PARTITIONING OF TRANSURANIC METAL IONS TO IONIC LIQUIDS CONTAINING THE IONIZABLE COMPLEXANT CYANEX-272

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ABSTRACT

Extraction of americium(III) ions with ionizable dialkylphosphoric or dialkylphosphinic acids from aqueous solutions to the ionic liquid, 1-decy1-3-methylimidazolium bis(trifluoromethanesulfonfyl)imide have been investigated. The results are compared with the analogous traditional molecular solvent systems and show similar patterns for the distribution ratios in each system. Studies indicate that the metal ion coordination environments, elucidated from EXAFS and UV-visible spectroscopy measurements on Nd³⁺ and Eu³⁺ respectively, as stand-ins for Am³⁺, are equivalent in the two systems with coordination of the metal ion with three extractant dimers forming a neutral complex. Extraction equilibria and metal coordination studies demonstrate that with these complexants, the extraction mode and metal coordination environment are conserved in the IL and molecular organic solvent systems.

INTRODUCTION

Room temperature Ionic Liquids (ILs) have been investigated extensively as solvents for synthetic, catalytic, biochemical and electrochemical applications and as liquid phases for separations processes (1,2), in most cases, as potential alternatives to conventional solvents, especially volatile organic compounds (VOCs). ILs have, in general, no measurable vapor pressure and are not flammable. These are significant characteristics with regard to reduction of chemical and environmental hazards associated with exposure and the increasing restrictions on the uses of VOCs. In addition, the composition of ILs, being wholly ionized and dissociated cations and anions, makes them unique systems for studying the coordination chemistry and extraction mechanisms of metal ions, particularly actinides (3). From the perspective of use in radiochemical separations and applications, radiolytic studies also indicate that some imidazolium-based ILs may have superior stability to radiation compared to traditional organic solvents (4).

Metal ion extraction and partitioning has been investigated with a varied range of IL systems and extractants (5—14). In the majority of examples, neutral complexants such as crown ethers have been studied. In several cases, significantly higher distribution...
ratios of metal ions to the IL phase have been observed compared to those using traditional organic solvents as the extracting phase (5,7,13), however these initial studies tended to make the assumption that the IL would behave as an inert, solvent. Since the IL phase consists of cations and anions which can not necessarily be expected to take a passive role in the separations process, this is clearly not the case. The relative roles and importance of different transport and exchange mechanisms on metal ion partitioning have been shown, more recently, to change depending on complexant, metal, and IL cation and anion (5,9,14).

The extraction of uranyl nitrate with CMPO (diisobutyl-carbamoylmethylphosphine oxide) and tributylphosphate in dodecane and the hydrophobic ILs, [C4mim][PF6] and [C4mim][NTf2] was shown to follow a cation exchange mechanism with the transfer of the imidazolium cation in the aqueous phase in contrast to the conventional ion pair transport mechanism in dodecane. Additionally, and consistent with differing transport mechanisms, the coordination sphere for the metal in the ILs was different from that in molecular organic solvents (9). Although cation exchange mechanisms for metal ion transport in aqueous/IL systems are the most widely observed to date, Dietz et al. shown that this is not always the case. Strontium ion partitioning with crown from aqueous to bistrifylimide ILs can be changed from cation exchange in systems containing ILs with hydrophilic cations to an ion pair transfer via formation of neutral, lipophilic Sr2+ nitrate-crown complexes with ILs containing more hydrophobic cations. In these systems, ILs such as 1-decyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (Figure 1) appear to behave similarly to conventional organic solvents such as octanol (10). A third transport mechanism, anion exchange, was identified when the partitioning of trivalent lanthanides using Htta (1-(2-thienyl)-4,4,4-trifluoro-1,3-butadione) in [C4mim][NTf2] was investigated (15). Coordination of Ln3+ with the ionizable Htta complexants resulted in formation of anionic [Ln(tta)4]− in the IL system which transferred to the IL phase by an anion exchange process with [NTf2]− anions from the IL.

Figure 1. 1-Alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C10mim]-[NTf2])

To develop practical application for ILs in biphasic metal ion separations, a better understanding of ILs anion and cation and complexant effects in IL/1 metal extraction is needed. We are investigating here, Am3+ ion separation from aqueous nitric acid to the hydrophobic [C10mim][NTf2], using a protonated ligand, Cyanex 272 (HC-272) which is a commercial phosphinic acid extractant (16) comprising predominantly of bis(2,4,4-trimethylpentyl)phosphinic acid (Figure 2). Distribution ratios for the metal ions have been determined using the radio-tracer approach and are compared to equivalent data taken using a more conventional dodecane extracting solvent. The metal-coordination environment has been probed by uv/vis spectroscopy and by EXAFS in model systems containing Nd3+ (uv/vis) and Eu3+ (EXAFS) with HDEHP (bis(2-ethylhexyl)phosphoric acid) in both [C10mim][NTf2] and dodecane.
Figure 2. Bis(2,4,4-trimethylpentyl)phosphinic acid (left) the major component of Cyanex 272, and HDEHP (bis(2-ethylhexyl)phosphoric acid) (right).

EXPERIMENTAL

Materials

Cyanex-272® and lithium bis(trifluoromethanesulfonyl)imide (Li[NTf₂]) were gifts from Cytec Inc., (Niagara Falls, Canada) and 3M (Minneapolis, MN) respectively and were used as received. ²⁴¹AmCl₃ tracers were purchased from Isotope Products Laboratories, Valencia, CA. All other chemicals were of reagent grade, and were obtained from Aldrich (Milwaukee, WI) and used as received. All solutions were prepared using deionized water, purified with a Barnsted deionization system (Dubuque, IA) and polished to 18.3 MΩ-cm.

Gamma ray emission analysis was used for ²⁴¹Am counting and was carried out on a Packard Cobra II Auto-Gamma spectrometer (Packard Instrument Co., Downers, Grove, IL).

Synthesis of 1-decyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide. [C₁₀mim][Br] was prepared using literature methods described for 1-butyl-3-methylimidazolium bromide (17). A 1:1.1 molar ratio of [C₁₀mim][Br] and Li[NTf₂] dissolved in water were mixed and stirred overnight. A two phase system was formed, the top phase being aqueous LiBr and the bottom phase [C₁₀mim][NTf₂]. The top phase was decanted and then the IL phase was washed with water 20 times to remove any remaining LiBr. The final product was equilibrated and stored under DI water in order to ensure that the consistent, equilibrium water content for the IL was achieved in each case before partitioning experiments were conducted. Prior to the leaching experiment, samples of the IL were heated under reduced pressure on a rotary evaporator for 4 h at 90 °C, followed by drying under high vacuum for 8 h at 80 °C to ensure that the samples were initially completely dry. ¹H and ¹³C NMR spectra and melting points of the dried IL were comparable with the literature (17,.19). The chemical shifts δ/ppm relative to TMS for ¹H-NMR spectrum in CDCl₃ at 360.13 MHz are: 8.730 (s, 1H), 7.33 (d, 1H), 7.30(t, 1H), 4.15 (t, 2H), 3.93 (s, 3H), 1.85 (m, 2H), 1.29 (m, 14H), and 0.87 (t, 3H).

Partitioning experiments. Two phase systems were prepared using equal volumes of nitric acid solutions and [C₁₀mim][NTf₂] containing Cyanex-272. After vortexing the
vials for 30 seconds and allowing to equilibrate for 30 minutes. 3 μL of $^{241}$AmCl$_3$ tracer was added to the systems. The samples were vortexed and centrifuged twice, then allowed to sit for 24 hours. 100 μL from each phase was counted for partitioning measurements. The radiometric distribution ratio ($D$) was calculated from the number of counts per minute in the IL phase divided by the number of counts per minute in the aqueous phase. Comparison studies using dodecane as the extracting phase were made using the same methodology, substituting water equilibrated dodecane for the IL.

**Leaching experiments.** Leaching of 1-decyl-3-methylimidazolium into the aqueous phase as a function of nitric acid concentration was studied using uv/vis spectroscopy. Spectra were obtained on a Cary 3C spectrophotometer (Varian Optical Spectroscopy, Multigrave, Victoria, Australia). A baseline was automatically subtracted for each experiment. The amount of $[\text{C}_{10}\text{mim}]^+$ was calculated from a standard calibration plot made with $[\text{C}_{10}\text{mim}]\text{Br}$, which is water soluble, using the absorbance maxima centered at 211 nm from the imidazolium cation. We used 0.1 mM-6 mM $[\text{C}_{10}\text{mim}]\text{Br}$ diluted 10,000 times for initial concentrations between 0.01 M and 0.1 M HNO$_3$ and 1,000,000 times for initial concentrations higher than 4 M HNO$_3$. Over this concentration range, in the uv/vis spectra, Beer’s Law is obeyed and thus the solutions are below the critical micelle concentration for $[\text{C}_{10}\text{mim}]\text{Br}$. Using the calibration curve for $[\text{C}_{10}\text{mim}]\text{Br}$, the concentration of $[\text{C}_{10}\text{mim}]^+$ in the aqueous phase was calculated for $[\text{C}_{10}\text{mim}][\text{NTf}_2]$ leaching. For leaching determination of $[\text{C}_{10}\text{mim}][\text{NTf}_2]$, 5 ml of 0.1 M Cyanex-272 in $[\text{C}_{10}\text{mim}][\text{NTf}_2]$ solution were contacted with 5 mL of HNO$_3$ solutions of different concentrations, stirred for 24 hours and then the aqueous phases were diluted and used for uv/vis determinations.

**RESULTS AND DISCUSSION**

Distribution of Am$^{3+}$ between aqueous acidic solutions and $[\text{C}_{10}\text{mim}][\text{NTf}_2]$, using Cyanex-272 as an extractant was investigated as a function of acid concentration. The metal coordination environment and structure have been studied in detail by uv/vis spectroscopy and by EXAFS using HDEHP as a higher purity alternative to commercial Cyanex-272. Both HDEHP and Cyanex-272 coordinate in the same way to trivalent f-elements cations and they can be used interchangeably (20,21). Cyanex-272 is a readily available and widely used commercial complexant, whereas HDEHP offers greater purity which holds advantages for studies such as the spectroscopic studies conducted here.

The suite of Cyanex® complexants, distributed by Cytec, Inc., are phosphorus-based materials that have primary uses in metal extraction and separations. Cyanex-272, or bis(2,4,4-trimethylpentyl)phosphinic acid, is an ionizable complexant that is an effective extractant for transition metals, and is used commercially for primary separation of Co and Ni. The use of Cyanex extractants for lanthanide and actinide complexation and separation has also been investigated, excellent extractive abilities for actinide ions with a range of valencies have been found, with discrimination possible between lanthanides and actinides for some related Cyanex complexants.
Distribution of Am$^{3+}$ in IL/Cyanex-272 systems

Distribution ratios ($D$) for Am$^{3+}$ between [C$_{10}$-mim][NTf$_2$] containing 0.1 M Cyanex-272 as an extractant and aqueous acidic solutions (0.001-10 M) were determined using radiotracer methods with equal volumes of IL and aqueous phases. The distribution results for both IL and dodecane extracting phases are shown in Figure 3 indicate that partitioning of Am$^{3+}$ using Cyanex-272 in the two systems, IL/aqueous and dodecane/aqueous, is roughly comparable over the acid concentration range 0.001 M to 10 M.

Figure 3. Distribution Ratios for $^{241}$Am in 0.1 M Cyanex-272 vs. [HNO$_3$]. □ Dodecane, ○ [C$_{10}$mim][NTf$_2$].

At low nitrate concentration, with both IL and dodecane extracting phases, the $D$ is high, showing preferential extraction in the IL/organic phase. With increasing nitrate concentrations, $D$ progressively decreases until 1 M HNO$_3$ and is then followed by an upturn in $D$ at high acid concentration. Cyanex-272 is an weak acid with pKa = 3.6, and at low concentrations of nitric acid, dissociation of Cyanex-272 supports a cation exchange mechanism, where the metal ion is exchanged with the dissociated proton from complexant. With increasing of nitric acid, above approximately 1 M, dissociation of Cyanex-272 is suppressed and the extraction mechanism seems to change from cation exchange to a different extraction process.

To have a better understanding of the separation pathway, ligand dependency of the extraction process was determined at 0.001 M nitric acid concentration by measuring $D$ as a function of extractant concentration and is shown in Figure 4 for both dodecane and IL systems. It can be seen that log$D$ increases with the logarithm of extractant concentration and shows a linear dependency with a slope of about two. The slope analysis for log$D$ vs. log[Cyanex-272]$_{initial}$ in dodecane has been previously reported in the literature as 2 (21,22). However, Cyanex-272 is known as a hydrogen-bonded dimer and Jensen, et al. (21) have shown that the second power dependence of $D$ on extractant concentration doesn’t support a simple 2:1 ligand:metal (equation 1) ratio when the ligand is the dimer form of Cyanex-272, and taking into consideration aggregation formation determined a true 3:1 ligand:metal ratio (equation 2) for americium in
dodecane where the ligand is the bidentate hydrogen-bond bridged dimer form of Cyanex-272. This is supported by EXAFS studies on the Am³⁺/Cyanex-272 coordination environment in dodecane, where a 3:1 ligand:metal ratio was calculated (21).

\[
\begin{align*}
\text{Am}^{3+} + 2(\text{HA})_{2(\text{org})} & \rightleftharpoons \text{Am}(\text{A})_{3}\text{HA}_{\text{(org)}} + 3\text{H}^+ \quad [1] \\
\text{Am}^{3+} + 3(\text{HA})_{2(\text{org})} & \rightleftharpoons \text{Am}(\text{HA})_{2(\text{org})} + 3\text{H}^+ \quad [2]
\end{align*}
\]

![Figure 4. Ligand Dependency for $^{241}$Am in in [C₁₀mim][NTf₂] (○, slope = 2.19) and dodecane (□, slope = 2.09) from 0.001M HNO₃.](image-url)

While cation exchange processes involving the imidazolium cations of the IL phase have been identified in a number of two-phase systems, the cation exchange mechanism of metal cation with a component of the ligand (here, the hydrogen ion) has rarely been observed in IL biphasic separation systems. Recognition and application of this mode of separation offers significant opportunities to develop more optimal separation systems in ILs since neither the ILs cation nor anion are involved in the extraction mechanism.

Imidazolium ions are not involved in the extraction mechanism, but it is well known that imidazolium salts can leach to some degree in the aqueous phase. To quantify the loss of the IL in the aqueous phase due to the leaching of the imidazolium cation, the concentration of the IL cation has been measured and it doesn’t appear to be significant. The concentration of imidazolium ions in the aqueous phase increases linearly (Figure 5) with nitrate concentration, reaching a maximum of 0.06 M in 10 M nitric acid. Since imidazolium cations are much more hydrophobic that the proton liberated from each coordinating Cyanex-272 complexant, it is not unsurprising that the transport mechanism operates with ion exchange of the most hydrophilic cation to the aqueous phase, namely the proton, and that proton transfer to the aqueous phase decreases with increasing acidity following simple equilibrium principles.
From the combination of $D$ and ligand dependencies, the extraction of $\text{Am}^{3+}$ by Cyanex-272 in $[\text{C}_{10}\text{mim}][\text{NTf}_2]$ IL appears to be similar to that of the analogous liquid/liquid system using dodecane as the extractant phase.

**Coordination of Nd$^{3+}$ and Eu$^{3+}$, in IL/HDEHP and IL/Cyanex-272 systems**

The metal ion coordination environment of Am$^{3+}$ stand-ins, Nd$^{3+}$ and Eu$^{3+}$, in IL systems was investigated using uv/vis spectroscopy and EXAFS. The uv/vis absorption spectra for Nd$^{3+}$, a stand-in element for Am$^{3+}$, in both Cyanex-272/$[\text{C}_{10}\text{mim}][\text{SO}_2\text{CF}_2\text{SO}_2\text{N}]$ and HDEHP/toluene are shown in Figure 6. The spectra overlap perfectly in the range 560-600 nm, suggesting identical coordination environments in both the IL and toluene. HDEHP provides a coordination environment that is identical to Cyanex-272, but is obtainable in a chemically pure form.

![Figure 5](image5.png)

**Figure 5.** Leaching of $[\text{C}_{10}\text{mim}]^+$ cations from $[\text{C}_{10}\text{mim}][\text{NTf}_2]$ IL in contact with aqueous phases as a function of HNO$_3$ concentration.

![Figure 6](image6.png)

**Figure 6.** Absorption spectra for Nd$^{3+}$ in Cyanex 272/$[\text{C}_{10}\text{mim}][\text{NTf}_2]$ and HDEHP/toluene showing the exact overlap in the visible range.
This is confirmed by EXAFS data collected on Eu\(^{3+}\) (as a non-radioactive stand-in for Am\(^{3+}\)) in HDEHP/[C\(_{10}\)mim][NTf\(_2\)] (Figure 7). Preliminary analysis of the EXAFS data and comparison with that in the literature for lanthanide Am(III)-stand-ins coordination in Cyanex-272/dodecane suggests that the coordination environments in each case are identical with a Eu(III) coordination number of six in an octahedral environment (Figure 8).

![EXAFS data for Eu\(^{3+}\) in HDEHP/[C\(_{10}\)mim][NTf\(_2\)].](image)

Figure 7. EXAFS data for Eu\(^{3+}\) in HDEHP/[C\(_{10}\)mim][NTf\(_2\)].

![Proposed coordination environment for Eu\(^{3+}\) with Cyanex-272, with 3 complexant dimers.](image)

Figure 8. Proposed coordination environment for Eu\(^{3+}\) with Cyanex-272, with 3 complexant dimers.

Further work is being undertaken to probe the nucleation of the complex (i.e., mononuclear vs. dinuclear) as well as aggregation effects of the extractant. In contrast to the results for [UO\(_2\)]\(^{2+}\) with CMPO/IL, this data shows an example where ILs can provide an environment that is identical to molecular solvents, presumably because of dominating coordination effects from the ionized complexant. Thus, once again, it becomes critical to elucidate the interactions that are important in ILs with regard to extractant binding and coordination. Additionally, investigations with lanthanide analogs as stand-in elements will continue to be important and require further study, especially with regard to macroscopic studies for TRU elements.
CONCLUSIONS

The separation results for $^{241}$Am and in this study indicate that using the protonated extractant, Cyanex-272, in two-phase partitioning systems with either dodecane or $[\text{C}_{10}\text{mim}]\text{[NTf}_2\text{]}$ as the extracting phase give similar results. The transfer of uranium and americium from nitric acid media to the IL phase is controlled by ionization of the Cyanex-272 extractant dimer releasing protons which can participate in an ion exchange process, rather than by the IL. These results show that in this system, the ion exchange mechanism involves sacrificial exchange of the extractant-sourced protons to the aqueous phase in a manner that resembles that in conventional molecular organic solvents, and that transfer of the imidazolium cation or bistrifylimide anion to the aqueous phase or solvent extraction processes (7) are not the only mechanisms by which metal-ions can be partitioned to ILs.

Distribution ratios results combined with absorption spectroscopy and the confirmation of coordination number determined from EXAFS data show that the extraction equilibria and coordination mode of the Am$^{3+}$ cation is conserved in both $[\text{C}_{10}\text{mim}]\text{[NTf}_2\text{]}$ and dodecane systems with these phosphinic acid or phosphoric acid ligands. The net the transport mechanism is ionic exchange, with a proton from the complexant as the hydrophilic migratory ion, and formation of a neutral extracting species at acid concentrations below 1 M. This data shows an example where ILs can provide an environment that is identical to molecular solvents, presumably because of dominating coordination effects from the ionized complexant.

These results demonstrate an example of an IL/aqueous biphasic system in the extraction behavior, right down to the coordination environment, has been shown to be identical to that of a conventional molecular organic solvent, despite the structural differences between the IL and dodecane.

Separations systems utilizing ILs as the extracting phase are potentially much more complex that those with simple organic solvents as extracting phases. This arises from the potential for either, or, both cations and anions from the IL to contribute in the extraction processes. In contrast to organic extracting phases, ionic liquids can not necessarily be considered to be passive carrier fluids. Ion pair, cation, anion, and sacrificial ion exchange mechanisms have been observed, and vary depending on the nature of the ionic liquid components and of the complexants used. Ionic liquids can be considered as solvents for actinide chemistry. However, the current results are indicating that if ILs are to be used as alternatives to traditional organic solvents in liquid/liquid separations of metal salt complexes, great attention to the design of appropriate ILs and selection of ligand systems is required.

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