aromatic solutes contained ionizable groups, a change in the aqueous phase pH revealed the distribution ratio for the uncharged form to be higher than for the charged form.

Two other reports of the utility of RTIL for separations have appeared. Brennecke, *et al.* have exploited the non-volatile aspect of RTIL to show how supercritical CO_2 can be used to strip non-volatile organics from that phase (13). Recently, Dai, *et al.* used dicyclohexyl-18-crown-6 to produce "unprecedentedly large" distribution ratios for Sr^{2+} from dilute nitrate media in both [C_2mim][bis(triflyl)amide] and [C_3mim][bis(triflyl)amide] RTIL (11). As a neutral extractant, this crown ether has higher affinity for the RTIL compared to the aqueous phase.

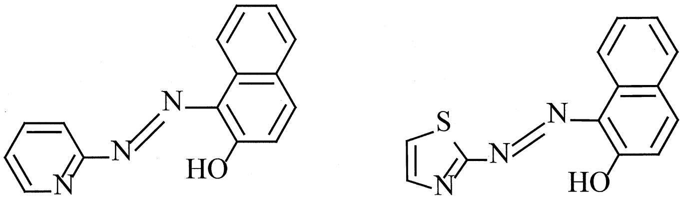
The hydrated nature of many hard metal cations suggests they would remain in the aqueous phase and require the addition of an extractant to enhance their affinity for the extracting phase. Table 1, summarizing the partitioning of several metal cations in [C_4mim][PF_6] and [C_6mim][PF_6]/aqueous systems over a wide pH range, bears this out. We have recently demonstrated that the sulfonated aromatic, azo dye thymol blue preferred [$C_n$mim][PF_6] (n = 4, 6, 8) phases over H_2O in the red zwitterionic and yellow mono-anionic form, but was quantitatively partitioned to the aqueous phase in the blue di-anionic form at high pH (27). This work suggested that with careful choice and control of pH, metal ion extractants could be utilized in RTIL.

In traditional liquid/liquid separations, common methods used to increase the partitioning of metal ions to the hydrophobic phase include organic molecules with metal ion chelating groups (10,28-30) and, separately, complexing anions that form anionic complexes with the metal ions (8,9,31). The azo functionality in combination with an *ortho* aromatic hydroxyl group are a common metal ion chelating group, particularly with cations of both heavy and transition metals (10). We have chosen to study PAN and TAN (Fig. 2) as they are noted metal ion extractants with limited water solubility, but can be extracted into organic solvents

Table 1. Distribution Ratios for Metal Ions Between Aqueous and [C_4mim][PF_6] or [C_6mim][PF_6] Phases

Metal	ΔG_{hyd} (kJ/mol)[a]	Aqueous pH	D ([C_4mim][PF_6])	D ([C_6mim][PF_6])
Na^+	-385	1	0.025	0.013
		7	0.023	0.011
		13	0.023	0.013
Hg^{2+}	-1495	1	0.85	0.72
		7	0.81	0.51
		13	0.73	0.61
Cd^{2+}	-1575	1	0.027	0.018
		7	0.031	0.023
		13	0.076	0.022
Co^{2+}	-1880	1	0.013	0.017
		7	0.011	0.018
		13	0.017	0.025
Ni^{2+}	-2005	1	0.0034	0.0016
		7	0.0018	0.0030
		13	0.011	0.0017
Fe^{3+}	-4580	1	0.067	0.067
		7	0.073	0.085
		13	0.049	0.050
Cl^-	-270	1	0.076	0.044
		7	0.058	0.037
		13	0.061	0.051
I^-	-220	1	0.16	0.36
		7	0.17	0.47
		13	0.23	0.76

[a] Reference (50).



1-(Pyridylazo)-2-napthol (PAN) **1-(Thiazolylazo)-2-napthol (TAN)**

Figure 2. Extractants PAN and TAN.

(32,33). We also have some experience with these extractants having demonstrated their utility in such non-traditional biphasic systems as polyethylene glycol-based aqueous biphasic systems (34). Despite ionization of both molecules (PAN pKa = 1.9 and 12.2; TAN pKa = 2.3 and 8.5) (10), we have spectrophotometrically determined that both PAN and TAN quantitatively partition to $[C_4mim][PF_6]$ and $[C_6mim][PF_6]$ RTIL from aqueous phases of pH 1 to 12.

Without extractants (Table 1) the distribution ratios between $[C_4mim][PF_6]$/aqueous phases at pH 1 to 13 of Na^+, Ni^{2+}, Co^{2+}, Cd^{2+}, Hg^{2+}, and Fe^{3+} are all relatively low, indicating retention in the aqueous phase. The distribution ratios for Hg^{2+} are approximately an order of magnitude higher than the others, reflecting the softer nature of this large ion.

In the presence of 0.1 mM PAN in the RTIL phase at pH 1 (Fig. 3), distribution ratios are relatively low increasing in the order Ni^{2+} (D = 0.0017), Cd^{2+} (D = 0.0054), Co^{2+} (D = 0.014), Fe^{3+} (D = 0.036). All four ions exhibit a large increase in distribution ($D_{Co}{}^{2+} = 4.2$) to the RTIL phase as the pH is increased to 13, consistent with deprotonation and complexation of PAN to the ions. In the same system at pH 13, there is a change in the extraction such that Co^{2+} has higher distribution ratios than Fe^{3+}. The use of 0.1 mM TAN (Fig. 4) gives similar results.

The partitioning data for PAN and TAN, and for metal ions in the presence of PAN and TAN, suggest a pH reversible extraction; at high pH the metal ions

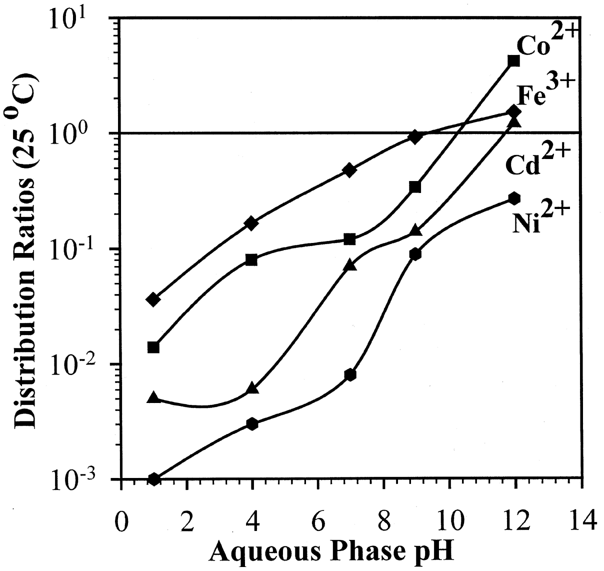


Figure 3. Metal ion partitioning with 0.1 mM PAN in $[C_6mim][PF_6]$ as a function of aqueous phase pH.

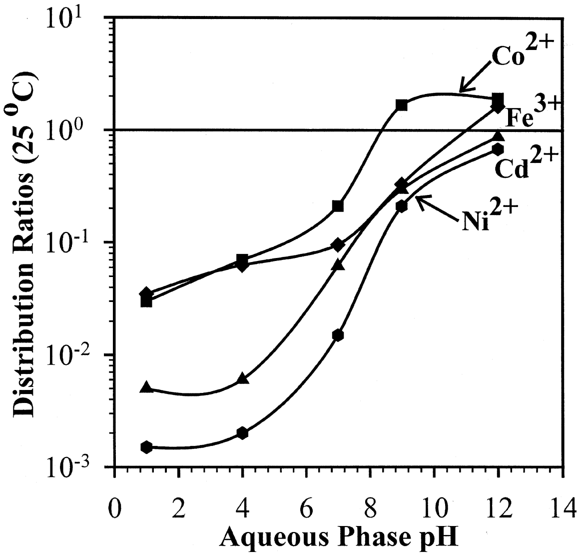


Figure 4. Metal ion partitioning with 0.1 mM TAN in [C_6mim][PF_6] as a function of aqueous phase pH.

would be loaded to the RTIL phase and could be stripped upon contact with an acidic aqueous phase. Both PAN or TAN would remain in the ionic liquid.

Extraction stoichiometries for the RTIL/aqueous systems were determined for both PAN and TAN at pH 12 and are shown in Fig. 5 and 6, respectively. In previously reported metal ion extraction with these ligands, the most common metal:ligand ratios are 1:1 and 1:2 (10) where the extracted species have been proposed to be M(PAN)(X), where X is an anion, and M$(PAN)_2$, respectively (10,35). Similar results were obtained for the extraction stoichiometry involving TAN. All of the metal ions studied here were extracted as a 1:2 complex with both the PAN and TAN ligands, suggesting concomitant extraction of OH^- to form a neutral complex only in the case of Fe^{3+}. Previous work has focussed on the metal ion extraction with the ligands at lower pH ranges (32,35-40) although the high D values observed here may indicate the heightened stability of the metal-PAN and metal-TAN complexes at alkaline pH in the RTIL/aqueous systems.

In addition to the use of organic extracts, we are interested in extraction of complex metal anions. Our previous work utilizing halides and pseudohalides as anionic extractants in alternative extraction systems (ABS (9,41)), prompted the investigation of their use in RTIL-based liquid/liquid separations. Due to the water solubility of the anions and the ionic nature of the extracting solvent, inorganic

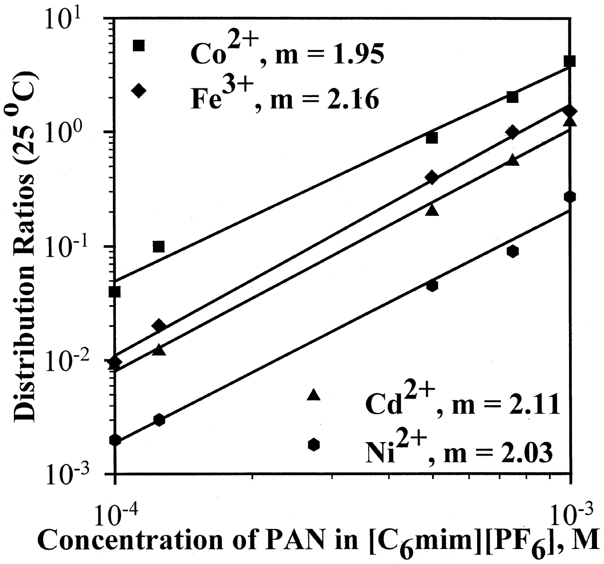


Figure 5. Metal ion distribution ratios as a function of PAN concentration in $[C_6mim][PF_6]$ at an aqueous phase pH of 12.

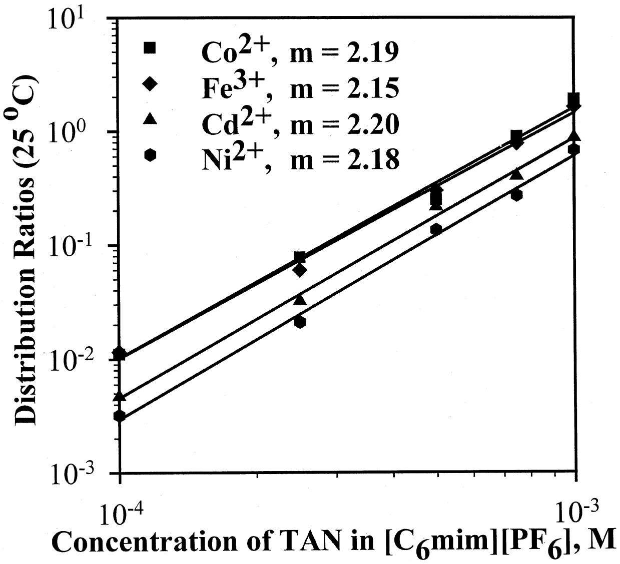


Figure 6. Metal ion distribution ratios as a function of TAN concentration in $[C_6mim][PF_6]$ at an aqueous phase pH of 12.

extractants were studied in the aqueous phase. These anions would act as extractants by forming an anionic complex with the metal ion, subsequently increasing the hydrophobicity of the metal-anion complex and increasing its affinity for the RTIL phase. An example of the utility of such an approach is the extraction of metal anionic complexes from salt solutions in mining and hydrometallurgical processes (42,43).

In general, halides and pseudohalides are known extractants and complex with soft metals to form a variety of species (44). As the size of the complex anions increases, they become less hydrated and their extraction to a hydrophobic phase increases. Alternatively, certain platinum group metals (e.g., Au, Pd, and Pt) can be removed from sulfide matte residue by forming stable anionic chloro species that can be separated from other metals (e.g., Ir and Rh) as they form chloro-complexes that partition differently. In another example, an intermediate step in gold refinement is the formation and subsequent liquid/liquid purification of gold from hydrochloric acid solutions (42). In addition to the use of halides as extractants, the pseudohalides (e.g., CN^-, OCN^-, and SCN^-) may promote the complexation of metal ions due to the presence of N and S atoms, both of which strongly coordinate Hg^{2+} ions and could prove beneficial for the complexation of such soft metal ions (45-47).

In the absence of extractant, the distribution ratio for Hg^{2+} in a $[C_4mim][PF_6]/H_2O$ system at $pH = 7$ is 0.81. For the series of NaX salts ($X = F^-$, Cl^-, Br^-, I^-), the iodide anion has the smallest magnitude of ΔG_{hyd} and the highest formation constant with Hg (49,50). The values of ΔG_{hyd} (50) become increasingly more negative $I^- > Br^- > Cl^- > F^-$, which follows both the trends in formation constants and the partitioning of Hg^{2+} halide complexes to a RTIL phase in the presence of these anions (Fig. 7). Fluoride and chloride apparently depress $D_{Hg^{2+}}$ at low halide concentrations. Only at the higher halide concentrations studied do the distribution ratios of Hg^{2+} return to *ca.* 1. The presence of the softer, more hydrophobic anions Br^- and I^- results in a marked increase in the D values for their Hg complexes, increasing to 96 with 0.5 M Br^- and 524 for 0.5 M I^-.

Some applications of mercury separations are based in hydrometallurgy and involve the removal of Hg^{2+} from sulfuric acid solutions. For example, in the CENIM-LNETI process there is the production of sulfates which may interfere with the leaching step (51). From the results in Fig. 7, the presence of 2 M H_2SO_4 in the NaX solutions has little effect on the distribution ratios for Hg^{2+}, thus extending the application of these liquid/liquid separation conditions. When similar studies are carried out in polyethylene glycol-based aqueous biphasic systems (9), the partitioning of Hg^{2+} halide species increases in the presence of H_2SO_4 due to the possible enhancement of the formation constants in the acidic environment.

Elucidating the metal ion speciation in the presence of these inorganic extractants is a key factor towards understanding the results. As shown in Table 2,

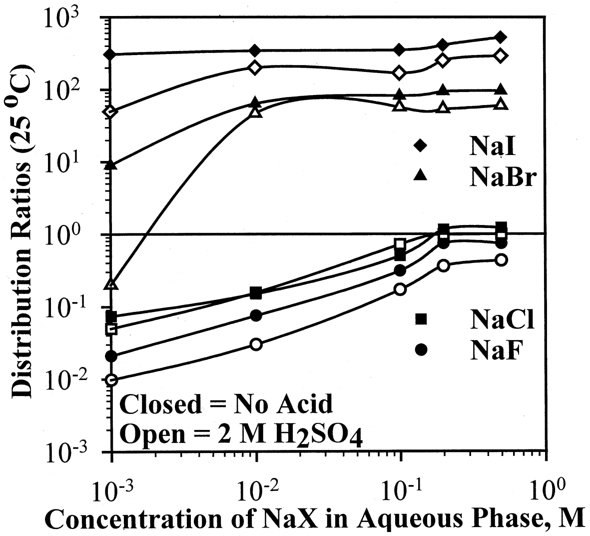


Figure 7. Distribution ratios for Hg^{2+} to $[C_4mim][PF_6]$ from increasing concentrations of aqueous NaX. Open symbols indicate that the aqueous phases are 2 M in H_2SO_4.

the HgX_4^{2-} species is predicted to be dominant with Cl^-, Br^-, and I^- in accordance with their formation constants, whereas the values indicate HgF^+ is the only complex that forms with the fluoride anion (9). The iodide ion has the smallest ΔG_{hyd} (50) and, thus, the largest formation constant with Hg^{2+}, although I^- itself prefers the aqueous phase ($D_{I^-} = 0.2$, $[C_4mim][PF_6]$; Table 1). The remaining halides have increasingly negative ΔG_{hyd} values, indicating their increasing hydrophobicities. As a result, Hg^{2+} complexes with I^- would be the most chaotropic for all complexes with the halides (9). The formation constants are determined for aqueous systems and, in light of the novel environment of RTIL, may not be a true representation of the actual speciation that is present in that phase. Hence, the presence of other species can not be ruled out and is currently a topic of further research in our laboratories.

We have also measured the distribution ratios for Hg^{2+}, Co^{2+}, Cd^{2+}, Ni^{2+}, and Fe^{3+} ions in $[C_4mim][PF_6]$/aqueous systems in the presence of the pseudohalides SCN^-, OCN^-, and CN^-. Table 3 summarizes the complexation constants and associated speciation for the metal ions with each anion in water. The results for thiocyanate are shown in Fig. 8. When 0.001 M SCN^- is present, the D values for Hg^{2+} rise sharply, indicating the stability and hydrophobicity of those complexes. The largest formation constants for these metals with SCN^- decrease in the order $Hg^{2+} > Fe^{3+} > Ni^{2+} > Cd^{2+} > Co^{2+}$ (49), and represent the most stable form of each metal with SCN$^-$ (i.e., Hg(SCN)$_4^{2-}$, Fe(SCN)$_4^-$, Ni(SCN)$_3^-$, Cd(SCN)$_4^2$, and Co(SCN)$_2$ (49)). In the presence of SCN$^-$, the affinity of smaller, harder cations for the RTIL phase also increases, but more slowly, illustrating how a combination of speciation and the resulting hydration of the metal ion complex can affect the partitioning. In the RTIL phase, the speciation is rather complex and several forms of the metal complex may be present since radiometrically determined distribution ratios are a simple measurement of the total amount of metal ion in each phase, not a specific moiety.

The cyanate ion at higher concentrations can result in the extraction of Hg^{2+} ions by increasing D_{Hg} an order of magnitude (Fig. 9). The remaining metal ions studied show some increases in D_M at 0.2 M and 0.5 M NaOCN, however, in general the distribution ratios remain low. The trend in formation constants with OCN$^-$ for these metals is $Hg^{2+} > Fe^{3+} > Ni^{2+} > Co^{2+} > Cd^{2+}$ (49).

Table 2. Distribution Ratios for Hg^{2+} in the Presence of Halides in 0.5 M NaX/[C$_4$mim][PF$_6$] Systems and log K in Aqueous Media

Anion	Complex	ΔG_{hyd} (kJ/mol)[a]	D Hg^{2+} (0.5 M NaX)	Log K[b] ($\mu = 0.5$)
None	Hg(II)	-1495	0.81	
F$^-$		-345	0.74	
	HgF$^+$			1.03
Cl$^-$		-270	1.2	
	HgCl$^+$			6.74
	HgCl$_2$			13.2
	HgCl$_3^-$			14.2
	HgCl$_4^{2-}$			15.2
Br$^-$		-250	96	
	HgBr$^+$			9.07
	HgBr$_2$			17.3
	HgBr$_3^-$			19.7
	HgBr$_4^{2-}$			21.2
I$^-$		-220	520	
	HgI$^+$			12.9
	HgI$_2$			23.8
	HgI$_3^-$			27.6
	HgI$_4^{2-}$			29.8

[a] Reference (50).
[b] Reference (49).

Table 3. Distribution Ratios for Metal Ions in the Presence of Pseudohalides in 0.5 M X(aq)/[C_4mim][PF_6] Systems and log K in Aqueous Media

Metal	Pseudohalide	Complex	ΔG_{hyd} (kJ/mol)[a]	D Value (0.5 M anion)	log K ($\mu = 0.1$)[b]
Fe^{3+}					
	CN^-		-260	0.52	
		$Fe(CN)_6^{3-}$			43.6
	OCN^-		-240	0.077	
	SCN^-		-220	0.89	
		$FeSCN^{2+}$			2.4
		$Fe(SCN)_2^+$			3.6
		$Fe(SCN)_3$			3.9
		$Fe(SCN)_4^-$			6.4
Ni^{2+}					
	CN^-		-260	0.76	
		$Ni(CN)_4^{2-}$			30.5
	OCN^-		-240	0.021	
		$NiOCN^+$			1.97
		$Ni(OCN)_2$			1.56
		$Ni(OCN)_3^-$			1.37
		$Ni(OCN)_4^{2-}$			1.3
	SCN^-		-220	0.26	
		$NiSCN^+$			1.3
		$Ni(SCN)_2$			2.2
		$Ni(SCN)_3^-$			3.5
Co^{2+}					
	CN^-		-260	0.015	
		$Co(CN)_3^-$			13.7
		$Co(CN)_5^{3-}$			23.0
	OCN^-		-240	0.094	
		$Co(OCN)_4^{2-}$			2.7
	SCN^-		-220	49	
		$CoSCN^+$			1.4
		$Co(SCN)_2$			2.0
Cd^{2+}					
	CN^-		-260	0.19	
		$CdCN^+$			6.01
		$Cd(CN)_2$			11.60
		$Cd(CN)_3^-$			16.37
		$Cd(CN)_4^{2-}$			18.89
	OCN^-		-240	0.014	
		$Cd(OCN)_4^{2-}$			
	SCN^-		-220	5.4	

Table 3. Continued

Metal	Pseudohalide	Complex	ΔG_{hyd} (kJ/mol)[a]	D Value (0.5 M anion)	log K ($\mu = 0.1$)[b]
		$CdSCN^+$			1.64
		$Cd(SCN)_2$			2.42
		$Cd(SCN)_3^-$			2.08
		$Cd(SCN)_4^{2-}$			2.3
Hg^{2+}					
	CN^-		-260	0.90	
		$HgCN^+$			17.97
		$Hg(CN)_2$			34.71
		$Hg(CN)_3^-$			38.54
		$Hg(CN)_4^{2-}$			41.52
	OCN^-		-240	6.8	
		$Hg(OCN)_4^{2-}$			
	SCN^-		-220	140	
		$HgSCN^+$			9.08
		$Hg(SCN)_2$			16.43
		$Hg(SCN)_3^-$			19.1
		$Hg(SCN)_4^{2-}$			21.2

[a] Reference (50).
[b] References (10,49).

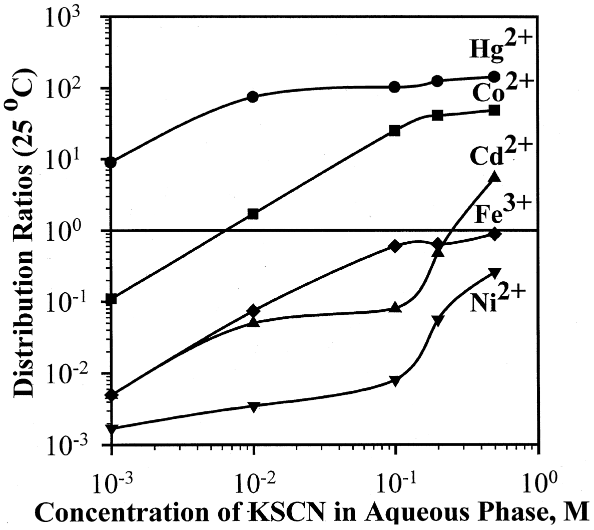


Figure 8. Distribution ratios to $[C_4mim][PF_6]$ from increasing concentrations of aqueous KSCN.

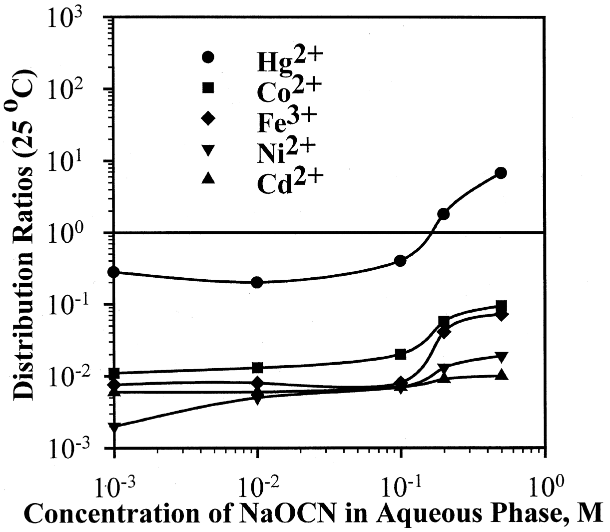


Figure 9. Distribution ratios to [C_4mim][PF_6] from increasing concentrations of aqueous NaOCN.

The cyanide ion results in increases in D_M for Ni^{2+} and Fe^{3+} to near 1 at 0.5 M concentration (Fig. 10). Partitioning of Co^{2+} is not affected by the presence of CN^- although Hg^{2+} and Cd^{2+} show a slight increase in partitioning as the concentration of CN^- increases. The trend in formation constants with CN^- for these metals is $Hg^{2+} > Fe^{3+} > Ni^{2+} > Co^{2+} > Cd^{2+}$ (49). Successful application of this anion as a metal ion extractant in RTIL systems is limited since the resulting metal-anion complexes are not sufficiently hydrophobic to partition to the RTIL phase.

The complex results presented here are a product of several competing factors, including speciation, hydration of metal ions, the hydrophobicity of the resulting metal ion complexes, and the chemistry of the ionic systems. Review of the formation constants for each metal ion with the anions studied (Tables 2 and 3), reveals that higher log K values do not guarantee higher D values. For example, $Hg(CN)_4^{2-}$ and $Hg(SCN)_4^{2-}$ have log K values of 41.5 and 21.2, respectively, despite the thiocyanate distribution ratio being two orders of magnitude larger than for the corresponding distribution ratio with cyanide ion. It is likely that due to the anionic nature of the extracting solvents, the charge on the metal-anion complex is a contributing factor to the partitioning, as well as any counter-ions necessary to balance charge in partitioning.

Of particular concern when interpreting the results presented here is the possibility that the RTIL may be participating in a liquid ion exchange process in

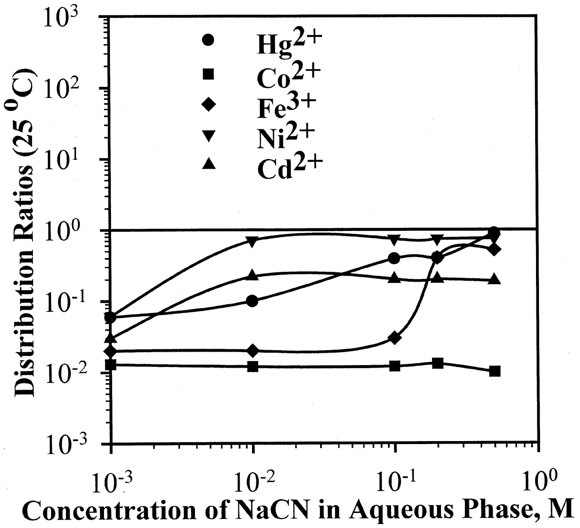


Figure 10. Distribution ratios to [C_4mim][PF_6] from increasing concentrations of aqueous NaCN.

which PF_6^- is replaced by a more hydrophobic metal-anion complex formed in the aqueous phase. This would result in irreversible loss of the extracting solvent to the aqueous phase and preclude 100% solvent recycle. Additional loss of either the [C_4mim]$^+$ or PF_6^- ions via leaching to the aqueous phase would also deter use of RTIL as solvents in liquid/liquid extraction. We are currently investigating both potential liquid ion exchange properties and solvent leaching. Since the ΔG_{hyd} values vary with the inverse of the ionic radius (31), the partitioning is likely to occur via an anion exchange mechanism including the loss of PF_6^- from the RTIL when the radius of the anions in the aqueous phase is larger than that of PF_6^-. A total understanding of RTIL-based liquid/liquid systems at the molecular level and associated behavior of inorganic solutes could uncover a parameter to correlate the behavior of these types of solutes and help to unravel the complexity of partitioning metal ion complexes in these systems.

CONCLUSIONS

While the majority of organic-based metal ion complexants are designed for use in traditional liquid/liquid systems which use VOC diluents, the concepts remain the same when a RTIL such as [C_4mim][PF_6] is used as the hydrophobic phase; the metal ion extractant should quantitatively partition to the extracting phase to optimize the separation over a variety of conditions. We have demonstrated partitioning of metal ions from aqueous to RTIL phases using both organic and inorganic extractants, with particular observation as to how the hydrophobicity of the latter group may affect the interactions with water and complexing ability of the anions. When halides are used as extractants for soft metals such as Hg^{2+}, the partitioning decreases from I^- to F^- in a predictable fashion because size, stability, and hydration of the complexes are all changed in the same direction. Corresponding trends are currently more difficult to predict when using hard metal ions. Further work using the anionic extractants may focus on heavier transition metals to enhance the complexation between large anions and large cations and continuing to explore other anionic extractants.

In addition, it will be necessary to elucidate the nature of each extracted species and determine if a partitioning ion exchange mechanism is operating. Further detailed investigation of the solvent and physical properties of RTIL are also clearly needed before any serious effort can be warranted to deploy these neoteric solvents in an industrial separations technology.

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