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Room-temperature ionic liquids: new solvents for *f*-element separations and associated solution chemistry

Ann E. Visser and Robin D. Rogers*

Department of Chemistry and Center for Green Manufacturing, The University of Alabama, Tuscaloosa, AL 35487, USA

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Abstract

Ionic liquids (ILs) are composed of organic cations and either organic or inorganic anions that remain liquid over a wide temperature range, including room temperature. IL characteristics can be dramatically adjusted (e.g., hydrophobic vs. hydrophilic) by changing the anion type, or subtly altered by changing the length or number of alkyl groups appended to the cation. Changing alkyl chain lengths in the 1-alkyl-3-methylimidazolium cation, in combination with PF_6^- or $N(SO_2CF_3)_2^-$ anions, produces hydrophobic ILs with rheological properties suitable for their use in liquid/liquid separations. Actinides exhibit significant partitioning to these ILs from aqueous solutions with the addition of an extractant (e.g., octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyl phosphine oxide) to the IL. Ionic liquids can, thus, be considered for actinide chemistry as a new class of materials with adjustable solvent characteristics, unique properties, and the potential for enhancing the principles of "green" chemistry in various chemical processes. Here we highlight the unique physical properties of some ILs and their use in liquid/liquid separations.

Keywords: Ionic liquids; CMPO; Actinide separations; Alternative solvents; Imidazolium salts; Crown ethers

1. Introduction

Separations are common in the chemical industry and, over the course of a synthesis or processing scheme, the chemical component of interest may encounter several different separation techniques before completing its journey through the system. Although a variety of separation technologies are available, the efficacy of liquid/liquid separations is virtually unparalleled. The ability to subtly or dramatically change system conditions, associated rapid kinetics, and the large selection of organic solvents available, are several factors contributing to liquid/liquid separations as a mainstay for separation technologies.

The exploration of various actinide separation routes has been driven by the need for technology to successfully process the large quantity of high-level nuclear wastes compiled within the US. Abundant alpha-emitting isotopes are present in the waste, including ^{239}Pu, ^{237}Np, ^{233}U, and ^{241}Am. Fission products, including ^{137}Cs and ^{90}Sr, contribute to significant γ-ray emission. Since the majority of high-level waste is aqueous or will be solubilized in water, successful actinide removal from aqueous solutions will undoubtedly play an important part in developing a treatment strategy. SREX, CSEX, PUREX, REDOX, and combined CSEX–SREX are just a few of the processes, many relying on solvent extraction, that were developed to target the separation of actinides and/or their fission products from aqueous solutions [1].

Both the REDOX and the PUREX processes have been used for nuclear waste treatment [1] where methylisobutylketone and tributylphosphate are used as solvents, respectively [1,2]. SREX, CSEX, and combined CSEX–SREX focus on the extraction of the highly radioactive nuclides ^{137}Cs and ^{90}Sr [3,4]. An in-tank precipitation procedure involving sodium tetraphenylborate (NaTPB) was proposed and tested for ^{137}Cs precipitation in the form of ^{137}CsTPB [5]. An unexpected result was the "higher than expected rates of benzene generation" attributed to metal catalysis reactions [5].

In the systems detailed above, the need to use volatile or semi-volatile organic compounds (VOCs) or the subsequent generation of VOCs, introduces risk associated with the solvent's toxic and flammable nature. In addition to the obvious health problems associated with

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*Corresponding author. Fax: +205-348-0823.
E-mail address: RDRogers@bama.ua.edu (R.D. Rogers).

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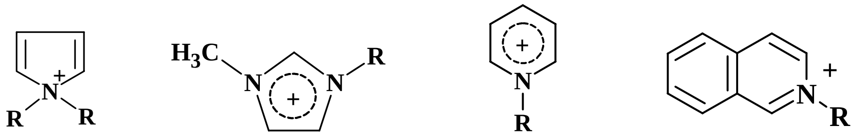
Cations



1,1'-alkyl-pyrolinium $[C_npyr]$	1-alkyl-3-methyl-imidazolium $[C_nmim]^+$	N-alkyl-pyridinium $[C_npy]^+$	N-alkyl-isoquinolinium $[C_nisoq]^+$

Anions

PF_6^-, $N(SO_2CF_3)_2^-$, $N(SO_2CF_2CF_3)_2^-$	BF_4^-	NO_3^-, Cl^-, ClO_4^-
Water-immiscible	Cation dependent [13]	Water miscible

Fig. 1. Representative cations and anions for IL composition (*n* indicates the number of carbons in the alkyl chain, e.g., $-CH_2CH_2CH_2CH_3$, $n = 4$). Tetraalkyl-ammonium and -phosphonium salts are also currently being used to prepare ILs.

organic diluents, strict environmental policies ensure a high cost of spent solvent disposal. Auxiliary issues can arise when designing a plant to safely contain and transport the solvents.

The development of novel solvents for use in separations provides an opportunity to extend the concepts and practices of "green" technology [6] to situations within the nuclear fuel cycle. A new generation of ionic liquids (ILs), comprised of cations and anions shown in Fig. 1, has received attention as solvent alternatives due to their low melting points, negligible volatility, and rheological properties that render them desirable for use in liquid/liquid separations and other applications. (Although ILs are currently being studied in a 'green chemistry' context, it should be noted that all of the toxicological and safety aspects of these new solvents are not yet known. Thus, care should be exercised in the use and study of these chemicals.)

Incorporating ILs as new solvent systems could offer advantages that surpass current practices and supplant traditional solvents such as kerosene, isopropylbenzene, and methylethylketone for use in actinide recovery and processing [1,7,8]. Despite the low volatility of kerosene, the use of ILs may provide unique benefits inherent to this new class of solvents.

Actinide chemistry in room-temperature ILs is a new area of investigation and appears to hold a great deal of potential for interesting results. Recent reports highlight electrochemistry and spectroscopy of uranium in tetrachloroaluminate ILs [9,10]; a patented process illustrates the dissolution of nuclear fuel cladding with $[C_4mim][NO_3]$ (defined in Fig. 1) with additional PUREX processing to recover uranium and plutonium [11]. Separately, the addition of nitric acid and acetone to $[C_4mim][NO_3]$ facilitated the precipitation of the first uranium complex from an IL [12]. The UO_2^{2+} crystal structure contained a bridging oxalate group and, since the precipitation of other metal complexes was not successful, a method to separate the uranium by precipitation could be envisioned [12].

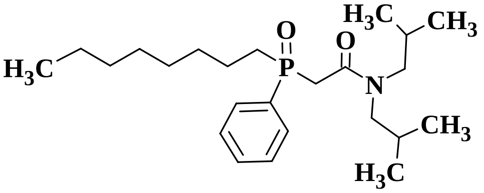


Fig. 2. Octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO).

In contrast to high-temperature melts, certain ILs are moisture stable, have miniscule volatility, and are water immiscible. The cations shown in Fig. 1 each contain at least one alkyl group (*R*) attached to the cation. Variations in the length of the alkyl chain and the introduction of different anions allow for adjustment of the IL properties [13–18]. For example, we have shown that increasing the alkyl chain length increases the hydrophobicity for a series of $[C_nmim][PF_6]$ ILs [14], with concomitant increases in the partition of hydrophobic solutes from aqueous to IL phases [19–21].

Typical ILs are in general non-coordinating and, in the absence of an extractant, do not extract metal ions from the aqueous phase to the IL phase. Extractants, such as crown ethers can be added to the IL phase to enhance Sr^{2+} and Cs^+ distribution ratios [20,22] and, similarly, azo molecules increase the affinity of transition metals for the IL [23]. Octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO, Fig. 2) has been successfully utilized as an actinide extractant in liquid/liquid separations with traditional organic solvents and significantly increases distribution ratios for actinides [24]. Its effect in IL-based liquid/liquid separation systems will be discussed here.

2. Experimental

HPF_6 was supplied by Ozark-Mahoning Co. (Tulsa, OK) and was used as received. CMPO was obtained from Strem Chemicals (Newburyport, MA) and used without purification. All other chemicals (unless otherwise indicated) were obtained from Aldrich (Milwaukee, WI), were of reagent grade, and were used without further purification. Synthesis and characterization of the ILs were performed as detailed elsewhere [14].

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. Acid and salt solutions were prepared as molar concentrations by transferring a known amount of material to a volumetric flask and diluting to the specified volume with deionized water. Each CMPO and/or TBP solution was prepared at molar concentration by weighing out a known amount of material and transferring it to a volumetric flask and diluting to the specified volume with $[C_4mim][PF_6]$.

Each actinide tracer was prepared from stock solutions maintained in the Chemistry Division at Argonne. Due to the presence of ^{229}Th daughters in the ^{233}U stock solution, UTEVA (Eichrom Industries, Darien, IL) and Amberlite XAD-7 resins were used to purify the solution prior to use. For $^{238}Pu^{4+}$ partitioning experiments, each aqueous phase also contained 0.01 M $NaNO_2$. (The actinide partitioning experiments were repeated in our laboratories at The University of Alabama utilizing different tracer stock solutions. The partitioning results from the two laboratories agreed to within 5%.)

Equal volumes of the IL and aqueous phases were contacted 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 $^{230}ThCl_4$, $^{241}AmCl_3$, $^{238}PuCl_4$, or $^{233}UO_2Cl_2$ (0.01 μCi, ~3 μL in dilute HNO_3) 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. Gamma-ray emission analyses were carried out on a Beckman Biogamma (Fullerton, CA) counter or a Packard Cobra Auto-Gamma Spectrometer (Packard Instrument Company, Downers Grove, IL). Alpha counting was performed via liquid scintillation on a Packard model 2000CA liquid scintillation counter.

Since equal volumes of both phases were analyzed, metal ion distribution ratios were calculated as follows:

$$D = \frac{\text{Counts per minute in the IL (lower) phase}}{\text{Counts per minute in the aqueous (upper) phase}}.$$

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

3. Results and discussion

3.1. Physical properties of ILs

IL properties are determined by the component cations and anions, and here we have focused on those combinations that result in hydrophobic ILs that remain liquid close to room temperature. Like other solvents, various amounts of water are soluble in hydrophobic ILs after a period of contact. After equilibration with water, the water content decreases from $[C_4mim][PF_6]$ (11,700 ppm) to $[C_6mim][PF_6]$ (8837 ppm) to $[C_8mim][PF_6]$ (6666 ppm), indicating how the alkyl chain length affects the hydrophobicity of the IL phase [14].

Our previous results indicate that many aromatic solutes have a high affinity for the IL phase and that increasing the hydrophobicity (e.g., by using $[C_6mim][PF_6]$ instead of $[C_4mim][PF_6]$) slightly increases the distribution ratios [14]. Changing the parent cation from 1-alkyl-3-methylimidazolium to *N*-alkyl-isoquinolinium also increases the distribution ratios for hydrophobic organic solutes [25].

In contrast to the partitioning of organic solutes to the IL phase, metal ions remain in the aqueous phase and require an extractant molecule to form a more hydrophobic complex to increase their affinity for the extracting phase. Given the affinity of certain organic molecules for the IL phase [19,23,26], the use of extractants that reside quantitatively in the extracting phase appears to be a promising method to increase actinide distribution ratios.

3.2. Organic extractants

The use of crown ethers as extractants for actinide fission products, Sr^{2+} and Cs^+, gave unexpected results in $[C_4mim][PF_6]$ systems. Using 4,4′-(5′)-di-(*t*-butylcyclohexano)-18-crown-6 (dtb18C6), we observed Sr^{2+} and Cs^+ partitioning that was contrary to literature results in the selectivity and trend with increasing aqueous acid concentrations [20]. A more in-depth study using $[C_4mim][PF_6]$ determined that the stability and composition of the IL phase changes with increasing aqueous acid concentrations. In fact, $[C_4mim][PF_6]$ in contact with 8 M HNO_3 becomes monophasic after several hours due to the acid-catalyzed hydrolysis of the PF_6^- to form PO_4^{3-}, producing a water-soluble IL which results in the degradation of the biphasic system [20]. The stability of ILs containing the PF_6^- anion may impact their use in separation systems where optimal conditions are often encountered in the presence of elevated aqueous acid concentrations. However, separations in IL systems may require lower acid concentrations to achieve similar distribution ratios or, alternatively, other IL anions (e.g., $N(SO_2CF_3)_2^-$), can be used [22].

The TRUEX process incorporates 0.2 M CMPO and 1.2–1.4 M tri-*n*-butylphosphate (TBP) with paraffinic hydrocarbons as the diluent [27]. One of the appealing features of the TRUEX process is that selective partitioning of trivalent actinides from tetra- and hexavalent actinides can be achieved through proper selection of aqueous-phase composition. Using this TRUEX formulation and partitioning from increasing HNO_3 concentrations, Schulz and Horwitz report the magnitude of distribution ratios decreases in the order Pu^{4+} (10^4 at 5 M HNO_3), NpO_2^+ (10^4 at 1 M HNO_3), UO_2^{2+} (10^3 at 6 M HNO_3) and Am^{3+} (10 at 6 M HNO_3) [27]. With dodecane as the diluent, Mathur et al. indicate distribution ratios with 0.2 M CMPO and 1.2 M TBP from 1 M HNO_3 decrease in magnitude from Pu^{4+} (10^3), UO_2^{2+} (10^2), to Am^{3+} (10) [28]. Since TBP is a phase modifier and not part of the extracted species, changing the concentration of TBP does not have an affect on the results [28].

We recently extended the possibilities for application of IL-based separations to actinides by incorporating CMPO as the extractant. As with other metal ions (e.g., Hg^{2+} [29], Cd^{2+} [29], Fe^{3+}, Eu^{3+}, Ni^{2+}, Co^{2+}, and Cs^+ [23]) in IL/aqueous systems, all actinides have distribution ratios significantly below 1, indicating their preference for the aqueous phase. The addition of 0.1 M CMPO and 1 M tri-*n*-butyl phosphate (TBP) to $[C_4mim][PF_6]$ significantly enhances the distribution ratios in comparison to the same concentrations of CMPO and TBP in dodecane, as shown in Fig. 3.

Distribution ratios for Am^{3+}, Pu^{4+}, Th^{4+}, and UO_2^{2+} are all at least an order of magnitude higher in $[C_4mim][PF_6]$ compared to similar extractant conditions in dodecane as the extracting phase. ILs apparently present a unique environment which contributes to the performance of CMPO in IL systems. An important consideration lies in the fact that the distribution ratios shown in Fig. 3 were obtained at no greater than 1 M HNO_3, below optimal conditions that are traditionally used for CMPO as an actinide extractant [27]. The chemistry associated with the PF_6^- anion limits the region of aqueous acid concentrations available for separation experiments and it is possible that using ILs with other hydrophobic anions may extend the range of system conditions available to surpass the results shown here.

The maximum solubility of CMPO in $[C_4mim][PF_6]$ is 0.1 M, and thus the CMPO and TBP concentrations used for comparison in dodecane (Fig. 3) are lower than optimal concentrations used in the literature [27] and serve only as a comparison to IL systems. Using 0.1 M CMPO/1 M TBP in dodecane, distribution ratios at 1 M HNO_3 decrease in magnitude from UO_2^{2+} (10^2), Th^{4+} and Pu^{4+} [10], to Am^{3+} which shows little affinity for the dodecane phase under these conditions. Increasing the concentration of CMPO from 0.1 to 0.2 M with 1.2 M TBP in dodecane, UO_2^{2+} distribution ratios from 3 M HNO_3 increase from approximately 120 to over 230 [28].

3.3. Assessment

CMPO and CMPO/TBP in ILs do enhance distribution ratios for selected actinide elements from low HNO_3 concentrations. At the studied concentrations, there is an enhancement of actinide distribution ratios to the ILs over dodecane as the diluent. Nonetheless, there are several facets of this work which will require much further study. Some of these include the following.

3.3.1. Radiolysis

A recent report in the literature indicates that due to the ability of aromatic rings to absorb energy, radiolysis of $[C_n mim]^+$ cations does not appear to present a problem [30]. The preliminary assessment of radiation stability of $[C_n mim]Cl$ and $[C_4mim][NO_3]$ ILs to α, β, and γ radiation indicated no significant decomposition [30]. The $[C_n mim]Cl$ and $[C_4mim][NO_3]$ ILs appeared to be much more stable than TBP/kerosene mixtures after similar irradiation conditions [30]. Although certain IL cation and anion combinations are becoming well-known and characterized, additional ILs resulting from

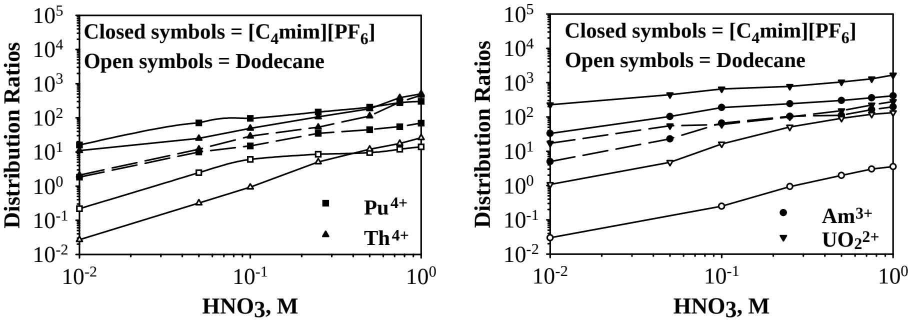


Fig. 3. Distribution ratios for $^{241}Am^{3+}$, $^{233}UO_2^{2+}$, $^{238}Pu^{4+}$, and $^{230}Th^{4+}$ in $[C_4mim][PF_6]$/aqueous (solid symbols) or dodecane/aqueous (open symbols) liquid/liquid systems. The extracting phase is either 0.1 M CMPO in $[C_4mim][PF_6]$ (- - -) or 0.1 M CMPO and 1 M TBP in $[C_4mim][PF_6]$ (—).

different cation and anion combinations and process conditions (i.e., physical contact with highly radioactive materials) need to be investigated. Thus, several aspects regarding chemistry in ILs and applications of the science remain wide open.

3.3.2. Stripping

Despite the positive results for actinide separations, stripping the actinides from the IL phase has not been addressed and, as the results in Fig. 3 show, a simple change in aqueous-phase pH may not be sufficient to induce stripping. Further research is needed to understand the mechanism, responsible for the results observed here, and to use the results to find appropriate conditions for stripping.

3.3.3. Task-specific ILs (TSILs)

The success with CMPO as an extractant prompted us to extend the concept of TSILs [29] to actinide separations by including a phosphine oxide functional group in the pendant arm of the cation. Such TSILs could help reduce or eliminate extractant loss to the aqueous phase. Our initial results in collaboration with Prof. Jim Davis at the University of South Alabama [31] with such a moiety appear promising, but the mechanism of the extraction process is still unclear.

3.3.4. Mechanisms

We are currently investigating the actinide coordination environment in ILs to determine whether unique extractant behavior or solvent effects (e.g., liquid ion exchange) underlie the results shown here. A fundamental understanding of systems based on traditional extractant molecules in ILs is a paramount objective towards optimizing the potential for these novel solvent alternatives in a variety of applications.

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