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Article

Formation of Higher Chloride Complexes of Np(IV) and Pu(IV) in Water-Stable Room-Temperature Ionic Liquid [BuMeIm][Tf$_2$N]

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A UV/vis/near-IR spectroscopic study shows that in [BuMeIm][(CF$_3$SO$_2$)$_2$N] hydrophobic room-temperature ionic liquid solutions, [BuMeIm]$_2$[AnCl$_6$] complexes, where BuMeIm$^+$ is 1-*n*-butyl-3-methylimidazolium and An(IV) is Np(IV) or Pu(IV), have an octahedral An(IV) environment similar to that observed in solid complexes. Water has no influence on the absorption spectra of AnCl$_6{}^{2-}$ complexes, indicating their stability to hydrolysis in ionic liquid. Adding [BuMeIm]Cl modifies the UV/vis/near-IR absorption spectra of An(IV) in the ionic liquid and causes solids to precipitate. The solid-state reflectance spectra of the precipitates reveal considerable differences from the corresponding An(IV) hexachloro complexes. A voltammetric study indicates that AnCl$_6{}^{2-}$ complexes are electrochemically inert in [BuMeIm][(CF$_3$SO$_2$)$_2$N] at the glassy carbon working electrode. By contrast, quasi-reversible electrochemical reduction An(IV)/An(III) and An(IV) oxidation are observed in ionic liquids in the presence of [BuMeIm]Cl. The oxidation wave of noncoordinated chloride ions interferes with the An(IV) oxidation waves. The spectroscopic and voltammetric data clearly indicate the formation of nonoctahedral actinide(IV) chloride complexes with a Cl$^-$/An(IV) ratio exceeding 6/1 in [BuMeIm][(CF$_3$SO$_2$)$_2$N] in excess chloride ions.

Introduction

Room-temperature ionic liquids (RTIL) have a considerable potential for the recovery and purification of actinides due to their negligible vapor pressure, good electrical conductivity, wide electrochemical window, high thermal stability, and ability to dissolve both organic and inorganic compounds.[1–3] Most published studies on actinide behavior in ionic liquids have focused on spectroscopic and electrochemical investigations of UCl$_6{}^{2-}$,[4] UCl$_6{}^-$,[5a] UCl$_5\cdot$SOCl$_2$,[5b] UO$_2{}^{2+}$,[6] NpCl$_6{}^{2-}$,[7] and PuCl$_6{}^{2-}$ [6d] in water-sensitive ionic

liquids comprising AlCl$_3$ and organic chloride salts. Water and oxygen impurities are known to react with chloroaluminate anions, which cause unwanted side reactions and possess considerable potential for corrosion. Recently prepared water-stable RTILs are composed of bulky organic cations, such as dialkylimidazolium, alkylpyridinium, tetraalkylammonium, etc., and various inorganic anions, e.g., PF$_6{}^-$, CF$_3$SO$_3{}^-$, (CF$_3$SO$_2$)$_2$N$^-$ (Tf$_2$N$^-$), etc.[1,8] Although the unique properties of water-stable RTILs create an opportunity

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to obtain the fundamental data on actinide chemistry without interference from the hydrolysis reactions, only a few studies of actinides in such ionic liquids have appeared. X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) studies indicated coordination of Tf_2N^- ligands to UO_2^{2+} and U(IV) in solutions of hydrated complexes $UO_2(Tf_2N)_2 \cdot xH_2O$ and $U(Tf_2N)_4 \cdot xH_2O$, respectively, in $[Me_3BuN][Tf_2N]$.[9] It was shown also that Np(IV) is oxidized spontaneously to NpO_2^+ in solutions of $Np(Tf_2N)_4 \cdot xH_2O$ in $[Me_3BuN][Tf_2N]$.[9a] In this paper we report a spectroscopic and voltammetric study of neptunium(IV) and plutonium(IV) chloride complexes in hydrophobic RTIL $[BuMeIm][Tf_2N]$, where $BuMeIm^+$ is 1-n-butyl-3-methylimidazolium. For the first time it has been shown that An(IV) are able to form chloride complexes with a Cl^-/An(IV) ratio above 6/1.

Experimental Section

The ionic liquid was prepared by a metathesis reaction from $[BuMeIm]Cl$ and HTf_2N in an aqueous medium. $[BuMeIm]Cl$ was synthesized via quaternization of 1-methylimidazole by 1-chlorobutane and washed with ethyl acetate as recently described.[1] Initial chemicals (Aldrich, highest purity) were used in the synthesis without additional purification. The as-prepared RTIL was washed with deionized water (18 $M\Omega \cdot cm$) to neutral reaction and to the absence of chloride ions. The control of chloride ions was performed by an $AgNO_3$ test of the aqueous phase preequilibrated with RTIL. Organic impurities were removed from the RTIL with activated charcoal for 12 h, after which the mixture was passed through a column with small amounts of acidic alumina. ^1H NMR analysis revealed the absence (<1%) of residual reagents in the purified ionic liquid. The RTIL was dried overnight under reduced pressure (~5 mbar) at 70 °C. The water concentration in the dried RTIL was measured by coulometric Karl-Fisher titration and found to be equal to 0.008(2) M. The stock solution of $[BuMeIm]Cl$ in ionic liquid with concentration 0.5 M was prepared by the dissolution of dried solid $[BuMeIm]Cl$ (70 °C, 24 h, reduced pressure) in anhydrous $[BuMeIm][Tf_2N]$ under slight heating. Obtained solution was then dried again at the conditions similar to those for $[BuMeIm]$-$[Tf_2N]$ to remove water adsorbed during dissolution of highly hygroscopic $[BuMeIm]Cl$.

$[BuMeIm]_2[AnCl_6]$ complexes [where An(IV) = Np(IV) or Pu(IV)] have been prepared for the first time by precipitation from the corresponding An(IV) solutions in HCl in the presence of $[BuMeIm]Cl$. Neptunium(IV) and plutonium(IV) were purified prior to synthesis on anion-exchange resin from nitric acid solutions by conventional procedures.[12] Solution of Np(IV) in HCl was obtained by $NpO_2OH \cdot xH_2O$ ($x \approx 2.5$) dissolution in 5 M HCl followed by

Np(V) reduction to Np(IV) with 0.5 M NH_2OH at 70 °C. Plutonium(IV) after purification by anion exchange was precipitated with ammonia from nitric acid solution as $PuO_2 \cdot xH_2O$. Freshly obtained precipitate was washed with diluted ammonia and diluted HCl and then redissolved in concentrated HCl. This procedure was repeated twice to remove all nitrate ions.

Complexes $[BuMeIm]_2[AnCl_6]$ were obtained by addition of 0.5 M $[BuMeIm]Cl$ in concentrated HCl to corresponding An(IV) solutions in concentrated HCl at the molar ratio 2.2/1.0, respectively. Concentration of An(IV) was about 10 $g \cdot L^{-1}$. Temperature was kept about 5 °C during precipitation. The precipitates were washed with cold acetone and dried in a desiccator over silica gel. $[BuMeIm]_2[NpCl_6]$ and $[BuMeIm]_2[PuCl_6]$ complexes are putty-colored and yellow-green powders, respectively. Fourier transform infrared (FTIR) spectra of the solids reveal the presence of $BuMeIm^+$ cation [ν(C−H) aromatic, s 3171, 3124 cm^{-1}; ν(C−H) aliphatic, s 2966, 2939, 2878 cm^{-1}; ν(ring), s sym 1575, 1467 cm^{-1}; MeC−H asym 1431, 1386 cm^{-1}; ν(ring), s sym 1170 cm^{-1}). Water molecule vibration modes (ν_1 and ν_3, 3000−3800 cm^{-1}; ν_2, 1595−1650 cm^{-1}) were not observed, indicating that the prepared hexachlorocomplexes are anhydrous. Stretch vibrations of An−Cl bonds (265−280 cm^{-1}) were outside the measurement range (4000−400 cm^{-1}).

UV/vis/near-IR spectra were collected by a Shimadzu UV-3101 PC spectrophotometer by use of 1 cm or 1 mm quartz cells, respectively, for the vis/near-IR and UV spectral ranges. The spectrophotometric cells were sealed airtight by Teflon stoppers. The diffuse solid-state reflectance spectra were measured with a U-3000 Hitachi device equipped with a 60 mm diameter integrating sphere. FTIR spectra were collected by a Nicolet Magna-IR spectrometer in KCl pellets.

The voltammetric study was carried out with a Volta Lab PST 050 device. A three-electrode thermostated Pyrex commercial cell (V = 4 mL) was used with a glassy carbon (GC, d = 3 mm, from Radiometer) disk working electrode, Ag/Ag(I) reference electrode, and Pt counterelectrode. The reference electrode was prepared by immersing Ag wire in 0.01 M solution of $Ag(CF_3SO_3)$ in RTIL. Reference solution was placed in a glass tube having a fine porosity frit (from Radiometer). The working electrode was polished with a damp cloth and then washed in dioxane before use. Argon (<3 ppm O_2 and H_2O) was supplied to the electrochemical cell through the fine Teflon tube. Appropriate gases were bubbled for 2 h into the ionic liquids before the experiments and then sparged during the electrochemical data acquisition. All measurements were performed at 25 ± 1°C.

Several voltammetric measurements were performed with ferrocene, $FeCp_2$, in $[BuMeIm][Tf_2N]$, since the redox couple $FeCp_2/FeCp_2^+$ is often used as a reference electrode for redox reactions in ionic liquids.[1] One-electron oxidation of $FeCp_2$ was found be quasireversible, having $E_{1/2}$ = −0.383 V vs Ag/Ag(I) at 25 °C. The $E_{1/2}$ value obtained fits well with the published data.[1]

Results and Discussion

Spectroscopic Study. The dissolution of $[BuMeIm]_2$-$[AnCl_6]$ in $[BuMeIm][Tf_2N]$ gives almost colorless and green solutions for Np(IV) and Pu(IV), respectively. The vis/near-IR absorption spectra of these solutions and the diffuse solid-state reflectance spectra of the corresponding $[BuMeIm]_2AnCl_6$ are shown in Figures 1 and 2 (and Supporting Information), respectively. The vis/near-IR absorption spectra of Np(IV) and Pu(IV) in RTIL are characteristic of octahedral complexes in which the actinide(IV) environment has a center
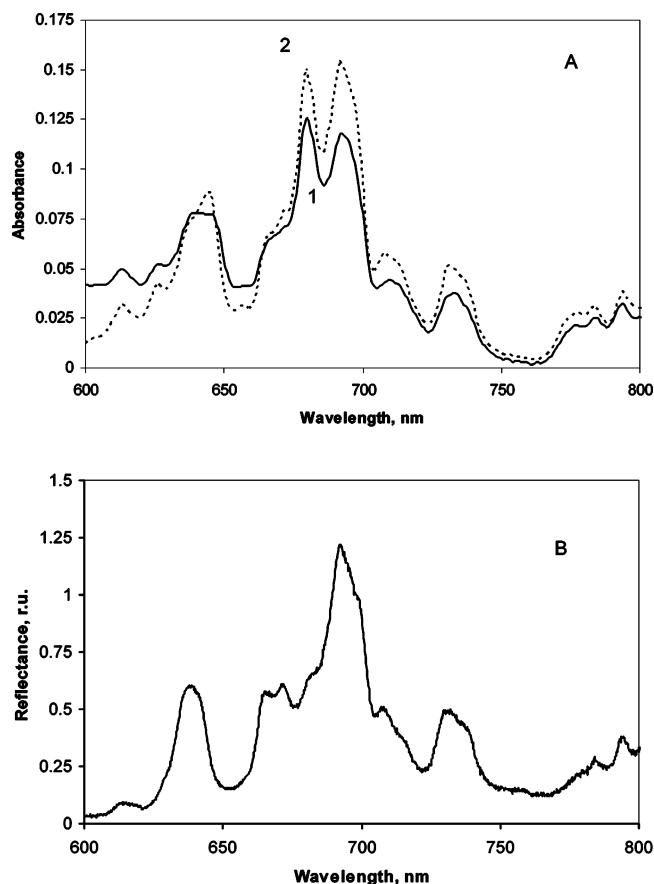
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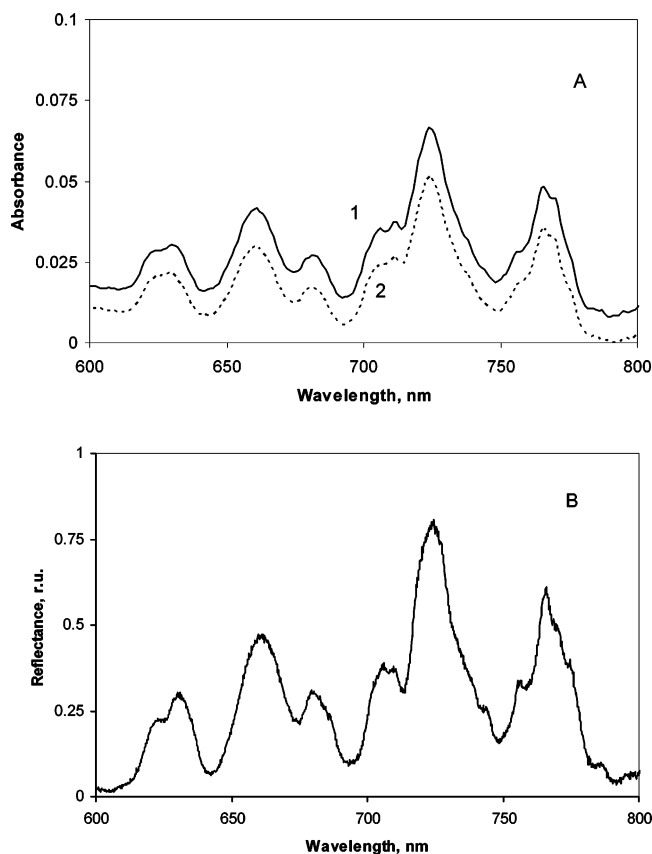
Figure 1. (A) Vis/near-IR spectra of 0.01 M [BuMeIm]$_2$NpCl$_6$ in dried [BuMeIm][Tf$_2$N] (1) and in the presence of 0.5 M H$_2$O (2), l = 1.0 cm. (B) Solid-state reflectance spectrum of [BuMeIm]$_2$NpCl$_6$.

Figure 2. (A) Vis/near-IR spectra of 0.01 M [BuMeIm]$_2$PuCl$_6$ in dried [BuMeIm][Tf$_2$N] (1) and in the presence of 0.5 M H$_2$O (2), l = 1.0 cm. (B) Solid-state reflectance spectrum of [BuMeIm]$_2$PuCl$_6$.

of symmetry. The electron $f \rightarrow f$ transitions are Laporte-forbidden, and the spectra are weak because the bands are of vibronic origin.[10] The solid-state spectra of the prepared complexes are also very close to those of other neptunium(IV) and plutonium(IV) hexachlorides with different cations.[10] The strong similarity of the solid and solution spectra suggests that AnCl$_6^{2-}$ is the largely predominant chemical form of actinides(IV) in [BuMeIm][Tf$_2$N] solutions. Figure 3 illustrates UV spectra of AnCl$_6^{2-}$ solutions in ionic liquid corresponding to the first electron transfer (FET) absorption bands of An(IV). Table 1 shows that the electron transfer bands in RTIL practically coincide with those published for acetonitrile.[10]

Figures 1−3 and Table 1 indicate that addition of water to AnCl$_6^{2-}$ solutions in RTIL up to 0.5 M has no influence on the position of the peaks in UV/vis/near-IR absorption spectra, implying that the AnCl$_6^{2-}$ complexes are stable with respect to hydrolysis in [BuMeIm][Tf$_2$N]. This is somewhat surprising since these complexes are known to be sensitive to hydrolysis.[12] Thus, even in concentrated aqueous HCl, the AnCl$_6^{2-}$ species are formed only to some extent due to hydration.[10b] Such behavior of AnCl$_6^{2-}$ can be explained by solvation of H$_2$O molecules and AnCl$_6^{2-}$ in the ionic liquid. It is known that water molecules are strongly bound via H-bonding with Tf$_2$N$^-$ anions in RTIL ($\Delta H_H = -10.5$ kJ·mol^{-1}).[11] No thermodynamic data concerning the hydration of AnCl$_6^{2-}$ complexes were found in the literature. However, a theoretical molecular dynamics study showed

that a EuCl$_6^{3-}$ complex in water-preequilibrated ionic liquid [BuMeIm][PF$_6$] is embedded in a water shell completed by BuMeIm$^+$ cations whose C$_2$H, C$_4$H, and C$_5$H aromatic protons are hydrogen-bonded to Cl$^-$ ligands of the complex.[13] In a dried RTIL complex, EuCl$_6^{3-}$, is solvated only by BuMeIm$^+$ cations. The hexachloro complex is better solvated in humid than in dried ionic liquid. The energy difference between EuCl$_6^{3-}$ solvation in [BuMeIm][PF$_6$]·H$_2$O and [BuMeIm][PF$_6$] was estimated to be 180 ± 49 kJ·mol^{-1}. Assuming similar behavior of EuCl$_6^{3-}$ and AnCl$_6^{2-}$, the stability of AnCl$_6^{2-}$ to hydrolysis in ionic liquids may be considered related to their strong solvation as well as to H-bonding of water molecules with the RTIL anions.

The slight decrease of FET band intensities after water addition may be related to some change in AnCl$_6^{2-}$ solvation. This observation is in consistent with the molecular dynamic calculations cited above. Solutions of AnCl$_6^{2-}$ in dried or hydrated RTIL are stable in time. No variation has been observed in their absorption spectra even after 1 month of storage under argon.

By contrast with the insignificant effect of water, the behavior of AnCl$_6^{2-}$ in [BuMeIm][Tf$_2$N] exhibits strong dependence on chloride ions. The Np(IV) solution in RTIL changes from almost colorless to green after addition of 0.04 M [BuMeIm]Cl. Initially green PuCl$_6^{2-}$ solution does not

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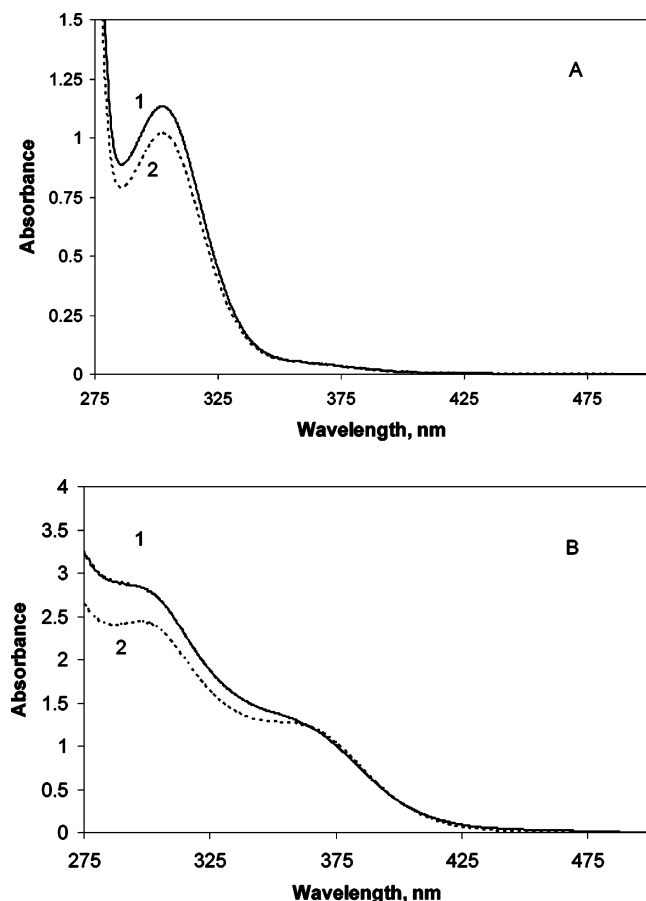
**Figure 3.** First electron-transfer absorption bands of $NpCl_6^{2-}$ (A) and $PuCl_6^{2-}$ (B) in dried [BuMeIm][Tf$_2$N] (1) and in the presence of 0.5 M H$_2$O (2), l = 1.0 mm.

Table 1. First Charge-Transfer Absorption Bands of 0.01 M AnCl$_6^{2-}$ in [BuMeIm][Tf$_2$N] and Acetonitrile

complex	solvent	λ_{et}, nm
NpCl$_6^{2-}$	dried [BuMeIm][Tf$_2$N]	300
NpCl$_6^{2-}$	[BuMeIm][Tf$_2$N] + 0.5 M H$_2$O	300
NpCl$_6^{2-}$	acetonitrile	302[a]
PuCl$_6^{2-}$	dried [BuMeIm][Tf$_2$N]	363
PuCl$_6^{2-}$	[BuMeIm][Tf$_2$N] + 0.5 M H$_2$O	363
PuCl$_6^{2-}$	acetonitrile	367[a]

[a] Reference 10d.

show any visible color change after [BuMeIm]Cl addition. However, Figures 4 and 5 (and Supporting Information) demonstrate the significant changes in both UV/vis/near-IR spectra of AnCl$_6^{2-}$ in the presence of [BuMeIm]Cl. The spectra were measured approximately 3 h after chloride addition when equilibrium was reached. The FET bands of Np(IV) and Pu(IV) are shifted to shorter wavelengths after chloride addition. In the case of Np(IV) a broad band is also observed at approximately 360 nm. This band cannot be assigned to $f \rightarrow f$ transition and is most probably related to the positively shifted first electron transition band. Obviously, the green color of Np(IV) solution is due to this absorption band. The appearance of two FET bands in the spectrum of Np(IV) suggests the presence of at least two species of Np(IV) in the ionic liquid. The concentration of complex with λ_{et} = 360 nm increases with the chloride concentration. The very big difference in the position of the two FET bands
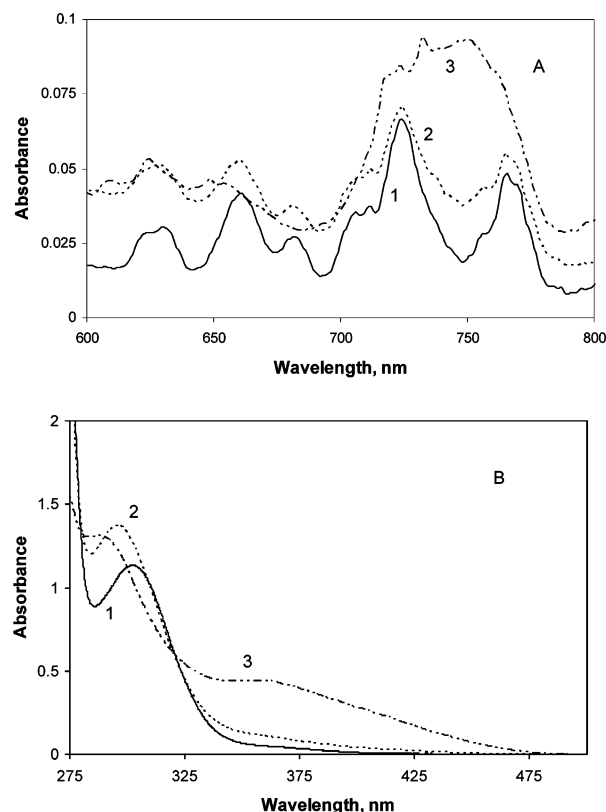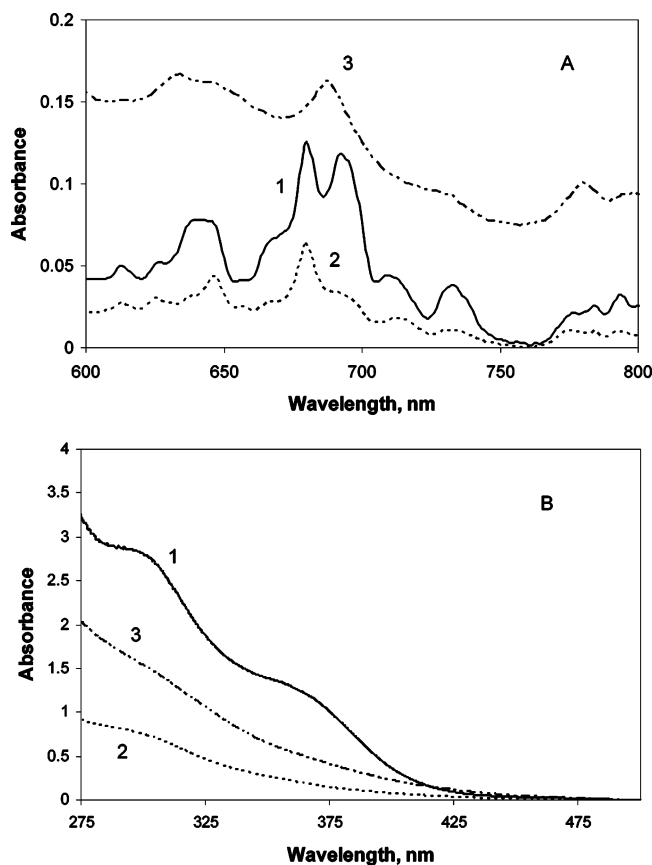
Figure 4. Vis/near-IR (A) and UV (B) spectra of Np(IV) in dried [BuMeIm][Tf$_2$N] as a function of [BuMeIm]Cl concentration: 0 M (1), 0.04 M (2), and 0.06 M (3). Initial 0.01 M Np(IV) solution was prepared by dissolution of [BuMeIm]$_2$NpCl$_6$ in neat RTIL.

(about 73 nm) implies a considerable difference in the structure of the two Np(IV) complexes. Moreover, this is the first example of Np(IV) complexes having an FET band in the visible range of the optical spectrum.

The wavelengths of major absorption bands in the vis/near-IR spectra of the solutions with and without [BuMeIm]Cl and the reflectance bands of solids are summarized in Table 2 for Np(IV) and Table 3 for Pu(IV). The Np(IV) spectra show increasing absorbance near 740 ($^2G_{7/2}$) and 911 ($^2H_{9/2}$) nm as the chloride concentration increases. These $f \rightarrow f$ absorption bands are known to be characteristic of nonoctahedral Np(IV) complexes.[12] Increasing the [BuMeIm]Cl concentration to 0.08 M leads to the precipitation of a green amorphous solid. The reflectance spectrum of this precipitate (Figure 6A and Table 2) is quite different not only from that of solid [BuMeIm]$_2$[NpCl$_6$] but also from the spectrum of Np(IV) in solution in the presence of 0.06 M [BuMeIm]Cl. In particular, the absorption band at 740 nm in solution is shifted to 711 nm in the spectrum of solid.

The effect of chloride ions on Pu(IV) absorption spectra in RTIL is somewhat different from their effect on Np(IV). Adding [BuMeIm]Cl to 0.04 M causes only a short-wavelength shift of FET bands followed by a decrease in the total absorbance compared with the spectra of PuCl$_6^{2-}$ without excess chloride. Although the vis/near-IR spectra of Pu(IV) in the presence of [BuMeIm]Cl have a less distinct structure than the similar spectra of Np(IV), they clearly indicate the formation of species different from PuCl$_6^{2-}$ in excess chloride ions. The abnormally high ground absorbance

Figure 5. Vis/near-IR (A) and UV (B) spectra of Pu(IV) in dried [BuMeIm][Tf$_2$N] as a function of [BuMeIm]Cl concentration: 0 M (1), 0.04 M (2),and 0.06 M (3). Initial 0.01 M Pu(IV) solution was prepared by dissolution of [BuMeIm]$_2$PuCl$_6$ in neat RTIL.

Table 2. Most Intensive Vis/Near-IR Bands for 0.01 M NpCl$_6$$^{2-}$ Solutions in [BuMeIm][Tf$_2$N] and Solid-State Reflectance Spectra of Np(IV) Solid Complexes

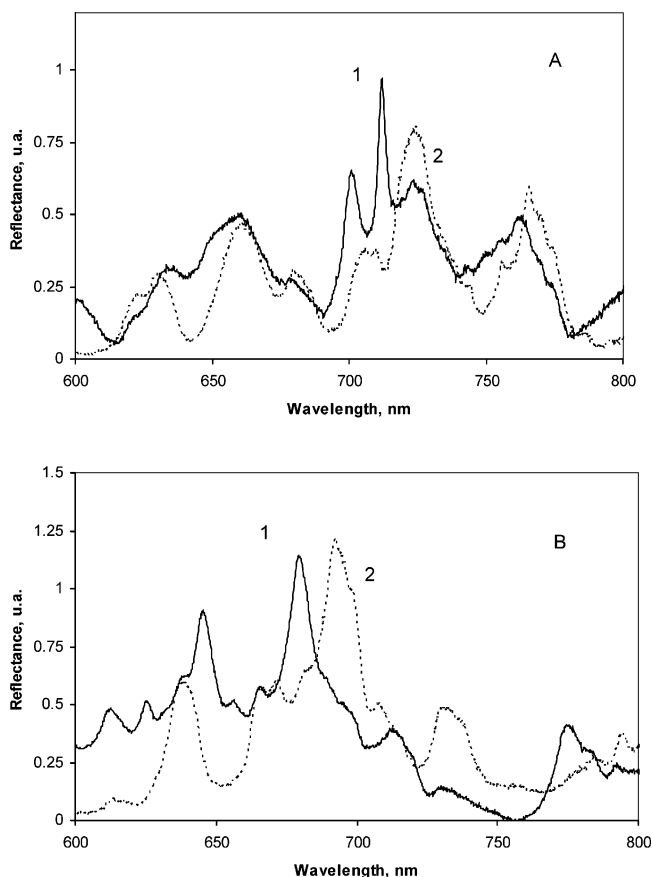|	wavelength, nm		
	Np(IV) in solution		
solid compound [BuMeIm]$_2$NpCl$_6$	without [BuMeIm]Cl	0.06 M [BuMeIm]Cl	solid product at 0.08 M [BuMeIm]Cl
522	517	512	517
629	621	621	600
659	667	643	655
678	673		
704	700	717	700
			711
723		740	721
765	764		760
			819
827	830	837	825
a	892		*a*
		911	
	921		
	951	987	

a Spectral range for the solid samples was 400−850 nm.

in the spectra of Pu(IV) at a [BuMeIm]Cl concentration of 0.06 M can be related to the formation of solid particles suspended in the ionic liquid. Increasing the chloride concentration to 0.08 M leads to the precipitation of green amorphous solids, as in Np(IV) solutions. Figure 6B and Table 3 show the reflectance spectrum of the solid Pu(IV) complex. This spectrum is different from the solid-state reflectance spectrum of [BuMeIm]$_2$[PuCl$_6$] as well as from

Table 3. Most Intensive Vis/Near-IR Bands for 0.01 M PuCl$_6$$^{2-}$ Solutions in [BuMeIm][Tf$_2$N] and Solid-State Reflectance Spectra of Pu(IV) Solid Complexes

	wavelength, nm		
	Pu(IV) in solution		
solid compound [BuMeIm]$_2$PuCl$_6$	without [BuMeIm]Cl	0.04 M [BuMeIm]Cl	solid product at 0.08 M [BuMeIm]Cl
610			610
	620	626	623
636	637	635	644
664	679	683	678
691	690		709
729	725		726
792	783	776	773
	833		831
a	884		*a*
	900		

a Spectral range for the solid samples was 400−850 nm.

Figure 6. Reflectance spectra of the slurry of the solids precipitated from Np(IV) (A-1) and Pu(IV) (B-1) solutions in [BuMeIm][Tf$_2$N] in the presence of 0.08 M [BuMeIm]Cl. Initial 0.01 M An(IV) solutions were prepared by the dissolution of corresponding [BuMeIm]$_2$AnCl$_6$ in neat RTIL. Solid-state reflectance spectra of (A-2) [BuMeIm]$_2$NpCl$_6$ and (B-2) [BuMeIm]$_2$-PuCl$_6$ are also shown.

the vis/near-IR spectrum of Pu(IV) in RTIL solution at 0.06 M [BuMeIm]Cl.

The spectroscopic data indicate that An(IV) are able to form chloride complexes with a Cl$^-$/An(IV) ratio higher than 6/1 in hydrophobic ionic liquid [BuMeIm][Tf$_2$N]. No published data could be found concerning the higher chlorides of An(IV). Moreover, the octahedral AnCl$_6$$^{2-}$ complexes are considered as a limiting chemical form for actinide(IV) chlorides. There is only one indirect indication of the
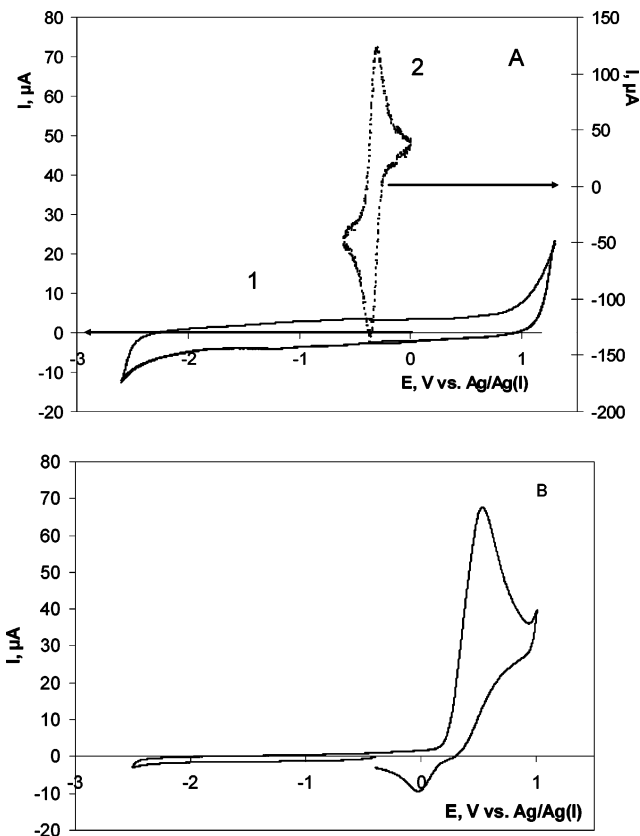
possibility to form neptunium(IV) chlorides different from $NpCl_6^{2-}$ in LiCl−KCl eutectic at 400 °C.[14] The Np(IV) absorption bands near 750 and 950 nm in the high-temperature melt were assigned to nonoctahedral chloride complexes of Np(IV). It should be emphasized that the absorption bands observed in molten chlorides closely resemble the maxima observed in the present study at 740 and 911 nm for Np(IV) in [BuMeIm][Tf$_2$N] in excess chloride ions.

The formation of nonoctahedral higher chlorides assumes that the An(IV) coordination number is higher than six in these species. Taking into account that uranium(IV) easily forms dimeric chlorides in aprotic solvents (e.g., tetra-hydrofuran, THF) and molten chlorides ([U$_2$Cl$_8$(THF)$_2$], [U$_2$Cl$_9$]$^-$),[15] it can be assumed that higher chlorides of An(IV) in [BuMeIm][Tf$_2$N] consist of a mixture of polymeric species with the general formula $[An_xCl_{(6x+y)}]^{(4x-(6x+y))}$, where $x \geq 1$ and $y > 1$. Variations in absorption spectra indicate the evolution of the complex composition with the chloride concentration, followed by precipitation of the polymers insoluble in RTIL. The quite different behavior of FET bands versus the chloride ion concentration for Np(IV) and Pu(IV) suggests some difference in the composition of the complexes for neptunium and plutonium.

In principle, the presumed $[An_xCl_{(6x+y)}]^{(4x-(6x+y))}$ complexes can be stabilized in RTILs by ion pairing with the organic cations of solvents since the overall negative charge of nonoctahedral actinide(IV) chlorides is higher than that of $AnCl_6^{2-}$. It has been shown that the diffusion coefficients of anionic complexes for various transition metals in chloro-aluminate ionic liquids decreased as the complex charge increased, indicating the possible formation of ion pairs.[19] This was also confirmed by molecular dynamic calculations showing strong interactions of anionic metal complexes with BuMeIm$^+$ cation in [BuMeIm][PF$_6$].[13]

Voltammetric Study. The cyclic voltammogram in Figure 7A demonstrates that the electrochemical window of dried [BuMeIm][Tf$_2$N] spans the potential range from −2.5 to +1.5 V versus Ag/Ag(I) at GC electrode in the presence of Ar. Figure 7B shows the cyclic voltammogram of [BuMeIm]Cl solution in ionic liquid in the absence of actinides. The anodic wave at $E_{1/2} = +0.610$ V vs Ag/Ag(I) is attributed to Cl$^-$ ions electrochemical oxidation in accordance with published data.[16]

The cyclic voltammogram of 0.01 M $NpCl_6^{2-}$ solution in [BuMeIm][Tf$_2$N] in Figure 8A shows no significant or well-

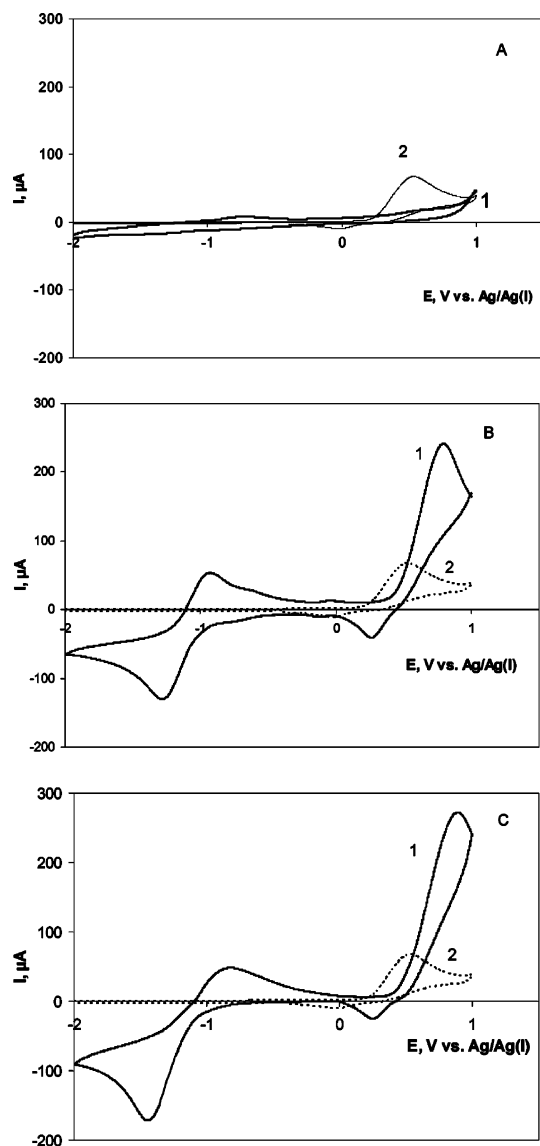(14) Barbanel, Yu. A. *J. Inorg. Nucl. Chem.* **1976** (Suppl. Vol.), 79.
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Figure 7. Cyclic voltammograms of dried neat [BuMeIm][Tf$_2$N] (1) and 0.01 M FeCp$_2$/FeCp$_2^+$ (2) (A) and 0.06 M [BuMeIm]Cl in [BuMeIm][Tf$_2$N] (B) ($v = 50$ mV·s^{-1}), at glassy carbon electrode in argon.

defined peaks, indicating that $NpCl_6^{2-}$ [Np(IV) and Cl$^-$] is electrochemically inert. The $PuCl_6^{2-}$ complex in neat RTIL exhibits similar behavior, and its voltammogram is not presented here. The voltammograms shown in Figures 8 and 9 reveal that adding [BuMeIm]Cl to $AnCl_6^{2-}$ solutions results in several irreversible redox processes. The peak currents increased with increasing $NpCl_6^{2-}$ or $PuCl_6^{2-}$ concentrations, confirming that the observed electrochemical processes are related to Np(IV) and Pu(IV), respectively.

Steady-state linear sweep voltammograms of Np(IV) recorded in the negative potential direction (Figure 9A) exhibit two well-defined cathodic waves, which most prob-ably are attributable to the reduction of two different species of Np(IV) to Np(III). For both waves, the limiting currents, i_l, increased linearly with the square root of the electrode rotation speed, $\omega^{1/2}$. According to Levich's equation, this indicates diffusion control of cathodic processes.[17] Figure 9B shows that Pu(IV) has a single major cathodic wave at the same [BuMeIm]Cl concentration as for Np(IV). Similar to Np(IV), the function of i_l versus $\omega^{1/2}$ for Pu(IV) → Pu(III) reduction is linear, indicating that the cathodic reaction is diffusion-controlled. The linear sweep voltammogram for Pu(IV) reduction recorded at a relatively low electrode rotation speed (250 rpm) does not show a current plateau but shows some current maxima. This phenomenon already described for RTILs[1] is related to the high viscosity of ionic liquids when the steady state cannot be reached at low rotation speeds. The voltammetric data thus confirm the
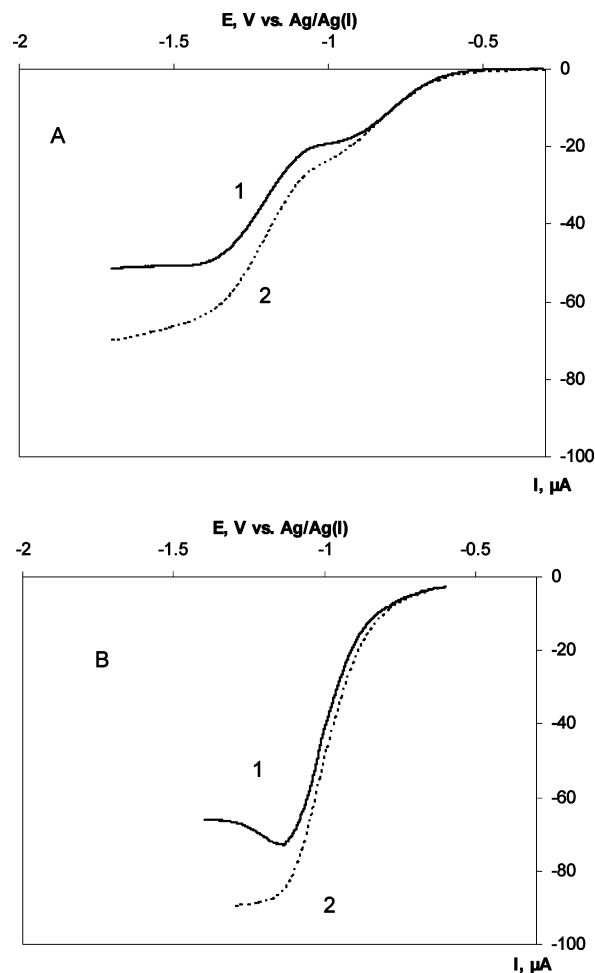
Figure 8. Cyclic voltammograms of 0.01 M $NpCl_6^{2-}$ (1) and 0.06 M [BuMeIm]Cl alone (2) in RTIL (A), in 0.01 M $NpCl_6^{2-}$ in the presence of 0.06 M [BuMeIm]Cl (B), and in 0.01 M $PuCl_6^{2-}$ in the presence of 0.06 M [BuMeIm]Cl (C). $V = 50$ mV·s^{-1}.

Figure 9. Steady-state linear sweep voltammograms for Np(IV) (A) and Pu(IV) (B) reduction in [BuMeIm][Tf$_2$N] in the presence of 0.06 M [BuMeIm]Cl. $V = 5$ mV·s^{-1}; $\omega = 250$ (1) and 500 (2) rpm.

Table 4. Dependence of $E_{1/2}$ and i_l for An(IV) Electrochemical Reduction on [BuMeIm]Cl Concentration

redox couple	[BuMeIm]Cl, M	$E_{1/2}$,^{a} V	i_l,^{b} mA
Np(IV)/Np(III)^c	0.04	$-0.97, -1.29$	$-16.5, -63.7$
Np(IV)/Np(III)^c	0.06	$-0.82, -1.21$	$-23.7, -64.4$
Pu(IV)/Pu(III)^d	0.06	-1.01	-89.0

^{a} Versus Ag/Ag(I). ^{b} $\omega = 500$ rpm. ^{c} $E° = +0.1550$ (V/ ENH).[12] ^{d} $E° = +0.9818$ (V/ ENH).[12]

conclusion drawn from the spectroscopic measurements concerning the composition difference of higher chlorides of Np(IV) and Pu(IV). Presumably two electroactive complexes of Np(IV) are formed in RTIL in comparable concentrations, whereas only a single predominant higher chloride of Pu(IV) is reduced electrochemically to Pu(III).

The values of the half-wave potentials, $E_{1/2}$, and i_l are summarized in Table 4 for Np(IV) and Pu(IV) reduction at different chloride ion concentrations. Increasing the [BuMeIm]Cl concentration causes a positive potential shift for both reduction waves of Np(IV), which means that the number of chloride ions coordinated to Np(III) is different from those of Np(IV). In principle, Np(III) can exist not only as $NpCl_6^{3-}$ but also as $NpCl_6(Tf_2N)_x^{-(3+x)}$ due to the Np(III) complexation with Tf$_2$N$^-$. This ligand is not able to replace the Cl$^-$ anion from the coordination octahedron of $NpCl_6^{2-}$. However, the stability of $AnCl_6^{3-}$ complexes in general is lower than that of $AnCl_6^{2-}$. The Tf$_2$N$^-$ anion concentration is much higher than that of chloride in solutions of 0.01 M [BuMeIm]$_2$[NpCl$_6$] in ionic liquids ([Tf$_2$N$^-$] = 3.5 M in neat [BuMeIm][Tf$_2$N]). One can conclude that at least, part of the $NpCl_6^{-3}$ can be transformed to $NpCl_6(Tf_2N)_x^{-(3+x)}$. Increasing the chloride ion concentration should lead to a higher $NpCl_6^{3-}$ yield followed by a positive shift in $E_{1/2}$ values due to the formation of thermodynamically more stable species of Np(III).

Table 4 demonstrates also that an increase in the [BuMeIm]Cl concentration leads to a relative increase in the limiting current for the first Np(IV) reduction wave compared with the second Np(IV) reduction wave observed at more negative potential. Spectroscopic studies showed that the yield of Np(IV) complex for which $\lambda_{et} = 360$ nm increases with the [BuMeIm]Cl concentration (Figure 4). The first

Table 5. Parameters of Steady-State Sweep Voltammetry for An(IV) and Cl⁻ Oxidation in [BuMeIm][Tf₂N] at GC Rotating Electrode in the Presence of 0.06 M [BuMeIm]Cl[a]

|	Np(IV)/Np(V)		Pu(IV)/Pu(V)		Cl⁻/Cl°	
ω, rpm	i_l, mA	$E_{1/2}$,[b] V	i_l, mA	$E_{1/2}$,[b] V	i_l, mA	$E_{1/2}$,[b] V
250	107	+0.530	112	+0.772	49	+0.572
500	118	+0.546	131	+0.786	67	+0.584
1000	184	+0.593	195	+0.801	104	+0.610

[a] [BuMeIm]₂AnCl₆ 0.01 M; ν = 5 mV·s⁻¹. [b] Versus Ag/Ag(I).

cathodic process can be thus attributed to the reduction of Np(IV) species with the FET band at 360 nm. The positive shift in the Np(IV) reduction potential with increasing λ_{et} is consistent with the linear relationship between the standard An(IV)/An(III) redox potential and the energies of the first electron-transfer bands established for the various actinide complexes in aqueous solutions.[18]

Voltammetric data reveal that Pu(IV) reduction occurs in RTIL in the same potential range as Np(IV). This result is very surprising since the difference in Pu(IV)/Pu(III) and Np(IV)/Np(III) standard redox potentials is about 0.82 V.[12] A possible explanation of this observation is related to the difference in complex composition for Np(IV) and Pu(IV) in the presence of [BuMeIm]Cl. Spectroscopic data demonstrate the opposite effects of [BuMeIm]Cl on the FET bands for Pu(IV) and Np(IV): Pu(IV) exhibits a dramatic low-wavelength shift, while Np(IV) shows some low-wavelength shift (7−11 nm, but also a strong high-wavelength shift at about 60 nm. Nugent's relation between $E°$ and λ_{et}[18] predicts in this case a significant positive potential shift for Np(IV)/Np(III) with respect to Pu(IV)/Pu(III). It should be noted that the strong effect of complexation on redox potential values is well-known for An(IV) solutions in different media. For example, the difference in U(IV)/U(III) reduction peak potentials reached 0.75 V for UCl₄ and [UCl₅(THF)]⁻ in THF solutions.[15d] Another possible explanation for the resemblance in redox potentials of Np(IV) and Pu(IV) may be related to the significant difference in the stabilities of Np(III) and Pu(III) chloride complexes in RTILs. However, in the literature there are no data on the stability and structure of An(III) chlorides in hydrophobic ionic liquids. Indeed, additional investigations will be necessary to establish the composition and the structure of An(IV) and An(III) chloride complexes in such solvents.

The typical steady-state voltammograms of Np(IV) and Pu(IV) in the presence of 0.06 M [BuMeIm]Cl recorded in the positive potential direction exhibit a single oxidation wave approximately at the same potential range as for the Cl⁻ electrochemical oxidation. The steady-state voltammetry parameters for the oxidation processes are presented in Table 5. The half-wave potentials for Np(IV) and Pu(IV) are shifted

to lower and higher values, respectively, compared with the $E_{1/2}$ value for chloride ion oxidation. The limiting currents of the oxidation waves in the presence of An(IV) are higher than those for chloride ions under similar experimental conditions. According to the voltammetric studies, we can conclude that the oxidation waves represent the superposition of An(IV) oxidation and oxidation of noncoordinated chloride ions. Oxidation of An(IV) could thus include chemical and electrochemical stages corresponding to the following scheme:

$$Cl^- - e^- \rightarrow Cl° \quad (1)$$

$$An(IV) + Cl° \rightarrow An(V) + Cl^- \quad (2)$$

$$An(IV) - e^- \rightarrow An(V) \quad (3)$$
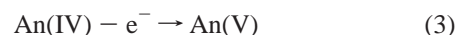
The i_l values increased linearly with $\omega^{1/2}$, indicating diffusion control of anodic processes.[17] However, an increase in $E_{1/2}$ with the electrode rotation speed demonstrates that the oxidation reactions are not totally reversible. The oxidation half-wave potentials of Np(IV) and Pu(IV) cannot be obtained from the voltammetric data presented in Table 5 due to interference from Cl⁻ oxidation.

Conclusions

The dissolution of [BuMeIm]₂AnCl₆ in hydrophobic room-temperature ionic liquid [BuMeIm][Tf₂N] yields solutions of octahedral actinide(IV) hexachloro complexes. AnCl₆²⁻ are stable to hydrolysis in [BuMeIm][Tf₂N].

Adding [BuMeIm]Cl to the solution of AnCl₆²⁻ in RTIL modifies the UV/vis/near-IR absorption spectra and causes solids to precipitate, indicating the formation of higher chloride complexes with a Cl⁻/An(IV) ratio higher than 6/1. Spectrosopic and voltammetric studies suggest a difference in the complex composition for Np(IV) and Pu(IV).

NpCl₆²⁻ and PuCl₆²⁻ complexes are electrochemically inert in [BuMeIm][Tf₂N] solutions at the glassy carbon electrode. However, the addition of [BuMeIm]Cl causes several redox processes to appear for Np(IV) and Pu(IV) in this medium.

Supporting Information Available: Spectroscopic data in the extended range (from 400 to 1050 nm) of Np(IV) and Pu(IV) in [BuMeIm][Tf₂N] at different chloride ion concentrations. This material is available free of charge via the Internet at http://pubs.acs.org.

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