Inorganic Chemistry

Forum Article

pubs.acs.org/IC

Actinide Chemistry in Ionic Liquids

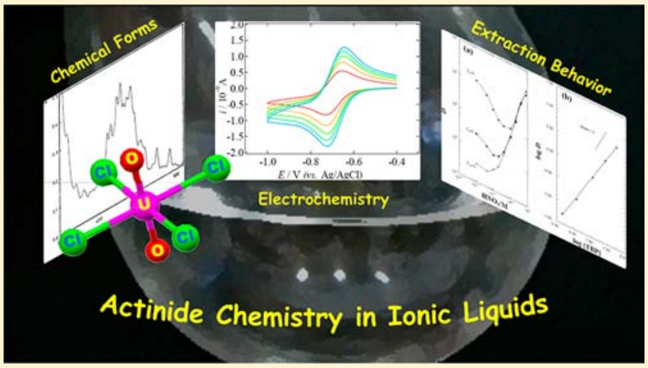
Koichiro Takao,[†] Thomas James Bell,[‡] and Yasuhisa Ikeda*,[‡]

[†]Department of Materials and Life Science, Seikei University, 3-3-1 Kichijoji-Kitamachi, Musashino-shi, Tokyo 180-8633, Japan

[‡]Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, 2-12-1-N1-34 O-okayama, Meguro-ku, Tokyo 152-8550, Japan

Ⓢ *Supporting Information*

ABSTRACT: This Forum Article provides an overview of the reported studies on the actinide chemistry in ionic liquids (ILs) with a particular focus on several fundamental chemical aspects: (i) complex formation, (ii) electrochemistry, and (iii) extraction behavior. The majority of investigations have been dedicated to uranium, especially for the 6+ oxidation state (UO_2^{2+}), because the chemistry of uranium in ordinary solvents has been well investigated and uranium is the most abundant element in the actual nuclear fuel cycles. Other actinides such as thorium, neptunium, plutonium, americium, and curiumm, although less studied, are also of importance in fully understanding the nuclear fuel engineering process and the safe geological disposal of radioactive wastes.



1. INTRODUCTION

Ionic liquids (ILs) are commonly defined as compounds that are composed of cations and anions and melt at temperatures below 100 °C. The majority of ILs consist of organic cations such as 1,3-dialkylimidazolium, *N*-alkylpyridinium, quaternary ammonium, *N*,*N*′-dialkylpyrrolidinium, and alkylphosphonium and organic or inorganic anions, as shown in Figure 1. ILs have been shown to have a number of attractive properties, such as thermal stability, nonflammability, high ionic conductivity, low vapor pressure, and wide electrochemical potential windows.[1] Therefore, ILs are expected to be used in a wide variety of processes, including in the syntheses of organic compounds, liquid−liquid extraction and separation of metal ions, CO_2 capture, biomass pretreatment, and dry-sensitized solar cells and as electrolytes for electrochemical devices such as in the lithium battery.[2−7]

In the nuclear chemistry field, applications of ILs as media for the reprocessing of spent nuclear fuels and radioactive waste treatment have also been expected. Commercial reprocessing is performed by the PUREX method. In this method, the spent nuclear fuels are dissolved in a concentrated HNO_3 aqueous solution, uranium(VI) and plutonim(IV) are extracted using tri-*n*-butyl phosphate (TBP) in *n*-dodecane, and then the uranium and plutonium species are stripped from the *n*-dodecane phase using a dilute HNO_3 solution.[8] If ILs will be applied to the reprocessing processes as alternative media to the conventional extractant consisting of volatile organic compounds, the processes are expected to become safer because of their properties mentioned above. However, in order to evaluate ILs as diluents, basic studies on their density, viscosity, phase disengagement time, solubility in aqueous phase, and so on are necessary.[9] In addition to the PUREX process based on an aqueous solution, a pyroreprocessing method for spent nuclear fuels has been developed.[10] In this process, the fuels are dissolved into molten chloride salts at a temperature greater than 600 °C, and then uranium and plutonim are recovered as their metals or oxides using an electrodeposition method. The use of ILs as media in the pyroreprocessing method is expected to lead to milder process conditions and an easier treatment of wastes due to media. In order to realize the use of ILs as media in pyroreprocessing, however, data on the physical and electrochemical properties of ILs, dissolution behavior of nuclear fuels in ILs, electrochemical properties of actinide species in ILs, etc., must be accumulated.

From these backgrounds, the structural and electrochemical properties of actinide species in ILs, the extraction behavior of actinide species from acidic aqueous solutions to the IL phase, radiochemical stability of ILs, etc., have been widely studied. Therefore, some review papers related to these matters have already been published.[11] The aim of this Forum Article is to provide a review of basic studies foreseeing the application of ILs as media to the reprocessing and waste treatment processes in nuclear fuel cycles, with a particular focus on the fundamental coordination chemistry of uranium and other actinide species in ILs.

The schematic structures and abbreviations of all of the organic ligands, extractants, and task-specific ILs dealt with in this article are shown in Chart 1 (full names of the compounds in this chart are listed in the Supporting Information).

Special Issue: Inorganic Chemistry Related to Nuclear Energy

Received: April 20, 2012
Published: August 8, 2012

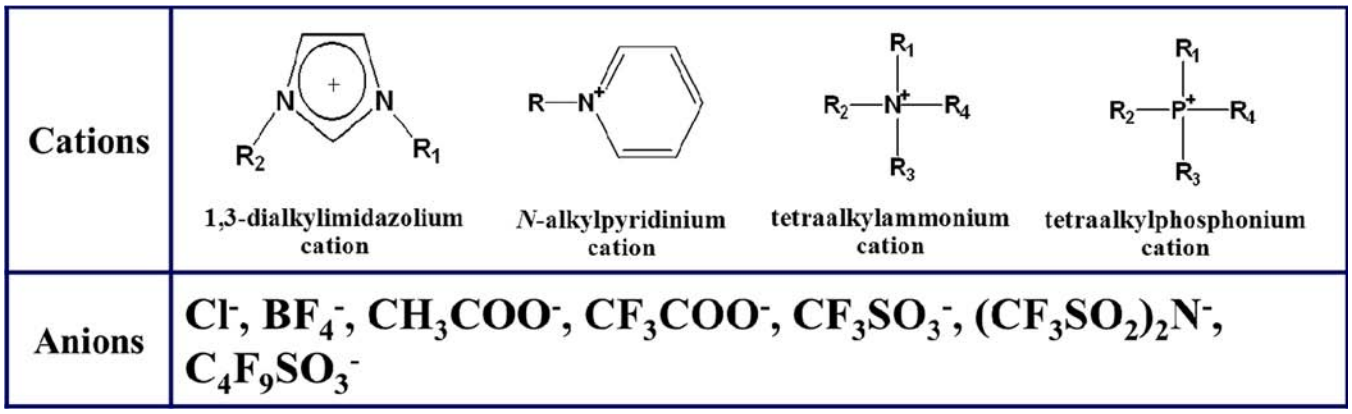
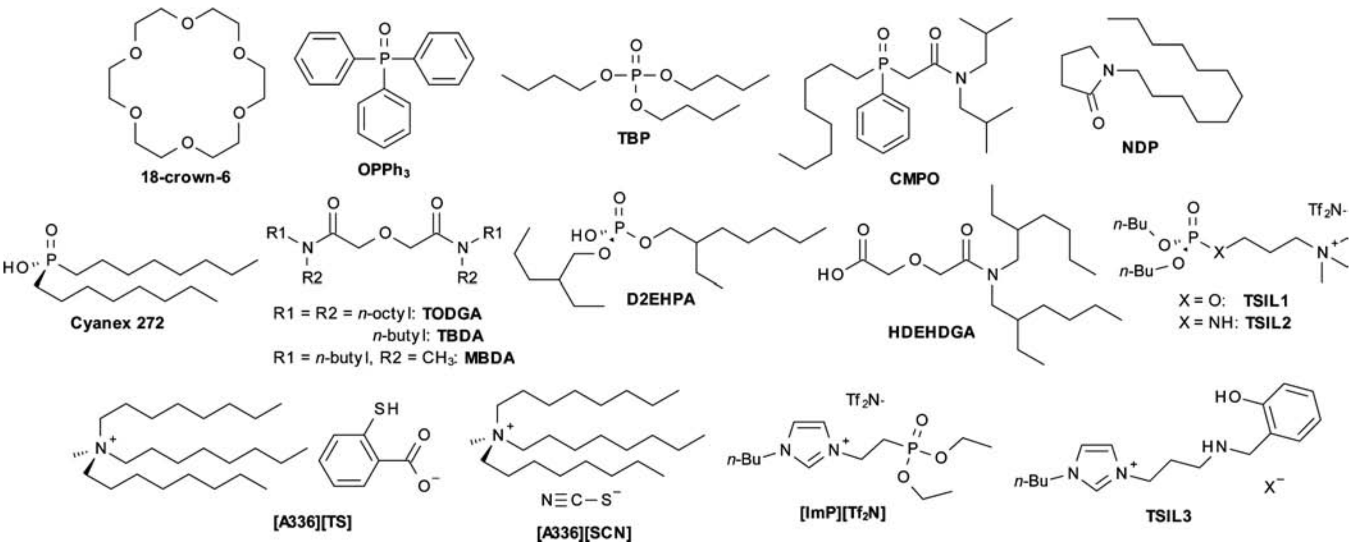


Figure 1. Examples of cations and anions commonly used in ILs.

Chart 1



2. URANIUM SPECIES IN ILS

2.1. Complex Formation of Uranium in ILs. Complexation of UO_2^{2+}, UO_2^{+}, and U^{4+} in ILs and the molecular structures of the species formed are of great interest. The studies reported so far concerning uranium as a nuclear fuel have tended to focus exclusively on its interaction with Cl^- and NO_3^- because these anions are strongly related to the reprocessing of spent nuclear fuels; high-temperature chloride melts are usually used in the pyroreprocessing methods, and HNO_3 solutions are used as dissolution media for the spent nuclear fuels in wet reprocessing systems such as the PUREX method. Normally, an anion different from either Cl^- or NO_3^- tends to be preferred as an anionic component of IL solvents because of the relatively high melting points of Cl^-- and NO_3^--based ILs.[12] Therefore, a Cl^- or NO_3^- salt bearing the same cation as the solvent was often added to an IL solution dissolving a parent uranium salt. There are also several studies on the complex formation of UO_2^{2+} with a variety of other inorganic and organic ligands.

Chloride. As a general trend, the tetrachloro species, $[UO_2Cl_4]^{2-}$ in D_{4h} symmetry, is formed, when excess Cl^- is present in solution. To our knowledge, the earliest study on the UO_2^{2+}−Cl^- interaction in chloroaluminate-based ILs, which are so moisture-sensitive that their handling always requires special care because of the strong tendency of the anions (e.g., $AlCl_4^-$, $Al_2Cl_7^-$) toward hydrolysis, was performed by Heerman et al.[13] The formation of $[UO_2Cl_{4+x}]^{(2+x)-}$ (x = 0−2) in basic $[BuPy][Cl/AlCl_3]$ (53:47; BuPy = N-butylpyridinium)[14] was suggested by means of UV−vis absorption spectroscopy in which the characteristic fine structures due to ligand-to-metal charge transfer (LMCT) in UO_2^{2+} were observed around 440 nm (Figure 2). However, now it is widely accepted that $[UO_2Cl_4]^{2-}$ is the species formed. A similar study was also reported by Dai et al.,[15] for basic $[EMI][Cl/AlCl_3]$ and $[DMPI][Cl/AlCl_3]$ ILs (48:52; EMI = 1-ethyl-3-methylimidazolium; DMPI = 1,2-dimethyl-3-propylimidazolium). The C−H···Cl hydrogen bonding in C(2)−H of $[EMI]^+$ and $[UO_2Cl_4]^{2-}$ was suggested by the peak intensity ratios of the fine structures in the UV−vis absorption spectrum. A more detailed assignment of the structured spectrum of $[UO_2Cl_4]^{2-}$ in the basic $[EMI][Cl/AlCl_3]$ (60:40) was attempted by Hopkins et al.[16] They combined UV−vis absorption spectroscopy with emission, one- and two-photon excitation, and Raman spectroscopy to analyze the vibronic transition of $[UO_2Cl_4]^{2-}$ in IL at 25 and −198 °C (frozen glass). Both one- and two-photon excitation spectra observed indicated a small deviation from a center of symmetry of $[UO_2Cl_4]^{2-}$ in $[EMI][Cl/AlCl_3]$ (60:40). This could be related to a noncentrosymmetric interaction between the tetrachloro complex and the IL solvent used. As shown in these studies,

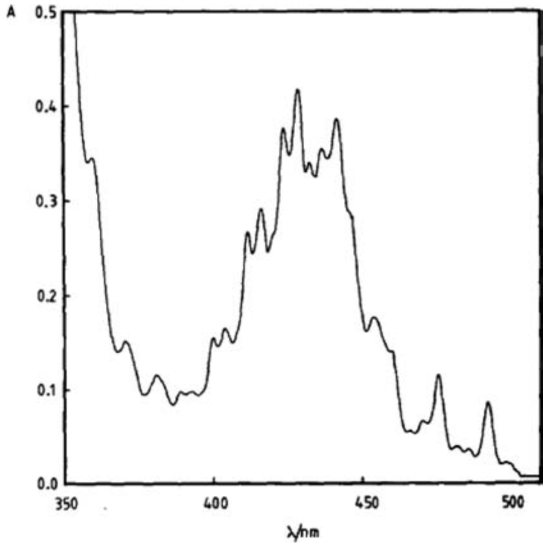


Figure 2. Absorption spectrum of $[UO_2Cl_4]^{2-}$ in a [BuPy][Cl/AlCl$_3$] (53:47) basic melt. Reprinted with permission from ref 13.

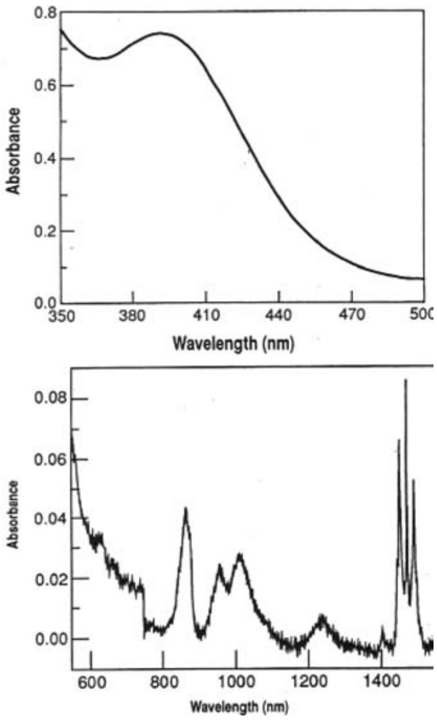


Figure 3. Absorption spectrum of $[UCl_6]^-$ in a [EMI][Cl/AlCl$_3$] (45:55) solution 5 days later from dissolution of UO_2Cl_2: top, visible; bottom, NIR. Reprinted with permission from ref 17a.

$[UO_2Cl_4]^{2-}$ is present as a stable species in the basic [EMI][Cl/AlCl$_3$], where excess Cl^- served for the formation of the limiting tetrachloro species is available. In contrast, UO_2^{2+} is not stable in the acidic [EMI][Cl/AlCl$_3$] (45:55) and reacts with $[Al_2Cl_7]^-$ arising from the excess $AlCl_3$ in the medium.[17] Finally, removal of the axial oxygen atoms is initiated to give UO^{4+} and U^{6+} (ca. 10 min half-life), followed by a slow reduction to U^{5+} (ca. 2 days half-life). The final U^{5+} product was assigned as $[UCl_6]^-$ on the basis of similarity in the absorption spectrum (Figure 3) with the same species in various solvents,[18] while any detailed discussion on the coordination structures around the uranium atom in other occurring species was not given.

Complexation of UO_2^{2+} with Cl^- has also been studied in various air- and moisture-stable ILs. This is in contrast to the chloroaluminate-based ILs, which are readily hydrolyzed upon contact with moisture, resulting in fumes of HCl, and are not simple to handle. Giridhar et al. dissolved $M_2[UO_2Cl_4]$ (M = Cs and Na) in [BMI][Cl] (BMI = 1-butyl-3-methylimidazolium) at 70 °C.[19] Tetrachloro equatorial coordination around UO_2^{2+} is supposed to remain unchanged in [BMI][Cl]. This could be reasonable in accordance with the presence of a large excess of Cl^- in the system. The detailed $UO_2^{2+}-Cl^-$ complexation in the nonhaloalminate ILs was repeatedly investigated by using different techniques: UV–vis, emission, and extended X-ray absorption fine structure (EXAFS).[20] All of the investigations reached the same conclusion: that $[UO_2Cl_4]^{2-}$ is predominantly formed even in the use of different ILs ([BMI][Tf$_2$N], [BMI][PF$_6$], [MeBu$_3$N][Tf$_2$N], and [BuMePyr][Tf$_2$N], where $Tf_2N^- = (CF_3SO_2)_2N^-$ and BuMePyr = *N*-butyl-*N*-methylpyrrolidinium) and different starting UO_2^{2+} salts (NO_3^-, $CF_3SO_3^-$, ClO_4^-, and Tf_2N^-) as long as stoichiometric or more Cl^- (i.e., $[Cl^-]/[UO_2^{2+}] \geq 4$) is present in a system. The EXAFS experiments provided the interatomic distances in $[UO_2Cl_4]^{2-}$; U–O = 1.76–1.78 Å; U–Cl = 2.69–2.70 Å. The molecular dynamics study explains the preferential coordination of Cl^- to UO_2^{2+} compared to other anions in the starting UO_2^{2+} salts (NO_3^-, $CF_3SO_3^-$, ClO_4^-, and Tf_2N^-); i.e., the formation of $[UO_2Cl_4]^{2-}$ is more favorable in energy than the coordination of other anions.[20b] The competitive complexation of Cl^- and NO_3^- to UO_2^{2+} in [BMI][Tf$_2$N] investigated by Gaillard et al.[21] indicated the same trend, although the mixed-ligand complexes like $[UO_2Cl_n(NO_3)_m]^{(2-n-m)}$ (n:m = 1:2, 3:1) were also suggested to be formed in the systems with the lower Cl^- ratio with respect to UO_2^{2+} and NO_3^-. The chemistry of $UO_2^{2+}-Cl^-$ in ILs was further expanded to solvation in the second coordination sphere of $[UO_2Cl_4]^{2-}$ and related species in [EMI][AlCl$_4$], [BMI][Tf$_2$N], [MeBu$_3$N][Tf$_2$N], [BMI][PF$_6$], and [OMI][PF$_6$] (OMI = 1-octyl-3-methylimidazolium) by using the molecular dynamics investigations conducted by Wipff's group.[21,22]

In contrast, the number of reports dealing with $UO_2^+-Cl^-$ complexation in ILs is very limited. To our knowledge, our recent communication on the spectroelectrochemical identification of $[UO_2Cl_4]^{3-}$ in a mixture of [EMI][Cl] (mp = 89 °C) and [EMI][BF$_4$] (mp = 15 °C) with a molar ratio (%) = 50:50 [abbreviated as [EMI][BF$_4$/Cl] (50:50)] is the first report.[23] This uranium(V) species has been electrochemically generated from the well-established parent uranium(VI) species $[UO_2Cl_4]^{2-}$ and exhibits an intense metal-to-halogen charge-transfer band centered at 406 nm (ε = 832 M^{-1} cm^{-1}; M = mol dm^{-3}) and much weaker absorption bands at 630 and 770 nm (ε = 9.5 and 7.1 M^{-1} cm^{-1}, respectively) attributable to the electric-dipole-forbidden transitions of LMCT and f–f in UO_2^+ (Figure 4). These spectroscopic properties are common to those in high-temperature chloride melts.[24] The above-mentioned $[UCl_6]^-$ in the acidic [EMI][Cl/AlCl$_3$] is another form of uranium(V) found in ILs (Figure 3).[17b] The hexachlorouranate(V) complex was also found in the electrochemical oxidation of uranium(IV) in acidic [BuPy][Cl/AlCl$_3$] ILs (33:67 and 38:62).[18a]

The first study on $U^{4+}-Cl^-$ complexation has also been conducted in the acidic [BuPy][Cl/AlCl$_3$] of different compositions (48:52–33:67).[18a] Variation of the uranium-

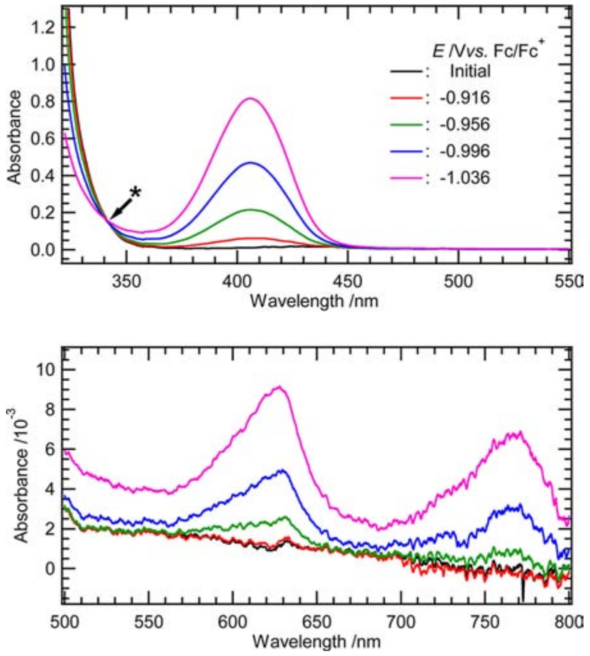


Figure 4. UV−vis−NIR absorption spectra of a [EMI][BF_4/Cl] (50:50) solution prepared by dissolving $[EMI]_2[UO_2Cl_4]$ (5.48 × 10^{-2} M in total) at 25 °C and different potentials. Wavelength range: 320−550 nm (top); 500−800 nm (bottom). The asterisk indicates the isosbestic point at 342 nm. This figure was taken from ref 23.

(III/IV) formal redox potential as a function of pCl^- suggested that partial dissociation of Cl^- from the starting UCl_4 occurs in the system tested and chloro complexes $[UCl_x]^{(4-x)}$ with $3 \geq x \geq 1$ are formed. Cl^- dissociation tends to be more significant as the acidity of the medium increases (i.e., $AlCl_3$ fraction increases). The major species in [BuPy][Cl/$AlCl_3$] (33:67) is UCl^{3+}. Although further neutralization of the [BuPy][Cl/$AlCl_3$] melt causes precipitation of UCl_4,[18a] the basic [BuPy][Cl/$AlCl_3$] (53:47) again can dissolve U^{4+} in the solution. In this basic IL, it was supposed that excess Cl^- toward U^{4+} may promote the formation of $[UCl_n]^{4-n}$ ($n \geq 5$).[13] The UV−vis absorption spectrum recorded after the exhaustive electrolysis of $[UO_2Cl_4]^{2-}$ in the basic melt was indicative of the formation of $[UCl_6]^{2-}$. Nikitenko et al. isolated the $[cation]_2[UCl_6]^{2-}$ (cation = BMI and $MeBu_3N$) and performed their structure characterization in the crystalline state and Tf_2N^--based IL solutions.[25] The EXAFS experiment clarified that the octahedral structure of $[UCl_6]^{2-}$ remains unchanged even in the ILs without the further addition of a Cl^- source. The estimated U−Cl interatomic distance is 2.63−2.66 Å. The hydrogen-bonding interactions of C(2)−H of $[BMI]^+$ and α-$CH_{2/3}$ of $[MeBu_3N]^+$ with the coordinated Cl^- of $[UCl_6]^{2-}$ in the corresponding IL solutions were revealed by means of ^1H NMR and UV−vis absorption spectroscopy. The authors described that $[UCl_6]^{2-}$ in these IL solutions are stable toward hydrolysis and that the spectral change observed after the addition of 0.5 M H_2O arises from different solvations around the complex. The solvation around $[UCl_6]^{2-}$ in dry and wet [cation][Tf_2N] (cation = BMI and $MeBu_3N$) was discussed in the molecular dynamics investigation by Schurhammer and Wipff.[26]

Nitrate. All of the studies dealing with the interaction of U with NO_3^- have been performed in nonhaloaluminate ILs. In the solution chemical research, the addition of extractants like octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) and TBP, shown in Chart 1, have also been investigated in hydrophobic ILs, foreseeing the application of ILs as a nonvolatile organic phase in conventional extraction processes. Crystal deposition of UO_2^{2+} from NO_3^--based ILs is also of interest in the selective recovery of uranium (and plutonium) from fission products and minor actinides in HNO_3 dissolving the spent nuclear fuels.

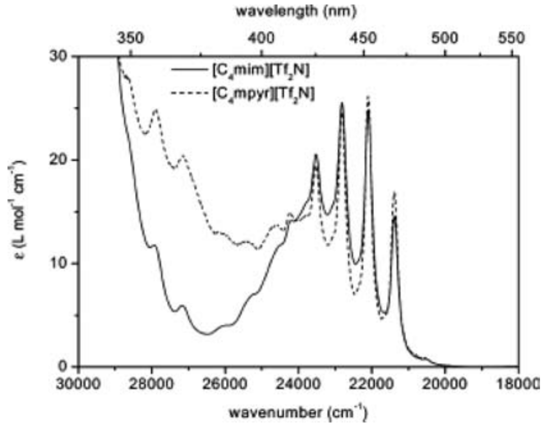


Figure 5. UV−vis absorption spectra of $[UO_2(NO_3)_3]^-$ in [BMI]-[Tf_2N] and [BuMePyr][Tf_2N] at room temperature, where $[UO_2^{2+}]$:$[NO_3^-]_{tot}$ = 1:4. The uranyl concentrations are 5 × 10^{-2} M in [BMI][Tf_2N] and 10^{-2} M in [BuMePyr][Tf_2N]. This figure was taken from ref 27b.

UO_2^{2+}−NO_3^- coordination in [BMI][Tf_2N] and [BuMePyr][Tf_2N] without any additional ligands has been studied by the Belgium group and collaborators.[27] In these systems, a trinitrato complex, $[UO_2(NO_3)_3]^-$, is formed under the presence of excess NO_3^-, which has been evidenced by the observation of its characteristic absorption bands around 22000 cm^{-1} (ca. 450 nm), as shown in Figure 5. The EXAFS experiment for the [BMI][Tf_2N] sample provided the structural information of this species; i.e., U═O(axial) = 1.77 Å; U−O(equatorial) = 2.49 Å; U···N = 2.92 Å; U−O(distal) = 4.18 Å. The U···N distance indicated that each NO_3^- ligand in this complex is bound to uranium in a bidentate manner. As other UO_2^{2+}−NO_3^- species in ILs, Pasilis et al. suggested the formation of $UO_2(NO_3)_2$ in [BMI][Tf_2N] and [EMI][Tf_2N] containing $[NO_3^-] < 3[UO_2^{2+}]$, although it is still uncertain if the remaining coordination sites in the equatorial plane of this species in anhydrous IL systems are vacant.[28] Their attenuated total reflection Fourier transform infrared (ATR-FTIR) experiments combined with Raman and NMR spectroscopy did not detect the mononitrato complex, $[UO_2(NO_3)]^+$, while the EXAFS study by Gaillard et al.[20b] provided an indication of its presence in [BMI][Tf_2N] and [Me_3BuN][Tf_2N]. According to the interpretation by the latter authors, disproportionation of $UO_2(NO_3)_2$ proceeds after dissolution of $UO_2(NO_3)_2 \cdot 6H_2O$ in these ILs to give a mixture of $[UO_2(NO_3)]^+$, $UO_2(NO_3)_2$, and $[UO_2(NO_3)_3]^-$. A study on the stepwise equilibria of the UO_2^{2+}−NO_3^- complexation in [BMI][Tf_2N] was conducted by Georg et al.[29] The estimated conditional gross stability constants of $[UO_2(NO_3)_n]^{2-n}$ (β_n, n = 1−3) in [BMI][Tf_2N] at 18.5 °C were log β_1 = 4.81 ± 0.45, log β_2 = 8.31 ± 0.65, and log β_3 = 12.17 ± 0.81. Assuming that these constants are also supported by the samples of the other publications, the equilibrium calculation at $[UO_2^{2+}]$ = 0.1 M and $[UO_2^{2+}]$:

$[NO_3^-]$ = 1:2 (dashed line in Figure 6) gives a species distribution consisting of 2% UO_2^{2+}, 34% $[UO_2(NO_3)]^+$, 24% $UO_2(NO_3)_2$, and 39% $[UO_2(NO_3)_3]^-$ in [BMI][Tf_2N], which is in line with the suggestion by Gaillard et al.[20b]

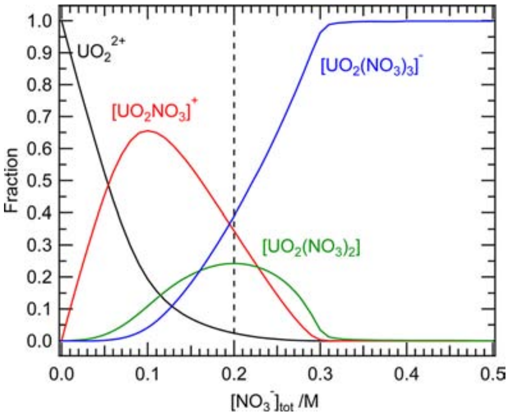


Figure 6. Species distribution diagram of $[UO_2(NO_3)_n]^{2-n}$ (n = 0−3) complexes at $[UO_2^{2+}]_{tot}$ = 0.1 M, $[NO_3^-]_{tot}$ = 0−0.5 M, and 18.5 °C in [BMI][Tf_2N]. This diagram was computed on the basis of the stability constants reported by Georg et al.[29]

The addition of the extractants drastically modifies the coordination chemistry of the UO_2^{2+}−NO_3^- system in ILs. The UO_2^{2+} species extracted from a 1 M HNO_3 aqueous solution to [BMI][PF_6] containing 0.1 M CMPO and 1 M TBP, which are the same conditions as those used in the TRUEX process, was characterized as $[UO_2(NO_3)(CMPO)]^+$, although the denticity of NO_3^- and CMPO, i.e., unidentate versus bidentate, is still uncertain.[30] To provide an answer to this question, Chaumont and Wipff performed a molecular dynamics study and suggested that both NO_3^- and CMPO are unidentate and three additional water molecules are also bound to uranium to give $[UO_2(NO_3)(CMPO)(H_2O)_3]^+$ with five-coordination in the UO_2^{2+} equatorial plane.[31] The dissolution of a UO_2 powder in [BMI][Tf_2N] containing an oxidant like HNO_3 or a $TBP(HNO_3)_{1.8}(H_2O)_{0.6}$ complex[32] was investigated by Billard et al.[33] and Wai et al.[34] According to the former, the trinitrato complex $[UO_2(NO_3)_3]^-$ is formed in IL even in the presence of water. When TBP is present in the system, $[UO_2(NO_3)_x(TBP)_2]^{2-x}$ (x = 1−3) was supposed to be formed.

The precipitation of UO_2^{2+}−NO_3^- species from ILs was attempted by Bradley et al.[35] The precipitate isolated from [BMI][NO_3] dissolving UO_2 powder is considered to consist of an anionic dinuclear complex, $[(UO_2)_2(NO_3)_4(\mu_4\text{-}C_2O_4)]^{2-}$, and $[BMI]^+$, although the single crystals suitable for X-ray diffraction (XRD) were deposited from acetonitrile. The bridging oxalate was postulated to arise from oxidation of the acetone remaining in the [BMI][NO_3] used, being evidenced by their later ^{13}C-labeled experiment.[35b] The same authors also expanded this chemistry to other [XMI][NO_3] IL systems (XMI = 1-X-3-methylimidazolium, where X = n-C_mH_{2m+1}, with m = 1−8, 10, 12, 16, and 18), and succeeded in X-ray structure determination of the crystals obtained of $[(UO_2)_2(NO_3)_4(\mu_4\text{-}C_2O_4)][XMI]_2$ for m = 2−6 and 16. When m = 1 and 12, *trans*-$[UO_2(NO_3)_4]^{2-}$ with two bidentate and two unidentate NO_3^- was determined to be formed.

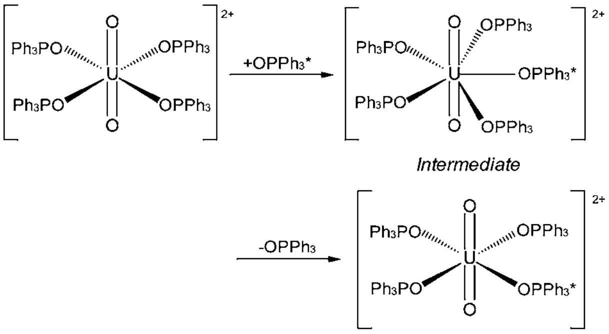
Other Ligands. The most fundamental, but still not well-studied, ligand coordination of UO_2^{2+} in ILs should be hydration. The only work clearly describing this issue is that of Nockemann et al.[27b] They found that $UO_2(Tf_2N)_2\cdot xH_2O$ in [HMI][Tf_2N] (HMI = 1-hexyl-3-methylimidazolium) and $UO_2(ClO_4)_2\cdot xH_2O$ in [BMI][Tf_2N] and [BuMePyr][Tf_2N] exhibit the same UV−vis absorption spectral features. In conclusion, a pentahydrated species, $[UO_2(OH_2)_5]^{2+}$, is formed in these IL solutions. Pasilis and Blumenfeld detected the hydration of UO_2^{2+} in [EMI][Tf_2N] from a shift of IR absorption due to a water molecule.[28b] We have also studied the hydration of UO_2^{2+} in [BMI][NfO] (NfO^- = n-$C_4F_9SO_3^-$), and additionally made an attempt to remove the coordinated water by heating under reduced pressure.[36] When the results from NMR, UV−vis, and Raman spectroscopy were combined, the dehydration from UO_2^{2+} was successfully confirmed. However, we have obtained no evidence that directly indicates any specific solvation around UO_2^{2+} in the dehydrated system. Hence, further characterization using a structure-sensitive technique like EXAFS is needed. Regarding solvation around UO_2^{2+} in "dry" Tf_2N^--based ILs, the interaction of Tf_2N^- to form $[UO_2(Tf_2N)_2]$ is also suggested by experimental and molecular dynamics studies.[37]

Another important aspect of the hydrated UO_2^{2+} is hydrolysis. Although no hydrolysis chemistry of UO_2^{2+} in IL solutions has been investigated so far, one article dealing with the crystallographic characterization of UO_2^{2+} hydrolysis product obtained from mixtures of IL-like compounds (1,3-dimethylimidazolium-2-carboxylate, [EMI][$CF_3SO_2NC(O)$-CF_3], [TMI][$MeOCO_2$], and [TMI][Cl], where TMI = 1,2,3-trimethylimidazolium) and molecular solvents (CH_3CN, CH_2Cl_2, and CH_3OH) is available.[38] In most cases of the hydrolysis product in this work, a dinuclear UO_2^{2+} complex bridged by two μ-hydroxo groups, $[(UO_2)_2(\mu\text{-}OH)_2(NO_3)_4]^{2-}$, was obtained as salts of the imidazolium cations.

In connection with Cl^-, the homologous halide, Br^-, was also of interest in the coordination to UO_2^{2+} in ILs. This chemistry in Tf_2N^--based ILs of $[BMI]^+$ and $[MeBu_3N]^+$ was investigated by Sornein et al.[39] The stoichiometric formation of $[UO_2Br_4]^{2-}$ in these ILs was revealed as a congener of $[UO_2Cl_4]^{2-}$ by UV−vis absorption spectroscopy. The interatomic mean distances extracted from EXAFS data were identical in both ILs ($U{=}O_{ax}$ = 1.77 Å; U−Br = 2.82 Å) and also consistent with those in the crystalline $[BMI]_2[UO_2Br_4]$. The $[UO_2Br_4]^{2-}$ salts of N-methylpyrrolidinium cations bearing long aliphatic chains or aromatic ones with a long alkyl fringe attract attention as IL crystals including a new type of uranium-containing metallomesogen.[40] With regard to the relevant problem about the concomitant extraction of UO_2^{2+} and TcO_4^- in nuclear fuel reprocessing, the interaction of the congener ReO_4^- in several Tf_2N^--based ILs has recently been clarified by Chaumont et al.[37] These authors also compared the complexing strengths of Cl^-, NO_3^-, and ReO_4^- to that of UO_2^{2+} in their ILs and ordered them as $Cl^- \approx NO_3^- > ReO_4^-$.

On coordination of the organic ligands to UO_2^{2+}, several reports are also available. Nockemann et al. studied the complexation of acetate and 18-crown-6 in [BMI][Tf_2N] and [BuMePyr][Tf_2N] by means of UV−vis absorption spectroscopy.[27b] The results were suggestive of the formation of $[UO_2(CH_3COO)_3]^-$ in D_{3h} symmetry and inclusion of UO_2^{2+} in the crown ether cavity, $[UO_2(18\text{-crown-}6)]^{2+}$. The crown ether complexation seems to be weaker than the Br^- one. In connection with the carboxylate coordination, Nockemann et al. studied dissolution of UO_3 in carboxyl-functionalized, namely, betaine-type, ILs and discussed the coordination structure around UO_2^{2+} in these solutions and isolated crystalline materials.[41] We also conducted a ^{31}P NMR study on the complexation of triphenylphosphine oxide ($OPPh_3$) to UO_2^{2+} in [BMI][NfO] and clarified that $[UO_2(OPPh_3)_4]^{2+}$ is formed under the presence of excess ligand.[42]

Kinetics is also one of the relevant aspects to estimate the reactivity of a species in media of interest. However, the number of studies on the kinetics of UO_2^{2+} complexes in ILs is few. As an exception, we have studied the ligand-exchange reaction of $[UO_2(OPPh_3)_4]^{2+}$ in [BMI][NfO].[42] This reaction proceeds through an *associative* mechanism in which a UO_2^{2+} complex with an additional ligand, $[UO_2(OPPh_3)_5]^{2+}$, is formed as an intermediate in the rate-determining step (eq 1).



(1)

The activation enthalpy and entropy in [BMI][NfO] are $\Delta H^{\ddagger} = 55.3 \pm 2.8$ kJ mol^{-1} and $\Delta S^{\ddagger} = 16.1 \pm 7.9$ J mol^{-1} K^{-1}, while the corresponding quantities in CD_2Cl_2 are $\Delta H^{\ddagger} = 7.1 \pm 0.3$ kJ mol^{-1} and $\Delta S^{\ddagger} = -122 \pm 1$ J mol^{-1} K^{-1}. These activation parameters result in large differences in the second-order rate constants (k) between these media, i.e., $k = 7.2 \times 10^3$ M^{-1} s^{-1} in [BMI][NfO] and 1.4×10^5 M^{-1} s^{-1} in CD_2Cl_2 at 298 K. In spite of the high viscosity of the former medium, the rate of this ligand-exchange reaction is kinetically controlled because the actual k in [BMI][NfO] is much lower than that estimated under diffusion control. A specific solvation of NfO^- around $[UO_2(OPPh_3)_4]^{2+}$ via the Coulombic attraction could disturb the insertion of the free $OPPh_3$ into the first coordination sphere of $[UO_2(OPPh_3)_4]^{2+}$.

2.2. Electrochemical Behavior of Uranyl Species. Early electrochemical studies on uranyl species were performed in ILs containing $AlCl_3$.[13,17a,43] Although these studies have not focused on the application of ILs to the nuclear fuel cycles, basic information related to the electrochemical behavior of uranyl species in ILs is available.

Electrochemical studies on uranium in basic [BuPy][Cl/$AlCl_3$] have indicated that UO_3 dissolves easily and the resulting $[UO_2Cl_4]^{2-}$ undergoes an irreversible two-electron reduction to form $[UCl_6]^{2-}$.[13] Hitchcock et al. have investigated the electrochemical reaction of [EMI][UO_2Cl_4] in [EMI][Cl/$AlCl_3$] (55.6:44.4) and observed two reduction waves in the cyclic voltammogram.[43] They proposed that the first reduction process corresponds to the reaction $[UO_2Cl_4]^{2-} + 2AlCl_4^- + 2e^- \rightarrow 2AlOCl_2^- + UCl_6^{2-} + 2Cl^-$ and the second reduction process is the reversible reaction $[UCl_6]^{2-} + e^- \leftrightarrow [UCl_6]^{3-}$. Similar studies on the redox behavior of UO_2Cl_2 in [EMI][Cl/$AlCl_3$] (45:55) have been performed using cyclic voltammetry.[17a] The cyclic voltammogram at 100 mV s^{-1} showed three reduction reactions corresponding to U^{VI}/U^{V}, U^{V}/U^{IV}, and U^{IV}/U^{III} redox couples, and at 5 mV s^{-1}, two waves assigned to U^{V}/U^{IV} and U^{IV}/U^{III} redox couples were observed. Recently, the electrochemical study of [EMI][Br/$AlBr_3$] (55.6:44.4) dissolved $[EMI]_2[UO_2Br_4]$ crystals has been performed using cyclic voltammetry[44] and gave results similar to those of Hitchcock et al.[43]

On the other hand, some research groups have carried out electrochemical studies on uranyl species in ILs to examine the feasibility of the application of ILs as media for the reprocessing or treatment of radioactive wastes. Rao and co-workers have investigated the electrochemical behavior of uranyl species in [BMI][Cl] to get basic data for recovering uranium as its oxide using an electrolytic deposition method.[19,45] The cyclic voltammograms of $M_2UO_2Cl_2$ (M = Na or Cs) in [BMI][Cl] were measured at 70 °C using a glassy carbon working electrode and a palladium wire quasi-reference electrode and showed one cathodic and two anodic waves observed around −0.85, −0.6, and +0.2 V versus palladium.[19] On the basis of these results, the controlled potential electrolysis on a platinum plate was carried out at −0.8 V. Black dense and fine particles were deposited on the surface of a platinum plate. Their energy-dispersive X-ray (EDX) and energy-dispersive X-ray fluorescence (EDXRF) analyses indicated that the deposited particles are amorphous and contain uranium. In addition, upon heating of the deposit to 1000 °C, the resulting materials showed the XRD pattern corresponding to U_3O_8. From these results, it was proposed that the uranyl(VI) species in [BMI][Cl] are reduced to UO_2 with a single-step two-electron transfer at the working electrode. Similarly, they have also investigated the electrochemical behavior of uranyl nitrate in [BMI][Cl] in the range of 70−100 °C using cyclic voltammetry, chronopotentiometry, and square-wave voltammetry and reported that the reduction of uranyl(VI) species occurs through an irreversible single-step two-electron transfer to the UO_2 deposit at the glassy carbon working electrode.[45]

Sornein et al. have reported cyclic voltammetric studies on $[UO_2][OTf]_2$ (0.01 M; OTf = CF_3SO_3) in [BMI][Tf_2N] and [Bu_3MeN][Tf_2N] at 60 °C using a glassy carbon working electrode and silver/silver(I) reference electrode.[20a] In a [BMI][Tf_2N] solution, two broad cathodic peaks and one anodic peak were observed at −0.6, −2.5, and 0.37 V, respectively. Similarly, the cyclic voltammogram in a [Bu_3MeN][Tf_2N] solution showed two cathodic peaks and one anodic peak at −0.6, −1.4, and 0.45 V, respectively. They proposed that the first cathodic peak corresponds to the reduction of UO_2^{2+} to UO_2^{+}, followed by the chemical reaction resulting in the formation of UO_2, that the second cathodic peak might be the direct reduction of UO_2^{2+} to UO_2, and that the anodic peak is due to the redissolution of the reduction product. The electrochemical behavior of $[UO_2][OTf]_2$ (0.01 M) in the mixtures of [BMI][Cl]−[BMI][Tf_2N] and [Bu_3MeN][Cl]−[Bu_3MeN][Tf_2N] ($[Cl^-]/[UO_2^{2+}] > 4$) were also studied by the same group.[20a] One redox couple was observed around −1.3 V in the mixture of [BMI][Cl]−[BMI][Tf_2N], while only one cathodic peak was observed at −1.44 V in the mixture of [Bu_3MeN][Cl]−[Bu_3MeN][Tf_2N]. It was suggested that $[UO_2Cl_4]^{2-}$ is reduced to $[UO_2Cl_4]^{3-}$ in these mixed ILs and that the resulting $[UO_2Cl_4]^{3-}$ seems more stable in the [BMI][Cl]−[BMI][Tf_2N] mixture than in the [Bu_3MeN][Cl]−[Bu_3MeN][Tf_2N] mixture.

We have also investigated the electrochemical behavior of uranyl chloride complexes in [BMI][Cl].[46] Cyclic voltammograms of $[UO_2Cl_4]^{2-}$ in [BMI][Cl] were measured at 80 ± 1 °C using a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode with a liquid junction filled with [BMI][BF_4] in a glovebox under an argon gas atmosphere. Peaks of one redox couple were observed around −0.73 (E_{pc}) and −0.65 V (E_{pa}), as shown in Figure 7. The potential differences (ΔE_p) at scan rates (v) in the range of 10−50 mV s^{-1} were 70−80 mV, which are close to the theoretical ΔE_p value (67 mV) for the reversible one-electron-transfer reaction at 80 °C. The $(E_{pc} + E_{pa})/2$ value was constant, −0.690 V, without depending on the scan rate, and the estimated standard rate constant was 1.8×10^{-3} cm s^{-1} at 80 °C. From these results, we proposed that the $[UO_2Cl_4]^{2-}$ species in [BMI][Cl] is reduced to $[UO_2Cl_4]^{3-}$ quasi-reversibly and that the reduction product $[UO_2Cl_4]^{3-}$ is relatively stable in [BMI][Cl]. This result is consistent with that reported by Sornein et al.[20a] Recently, in order to examine the redox behavior of $[UO_2Cl_4]^{2-}$ species in more detail, we carried out electrochemical and spectroelectrochemical experiments using sample solutions prepared by dissolving $[EMI]_2[UO_2Cl_4]$ (5.48×10^{-2} M) into $[EMI][BF_4/Cl]$ (50:50).[23] The cyclic voltammograms showed the coupled reduction and oxidation waves at −1.05 (E_{pc}) and −0.92 V (E_{pa}) versus ferrocene/ferricenium (Fc/Fc^+). The ΔE_p values increased from 0.101 to 0.152 V with an increase in v, while the $(E_{pc} + E_{pa})/2$ value was almost constant at -0.989 ± 0.002 V regardless of v.[23] From these results, it was suggested that the $[UO_2Cl_4]^{2-}$ species is reduced to $[UO_2Cl_4]^{3-}$ quasi-reversibly. The results of UV−vis−near-IR (NIR) spectroelectrochemical experiments are shown in Figure 4. The presence of an isosbestic point at 342 nm indicates that only the redox equilibrium of $[UO_2Cl_4]^{2-}$ exists in this system. From analyses of the absorption spectra based on the Nernst equation, it was confirmed that the spectrum recorded at the lowest E in Figure 4 (−1.036 V) is of an admixture of $[UO_2Cl_4]^{2-}$ and $[UO_2Cl]_4^{3-}$ ($[U^{VI}]$:$[U^{V}]$ = 17.4:82.6) and that the formal potential for $[UO_2Cl_4]^{2-} + e^- \leftrightarrow [UO_2Cl]_4^{3-}$ is -0.996 ± 0.004 V versus Fc/Fc^+.

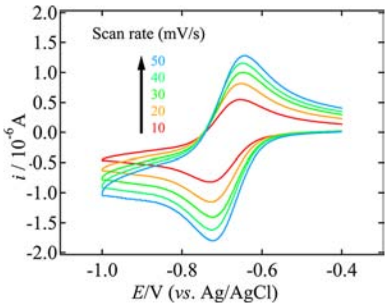


Figure 7. Cyclic voltammograms of the solutions prepared by dissolving $Cs_2UO_2Cl_4$ into [BMI][Cl] measured in the potential range from −0.1 to −0.4 V at different scan rates (v = 10−50 mV s^{-1}). $[UO_2^{2+}] = 1.47 \times 10^{-2}$ M. Temperature = 80 °C. Initial scan direction: cathodic.

Sornein et al. have also examined the electrochemical behavior of $[BMI]_2[UO_2X_4]^{2-}$ (X = Cl or Br) in the mixture of [BMI][Cl] or [BMI][Br] and $[BMI][Tf_2N]$ ($[Cl^-]$ = 0−0.1 M; $[Br^-]$ = 0−0.49 M) using cyclic voltammetry (a glassy carbon working electrode, a platinum wire counter electrode, and a reference electrode prepared by immersing a silver wire in a 0.01 M solution of AgOTf in $[BMI][Tf_2N]$). They reported that the reduction of $[UO_2Cl_4]^{2-}$ proceeded through the ECE mechanism, i.e., $[UO_2Cl_4]^{2-} + e^- \rightarrow [UO_2Cl_4]^{3-}$, $[UO_2Cl_4]^{3-} \leftrightarrow [UO_2Cl_{(4-x)}]^{x-3} + xCl^-$, and $[UO_2Cl_{(4-x)}]^{x-3} + e^- \rightarrow U^{IV} + (4-x)Cl^-$ (with $x \ll 4$).[47] It was also reported that the reduction of $[UO_2Cl_4]^{2-}$ in $[BMI][Tf_2N]$ seems irreversible and results in the formation of a deposit on the electrode surface and that, under the presence of a large excess of halide ions, (X^-) $[UO_2X_4]^{2-}$ is reduced to $[UO_2X_4]^{3-}$ quasi-reversibly without any successive chemical reactions.

The uranium recovery methods using ILs as media have been investigated.[46a,48] The cyclic voltammograms of uranyl species in [BMI][NfO] have been measured to evaluate the applicability of ILs as media for pyroreprocessing.[46a] Irreversible reduction peaks and one sharp oxidation peak were observed in the range of −0.6 to −0.2 V and around 0.85 V versus Ag/AgCl, respectively, as shown in Figure 8. The reduction peaks were assigned to the multistep reduction of U^{VI} to U^{IV}, i.e., $U^{VI} + e^- \rightarrow U^{V}$, $U^{V} + e^- \rightarrow U^{IV}$, and $U^{VI} + 2e^- \rightarrow U^{IV}$. On the basis of these data, bulk electrolysis of UO_2^{2+} in BMINfO was carried out at −1.0 V using the carbon electrode as the cathode. The formation of deposits on the carbon electrode was observed. From EDX analyses, it was found that the deposits are uranium oxides and uranium oxychlorides. Rao et al. have examined the feasibility of direct electrolysis of uranium(VI) species extracted from a HNO_3 solution using TBP diluted with ILs. The controlled potential electrolysis of uranyl nitrate extracted into 1.1 M TBP/$[BMI][Tf_2N]$ on a platinum plate has been performed at 70 °C. The black dense and fine particles were deposited on the surface of a platinum plate. The EDXRF and XRD analyses of the deposits showed that the uranyl species extracted undergo a single-step two-electron reduction to amorphous UO_2. Furthermore, to evaluate the feasibility of ILs as alternate electrolytes to the conventional high-temperature molten salts in the pyroreprocessing method, the dissolution properties of UO_2, U_3O_8, and UO_3 in $[Hbet][Tf_2N]$ (Hbet = protonated betaine) and the electrochemical behavior of uranium(VI) in the resultant solutions have been studied by cyclic voltammetry.[48b] Experimental results indicated that UO_3 is rapidly dissolved and, to the contrary, UO_2 and U_3O_8 are hardly dissolved and that U^{VI} is reduced to U^{V}, which undergoes a disproportionation reaction to give U^{VI} and U^{IV}.

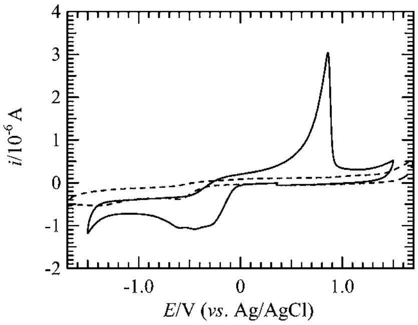


Figure 8. Cyclic voltammograms of neat [BMI][NfO] (dotted line) and uranyl chloride in [BMI][NfO] (solid line). Temperature = 80 °C. $[U^{VI}] = 8.7 \times 10^{-3}$ mol kg^{-1}. Scan rate = 50 mV s^{-1}.

From the results mentioned above, it is suggested that the reduction of $[UO_2X_4]^{2-}$ (X = Cl or Br) in ILs consisting of anions except for Cl^- and Br^- is irreversible, that by using appropriate ILs the uranyl species can be recovered electrolytically as uranium compounds such as oxides, and that UO_2 electrodeposition from uranium(VI) species extracted into IL phases is feasible.

2.3. Extraction of Uranyl Species from Aqueous Solutions. The potential for extracting U(VI) from spent

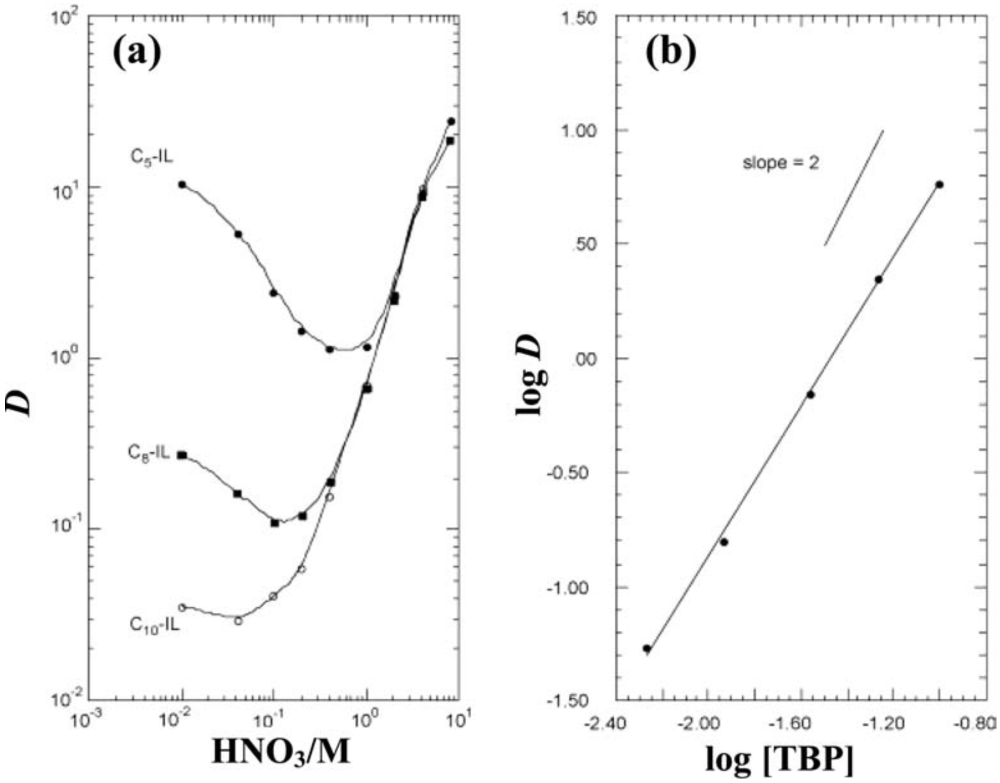


Figure 9. (a) Dependency of *D* on [HNO_3] at constant TBP (1.2 M) concentration in ILs and *n*-dodecane. (b) Dependency of *D* on TBP at constant [HNO_3] (3 M) concentration in [DMI][Tf_2N]. Reprinted with permission from ref 51.

nuclear fuel using ILs as alternative media to conventional solvents, such as *n*-dodecane, has been much studied over the past decade.[11g,49] Here, an overview of the main studies is introduced.

Extraction into IL Phases Containing Extractants. The extraction of uranium(VI) using ILs containing an extractant has been widely reported, with the vast majority of these studies focusing on imidazolium-based ILs containing TBP (Chart 1, 1.0−1.2 M). An example of early work by Giridhar et al. involved the use of the 1-alkyl-3-methylimidazolium hexafluorophosphates, [XMI][PF_6] (X = *n*-C_mH_{2m+1}, with m = 4 and 8), to extract uranium(VI) from HNO_3 media in the range of 0.01−8 M.[50] For both ILs, the distribution ratios (*D*) for uranium(VI) were observed to gradually increase from approximately 0.05 to 33 with an increase in [HNO_3]. The slope analysis of the log−log plot of *D* as a function of [TBP] indicates that the uranium(VI) complex extracted into [BMI][PF_6] is the neutral species $UO_2(NO_3)_2(TBP)_2$, which is the same species observed for the extraction of uranium(VI) into *n*-dodecane. The uranium(VI) species extracted into [OMI][PF_6] has not been assigned.

Recent studies have involved the use of [XMI][Tf_2N] as extraction media. One such example is the extraction of uranium(VI) from HNO_3 (0.01−8 M) into [XMI][Tf_2N] (X = *n*-C_mH_{2m+1}, with m = 5, 8, and 10) phases.[51] In these ILs, Dietz et al. observed that the *D* values vary considerably depending on the alkyl chain length of the IL cations (Figure 9a). In [DMI][Tf_2N] (DMI = 1-decyl-3-methylimidazolium), the *D* values were found to increase with increasing [HNO_3], with the uranium(VI) species reported to be extracted as $UO_2(NO_3)_2(TBP)_2$ based on the comparison of the shape of the curve for the [DMI][Tf_2N] system shown in Figure 9a with that observed in the extraction of uranium(VI) using alkanes as the extraction media and the result of the slope analysis in Figure 9b. For the [XMI][Tf_2N] systems (X = *n*-C_mH_{2m+1}, with m = 5 and 8), it was found that the *D* values decrease with an increase in [HNO_3] from 0.01 to approximately 1 M and then increase with increasing [HNO_3] up to 8 M (Figure 9a). This phenomenon has also been reported by Giridhar et al. for the [BMI][Tf_2N] system, where the *D* values decrease from 15.3 to 0.7 with an increase in [HNO_3] from 0.01 to 0.1 M and then increase again with a further increase in [HNO_3].[48a,52]

By a comparison with the results for the extraction of Sr^{2+} and Na^+ using DCH18C6[51] and taking into account that a value of 2 was obtained from the slope analysis and that there was no significant evidence of nitrate transfer from the aqueous to IL phases, it was proposed that the uranium(VI) species extracted into the [PMI][Tf_2N] (PMI = 1-pentyl-3-methylimidazolium) phase from HNO_3 solutions of low concentrations is the charged species $[UO_2(TBP)_2]^{2+}$ and that the uranium(VI) species extracted from HNO_3 solutions of high concentrations is principally the neutral complex $UO_2(NO_3)_2(TBP)_2$. Furthermore, it was proposed that the differences in the *D* values observed in the ILs with cationic components of different chain lengths were due to the relative hydrophobicity of the respective ILs.

In the [BMI][Tf_2N] system, no investigations for the extraction mechanisms or chemical forms of the extracted uranyl species were included in the original publications.[48a,52] However, recently, Wang et al. have provided evidence for the presence of $UO_2(NO_3)_2(TBP)_2$ in [BMI][Tf_2N] after extraction from HNO_3 solutions of concentrations more than 0.1 M following stripping studies undertaken with supercritical CO_2.[53] The $UO_2(NO_3)_2(TBP)_2$ complex was identified by comparing the UV−vis absorption spectra of the species extracted into both the IL and supercritical CO_2 phases with that obtained

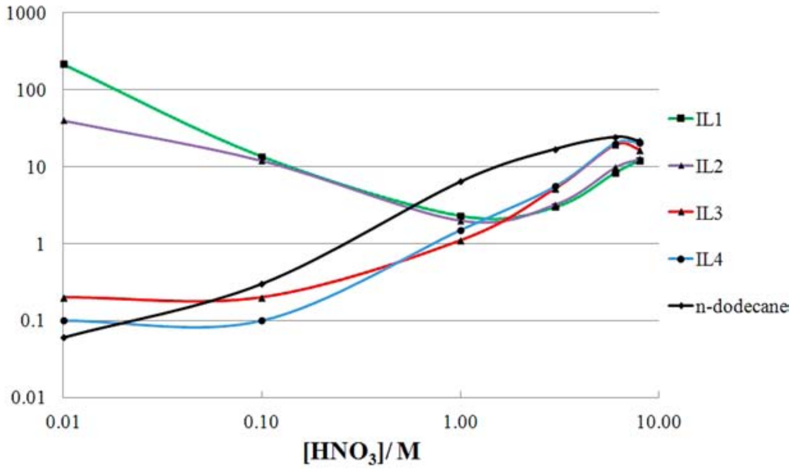


Figure 10. Dependency of *D* on [HNO$_3$] at a constant TBP (1.2 M) concentration in ILs and *n*-dodecane.

previously for the neutral compound[53] and also by examining the fluorescence spectrum of the complex recovered from the supercritical CO$_2$ phase.

Two further detailed studies on the mechanism and chemical forms of uranium(VI) species extracted into [XMI][PF$_6$] and [XMI][Tf$_2$N] containing TBP from aqueous HNO$_3$ solutions have been reported by Murali et al. and Billard et al., respectively.[54] For the [XMI][PF$_6$] system, the extraction behavior of uranium(VI) into [BMI][PF$_6$] and [OMI][PF$_6$] from a 1 M HNO$_3$ solution has been examined using slope analysis, UV–vis spectrophotometry, and matrix-assisted laser desorption ionization and electrospray ionization mass spectrometries.[54a] The results were compared to those obtained from studies involving a *n*-dodecane/aqueous extraction system. It was deduced that for the [BMI][PF$_6$] system the principal extraction mechanism is cationic exchange using predominately [UO$_2$(NO$_3$)(TBP)$_2$]$^+$, while for the [OMI][PF$_6$] system, the uranium(VI) species are transferred from the HNO$_3$ solution as UO$_2$(NO$_3$)$_2$(TBP)$_2$ via a neutral mechanism.

More recently, the extraction of uranium(VI) from HNO$_3$ media of various concentrations (0.1–8 M) into [BMI][Tf$_2$N] has been investigated by Billard et al.[54b] On the basis of studies on uranyl extraction using UV–vis spectrophotometry and H$_2$O/HNO$_3$ solubilization in [BMI][Tf$_2$N], it was proposed that the uranium(VI) extraction from HNO$_3$ solutions of low concentrations occurs through a cation-exchange mechanism and that from the concentrated HNO$_3$ solutions uranium(VI) species are extracted by an anion-exchange mechanism. By determination of the stoichiometry of the complexes using chemical modeling, it was deduced that the cationic species is [UO$_2$(TBP)$_2$]$^{2+}$ and the anionic species is [UO$_2$(NO$_3$)$_3$(TBP)$_2$]$^-$.

A few studies, where extractants other than TBP have been used with imidazolium-based ILs, have been reported. For example, Cocalia et al. studied the extraction of uranium(VI) from HNO$_3$ solutions (0.01–10 M) into [DMI][Tf$_2$N] containing Cyanex-272 (Chart 1, 0.005 M) as the extractant and compared the results to extractions carried out with *n*-dodecane.[55] For both the IL and *n*-dodecane systems, a high *D* value was obtained in a 0.01 M HNO$_3$ solution, which then steadily decreased until [HNO$_3$] reached 1 M and then slightly increased again up to 10 M HNO$_3$ concentration. The mechanism was proposed to proceed through the partitioning of neutral complexes in both systems at low acid concentrations. By using UV–vis spectrophotometry and EXAFS (using HDEHP instead of Cyanex-272), it was discovered that metal-ion coordination was equivalent in both the IL and *n*-dodecane systems.

Visser et al. have reported the extraction of uranium(VI) from an aqueous HNO$_3$ solution into [BMI][PF$_6$] and [OMI][Tf$_2$N] using a combination of CMPO (Chart 1, 0.1 M) and TBP (1 M) in the extracting phase.[30,56] The results were compared to a standard *n*-dodecane/aqueous HNO$_3$ system (based on the TRUEX process). From slope analysis, UV–vis spectrophotometry, and EXAFS data, it was determined that the extraction proceeds through a cationic-exchange mechanism involving the complex [UO$_2$(NO$_3$)(CMPO)]$^+$ in both IL systems, and in the *n*-dodecane system, the extracted complex is UO$_2$(NO$_3$)$_2$(CMPO)$_2$.

More recently, Shen et al. have examined the extraction of uranium(VI) from an aqueous HNO$_3$ solution (0.05–8 M) into [XMI][PF$_6$] (X = *n*-C$_m$H$_{2m+1}$, with m = 4, 6, and 8) containing *N*,*N*,*N*′,*N*′-tetrabutyl-3-oxapentanediamide (TBDA) and *N*,*N*′-dimethyl-*N*,*N*′-dibutyl-3-oxapentanediamide (MBDA) (Chart 1, 0.001–0.3 M) as extractants.[57] The results were compared to a chloroform/aqueous HNO$_3$ extraction system. Excellent *D* values in the region of 150 were obtained in the extraction from a 0.05 M HNO$_3$ solution into [BMI][PF$_6$] containing both TBDA and MBDA. However, the *D* values were lower for [HMI][PF$_6$] and [OMI][PF$_6$] systems when TBDA was used (95 and 3, respectively), and very poor results were obtained in [HMI][PF$_6$] and [OMI][PF$_6$] systems using MBDA. All IL systems showed almost no extractability in aqueous solutions of [HNO$_3$] > 1 M. These results are in contrast to the very little or no extraction that was observed with the chloroform system at all acidities. The extraction mechanism and extracted complexes were examined using slope analysis and IR spectroscopy. The results clarified that at low HNO$_3$ concentrations the mechanism is one of cationic exchange with the formation of a stable 2:1 complex involving the UO$_2$$^{2+}$ ion.

Our group has reported the use of non-imidazolium-based ILs for the extraction of uranium(VI).[58] This involved the extraction of uranium(VI) from HNO$_3$ solutions of various concentrations (0.01–8 M) using a range of ammonium-based hydrophobic ILs in concert with TBP, as shown in Figure 10. It was observed that significantly different *D* values are obtained depending on the hydrophobicity of the IL but with trends similar to those previously reported for imidazolium-based ILs (Figure 9a). For weakly hydrophobic ILs such as $[Me_3(MeOEt)N][Tf_2N]$ (MeOEt = 2-methoxyethyl, IL1) and $[Me_3PrN][Tf_2N]$ (Pr = *n*-propyl, IL2) at $[HNO_3]$ = 0.01 M, *D* values as high as 216 and 40, respectively, were obtained, which progressively decreased with an increase in $[HNO_3]$ from 0.01 to 2 M and then increased again up to $[HNO_3]$ = 6 M. Using ^1H and ^{19}F NMR, slope analysis, and UV−visible spectrophotometry, cationic exchange was identified as the predominant mechanism at low HNO_3 concentrations for IL1 with a mixture of anionic exchange and neutral partitioning occurring at high HNO_3 concentrations, with the former in the majority. For strongly hydrophobic ILs such as $[BzHdMe_2N][Tf_2N]$ (Bz = benzyl, Hd = *n*-hexadecyl, IL3) and $[BzMe_2RN][Tf_2N]$ [R = $-(CH_2)_2O(CH_2)_2OC_6H_4C(CH_3)_2CH_2{}^tBu$, IL4], low *D* values were obtained below a 0.1 M HNO_3 concentration but extractability increased progressively with an increase in $[HNO_3]$ from 0.1 to 6 M. By a comparison of the results to those obtained with *n*-dodecane and with the aid of ^{19}F NMR analysis, the extraction mechanism was shown to involve the partitioning of a neutral uranyl complex. The complexes identified were $[UO_2(TBP)_3]^{2+}$ for the cationic-exchange mechanism, $UO_2(NO_3)_2(TBP)_2$ for the neutral mechanism, and $[UO_2(NO_3)_3(TBP)]^-$ for the anionic-exchange mechanism.

More recently, investigations have been undertaken in our laboratory involving extractants other than TBP with an ammonium-based IL. The use of CMPO, *N*,*N*,*N*′,*N*′-tetraoctyldiglycolamide (TODGA; Chart 1), and *N*-dodecyl-2-pyrrolidone (NDP; Chart 1) produced promising results and good *D* values. Further work is currently continuing in this area.

Extraction into a Neat IL. The use of novel ILs that can extract uranium(VI) from an aqueous medium without utilizing a separate extractant, often known as task-specific ILs (TSILs), has much potential promise. However, only two studies have been reported to date.

Ouadi et al. synthesized a group of TSILs incorporating phosphoryl groups as a means of extracting uranium(VI) from a 3 M HNO_3 solution without using TBP.[59] In this work, three TSILs were synthesized in multistep procedures but two were found to be too viscous to be directly employed in liquid−liquid extraction. Although the remaining TSIL $[(BuO)_2OPO(CH_2)_2N(CH_3)_3][Tf_2N]$ (TSIL1; Chart 1) has an acceptable viscosity, its extractability to uranium(VI) was poor; that is, the *D* value was 1.78. In order to overcome the viscosity problems, the extractions were repeated using a 30% (v/v) mixture of each TSIL with the less viscous IL $[Me_3NBu][Tf_2N]$. The best result was obtained with $[(BuO)_2OPNH(CH_2)_3N(CH_3)_3][Tf_2N]$ (TSIL2; Chart 1), which gave an excellent *D* value of 170. Unfortunately, no work has been reported on the extraction mechanisms and the chemical form of extracted species.

The other study reported by Srncik et al. has involved the use of ILs containing the cation Aliquat 336 (A336), in combination with various anion substituents, to extract uranium(VI) from a purely aqueous solution.[60] For the ILs [A336][TS] (TS = thiosalicylate) and [A336][SCN] (SCN = thiocyanate) (Chart 1), which are both of low enough viscosity to allow direct application, exceptional *D* values of greater than 1000 were achieved. Unfortunately, this study has also not examined the extraction mechanisms and chemical forms of extracted species.

3. ACTINIDE SPECIES IN ILS

3.1. Chemical Forms of Actinide Species. Compared to the many structural studies on uranyl complexes in ILs, such studies on actinide species other than uranium are limited.

Nikitenko et al. have studied the chemical forms of neptunium(IV) and plutonium(IV) in $[BMI][Tf_2N]$ by measuring UV−vis−NIR spectra of $[BMI][Tf_2N]$ solutions dissolving $[BMI]_2[AnCl_6]$ (An = Np or Pu) and reported that neptunium(IV) and plutonium(IV) exist stably as $[AnCl_6]^{2-}$ with the octahedral structure in $[BMI][Tf_2N]$.[61] They have also examined the stability of $[AnCl_6]^{2-}$ (An = Th, Np, or Pu) in $[BMI][PF_6]$ and reported that vis−NIR spectra of $[BMI][PF_6]$ solutions dissolving $[BMI][AnCl_6]$ change with the elapse of time and that solid products are precipitated.[62] Solid-state NMR and IR spectroscopic studies on precipitates suggested that the instability of $[AnCl_6]^{2-}$ in $[BMI][PF_6]$ is related to the hydrolysis of the PF_6^- anion accelerated by $[AnCl_6]^{2-}$ and that fluorophosphates and phosphates formed from the PF_6^- anion cause precipitation of actinide(IV).

Stumpf and co-workers have studied the coordination structure of europium(III) and curium(III) in $[BMI][Tf_2N]$ solutions containing $Eu(OTf)_3$ or $Cm(ClO_4)_3$ by using time-resolved laser fluorescence spectroscopy (TRLFS) to understand the properties of trivalent lanthanides (Ln^{III}) and actinides (An^{III}) in ILs from the viewpoint of their mutual separation.[63] The TRLFS data indicated that europium(III) and curium(III) exist as two species; i.e., one is the species without water in the first coordination sphere, and the other is the $M^{III}[BMI][Tf_2N]$ (M = Eu or Cm) species with one water molecule in the first coordination sphere. The same group has also investigated the complexation of europium(III), americium(III), and curium(III) with N_3^- using TRLFS and X-ray absorption spectroscopy to examine differences and similarities in the properties of Ln^{III} and An^{III} in ILs.[64] It was clarified that europium(III) forms an instantaneously mixed complex with N_3^- and that the complex formations of americium(III) and curium(III) with N_3^- are relatively slow; i.e., the mixed $An^{III}-ClO_4^--N_3^-$ complexes are formed after several days. These phenomena were explained by the differences in reactivity between europium(III) and actinide(III), which are due to the increased delocalization of 5f orbitals in actinide(III) inner-sphere complexes resulting in a stronger metal-to-ligand bond compared to the corresponding lanthanide(III) complexes.

3.2. Electrochemical Behavior of Actenide Species. Limited information is available concerning electrochemical studies of actinide species.[61,65] Voltammetric studies on $[AnCl_6]^{2-}$ (An = Np or Pu) in $[BMI][Tf_2N]$ have been carried out by using a glassy working electrode.[61] It was reported that $[AnCl_6]^{2-}$ species are electrochemically inert in this IL and that quasi-reversible electrochemical reduction An^{IV}/An^{III} and An^{IV} oxidation are observed in $[BMI][Tf_2N]$ in the presence of [BMI][Cl].[61] The electrochemical behavior of $[Th(Tf_2N)_4(HTf_2N)]\cdot 2H_2O$ in $[Bu_3MeN][Tf_2N]$ has been examined by cyclic voltammetry with a glassy carbon disk working electrode, a platinum gauze counter electrode, and a silver wire quasi-reference electrode.[65] The results show that thorium(IV) is reduced to thorium(0) in $[Bu_3MeN][Tf_2N]$ in a single reduction step and that the formal potential for this reduction is −2.20 V (vs Fc/Fc^+; −1.80 V vs SHE).

3.3. Extraction of Actinide Species from Aqueous Solutions to the IL Phase. To examine the feasibility of the

Table 1. *D* Values for Plutonium(IV), Americium(III), and Uranium(VI) in Their Extraction from HNO_3 Aqueous Solutions to $[BMI][Tf_2N]$ or $[OMI][Tf_2N]$ Solutions Containing $[ImP][Tf_2N]$ (Chart 1)[70]

	D values									
	plutonium(IV)		americium(III)				uranium(VI)			
	[TSIL] in $[BMI][Tf_2N]$		[TSIL] in $[BMI][Tf_2N]$		[TSIL] in $[OMI][Tf_2N]$		[TSIL] in $[BMI][Tf_2N]$		[TSIL] in $[OMI][Tf_2N]$	
$[HNO_3]$ M	0.0 M	0.4 M	0.0 M	0.4 M	0.0 M	0.4 M	0.0 M	0.4 M	0.0 M	0.4 M
1	0.004	159	2×10^{-4}	6×10^{-4}	3×10^{-5}	2×10^{-3}	5×10^{-4}	0.305	1×10^{-3}	0.080
3	0.412	17	2×10^{-4}	6×10^{-4}	1×10^{-4}		8×10^{-3}	0.145	0.019	0.044
5	6.62	8	2×10^{-4}	9×10^{-4}	4×10^{-4}	2×10^{-3}	7×10^{-2}	0.200	0.135	0.135

use of ILs as alternatives to conventional organic solvents in aqueous reprocessing and radioactive waste treatment, some research groups have studied the extraction behavior of actinide species from aqueous phases to IL ones.

Rogers et al. have examined the extraction behavior of Am^{3+}, Pu^{4+}, Th^{4+}, and UO_2^{2+} from HNO_3 solutions ($[HNO_3] < 1$ M) to $[BMI][PF_6]$ containing 0.1 M CMPO or 0.1 M CMPO and 1 M TBP and determined that their *D* values ($10-10^2$) are at least 1 order of magnitude higher compared to similar extraction conditions in *n*-dodecane.[56] However, they have not explained the reasons why CMPO and CMPO/TBP in $[BMI][PF_6]$ enhance the extraction of actinide species. Rao and co-workers have carried out extraction experiments of europium(III) and americium(III) in aqueous solutions by using $[OMI][Tf_2N]$ containing bis(2-ethylhexyl)phosphoric acid (D2EHPA) or bis(2-ethylhexyl)diglycolamic acid (HDEHGA) as extractants (Chart 1).[66] The *D* values for the extraction of europium(III) and americium(III) from aqueous solution of pH 3 are 496 and 278 in a 0.05 M HDEHDGA/$[OMI][Tf_2N]$ system and 637 and 318 in a 0.05 M D2EHPA/$[OMI][Tf_2N]$ system. These are larger than the *D* values [216 for europium(III) and 181 for americium(III)] obtained in the systems when 0.1 M D2EHPA−octanol/*n*-dodecane was used.[67] These results indicate that the use of ILs as diluents leads to the more effective separation of Ln^{III} from An^{III}.

Recently, the extraction of actinide species using TSILs has been studied. Ouadi and co-workers have investigated the extraction of americium(III) from aqueous solutions by using TSILs shown in Chart 1.[68] Experimental results indicated that the *D* values for americium(III) are 10−30 in the pH range of 8.5−10, that the extracted species is a compound with americium(III):extractant = 1:2, and that the extraction occurs via an ion-exchange mechanism. Odinets et al. have synthesized various imidazolium-based TSILs with CMPO as a functional group and prepared solid-phase extractants by treating TSILs with solid supports such as PAN fiber and multiwalled carbon nanotubes in CH_2Cl_2 or C_2H_5OH, followed by air drying.[69] Extraction experiments of europium(III), uranium(IV), plutonium(IV), and americium(III) using the prepared sorbents clarified that these species are highly separated using the carbon-nanotube-based sorbents with TSILs as active agents. Rao et al. have synthesized a TSIL containing diethylethylphosphonate in the pendant arm of the imidazolium cation $[ImP][Tf_2N]$ (ImP = diethyl-2-(3-methylimidazolium)ethylphosphonate; Chart 1) and examined the extraction behavior of plutonium(IV), uranium(IV), and americium(III) from HNO_3 aqueous solutions to the $[BMI][Tf_2N]$ or $[OMI][Tf_2N]$ solution containing $[ImP][Tf_2N]$.[70] This TSIL was found to have a highly selective extractability to plutonium(IV). The *D* values of plutonium(IV) species are larger than those of uranium(VI) and americium(III), as shown in Table 1, and lead to unusually high separation factors for plutonium(IV) from uranium(VI) or americium(III). This result suggests that the highly selective separation of actinide species from other species becomes possible by using appropriately designed TSILs.

The extraction behavior of thorium(IV) in the separation of cerium(IV) from HNO_3 solutions containing thorium(IV) and Ln^{III} (Ln = Ce, Gd, Yb) has been investigated using neat $[OMI][PF_6]$ as the extracting phase.[71] The *D* values for cerium(IV) increase from 3 to 83 with an increase in $[HNO_3]$ (1−3.6 M), while that for thorium(IV) is around 10 at $[HNO_3]$ = 3 M and those for Ln^{III} are almost zero. It was proposed that cerium(IV) is extracted as an anionic species such as $[Ce(NO_3)_6]^{2-}$ and that the low *D* values for thorium(IV) or Ln^{III} are due to the difficulty in the formation of anionic complexes with NO_3^-. Recently, the extraction behavior of thorium(IV) from HNO_3 solutions to $[XMI][PF_6]$ ($X = n\text{-}C_mH_{2m+1}$, with m = 4, 6, and 8) containing TBDA or MBDA as extractants has been investigated by Shen and co-workers.[72] It was proposed that thorium(IV) species are extracted into ILs containing MBDA as a cation complex, $[Th(MBDA)_2]^{4+}$, and that extractions of thorium(IV) using $[BMI][PF_6]$ or $[HMI][PF_6]$ with TBDA proceed through a cation-exchange mechanism, i.e., the exchange between $[Th(TBDA)_2(NO_3)_n]^{(4-n)+}$ ($n < 4$) and $(4 - n)BMI^+$ or $(4 - n)HMI^+$. In the extraction of thorium(IV) using $[OMI][PF_6]$ with TBDA, the exchange mechanism was found to change from the cation-exchange mechanism to a mechanism including extraction of a neutral species, $Th(TBDA)_2(NO_3)_4$, with an increase in the concentration of NO_3^- in aqueous solution.

4. CONCLUSION

This Forum Article has reviewed the actinide fundamental chemistry in ILs foreseeing applications of these new materials as media in the spent nuclear fuel reprocessing and radioactive waste treatments. Especially, we put our focus on the coordination chemistry of uranium and other actinide species. General trends found so far are summarized as follows.

The coordination behavior of uranium in ILs seems not to be very different from that in ordinary solvents at a glance. When excess Cl^- is present in a given system, $[UO_2Cl_4]^{2-}$ is formed regardless of the type of ILs, i.e., chloroaluminate and nonchloroaluminate salts. In contrast, removal of the axial oxygen atoms of UO_2^{2+} followed by *autoreduction* to uranium(V) was observed in the acidic (i.e., Cl^- is scarce) chloroaluminate melt as an exotic chemistry in ILs. Although the NO_3^- coordination seems more complicated than Cl^-, the stepwise complexation of $[UO_2(NO_3)_m]^{2-m}$ is widely accepted. Interaction with other inorganic and organic ligands also shows more or less similar trends to those in the ordinary solvents.

Most of electrochemical studies of actinide in ILs have been focused on uranyl(VI) species to examine the feasibility for recovery of uranium as its oxide using electrolytic deposition. From such studies, it is proposed that the reduction reactions of uranyl(VI) species in ILs are strongly affected by the anionic components of ILs coordinated to the equatorial plane of the uranyl moiety; that is, the uranyl(VI) species whose equatorial sites are coordinated by the same anionic species are reduced to the corresponding uranyl(V) quasi-reversibly, and otherwise the uranyl(VI) species are reduced to uranium(IV) irreversibly. Hence, it must be difficult to recover uranium as its oxides on the surface of the electrode in the former system, while in the latter system, the recovery of uranium as UO_2 is expected to be possible.

A number of reports on the extraction of uranium(VI) into ILs containing TBP have been published. In several cases, their *D* values are comparable to or better than those obtained previously using *n*-dodecane as the diluent. Depending on the relative hydrophobicity of ILs and the concentrations of HNO_3 media used, the extraction reactions proceed through a neutral partitioning, comparable to that obtained with *n*-dodecane, cationic or anionic mechanism. The use of ILs containing alternative extractants to TBP has been proven to be promising because of their higher *D* values. Similar work has also been carried out into the extraction of other actinides including Am^{3+}, Pu^{4+}, and Th^{4+}. The *D* values obtained in many cases were significantly higher than those obtained using *n*-dodecane. Preliminary studies on TSILs have also been performed and have shown them to be promising as alternative extraction systems for actinide species.

In accordance with the above-mentioned findings, we propose what should be done in the next steps. At the moment, the accumulation of quantitative information seems not to be enough. For example, there are many publications on the coordination of Cl^- to UO_2^{2+}, while to our knowledge, there are no experimental works regarding the stepwise complexation equilibria of $[UO_2Cl_n]^{2-n}$ (n = 1−4) and the related stability constants. In the electrochemical aspects, the data on redox potentials of various reactions should be collected to construct a reprocessing system similar to the current pyroprocess in high-temperature melts. This is also the case to find a best combination of extractant and IL that offers the best partitioning of radionuclides as desired. All of these aspects ascribe to the thermodynamics and kinetics of actinide in ILs. Therefore, the accumulation of this knowledge including mechanistic information is essential to quantitatively differentiate ILs from other ordinary solvents. This would strongly promote finding the way to use ILs practically in the nuclear chemical engineering field. It is well-known that both thermodynamic and kinetic aspects depend on the ionic strength in a given medium. Because ILs consist only of ions, a species dissolved in this solvent will experience a very strong ionic atmosphere. It should be of interest how the chemistry behaves under such an extraordinary condition.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full names of chemicals with abbreviations in Chart 1. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: yikeda@nr.titech.ac.jp. Phone: +81 3-5734-3061.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Japan Society for the Promotion of Science for the award of a postdoctoral fellowship and the Japan Atomic Energy Agency for their support.

■ REFERENCES

(1) (a) Earle, M. J.; Seddon, K. R. *Pure Appl. Chem.* **2000**, *72*, 1391−1398. (b) Rogers, R. D.; Seddon, K. R.; Volkov, S. *Ionic Liquids Industrial Applications for Green Chemistry*; ASC Symposium Series 818; American Chemical Society: Washington, D.C., 2002. (c) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH: Darmstadt, Germany, 2008.

(2) (a) Welton, T. *Chem. Rev.* **1999**, *99*, 2071−2084. (b) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772−3789. (c) Gordon, C. M. *Appl. Catal., A* **2001**, *222*, 101−117. (d) Hallett, J. P.; Welton, T. *Chem. Rev.* **2011**, *111*, 3508−3576.

(3) (a) Shobukawa, H.; Tokuda, H.; Tabata, S.; Watanabe, M. *Electrochim. Acta* **2004**, *50*, 305−309. (b) Ohno, H. *Electrochemical Aspects of Ionic Liquids*; John Wiley & Sons, Inc.: Hoboken, NJ, 2005. (c) Fernicola, A.; Scrosati, B.; Ohno, H. *Ionics* **2006**, *12*, 95−102. (d) Fernicola, A.; Croce, F.; Scrosati, B.; Watanabe, T.; Ohno, H. *J. Power Sources* **2007**, *174*, 342−348. (e) MacFarlane, D. R.; Forsyth, M.; Howlett, P. C.; Pringle, J. M.; Sun, J.; Annat, G.; Neil, W.; Izgorodina, E. I. *Acc. Chem. Res.* **2007**, *40*, 1165−1173. (f) Hapiot, P.; Lagrost, C. *Chem. Rev.* **2008**, *108*, 2238−2264. (g) Le Bideau, J.; Viau, L.; Vioux, A. *Chem. Soc. Rev.* **2011**, *40*, 907−925.

(4) Tadesse, H.; Luque, R. *Energy Environ. Sci.* **2011**, *4*, 3913.

(5) (a) Keskin, S.; Kayrak-Talay, D.; Akman, U.; Hortaçsu, Ö. *J. Supercrit. Fluids* **2007**, *43*, 150−180. (b) Bara, J. E.; Camper, D. E.; Gin, D. L.; Noble, R. D. *Acc. Chem. Res.* **2010**, *43*, 152−159.

(6) (a) Gorlov, M.; Pettersson, H.; Hagfeldt, A.; Kloo, L. *Inorg. Chem.* **2007**, *46*, 3566−3575. (b) Gorlov, M.; Kloo, L. *Dalton Trans.* **2008**, 2655−2666.

(7) (a) Zhao, H.; Xia, S.; Ma, P. *J. Chem. Technol. Biotechnol.* **2005**, *80*, 1089−1096. (b) Pandey, S. *Anal. Chim. Acta* **2006**, *556*, 38−45. (c) Han, X.; Armstrong, D. W. *Acc. Chem. Res.* **2007**, *40*, 1079−1086. (d) Liu, Y.; Zhu, L.; Sun, X.; Chen, J. *AIChE J.* **2010**, *56*, 2338−2346.

(8) Choppin, G. R.; Liljenzin, J.; Rydberg, J. *Radiochemistry and Nuclear Chemistry*, 3rd ed.; Butterworth-Heinemann: New York, 2002.

(9) Giridhar, P.; Venkatesan, K. A.; Srinivasan, T. G.; Vasudeva Rao, P. R. *J. Nucl. Radiochem. Sci.* **2004**, *5*, 17−20.

(10) (a) Bychkof, A. V.; Volilov, S. K.; Skiba, O. V.; Porodnov, P. T.; Pravdin, A. K.; Popkov, G. P.; Suzuki, K.; Shoki, Y.; Kobayashi, T. In Proceedings of International Conference on Future Nuclear Systems (Global 1997), Yokoyama, Japan, 1997; p 912. (b) Inoue, T. *Prog. Nucl. Energy* **2002**, *40*, 547−554. (c) Malmbeck, R.; Nourry, C.; Ougier, M.; Souček, P.; Glatz, J. P.; Kato, T.; Koyama, T. *Energy Proc.* **2011**, *7*, 93−102.

(11) (a) Cocalia, V.; Gutowski, K.; Rogers, R. *Coord. Chem. Rev.* **2006**, *250*, 755−764. (b) Binnemans, K. *Chem. Rev.* **2007**, *107*, 2592−2614. (c) Billard, I.; Gaillard, C. *Radiochim. Acta* **2009**, *97*, 355−359. (d) Venkatesan, K. A.; Srinivasan, T. G.; Vasudeva Rao, P. R. *J. Nucl. Radiochem. Sci.* **2009**, *10*, R1−R6. (e) Mudring, A.-V.; Tang, S. *Eur. J. Inorg. Chem.* **2010**, *2010*, 2569−2581. (f) Ha, S. H.; Menchavez, R. N.; Koo, Y.-M. *Korean J. Chem. Eng.* **2010**, *27*, 1360−1365. (g) Sun, X.; Luo, H.; Dai, S. *Chem. Rev.* **2012**, *112*, 2100−2128. (h) Vasudeva Rao, P. R.; Venkatesan, K. A.; Rout, A.; Srinivasan, T. G.; Nagarajan, K. *Sep. Sci. Technol.* **2012**, *47*, 204−222. (i) Venkatesan, K. A.; Jagadeeswara Rao, C.; Nagarajan, K.; Vasudeva Rao, P. R. *Int. J. Electrochem.* **2012**, *2012*, 1−12.

(12) Poole, C. F. *J. Chromatogr. A* **2004**, *1037*, 49−82.

(13) Heerman, L.; De Waele, R.; D'Olieslager, W. *J. Electroanal. Chem. Interface Electrochem.* **1985**, *193*, 289−294.

(14) When an IL dealt with in a cited reference consists of two different anions (anion1 and anion2) and a common cation, a notation of this IL medium in this article is [cation][anion1/anion2] with a mole ratio of the anions in parentheses.

(15) Dai, S.; Shin, Y. S.; Toth, L. M.; Barnes, C. E. *Inorg. Chem.* **1997**, *36*, 4900−4902.

(16) Hopkins, T. A.; Berg, J. M.; Costa, D. A.; Smith, W. H.; Dewey, H. J. *Inorg. Chem.* **2001**, *40*, 1820−1825.

(17) (a) Anderson, C. J.; Choppin, G. R.; Pruett, D. J.; Costa, D.; Smith, W. *Radiochim. Acta* **1999**, *84*, 31−36. (b) Costa, D. A.; Smith, W. H. *Electrochem. Soc. Proc.* **1998**, *98*, 266−277.

(18) (a) De Waele, R.; Heerman, L.; D'Olieslager, W. *J. Electroanal. Chem. Interface Electrochem.* **1982**, *142*, 137−146. (b) Selbin, J.; Ortego, J. D.; Gritzner, G. *Inorg. Chem.* **1968**, *7*, 976−982. (c) Selbin, J.; Ortego, J. D. *Chem. Rev.* **1969**, *69*, 657−671.

(19) Giridhar, P.; Venkatesan, K. A.; Subramaniam, S.; Srinivasan, T. G.; Vasudeva Rao, P. R. *Radiochim. Acta* **2006**, *94*, 415−420.

(20) (a) Sornein, M. O.; Cannes, C.; Le Naour, C.; Lagarde, G.; Simoni, E.; Berthet, J. C. *Inorg. Chem.* **2006**, *45*, 10419−10421. (b) Gaillard, C.; Chaumont, A.; Billard, I.; Hennig, C.; Ouadi, A.; Wipff, G. *Inorg. Chem.* **2007**, *46*, 4815−4826.

(21) Gaillard, C.; Chaumont, A.; Billard, I.; Hennig, C.; Ouadi, A.; Georg, S.; Wipff, G. *Inorg. Chem.* **2010**, *49*, 6484−6494.

(22) (a) Chaumont, A.; Engler, E.; Wipff, G. *Inorg. Chem.* **2003**, *42*, 5348−5356. (b) Chaumont, A.; Wipff, G. *Inorg. Chem.* **2004**, *43*, 5891−5901. (c) Chaumont, A.; Wipff, G. *J. Phys. Chem. B* **2008**, *112*, 12014−12023.

(23) Ogura, T.; Takao, K.; Sasaki, K.; Arai, T.; Ikeda, Y. *Inorg. Chem.* **2011**, *50*, 10525−10527.

(24) (a) Adams, M. D.; Wenz, D. A.; Steunenberg, R. K. *J. Phys. Chem.* **1963**, *67*, 1939−1941. (b) Wenz, D. A.; Adams, M. D.; Steunenberg, R. K. *Inorg. Chem.* **1964**, *3*, 989−992. (c) Khokhryakov, A. A. *Radiochemistry (Moscow, Russ. Fed.)* **1998**, *40*, 413−415. (d) Nagai, T.; Fujii, T.; Shirai, O.; Yamana, H. *J. Nucl. Sci. Technol.* **2004**, *41*, 690−695. (e) Nagai, T.; Uehara, A.; Fujii, T.; Shirai, O.; Yamana, H. *J. Nucl. Sci. Technol.* **2006**, *43*, 1511−1516. (f) Volkovich, V. A.; May, I.; Sharrad, C. A.; Kinoshita, H.; Polovov, I. B.; Bhatt, A. I.; Charnock, J. M.; Griffiths, T. R.; Lewin, R. G. *Recent Adv. Actinide Sci.* **2006**, 485−490. (g) Volkovich, V. A.; Polovov, I. B.; Vasin, B. D.; Griffiths, T. R.; Sharrad, C. A.; May, I.; Charnock, J. M. *Z. Naturforsch.* **2007**, *62a*, 671−676. (h) Volkovich, V. A.; Aleksandrov, D. E.; Griffiths, T. R.; Vasin, B. D.; Khabibullin, T. K.; Maltsev, D. S. *Pure Appl. Chem.* **2010**, *82*, 1701−1717.

(25) (a) Nikitenko, S. I.; Hennig, C.; Grigoriev, M. S.; Naour, C. L.; Cannes, C.; Trubert, D.; Bossé, E.; Berthon, C.; Moisy, P. *Polyhedron* **2007**, *26*, 3136−3142. (b) Nikitenko, S. I.; Cannes, C.; Le Naour, C.; Moisy, P.; Trubert, D. *Inorg. Chem.* **2005**, *44*, 9497−9505. (c) Bosse, E.; Den Auwer, C.; Berthon, C.; Guilbaud, P.; Grigoriev, M. S.; Nikitenko, S.; Le Naour, C.; Cannes, C.; Moisy, P. *Inorg. Chem.* **2008**, *47*, 5746−5755.

(26) Schurhammer, R.; Wipff, G. *J. Phys. Chem. B* **2007**, *111*, 4659−4668.

(27) (a) Servaes, K.; Hennig, C.; Billard, I.; Gaillard, C.; Binnemans, K.; Görller-Walrand, C.; Van Deun, R. *Eur. J. Inorg. Chem.* **2007**, *2007*, 5120−5126. (b) Nockemann, P.; Servaes, K.; Van Deun, R.; Van Hecke, K.; Van Meervelt, L.; Binnemans, K.; Gorller-Walrand, C. *Inorg. Chem.* **2007**, *46*, 11335−11344.

(28) (a) Quach, D. L.; Wai, C. M.; Pasilis, S. P. *Inorg. Chem.* **2010**, *49*, 8568−8572. (b) Pasilis, S. P.; Blumenfeld, A. *Inorg. Chem.* **2011**, *50*, 8302−8307.

(29) Georg, S.; Billard, I.; Ouadi, A.; Gaillard, C.; Petitjean, L.; Picquet, M.; Solov'ev, V. *J. Phys. Chem. B* **2010**, *114*, 4276−4282.

(30) Visser, A. E.; Jensen, M. P.; Laszak, I.; Nash, K. L.; Choppin, G. R.; Rogers, R. D. *Inorg. Chem.* **2003**, *42*, 2197−2199.

(31) Chaumont, A.; Wipff, G. *Phys. Chem. Chem. Phys.* **2006**, *8*, 494−502.

(32) Enokida, Y.; Tomioka, O.; Lee, S.-C.; Rustenholtz, A.; Wai, C. M. *Ind. Eng. Chem. Res.* **2003**, *42*, 5037−5041.

(33) Billard, I.; Gaillard, C.; Hennig, C. *Dalton Trans.* **2007**, 4214.

(34) Wai, C. M.; Liao, Y. J.; Liao, W.; Tian, G.; Addleman, R. S.; Quach, D.; Pasilis, S. P. *Dalton Trans.* **2011**, *40*, 5039−5045.

(35) (a) Bradley, A. E.; Hatter, J. E.; Nieuwenhuyzen, M.; Pitner, W. R.; Seddon, K. R.; Thied, R. C. *Inorg. Chem.* **2002**, *41*, 1692−1694. (b) Bradley, A. E.; Hardacre, C.; Nieuwenhuyzen, M.; Pitner, W. R.; Sanders, D.; Seddon, K. R.; Thied, R. C. *Inorg. Chem.* **2004**, *43*, 2503−2514.

(36) Mizuoka, K.; Ikeda, Y. *Prog. Nucl. Energy* **2005**, *47*, 426−433.

(37) Chaumont, A.; Klimchuk, O.; Gaillard, C.; Billard, I.; Ouadi, A.; Hennig, C.; Wipff, G. *J. Phys. Chem. B* **2012**, *116*, 3205−3219.

(38) Cocalia, V.; Smiglak, M.; Kelley, S. P.; Shamshina, J. L.; Gurau, G.; Rogers, R. D. *Eur. J. Inorg. Chem.* **2010**, *2010*, 2760−2767.

(39) Sornein, M.-O.; Mendes, M.; Cannes, C.; Le Naour, C.; Nockemann, P.; Van Hecke, K.; Van Meervelt, L.; Berthet, J.-C.; Hennig, C. *Polyhedron* **2009**, *28*, 1281−1286.

(40) (a) Goossens, K.; Lava, K.; Nockemann, P.; Van Hecke, K.; Van Meervelt, L.; Pattison, P.; Binnemans, K.; Cardinaels, T. *Langmuir* **2009**, *25*, 5881−5897. (b) Goossens, K.; Lava, K.; Nockemann, P.; Van Hecke, K.; Van Meervelt, L.; Driesen, K.; Gorller-Walrand, C.; Binnemans, K.; Cardinaels, T. *Chem.—Eur. J.* **2009**, *15*, 656−674.

(41) Nockemann, P.; Van Deun, R.; Thijs, B.; Huys, D.; Vanecht, E.; Van Hecke, K.; Van Meervelt, L.; Binnemans, K. *Inorg. Chem.* **2010**, *49*, 3351−3360.

(42) Takao, K.; Takahashi, T.; Ikeda, Y. *Inorg. Chem.* **2009**, *48*, 1744−1752.

(43) Hitchcock, P. B.; Mohammed, T. J.; Seddon, K. R.; Zora, J. A.; Hussey, C. L.; Haynes Ward, E. *Inorg. Chim. Acta* **1986**, *113*, L25−L26.

(44) Deetlefs, M.; Hussey, C. L.; Mohammed, T. J.; Seddon, K. R.; van den Berg, J. A.; Zora, J. A. *Dalton Trans.* **2006**, 2334−2341.

(45) Giridhar, P.; Venkatesan, K.; Srinivasan, T.; Rao, P. *Electrochim. Acta* **2007**, *52*, 3006−3012.

(46) (a) Asanuma, N.; Harada, M.; Yasuike, Y.; Nogami, M.; Suzuki, K.; Ikeda, Y. *J. Nucl. Sci. Technol.* **2007**, *44*, 368−372. (b) Ikeda, Y.; Hiroe, K.; Asanuma, N.; Shirai, A. *J. Nucl. Sci. Technol.* **2009**, *46*, 158−162.

(47) Sornein, M.-O.; Cannes, C.; Naour, C. L.; Mendes, M.; Hennig, C. *J. Electroanal. Chem.* **2011**, *661*, 49−56.

(48) (a) Giridhar, P.; Venkatesan, K. A.; Subramaniam, S.; Srinivasan, T. G.; Vasudeva Rao, P. R. *J. Alloys Compd.* **2008**, *448*, 104−108. (b) Rao, C. J.; Venkatesan, K. A.; Nagarajan, K.; Srinivasan, T. G. *Radiochim. Acta* **2008**, *96*, 403−409.

(49) Billard, I.; Ouadi, A.; Gaillard, C. *Anal. Bioanal. Chem.* **2011**, *400*, 1555−1566.

(50) Giridhar, P.; Venkatesan, K. A.; Srinivasan, T. G.; Vasudeva Rao, P. R. *J. Nucl. Radiochem. Sci.* **2004**, *5*, 21−26.

(51) Dietz, M. L.; Stepinski, D. C. *Talanta* **2008**, *75*, 598−603.

(52) Giridhar, P.; Venkatesan, K. A.; Srinivasan, T. G.; Vasudeva Rao, P. R. *J. Radioanal. Nucl. Chem.* **2005**, *265*, 31−38.

(53) Wang, J. S.; Sheaff, C. N.; Yoon, B.; Addleman, R. S.; Wai, C. M. *Chem.—Eur. J.* **2009**, *15*, 4458−4463.

(54) (a) Murali, M. S.; Bonville, N.; Choppin, G. R. *Solvent Extr. Ion Exch.* **2010**, *28*, 495−509. (b) Billard, I.; Ouadi, A.; Jobin, E.; Champion, J.; Gaillard, C.; Georg, S. *Solvent Extr. Ion Exch.* **2011**, *29*, 577−601.

(55) Cocalia, V. A.; Jensen, M. P.; Holbrey, J. D.; Spear, S. K.; Stepinski, D. C.; Rogers, R. D. *Dalton Trans.* **2005**, 1966−1971.

(56) Visser, A. E.; Rogers, R. D. *J. Solid State Chem.* **2003**, *171*, 109−113.

(57) Shen, Y.; Tan, X.; Wang, L.; Wu, W. *Sep. Purif. Technol.* **2011**, *78*, 298−302.

(58) Bell, T. J.; Ikeda, Y. *Dalton Trans.* **2011**, *40*, 10125−10130.

(59) Ouadi, A.; Klimchuk, O.; Gaillard, C.; Billard, I. *Green Chem.* **2007**, *9*, 1160−1162.

(60) Srncik, M.; Kogelnig, D.; Stojanovic, A.; Korner, W.; Krachler, R.; Wallner, G. *Appl. Radiat. Isot.* **2009**, *67*, 2146−2149.

(61) Nikitenko, S. I.; Moisy, P. *Inorg. Chem.* **2006**, *45*, 1235−1242.

(62) Nikitenko, S. I.; Berthon, C.; Moisy, P. *C. R. Chim.* **2007**, *10*, 1122−1127.

(63) Stumpf, S.; Billard, I.; Panak, P. J.; Mekki, S. *Dalton Trans.* **2007**, 240−248.

(64) Stumpf, S.; Billard, I.; Gaillard, C.; Panak, P. J.; Dardenne, K. *Inorg. Chem.* **2008**, *47*, 4618−4626.

(65) Bhatt, A. I.; Duffy, N. W.; Collison, D.; May, I.; Lewin, R. G. *Inorg. Chem.* **2006**, *45*, 1677−1682.

(66) Rout, A.; Karmakar, S.; Venkatesan, K. A.; Srinivasan, T. G.; Vasudeva Rao, P. R. *Sep. Purif. Technol.* **2011**, *81*, 109−115.

(67) Suneesh, A. S.; Ravi, J.; Venkatesan, K. A.; Antony, M. P.; Srinivasan, T. G.; Vasudeva Rao, P. R. *J. Radioanal. Nucl. Chem.* **2010**, *285*, 653−658.

(68) Ouadi, A.; Gadenne, B.; Hesemann, P.; Moreau, J. J.; Billard, I.; Gaillard, C.; Mekki, S.; Moutiers, G. *Chem.—Eur. J.* **2006**, *12*, 3074−3081.

(69) Odinets, I. L.; Sharova, E. V.; Artyshin, O. I.; Lyssenko, K. A.; Nelyubina, Y. V.; Myasoedova, G. V.; Molochnikova, N. P.; Zakharchenro, E. A. *Dalton Trans.* **2010**, *39*, 4170−4178.

(70) Rout, A.; Venkatesan, K. A.; Srinivasan, T. G.; Vasudeva Rao, P. R. *Radiochim. Acta* **2010**, *98*, 459−466.

(71) Zuo, Y.; Liu, Y.; Chen, J.; Li, D. Q. *Ind. Eng. Chem. Res.* **2008**, *47*, 2349−2355.

(72) Shen, Y.; Wang, S.; Zhu, L.; Wang, J.; Wu, W. *Ind. Eng. Chem. Res.* **2011**, *50*, 13990−13996.