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Review

The coordination chemistry of actinides in ionic liquids: A review of experiment and simulation

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Contents

Abstract

Ionic liquids (ILs) have found widespread use in biochemical, electrochemical, catalytic, and synthetic applications, and have recently been applied to important areas of f-element chemistry. This review highlights the use of ILs in separation schemes for the sequestration of actinide ions (including lanthanides, where appropriate, as stand-ins for actinide ions), the solid-state chemistry of actinide complexes containing imidazolium cations, and the spectroscopy and electrochemistry of actinide cationic and anionic species. Particular emphasis is placed on the coordination environments that are present under a variety of conditions, such as acidic and basic tetrachloroaluminate melts. Also, this review touches on the recent use of computer simulations to elucidate the microscopic interactions that result in the preferential solvation of actinide ions in ILs.
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1. Introduction

Ionic liquids (ILs) are a distinct set of compounds which by most accepted definitions are composed of fully dissociated ions and melt at temperatures lower than $100\,^{\circ}\mathrm{C}$. The most common ILs are composed of organic cations, including imidazolium, pyridinium, pyrrolidinium, ammonium, and phosphonium (Fig. 1), and inorganic anions. Seddon [1] has remarked that over 10^{18} simple organic salts that might be potential ILs could be prepared by varying the substitution patterns and anion choices, even just within imidazolium and pyridinium systems, not to mention binary, ternary and higher order mixtures.

ILs have been investigated recently as solvents for synthetic, catalytic, biochemical and electrochemical applications and as liquid phases for separations processes, primarily as potential alternatives to conventional solvents, especially volatile organic compounds (VOCs) [2,3]. Some of the unique properties of the most widely studied ILs include negligible volatility, wide liquid temperature range, high thermal stability, electrical conductivity, and tunable physical properties. These are significant characteristics with regard to reduction of chemical and environmental hazards associated with exposure to VOCs, and the increasing restriction of their use, particularly in industry. In addition, ILs are composed of fully dissociated cations and anions, making

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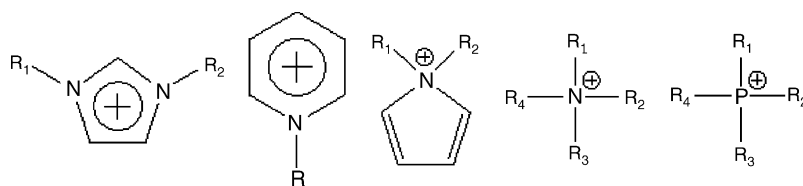 *E-mail address:* RDRogers@bama.ua.edu (R.D. Rogers).

Fig. 1. Common organic IL cations.

them unique systems for studying the coordination chemistry and extraction mechanisms of metal ions, particularly actinides [4]. Lanthanide ions, Ln(III), coordinate in the same way to similarly sized trivalent actinides with hard donor ligands, thus allowing many studies to be conducted using nonradioactive Ln(III) ions as stand-in elements for highly radioactive trivalent actinides [5,6].

Ionic liquids have started to gain high interest in actinide chemistry studies due to their potential applicability as solvents for actinide ion separations from spent fuel radioactive wastes, for electrochemical separation of actinides, and for solid-state studies of actinides. An important consideration in the use of ILs in areas such as f-element separations is solvent stability. In such separations, ILs may be subjected to large radiation fields from intense activity due to the radioactive decay of heavy actinides and short-lived fission products. A collaborative study by Allen et al. screened a series of ILs for their radiochemical stability, including 1-butyl-3-methylimidazolium nitrate, 1-ethyl-3-methylimidazolium chloride, and 1-hexyl-3-methylimidazolium chloride, towards alpha, beta, and gamma irradiation [7]. The results suggest that these ILs are comparable to benzene in terms of overall stability, and are significantly more stable than mixtures of tri-*n*-butylphosphate and odorless kerosene (historically important solvent systems in the nuclear industry) under similar degrees of irradiation. Overall, the imidazolium cation appears to be relatively radiation resistant, with no substantial decomposition of the organic components. Thus, ILs may be considered as potential solvents for use in a variety of nuclear-related applications where intense radiation is an important factor.

Here we review the use of ILs in several actinide-related applications, including separations, solid-state analysis, electrochemistry, spectroscopy, and computer simulations over the past 25 years. Particular emphasis is placed on describing the coordination environment around the actinide ion, and the effect that the IL itself has on this environment in comparison to more traditional solvents. The primary focus will be on 1-alkyl-3-methylimidazolium ($[C_n mim]^+$) and 1-alkylpyridinium ($[C_n pyr]^+$) based ILs, where n represents the length, in carbon atoms, of the alkyl chain.

2. Separations

Actinide coordination has been studied with a range of complexants in a number of IL/aqueous biphasic systems in the context of separations and me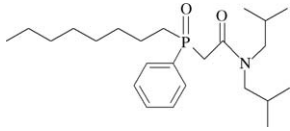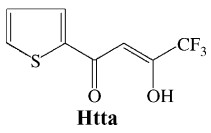tal ion extraction [8,9]. In contrast to systems comprised of purely molecular solvents, ILs have two components, a cation and an anion, both of which can be anticipated to have roles in metal ion extraction, a fact highlighted in the recent literature discussed below.

Metal ion separations have been of interest ever since the first reports of using extractants to partition metal ions from aqueous media to ILs appeared in 1999 [10,11]. Actinides are known to represent major components in nuclear tank wastes and the success of these initial studies with fission products such as Sr(II) led to conjecture that IL could be used as solvents in metal ions separation from aqueous media. Visser et al. [8] studied uranyl (UO_2^{2+}) extraction with CMPO and TBP into $[C_4 mim][PF_6]$ and $[C_8 mim][Tf_2N]$ (Tf_2N = bis(trifluoromethanesulfonyl)imide) from aqueous acidic media and showed enhancement for UO_2^{2+} ion extraction into ILs when compared to dodecane. Coordination studies to elucidate the nature of the metal ion coordination responsible for this enhancement were conducted. Extended X-ray absorbtion fine structure (EXAFS) measurements showed that UO_2^{2+}–CMPO complexes in $[C_4 mim][PF_6]$ and $[C_8 mim][Tf_2N]$ are similar, but different from those in dodecane. The UO_2^{2+}–CMPO coordination in dodecane consists of a hexagonal bipyramidal $UO_2(NO_3)_2(CMPO)_2$ complex with two U–O (CMPO) distances of 2.38(2) Å and four U–O (nitrate) distances of 2.53(2) Å. In the presence of the ILs, just a single equatorial U–O bond distance of 2.40(1) was observed by EXAFS with the average number of equatorially bound oxygen atoms approximately 4.5.

Slope analysis for the IL systems indicated that the extracted UO_2^{2+} complex was $UO_2(NO_3)(CMPO)^+$, while the extracted UO_2^{2+} complex in dodecane was the neutral $UO_2(NO_3)_2(CMPO)_2$. The different inner coordination sphere for extracted UO_2^{2+} species in $[C_4 mim][PF_6]$ and dodecane from 1 M HNO_3 with CMPO and TBP was probed also using UV–vis spectroscopy. The spectra containing extracted UO_2^{2+} complexes in $[C_4 mim][PF_6]$ and dodecane are not equivalent indicating that the primary coordination environments are different. These results demonstrated that the differences in UO_2^{2+} uptake into ILs compared to dodecane are due to a change in extraction equilibria from Eq. (2) in dodecane to Eq. (1) (Table 1) in the ILs. In Eq. (1) an imidazolium cation must migrate to the aqueous phase in a cation exchange process to maintain charge balance.

The origin of uptake enhancement for metal ions, including actinides, into ILs from aqueous media consequently results in loss of ILs cations in the aqueous phase, thus limiting the use of ILs for these applications. Further investigations have been

Table 1
Extraction mechanisms in IL/aqueous vs. organic/aqueous systems

Ligand	Equilibrium reaction for M^{n+} separation in ILs	Equilibrium reaction for M^{n+} separation in molecular solvents
CMPO	(1) $UO_{2(aq)}^{2+} + [C_n mim]_{IL}^+ + NO_{3(aq)}^- + L_{IL}$ $\Leftrightarrow [(UO_2)(NO_3)L]_{IL}^+ + [C_n mim]_{(aq)}^+$	(2) $UO_{2(aq)}^{2+} + 2NO_{3(aq)}^- + 2L_{org} \Leftrightarrow [(UO_2)(NO_3)_2 L_2]_{org}$
Htta	(3) $Ln_{(aq)}^{3+} + 4HL_{IL} + [C_4 mim][Tf_2 N]_{IL} \Leftrightarrow$ $[C_4 mim]^+[LnL_4]_{IL}^- + 4H_{(aq)}^+ + [Tf_2 N]_{(aq)}^-$	(4) $Ln(H_2 O)_{n(aq)}^{3+} + 3HL_{org} \Leftrightarrow [LnL_3(H_2 O)_{n-6}]_{org} + 3H_{(aq)}^+ + 6H_2 O_{(aq)}$
		(5) $Ln(H_2 O)_{n(aq)}^{3+} + 4HL_{org} \Leftrightarrow LnL_3 \cdot HL_{org} + 3H_{(aq)}^+ + nH_2 O_{(aq)}$

Eqs. (1) and (2) [8]; Eqs. (3)–(5) [6].

made to try to understand if this phenomenon is a general one for metal ion separation into ILs.

In contrast to previous results, Jensen and Bond [5] reported a study of trivalent lanthanide transfer into the IL using 2-thenoyltrifluoroacetone (Htta) as a charged complexant. Ln(III) form anionic complexes of the form $[Ln(tta)_4]^-$ in $[C_4 mim][Tf_2 N]$ (Eq. (3), Table 1), rather than the neutral $[Ln(tta)_3(H_2 O)_n]$ $n = 2$ or 3 (Eqs. (4) and (5), Table 1) complexes as observed in molecular solvents. Here the limitations for practical applications include the extraction of anionic complexes which requires the transfer of IL anions to the aqueous phase, thus depleting the IL and complicating the recovery of extracted metal.

In an effort to find metal ion coordination environments which would facilitate practical extractions, Cocalia et al. [9] studied the coordination and extraction behavior of Am(III) and UO_2^{2+} with Cyanex-272 and bis-(2-ethylhexyl) phosphoric acid (HDEHP) into $[C_{10} mim][Tf_2 N]$ from acidic aqueous solutions. The distribution ratios for both Am(III) and UO_2^{2+} versus nitric acid concentration follow the same trend in the IL and dodecane indicating that the same extraction equilibria take place. The coordination of the extracted metal ions was studied by UV–vis and EXAFS. The UV–vis spectra for the extracted UO_2^{2+} from 0.25 M HNO_3 with HDEHP into $[C_{10} mim][Tf_2 N]$ and dodecane exhibited similar peak shapes and energies of the vibronic fine structure for the uranyl complexes, indicating that the inner coordination sphere is the same in both solvents.

Nd(III) was used as a stand-in for Am(III) in the UV–vis spectroscopy measurements. The UV–vis spectra for extracted Nd(III) with HDEHP into the IL and into dodecane are similar in the visible region for the hypersensitive ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$, ${}^2G_{7/2}$ and ${}^4I_{9/2} \rightarrow {}^2H_{9/2}$, ${}^4F_{5/2}$ transitions centered at 281 and 803 nm. These results denote that Nd(III), and consequently trivalent actinides, coordinate in the same way to HDEHP and Cyanex-272 when extracted into $[C_{10} mim][Tf_2 N]$.

To corroborate the optical spectroscopy and obtain more structural information on the complexes studied, EXAFS measurements were carried out. EXAFS results for the Eu(III) (as a stand-in for Am(III)) extracted complex with 1 M HDEHP into $[C_{10} mim][Tf_2 N]$ are similar to the Cm(III) complexes with Cyanex-272 from the literature, demonstrating that the inner

coordination sphere of trivalent lanthanides and actinides is the same for HDEHP/Cyanex-272 complexes in both dodecane and $[C_{10} mim][Tf_2 N]$. The best fit for the Eu(III) data corresponds to 6.3 ± 0.6 coordinated O–P groups from 3.1 ± 0.3 HDEHP dimers. The Eu–O distance of 2.284(7) Å agrees with M–O distances corresponding to Cyanex-272 complexes of Nd(III), Sm(III) and Cm(III). The Eu–P distance of 3.78(2) Å and Eu–O–P angle of 150° both support the coordination of three monodeprotonated dimers of HDEHP or Cyanex-272 rather than bidentate monomers of the ligands.

EXAFS results for UO_2^{2+} complexes in dodecane and $[C_{10} mim][Tf_2 N]$ showed bond distances and coordination numbers consistent with four oxygens from HDEHP coordinated to UO_2^{2+} in both cases. The U=O bond distances corresponding to the two axial oxygens from UO_2^{2+} are 1.768(7) and 1.767(6) Å in $[C_{10} mim][Tf_2 N]$ and dodecane, respectively. The number of equatorially coordinated oxygens to UO_2^{2+} is 3.6 ± 0.4 in the IL and 3.7 ± 0.5 in dodecane corresponding to 1.8 ± 0.2 HDEHP dimers. The U–O distance corresponding to the oxygens bound equatorially to the UO_2^{2+} is 2.38(1) Å in both solvents. The similar extraction and coordination modes for trivalent and hexavalent actinides in ILs show that previous found limitations for using ILs in separation can be overcome by choosing the appropriate ligand–solvent combination.

3. Solid-state chemistry of actinide/imidazolium-based salts

Even though ILs have only recently enjoyed a high level of interest for actinide chemistries, there have been several earlier solid state studies with ILs or IL-based compounds, e.g. imidazolium-based salts, many of which are listed in Table 2. The first uranyl imidazolium salt was reported by Perry as a dimer, bis-μ-aquo-bis(dioxobis(nitrato)uranate(VI)) diimidazole, where two water molecules were reported to act as bridges between uranium atoms [12]. Later X-ray photoelectron and infrared studies indicated that the bridge between the uranium(VI) center is most probably hydroxide and not water [13]. The two $[(UO_2)(NO_3)_2]$ units are thus bound through two OH^- bridges and charge balanced by two imidazolium cations. The U–OH bridging distances were reported to be 2.35(1) and

Table 2
Actinide crystal structures containing imidazolium cations

Compound	References
Bis(imidazolium) bis-μ-hydroxo-bis[bis(nitrato-O,O)dioxouranate(VI)]	[12,13]
Bis(2-methylimidazolium) tetrachlorodioxouranate(VI)	[14]
Bis(imidazolium) tetrachlorodioxouranate(VI)	[15]
Bis(1-ethyl-3-methylimidazolium) hexachlorouranate(IV)	[16]
Bis(1-ethyl-3-methylimidazolium) tetrachlorodioxouranate(VI)	[16]
Bis(1,3-dimethylimidazolium) bis(nitrato-O,O)bis(nitrato-O)dioxouranate(VI)	[18]
Bis(1-ethyl-3-methylimidazolium) μ$_4$-(O,O,O',O'-oxalato)bis[bis(nitrato-O,O)dioxouranate(VI)]	[18]
Bis(1-propyl-3-methylimidazolium) μ$_4$-(O,O,O',O'-oxalato)bis[bis(nitrato-O,O)-dioxouranate(VI)]	[18]
Bis(1-butyl-3-methylimidazolium) μ$_4$-(O,O,O',O'-oxalato)bis[bis(nitrato-O,O)dioxouranate(VI)]	[17,18]
Bis(1-pentyl-3-methylimidazolium) μ$_4$-(O,O,O',O'-oxalato)bis[bis(nitrato-O,O)dioxouranate(VI)]	[18]
Bis(1-hexyl-3-methylimidazolium) μ$_4$-(O,O,O',O'-oxalato)bis[bis(nitrato-O,O)-dioxouranate(VI)]/1-hexyl-3-methylimidazolium nitrate (1/1)	[18]
Bis(1-dodecyl-3-methylimidazolium) bis(nitrato-O)bis(nitrato-O,O)dioxouranate(VI)]	[18]
Bis(1-hexadecyl-3-methylimidazolium) μ$_4$-(O,O,O',O'-oxalato)bis[bis(nitrato-O,O)dioxouranate(VI)]/acetonitrile (1/6)	[18]

2.37(1) Å and the uranium–axial oxygen bonds to be 1.78(1) and 1.76(1) Å.

Uranyl chloride hydrate reacts with imidazole or methylimidazole at a pH of about 2 to form tetrachlorodioxouranate(VI) ions stabilized by either two imidazolium or 2-methylimidazolium cations [14,15]. The imidazolium cations in these structures are planar entities and the chloride ions are situated in the equatorial positions around the UO_2^{2+} cation. The U–O distances in the two characterized compounds are within the reported values for tetrachlorodioxouranate ions.

Hitchcock et al. [16] synthesized $[C_2mim]_2[UCl_6]_2$ by treating $[C_2mim]Cl$ with UCl_4 in 6 M HCl in the absence of oxygen. In this structure, uranium is surrounded by six chloride ions in an octahedral environment with an average U–Cl distance of 2.61 Å. The oxidation of $[C_2mim]_2[UCl_6]$ in air led to $[C_2mim]_2[UO_2Cl_4]$, an octahedral complex with a mean uranium chlorine distance of 2.664 Å and an average distance between uranium and axial oxygens of 1.76 Å. Interestingly, only $[imidazolium]_2[UO_2Cl_4]$ is distorted from octahedral coordination [15]; the other two tetrachlorouranate complexes have O–U–O angles of 180° [14,16].

Recently, uranyl salts were demonstrated to precipitate from room temperature ILs [17]. Bradley et al. isolated and characterized a series of 1-alkyl-3-methylimidazolium salts of nitratodioxouranate(VI) from 1-alkyl-3-methylimidazolium nitrate, nitric acid, and usually an oxalate source [18]. The majority of the isolated complexes were oxalate-bridged dinuclear nitratodioxouranate 1-alkyl-3-methylimidazolium salts. Interestingly, the oxalate bridge was present even when no oxalate source was introduced in the media. It was suggested that the oxalate could be formed from acid impurities oxidized by nitric acid or from the oxidation of glyoxal (which was used in the synthesis of imidazolium ILs), by concentrated nitric acid.

When $[C_1mim][NO_3]$ and $[C_{12}mim][NO_3]$ ILs were used, the presence of oxalate was confirmed by NMR spectroscopy in the solution, but the precipitates obtained were characterized as 1,3-dialkylimidazolium bis(nitrato-O)bis(nitrato-O,O)dioxouranate(VI) salts (Fig. 2). This was explained as packing preferences of the $[C_1mim]^+$ IL with the smaller nitrate anions rather than the large oxalate dimer anions. In the
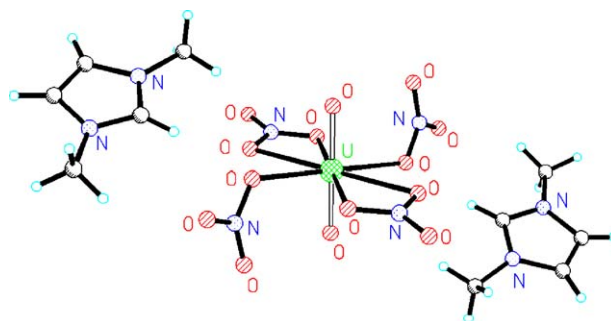

Fig. 2. Crystal structure of bis(1,3-dimethylimidazolium) bis(nitrato-O,O)bis(nitrato-O)dioxouranate(VI). (Diagram prepared from the coordinates in Ref. [18].)

$[C_{12}mim]^+$ IL, it was not clear why the precipitated compound contains the nitrate anions and not the oxalate anion. All of the other isolated salts contained $[\{UO_2(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]^{2-}$ anions and 1-alkyl-3-methylimidazolium cations.

The structure $[C_6mim]_2[\{UO_2(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]$ is the first published co-crystal with an IL and consists of $[C_6mim][NO_3]$ incorporated into the crystal lattice. When very long alkyl chains ($[C_{16}mim]^+$) were used in the ILs (Fig. 3), the anions associated with the headgroups of the cations formed channels between cationic layers which were filled with acetonitrile molecules.
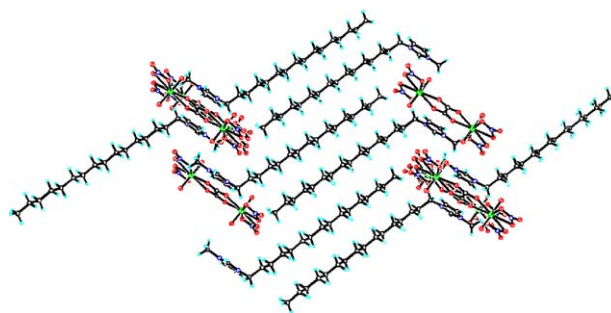

Fig. 3. Packing diagram of bis[1-hexadecyl-3-methylimidazolium] μ$_4$-(O,O,O',O'-oxalato)bis[bis(nitrato-O,O)dioxouranate(VI)]/acetonitrile (1/6), with acetonitrile molecules omitted. (Diagram prepared from the coordinates in Ref. [18].)

Bradley also studied the possibility of isolating the uranium from [C$_4$mim][NO$_3$] by reducing U(VI) to U(IV), but the attempt was unsuccessful due to the fact that UO$_2$ is an insulator at low temperatures and it could not be recovered. In this context, Bradley et al. studied the speciation of uranium following the oxidative dissolution of UO$_2$ in [C$_4$mim][NO$_3$]. The UV–vis spectrum of the solution indicated that U(VI) species are present in the solution and IR measurements indicated that oxalate participates as a tetradentate ligand in the metal binding.

EXAFS spectra of UO$_2$(NO$_3$)$_2$·6H$_2$O dissolved in [C$_4$mim][NO$_3$] suggested a number of possible structural arrangements, e.g. [UO$_2$(η^2-NO$_3$)$_2$(η^1-NO$_3$)(H$_2$O)]$^-$, or [UO$_2$(η^2-NO$_3$)$_2$(η^1-NO$_3$)$_2$]$^{2-}$. A comparison of the EXAFS results for oxidative dissolution of UO$_2$ in [C$_4$mim][NO$_3$] with those obtained for uranyl nitrate hexahydrate solution and bis[1-butyl-3-methylimidazolium] μ_4-(O,O,O′,O′-oxalato)bis[bis(nitrato-O,O)dioxouranate(VI)] solution in [C$_4$mim][NO$_3$] in the presence or absence of acetone, indicated that a mixture of nitrate monomer and oxalate bridged dimer is present in both cases. The best fit was obtained for a 15/85 mole ratio of a mononuclear nitrate complex/dinuclear oxalate complex [18].

4. Electrochemistry/spectroscopy

Ionic melts containing aluminum chloride (AlCl$_3$) have been used quite extensively as solvents for the electrochemical and spectroscopic study of organic and inorganic solutes, including lanthanides and actinides [19]. The earliest studies of various metal ions were performed in AlCl$_3$:MCl mixtures, where M$^+$ is an alkali metal cation. However, substitution of M$^+$ with an organic heterocycle, such as pyridinium or imidazolium, reduce the working temperature of the melt from greater than 200 °C to room temperature or lower. Melts that have working temperature at or below 100 °C will hereafter be referred to as ILs [20–22].

The acid–base properties of these ionic melts vary widely depending on their composition. Melts that contain greater than 50 mol% AlCl$_3$ are "acidic" melts because they contain the large, Lewis acidic anions AlCl$_4$$^-$ and Al$_2$Cl$_7$$^-$. Melts that contain less than 50 mol% AlCl$_3$ are "basic" melts because they contain free chloride ions that strongly complex with large metal cations [23].

The acidic melts stabilize metal cations of low oxidation state due to the presence of large AlCl$_4$$^-$ and Al$_2$Cl$_7$$^-$ anions of very low solvating power. Cations including Cd$_2$$^{2+}$, Pb$^+$, Sn$_2$$^+$, Bi$^+$, Bi$_5$$^{3+}$, Hg$_3$$^{2+}$, Te$_4$$^{2+}$, Te^{2+}, Te$_2$$^{2+}$, Se$_4$$^{2+}$, and Se$_8$$^{2+}$ have all been identified in the acidic alkali earth AlCl$_3$:NaCl and AlCl$_3$:KCl melts [24–30]. In fact, acidic sodium and 1-*n*-butylpyridinium chloroaluminates stabilize the divalent oxidation state in several of the lanthanides, a feat that has been accomplished only in anhydrous organic salts due to the high reactivity of these species with water. In very acidic melts, the low solvating power of these solvents has allowed for the stable preparation of Sm(II), Eu(II), Tm(II), and Tb(II) via reversible reduction of the trivalent oxidation state. However, as the acidity of the melt is decreased, precipitation of the trichloride or dichloride is typically observed due to the formation of cationic chlorocomplexes [31–33].

4.1. AlCl$_3$:1-butylpyridinium ionic liquids

Many of the early electrochemical and spectroscopic studies of actinide ions in low-temperature ionic melts were performed in AlCl$_3$:1-*n*-butylpyridinium chloride ([C$_4$pyr]Cl) systems of both acidic and basic character. An early Raman investigation [23] of this melt over the 0.75:1.0–2.0:1.0 molar composition range, established the equilibrium reaction as the following equation:

$$2AlCl_4^- + Al_2Cl_6 \leftrightarrow 2Al_2Cl_7^- \qquad (6)$$
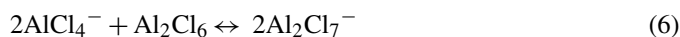
and that no molecular aluminum is present in the 2:0:1:0 melt. A subsequent potentiometric characterization [34] of the system determined the major acid–base equilibrium to be as in the following equation:

$$2AlCl_4^- \leftrightarrow Al_2Cl_7^- + Cl^- \qquad (7)$$

for which the equilibrium constant at 30 °C was estimated to be $K \leq 2.8 \times 10^{-13}$. Due to the more favorable properties of the AlCl$_3$:[C$_4$pyr]Cl system compared to the alkali halide melts (i.e. lower sublimation loss of Al$_2$Cl$_6$, even at high temperatures), many studies were performed to stabilize lower oxidation states in the acidic melts, as well as expand investigations into the basic regime.

The earliest electrochemical studies in the acidic AlCl$_3$:[C$_4$pyr]Cl room temperature IL (working temperature of ~30 °C) were performed on U(IV) in an attempt to reduce it and stabilize the U(III) species. In two papers published in 1982 [35] and 1986 [36], De Waele et al. studied the behavior of uranium over the 1.05:1.0–2.0:1.0 molar composition range. They found that the well-defined reduction of U(IV) to U(III) was irreversible. In the interpretation of the potentiometric data, it was concluded that U(IV) forms a series of chlorocomplexes in the acidic IL, while U(III) remains uncomplexed (and is only solvated by AlC$_4$$^-$ and Al$_2$Cl$_7$$^-$ ions). The uncomplexed nature of U(III) was established by noting that: (1) its absorption spectrum was independent of the melt composition and compared well with that in AlCl$_3$:NaCl melts, (2) high intensity bands which are characteristic for the formation of U(III) chlorocomplexes in solution and the solid state were absent in the melt, and (3) it was comparable to data obtained for Np(III) in the same IL.

The formation of U(IV) chlorocomplexes was supported by the large variation of the formal standard potential of the U(IV)/U(III) redox couple with melt acidity, particularly in the less acidic melts, suggesting different coordination environments with oxidation state. It was suggested that the U(IV) complexes exist as UCl(AlCl$_4$)$_m$$^{(3-m)+}$, UCl$_2$(AlCl$_4$)$_m$$^{(2-m)+}$, and UCl$_3$(AlCl$_4$)$_m$$^{(1-m)+}$ at the lower acidities, with Al$_2$Cl$_7$$^-$ likely replacing some of the AlCl$_4$$^-$ anions in the solvation shell at higher acidities.

Oxidation of U(IV) to U(V) in the same IL proceeded reversibly and was highly dependent upon melt acidity. The U(V) species likely exists as an octahedral chlorocomplex of the type UCl$_6$$^-$, since the absorption spectrum compared well with that in other solvents. Oxidation of U(V) to U(VI) was observed

beyond the electrochemical window of the melt, resulting in solvent breakdown and chlorine gas evolution.

An electrochemical and spectroscopic investigation of uranium in basic AlCl$_3$:[C$_4$pyr]Cl IL [37], revealed that U(VI) oxide readily dissolves and is stable in the melt, and the absorption spectrum supported the formation of [UO$_2$Cl$_{(4+x)}$]$^{(2+x)-}$ ($x = 0$–2) species. The U(VI) species readily underwent an irreversible two electron reduction to form UCl$_6^{2-}$ according to the following equation:

$$[UO_2Cl_{(4+x)}]^{(2+x)-} + 2AlCl_4^- + 2e^-$$
$$\rightarrow UCl_6^{2-} + 2AlOCl_2^- + (2+x)Cl^- \qquad (8)$$
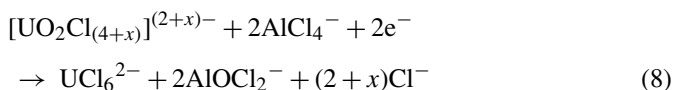
The spectrum of UCl$_6^{2-}$, obtained via oxidation, was identical to that of U(IV) chloride dissolved in the melt, and compared well with the same species reported in the literature. U(III) was found to be unstable in the basic IL, and resulted in the precipitation of solid UCl$_3$.

Neptunium has also been investigated in both the acidic and basic AlCl$_3$:[C$_4$pyr]Cl IL using electrochemical and spectroscopic means [38]. Dissolution of Cs$_2$NpCl$_6$ in the basic IL resulted in the precipitation of CsCl and the formation of NpCl$_6^{2-}$, as confirmed by comparing the absorbance spectrum to that in other chloride media. One-electron reduction of NpCl$_6^{2-}$ resulted in the formation of Np(III) as NpCl$_6^{3-}$, which had never previously been observed in chloride-rich media. This was supported by Raman and UV–vis spectra of the solid Cs$_2$NaNpCl$_6$ salt. In slightly acidic solutions, NpCl$_4$ and NpCl$_3$ precipitate, but redissolve when the IL is made more acidic (51–55 mol% AlCl$_3$). The absorption spectrum of Np(III) was observed to be independent of melt composition and comparable to that in non-complexing perchlorate media, thus suggesting the existence of the solvated Np(III) cation, similar to the U(III) case.

Oxidation of Np(III) to Np(IV) resulted in the formation of NpCl$_x^{(4-x)+}$ species, primarily NpCl$_3^+$ (in less acidic melts), NpCl$_2^{2+}$, and NpCl^{3+}. These were assigned based on the shift in the oxidation potential with melt composition, analogous to the situation in the U(IV)/U(III) redox couple, suggesting different coordination environments in both oxidation states. Spontaneous oxidation of the melt by Np(IV) with increasing melt acidity resulted in both Np(III) and Np(IV), with Np(III) becoming the only stable species at 57 mol% AlCl$_3$. Interestingly, using Nugent's potential linearization theory, the authors were able to predict that in acidic melts, the +4 oxidation state will not be stable for actinides beyond neptunium, while protactinium and thorium will not display the +3 oxidation state, even in this stabilizing medium.

4.2. AlCl$_3$:1-ethyl-3-methylimidazolium ionic liquids

The properties of actinide ions in tetrachloroaluminate ILs incorporating the 1-ethyl-3-methylimidazolium ([C$_2$mim]$^+$) cation have also been studied due to the low working temperature of these melts, as well as the large electrochemical window of the imidazolium cation. One of the earliest studies with this cation was performed by Schoebrechts and Gilbert [38] in the Raman characterization of NpCl$_6^{3-}$ in the AlCl$_3$:[C$_4$pyr]Cl melt where

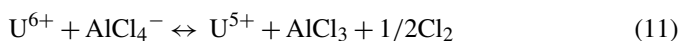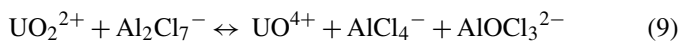a pyridinium cation band masked the presence of the actinide anion band. This masking band was absent in the [C$_2$mim]Cl melt, thus allowing for unambiguous assignment of the NpCl$_6^{3-}$ fingerprint.

Anderson et al. [39] performed spectroscopy and electrochemistry of U(VI)/U(III) in the basic AlCl$_3$:[C$_2$mim]Cl IL. U(IV) exhibited a one-electron reduction to form U(III), and the corresponding oxidation was reversible. Measurement and analysis of the potential of the U(IV)/U(III) redox couple as a function of melt composition suggested the presence of hexachloro complexes in each oxidation state (UCl$_6^{2-}$ and UCl$_6^{3-}$). The absorption spectrum of the U(IV) was identical to that in the AlCl$_3$:[C$_4$pyr]Cl IL, thus confirming the UCl$_6^{2-}$ species.

This species was also supported by Hitchcock et al. who irreversibly reduced UO$_2$Cl$_4^{2-}$ to UCl$_6^{2-}$ in the same IL [16]. Reduction of U(IV) resulted in a color change from pale green to deep blue, and the visible spectrum of the blue solution was similar to that in high-temperature molten chloride salts containing U(III) [39]. The trivalent uranium species was also suggested by Hitchcock et al. [16].

UO$_3$ dissolved in the basic room temperature melts, AlCl$_3$:[C$_2$mim]Cl and AlCl$_3$:1-propyl-2,3-dimethylimidazolium chloride, was found to form UO$_2$Cl$_4^{2-}$ species in both cases, but the interactions were stronger between UO$_2$Cl$_4^{2-}$ and [C$_2$mim]Cl than with 1-propyl-2,3-dimethylimidazolium chloride [40]. This difference was attributed to the stronger hydrogen bonding capabilities of [C$_2$mim]Cl than 1-propyl-2,3-dimethylimidazolium chloride.

In the acidic AlCl$_3$:[C$_2$mim]Cl IL (55:45 mol ratio), solutions of UO$_2^{2+}$ were found to be unstable, as evidenced by a distinct color change (pale yellow to bright orange) over 5–10 days [41]. UV–vis spectra of UO$_2^{2+}$ in the acidic IL minutes after preparation clearly indicated a reaction between the starting material and the IL, and after 5 days the spectrum was indicative of nearly complete conversion to UCl$_6^-$ (pentavalent uranium). A proposed mechanism that fit the experimental results for the decomposition of UO$_2^{2+}$ in the acidic melt is shown in the following equations:

$$UO_2^{2+} + Al_2Cl_7^- \leftrightarrow UO^{4+} + AlCl_4^- + AlOCl_3^{2-} \qquad (9)$$

$$UO^{4+} + Al_2Cl_7^- \leftrightarrow U^{6+} + AlCl_4^- + AlOCl_3^{2-} \qquad (10)$$

$$U^{6+} + AlCl_4^- \leftrightarrow U^{5+} + AlCl_3 + 1/2Cl_2 \qquad (11)$$

This suggested a distribution of di-oxo, mono-oxo, and non-oxo U(VI) species in the acidic IL. Prior to the reduction of UO$_2^{2+}$ in this acidic IL, Dai et al. [42] confirmed the stability of the U(V) oxidation state as UCl$_6^-$ (from optical spectroscopy) by dissolving UCl$_5$·SOCl$_2$ in a 62:38 melt and also studied its disappearance upon making the IL basic (45:55). The disappearance was attributed to the formation of UCl$_6^{2-}$ from oxidation of the IL itself, not a disproportionation reaction of the hexachloro complex.

A rare plutonium study in the basic and acidic AlCl$_3$:[C$_2$mim]Cl ILs was conducted by Costa et al. [43]. They observed a pseudo-reversible Pu(IV)/Pu(III) couple when studying the PuCl$_3$ and Cs$_2$PuCl$_6$ compounds in the basic IL, and a

second irreversible couple in $PuCl_3$ that may be attributed to a plutonium-oxo species. In the acidic melt, PuO_2Cl_2 underwent an irreversible redox couple and resulted in the formation of an insoluble precipitate, presumably Pu(IV), which has no solubility in the acidic IL. Costa et al. [44] have also looked at the electrochemistry and spectroscopy of uranium in non-$AlCl_3$ based ILs, namely $[C_2mim][Tf_2N]$ and $[C_4mim][Tf_2N]$, primarily as an alternative to aqueous-based decontamination and conversion systems for the electrolytic stripping of contaminated uranium surfaces.

5. Molecular dynamics simulations

There has been growing interest in ILs as solvents for f-element separations in nuclear waste remediation due to their favorable properties compared to traditional organic solvents. In many cases, the mechanisms involved in the solvent extraction or ion exchange of lanthanide and actinide ions are quite complex due to the wholly ionic nature of the solvents [6,8–10]. Thus, in order to grasp such difficult concepts, it is important to understand fundamental variables, such as complexation and solvation environments that, for example, stabilize lower oxidation states. Although high-temperature molten salts have been part of the nuclear industry for a long time [45], the same cannot be said about low-temperature, organic-based ILs, which in many cases have much more variability in terms of cation/anion components. In fact, little is known about the fundamental cation–anion interactions in the IL at the microscopic level, including their solvation properties, which may depend on active solvent ions, impurities, and the presence of water.

The elucidation of the fundamental properties of ILs may be aided by computer simulations, both of the bulk material, as well as, solutions with impurities or solute molecules and ions. Several studies have begun to emerge in the scientific literature using molecular dynamics (or Monte Carlo) simulations to probe pure ILs [46–49], as well as, metal ions [50,51] and small molecules [52,53] in ILs. Recent molecular dynamics simulations of actinide ions in ILs based on the imidazolium cation have also begun to shed light on the coordinating and solvating abilities of these notable solvent systems.

The first molecular dynamics simulation of UO_2^{2+} in an IL was performed by Chaumont et al. using $[C_4mim][PF_6]$ and neutral $[C_2mim][AlCl_4]$ as solvent media [54]. The potential energy (U) was described in the functional form shown in the following equation:

$$U = \sum_{\text{bonds}} k_b(b - b_0)^2 + \sum_{\text{angles}} k_\theta(\theta - \theta_0)^2$$
$$+ \sum_{\text{dihedrals}} \sum_n V_n[1 + \cos(n\varphi - \gamma)]$$
$$+ \sum_{i<j} \left[\frac{q_i q_j}{R_{ij}} - 2\varepsilon_{ij} \frac{R_{ij}^{*6}}{R_{ij}} + \varepsilon_{ij} \frac{R_{ij}^{*12}}{R_{ij}} \right] \quad (12)$$

where the first three terms describe bond, angle, and dihedral deformation energies, and the last three terms include pairwise additive 1–6–12 interactions between atoms for van der Waals and electrostatic energies. The force field parameters for the IL cations, as well as, the $AlCl_4^-$ anion were taken from De Andrade et al. [47], those for the PF_6^- anion were taken from the OPLS force field [55], and those for the UO_2^{2+} cation were taken from Guilbaud and Wipff [56], which accounts for the free energy of hydration of the uranyl cation. Details of the dynamics are available from Chaumont et al. [54].

The study examined: (1) dissociated UO_2^{2+} and NO_3^-, (2) associated (intimate) UO_2^{2+} and NO_3^-, and (3) UO_2Cl_2 and $UO_2Cl_4^{2-}$ in the ILs. In the first case, it was observed that the solvent anions, PF_6^- and $AlCl_4^-$, completely surround the UO_2^{2+} cation, with marked differences depending on the anion. The radial distribution functions (RDF) of the liquid around UO_2^{2+} are shown in Fig. 4.

In the hexafluorophosphate IL, UO_2^{2+} is surrounded, on average, by 6.0 ± 0.1 PF_6^- anions. The narrowness of the U–P peak at 4.0 Å in the RDF indicates that the P atoms are quasi-equidistant from the uranium atom, with approximate D_3 symmetry, and there is very little change in this coordination number (Fig. 4). The U–F RDF indicates a sharp peak at 2.6 Å containing 5.8 ± 0.6 F atoms. Interestingly, over the course of the dynamics, each of the 36 F atoms contributed to the primary coordination sphere due to dynamic anion rotation, and the anions exchanged between monodentate and bidentate coordination. Imidazolium cation contributions occur at 6 Å and beyond.

In the tetrachloroaluminate IL, the $AlCl_4^-$ anions exhibited very little rotation, thus contributing to a rigid coordination sphere around uranium of 5.0 ± 0.1 Cl atoms at 2.8 Å. There are 7.0 aluminum atoms at 4.85 Å from the uranium atom. Four of the five nearest chlorine atoms reside equatorially around the uranium, thus contributing to a $UO_2Cl_4^{2-}$ species. Imidazolium cations form an ill-defined shell beyond the $AlCl_4^-$ anions.

The intimate $UO_2^{2+}:2NO_3^-$ ion pairs in the hexafluorophosphate ionic liquid remained associated, with unchanged *trans* bidentate nitrate coordination. The remaining equatorial coordination sites on uranyl are occupied by 2.0 ± 0.2 F atoms at 2.5 Å from PF_6^- anions, which dynamically exchange (although slower than in the naked cation) with F atoms at 4.6 Å. Monodentate coordination is preferred, but bidentate occurs transiently. In the tetrachloroaluminate IL, the remaining equatorial coordination sites in uranyl are occupied by 2.0 ± 0.1 Cl atoms at 2.9 Å, and exchange of Cl atoms occurs less readily than in the PF_6^- case, with transient changes from monodentate to bidentate modes.

In the third case, both UO_2Cl_2 and $UO_2Cl_4^{2-}$ retain their coordinated Cl atoms over the course of the dynamics, with average U–Cl distances of 2.56 Å. In UO_2Cl_2, the remaining equatorial sites are filled by solvent anions. In the PF_6^- ILs, there are 2.7 ± 0.6 F atoms from 2.3 PF_6^- anions, leading to an average equatorial coordination number of 4.7. One anion is usually monodentate, while the other exchanges between monodentate and bidentate coordination modes. In the $AlCl_4^-$ IL, there are 2.9 ± 0.6 Cl atoms from 2.8 ± 0.6 anions, with primarily monodentate coordination modes. These results differ from the $UO_2(NO_3)_2$ dynamics due to the higher steric demand of the nitrate group. In $UO_2Cl_4^{2-}$, the imidazolium cations play
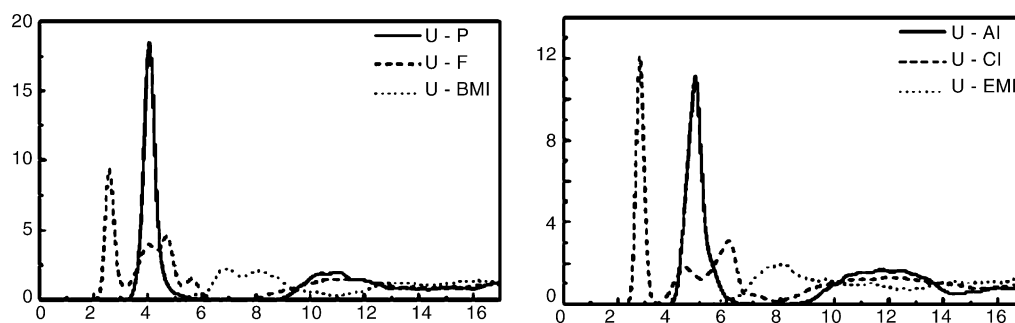
Fig. 4. Radial distribution functions for hexafluorophosphate (left) and tetrachloroaluminate (right) ILs around UO_2^{2+} (dissociated). Reprinted in part with permission from Inorg. Chem. 42 (2003) 5348–5356. Copyright 2003 American Chemical Society.

a greater role, with six $[C_4mim]^+$ and eight $[C_2mim]^+$ cations surrounding the solutes in each case.

Chaumont and Wipff have also investigated the solvation of UO_2^{2+} (including Eu^{3+}, which will not be discussed here, although may provide insight into trivalent actinide ion behavior) in the basic IL $AlCl_3$:$[C_2mim]Cl$, where the Cl^-:$AlCl_4^-$ ratios were about 1 and 3, respectively [57]. The same functional form of the potential energy and force field parameters were used as described previously. In these basic ILs, immersion of a single UO_2^{2+} moiety initially resulted in the formation of mixed $[UO_2Cl_3(AlCl_4)]^{2-}$ species which, after further dynamics, exchanged to form the thereafter stable $UO_2Cl_4^{2-}$ species. A mixing–demixing simulation further confirmed this observation.

A third simulation with nine UO_2^{2+} moieties gave mixed results. In the 1:1 Cl^-:$AlCl_4^-$ IL, $UO_2Cl_4^{2-}$, $[UO_2Cl_3 (AlCl_4)]^{2-}$, and $[UO_2Cl_2(AlCl_4)_2]^{2-}$ species were formed. However, in the 3:1 Cl^-:$AlCl_4^-$ IL, immediate formation of $UO_2Cl_4^{2-}$ occurred with all UO_2^{2+} cations. This indicates that in the more basic ILs, the tetrachloro UO_2^{2+} complexes are the more stable species. The imidazolium cations form a cage consisting of 8–9 ions around the $UO_2Cl_4^{2-}$ anion, with about two $AlCl_4^-$ anions residing in this shell, associated with the axial UO_2^{2+} oxygen atoms.

Finally, Chaumont and Wipff have also used molecular dynamics simulations to investigate the effect of water in the IL, or solvent "humidity", on the coordination environment of UO_2^{2+} (and Eu^{3+}/Eu^{2+}, which will not be described here) in $[C_4mim][PF_6]$ [58]. Once again, the same functional form for the potential energy and the same force field parameters were employed. The naked UO_2^{2+} cation was observed to form the $UO_2(H_2O)_5^{2+}$ aquo complex in less than 0.5 ns, and the same was observed with a more concentrated solution containing nine UO_2^{2+} cations. The PF_6^- anions form a shell around the aquo ion consisting of 6.9 anions (on average) within a distance of 7.2 Å, penetrated by water molecules, and nearly 11.7 imidazolium cations reside beyond this shell within 10.4 Å.

The UO_2Cl_2 and $UO_2Cl_3^-$ complexes coordinate with three and two water molecules, respectively, to achieve equatorial coordination numbers of five. The second shell is more complex, however. The former complex has 4.0 PF_6^- anions within 7.4 Å, 14 imidazolium cations within 10.6 Å, and 12 water molecules within 7.4 Å, while the latter has 11 water molecules, including loosely associated 2.7 PF_6^- anions and 2.9 imidazolium

cations. The $UO_2Cl_4^{2-}$ anion contains hydrogen bonds to an average first shell of 12.5 water molecules within a disordered shell of eight imidazolium cations (within 8.9 Å). The water molecules display both bridging and monodentate associations with the chlorine atoms. Energetic analysis indicates that uranyl interaction with the solvent increases with increasing number of bound Cl^- ligands and solvation forces are responsible for stabilizing the $UO_2Cl_4^{2-}$ species.

6. Conclusions

The study of actinides (and lanthanides) in ILs is a relatively new enterprise that has received only peripheral attention over the past two decades. Although there have been many important contributions in the areas of separations, solid-state characterization, electrochemistry, spectroscopy, and computer simulations, much has yet to be done. One of the most important facets of ILs as solvents is their ionic nature, making them fundamentally different from traditional molecular solvents. Although they have been investigated for their utility in processing and separations schemes, little is understood about the basic interactions between solute and solvent that may aid in ultimately tuning the properties of ILs for specific applications.

The use of ILs in actinide-related applications will be facilitated by obtaining a better understanding of solvent–solute interactions that govern important processes, such as solvent extraction or ion exchange. One key experimental technique that will continue to guide this understanding is extended X-ray absorption fine structure spectroscopy (EXAFS). EXAFS is one of the very few experimental techniques that provides direct clues about behavior in liquids or solutions, thus making it an invaluable resource for IL studies. EXAFS will continue to provide key information about the primary coordination environment of metal complexes in these solvents, including the coordinating and solvating ability of IL cations and anions. This will then aid in the development of ILs that have "tuned" physical properties that are ideal for specific applications, such as nuclear waste remediation.

One of the most promising areas in f-element research in ILs is computer-aided simulations that aim to elucidate the solvating power of ILs towards actinides, lanthanides, and even fission products, all or which are important components of nuclear wastes and processing streams. Although spectroscopic and

electrochemical investigations have given us a good understanding of the complexes that may be formed in, for example, tetrachloroaluminate ILs, only preliminary work has been done in extending this to water-stable ILs which show the most promise for routine use. Computer simulations of ILs, which have begun to receive widespread attention due to the development of reliable, accurate force fields and enhanced computing power, will ultimately provide a bridge with experiment by allowing for the direct energetic analysis and visualization of the solvating and coordinating power of individual IL components, thus allowing for the interpretation of complex experimental results.

Acknowledgements

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