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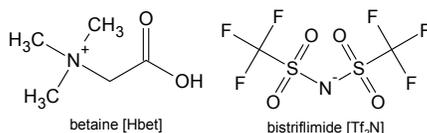
Unusual Redox Stability of Neptunium in the Ionic Liquid [Hbet][Tf₂N]Kristy Long,^a George Goff^b and Wolfgang Runde*^c

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The behavior of neptunium in the ionic liquid betaine bistriflimide, [Hbet][Tf₂N], has been studied spectroscopically at room temperature and 60 °C for the first time. An unprecedented complex redox chemistry is observed, with up to three oxidation states (IV, V and VI) and up to six Np species existing simultaneously. Both redox reactions and coordination of betaine are observed for Np(IV), (V) and (VI). Elevating the temperature accelerates the coordination of Np(V) with betaine and reduction reactions slow down.

Due to their advantageous properties ionic liquids (ILs) have attracted much interest for a variety of applications, and increasingly for potential utilization in nuclear fuel processing technologies. ILs have been demonstrated to exhibit properties desired for separation technologies such as low volatility and flammability, greater radiation stability and wider electrochemical windows needed for electrorefining processes. Examples that demonstrate the potential of ILs for *f*-element separation include the first successful electrodeposition of metallic uranium¹ or UO₂² from room-temperature ILs or the utilization of ILs to foster the solvent extraction of actinides and fission products which have recently been thoroughly reviewed.³ Significant solubility, which is prerequisite for utilizing ILs in separations technologies, has been reported in task-specific ILs. With the addition of limited amounts of HNO₃ Billard *et al* achieved dissolution of lanthanide and uranium oxides in [BMIm][Tf₂N], accompanied by the oxidation of U(IV) to U(VI).⁴ The hydrophilic, carboxyl-functionalized IL (trimethylammonio)acetate bistriflimide, [Hbet][Tf₂N] (see structure below), has garnered much recent interest due to its ability to coordinate with metal ions as well as its switchable phase behaviour.⁵ Rao *et al.* reported a theoretical solubility limit of 22 weight% U, but observed a 15% solubility limit when measuring UO₃ dissolution in [Hbet][Tf₂N] at 100 °C.⁶



Despite the promising results, the fundamental understanding of the oxidation state stability, solvation, reactivity and coordination of actinides in ILs remain to be unravelled. Few reports provide insight into the coordination chemistry of actinides in ILs such as [Hbet][Tf₂N]. Nockemann *et al.* reported the formation of monomeric U(VI) complexes in imidazolium-based [HbetmIm][Tf₂N] ([UO₂(betmIm)₃][Tf₂N]₂), dimeric nucleation in [Hbet][Tf₂N] ([UO₂(bet)₆(H₂O)₂][Tf₂N]₄), as well as extended polymeric U(VI) coordination in pyrrolidinium-based

ILs.⁷ Similar results were obtained by Chen *et al.* using a phosphonium betaine analogue to obtain single crystals of both monomeric and dimeric U(VI), [UO₂(CTMP)₃(H₂O)₂][Tf₂N]₂ and [UO₂(CTMP)₃][Tf₂N]₄.⁸

The majority of investigations on the behavior and separation of actinides using ILs have been performed with uranium in its +VI oxidation state, while few studies have involved the light transuranium elements neptunium (Np), plutonium, or americium.³ Neptunium is a key constituent in used nuclear fuel and is the most problematic actinide for the long-term storage and disposal of nuclear waste in geological settings. Neptunium may exist in the +III, IV, V and VI oxidation states, but only the +IV and V oxidation states are relevant to most environments.⁹ The soluble +V oxidation state is most common, and displays a lower affinity towards complexation or adsorption on minerals and ion exchange resins. To date, there are few reports on the stability, reactivity and coordination of Np in ILs. Nikitenko *et al.* showed that Np(IV) forms octahedral structures of AnCl₆²⁻ in the hydrophobic ILs [BuMIm][Tf₂N] and [BuMIm][PF₆] in the presence of concentrated HCl.¹⁰ The authors note the lacking influence of water on the NpCl₆²⁻ complex and its stability towards hydrolysis, which is quite contrary to its behaviour in aqueous systems. Charushnikova *et al.* crystallized a mixed valency Np(IV)-(V) compound, [BMIm]₅[Np(NpO₂)₃(H₂O)₆Cl₁₂] from an ethyl acetate-acetone mixture containing BMIm-Cl.¹¹ The Np(IV) atoms are surrounded by three neptunyl(V) oxygen atoms and 6 water molecules, while the inner coordination of the Np(V) atoms contains 2 axial neptunyl O atoms and 4 equatorial Cl atoms.

Both tetravalent and pentavalent oxidation states of Np have been reported in solid complexes; however, the valency of Np in the IL system from which the solids were isolated nor the general stability of Np in ILs have not been reported. In this study, we report for the first time on the stability of Np(IV), Np(V) and Np(VI) in water-saturated [Hbet][Tf₂N] at room temperature and at 60 °C. The characteristic electronic absorption bands in the region 950-1280 nm can be used to monitor changes in the inner coordination sphere around the Np atom in various oxidation states.¹² At room temperature, tetravalent Np exhibits a high stability towards oxidation in water-saturated [Hbet][Tf₂N] over a long period of time. The Np(H₂O)_x⁴⁺ cation has a characteristic absorbance at 960 nm in perchloric acid solutions.^{12c} After adding Np(H₂O)_x⁴⁺ to [Hbet][Tf₂N] the absorbance is shifted quickly to 971 nm due to the replacement of water molecules in the inner coordination sphere of the Np atom with betaine ligands (Fig. 1). Over a period of 26 days the initial Np(IV) betaine complex with an absorbance at 971 nm shifts further to 974 nm, which appears to be relatively stable towards oxidation to Np(V). Np(IV) is far more stable in [Hbet][Tf₂N] than in most aqueous systems, which requires reducing agents to avoid oxidation to the more stable

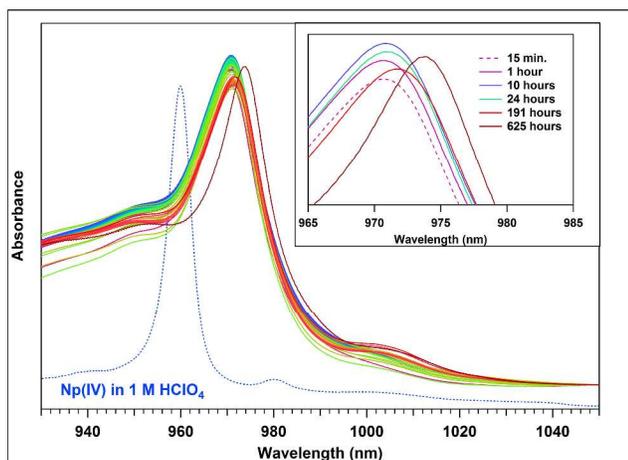


Fig. 1 Near-Infrared absorbance of 0.6 mM Np(IV) in acidic solution and in water-saturated [Hbet][Tf₂N]. Note that the small absorbance at 980 nm in the Np(IV) HClO₄ solution is due to an impurity of <1% Np(V).

Np(V). Over several weeks Np(IV) very slowly oxidizes to Np(V), observed via the increasing absorbance at 1008 nm which is characteristic of a Np(V) betaine complex (see below).

Neptunium(V) exhibits a much more complicated behavior in water-saturated [Hbet][Tf₂N] than Np(IV). The Np^VO₂(H₂O)₅⁺ cation has a very characteristic, intense absorbance at 980 nm in aqueous systems.^{12b, 9b} After adding Np^VO₂(H₂O)₅⁺ to [Hbet][Tf₂N], the intensity of the prominent peak at 980 nm decreases over weeks indicating slow changes in the coordination of Np(V) (Fig. 2). The in-growth of a new absorbance peak around 1008 nm is caused by the replacement of coordinated water in the equatorial plane of the O=Np=O⁺ moiety to form a Np(V)-betaine species. The complexation of Np(V) with betaine is significantly slower than the complexation kinetics of Np(IV) and after 7 days of reaction time only approximately 60% of the initial Np(V) is complexed with betaine. In contrast to the relatively stable Np(IV), Np(V) is also reduced to Np(IV) in addition to being complexed by betaine. The absorbance peaks at 963 and 973 nm indicate the reduction of Np(V) to Np(IV) with the 973 nm species being equivalent to the absorbance of the Np(IV)-betaine complex described above. After 135 days, the remaining Np(V) and Np(IV) fractions are complexed with betaine and only very small amounts of the 963 nm Np(IV) species remaining. Due to the slow reduction of the Np(V) betaine complex and the extremely slow oxidation of Np(IV) betaine, both Np(IV) and Np(V) are long-term stable oxidation states in [Hbet][Tf₂N]. This thermodynamic distribution poses the basis for the crystallization of the mixed Np(IV)-(V) solid complexes previously reported.¹¹

Quantitative analysis of the distribution of solution species requires knowledge of the molar extinction coefficients of the characteristic electronic absorbance bands. The extinction coefficients for several Np species in aqueous systems are well-known, but are unknown for unconventional solvents such as ILs. Initially, water in the IL outcompetes betaine for complexation ensuring a similar inner coordination sphere as found in acidic aqueous solutions. The absorbance maximum of NpO₂(H₂O)₅⁺ in [Hbet][Tf₂N] is shifting slowly to 983 nm^{9b} from the 980 nm in acidic perchlorate solutions. Similarly, the absorbance appears at 963 nm compared to 960 nm in HClO₄. It remains to be determined if these spectral features are caused by changes in the solvation or inner-coordination sphere of the Np atoms. The molar extinction coefficients for NpO₂(H₂O)₅⁺ are very similar in perchloric acid (395±5 L mol⁻¹ cm⁻¹)^{12b} and in water-saturated

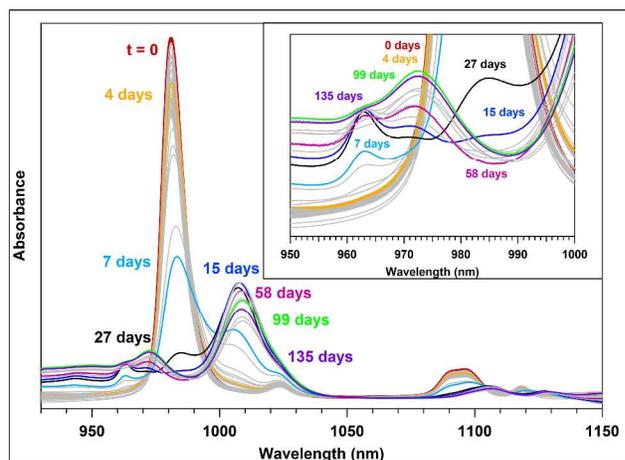


Fig. 2 Near-Infrared absorbance of 2.3 mM Np(V) in water-saturated [Hbet][Tf₂N].

[Hbet][Tf₂N]. Surprisingly, the molar extinction coefficient of the Np(IV)-betaine absorbance at 973 nm with $\epsilon = 219 \pm 20 \text{ L mol}^{-1} \text{ cm}^{-1}$ is slightly higher than that for the Np(H₂O)_x⁴⁺ ion in perchlorate solutions (206±10 L mol⁻¹ cm⁻¹).^{12c} In contrast, the molar extinction coefficient of the Np(V)-betaine complex at 1008 nm is significantly lower compared to that of the NpO₂(H₂O)₅²⁺ ion as evidenced by the significant decrease in intensity (Fig. 2), which is common for Np(V) complexation. A detailed quantitative analysis and speciation calculations will be presented in a future publication.

Higher temperature increases the stability of Np(IV) versus Np(V), and Np(IV) compounds can be prepared from Np(V) starting materials at elevated temperatures.^{9b} At 60 °C, Np(V) speciation is dominated by the fast complexation reaction with betaine as indicated by the two absorbances at 980 and 1008 nm (Figure 3). Within 3 days, about 90% of the initial NpO₂(H₂O)₅⁺ ions are complexed with betaine, compared to only about 15% at room temperature. The complexation reaction follows a pseudo-first order rate law, with a preliminary rate constant of 4.3×10⁻⁴ min⁻¹ (Fig. 3 inset). It should be considered that a faster evaporation of residual water in the IL at elevated temperature could contribute to the faster complexation kinetics. Although the absorbance for the NpO₂(H₂O)₅⁺ at 980 nm decreases continuously with time, both intensity and absorbance maximum increasingly fluctuate due to small amounts of water refluxing inside the sealed cuvettes. Evaporation of water fosters 80 complexation with betaine and thus reduction in the 980 nm

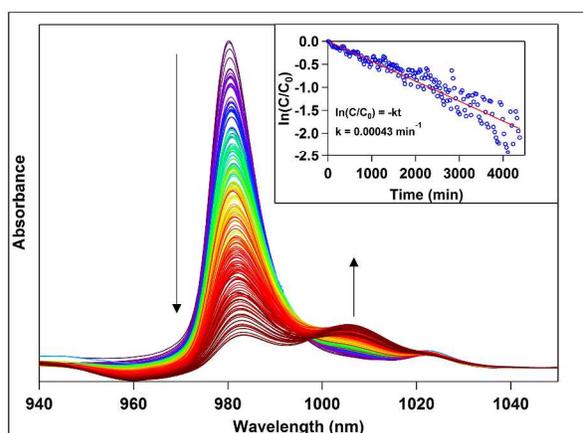


Fig. 3 Near-Infrared absorbance of Np(V) in water-saturated [Hbet][Tf₂N] at 60 °C over the course of three days.

absorbance; however, upon refluxing the water back into the IL the absorbance at 980 nm increases due to the fast coordination of water by Np(V). This was verified independently by adding water to the mixture to force the equilibrium back towards the hydrated Np(V) complex, as observed by an the immediate decrease of the 1008 nm absorbance and an increase in the 980 nm absorbance. Over time the Np(V) cation re-coordinates betaine, slowly intensifying the 1008 nm absorbance. The complexation of Np(V) with betaine stabilizes Np(V) in water-saturated [Hbet][Tf₂N]. No reduction to Np(IV) is detected within three days at 60 °C as the characteristic absorbances at 960-975 nm for Np(IV) are absent. Adding hydrazine to a mixture of about 10% NpO₂(H₂O)₅²⁺ and 90% Np(V)-betaine, quickly reduces the hydrated Np(V) to a Np(IV)-betaine complex. The Np(V)-betaine complex slowly transforms to a Np(IV)-betaine complex within several weeks.

Hexavalent Np is generally relatively unstable towards reduction to Np(V) and it requires oxidizing agents to keep Np(VI) in aqueous solution. Based on the observed slow reduction of Np(V) to Np(IV), Np(VI) is expected to quickly reduce to Np(V). Upon addition of Np^{VI}O₂(H₂O)₅²⁺ to [Hbet][Tf₂N] the broad absorbance at 1223 nm, characteristic for NpO₂(H₂O)₅²⁺ in perchloric acid,^{12a, 9b} is shifted to approximately 1231 nm indicating a fast complexation of Np(VI) with betaine (Fig. 4). We observed a similar fast coordination of betaine with the oxidation state-analogue U(VI). However, quantitative determination of the residual hydrated, non-complexed Np(VI) is complicated by the broad nature of the Np(VI) absorbance bands. Although Np(VI) is metastable for weeks, slow reduction to Np(V) can be monitored. Interestingly, the Np(VI)-betaine complex is reduced to the NpO₂(H₂O)₅⁺ ion first, before the Np(V)-betaine complex with its characteristic absorbance at 1010 nm appears. After about two weeks, three oxidation states of Np coexist in water-saturated [Hbet][Tf₂N] including an unusually stable Np(VI). The absorbance band at 963 nm indicates further reduction of Np(V) to Np(IV) with the Np(IV)-betaine complex (absorbance at 973 nm) forming subsequently. The fact that neither Np(IV) nor Np(V) are oxidized to Np(VI) suggests that Np(VI) is the least stable oxidation state and over time Np(IV) and Np(V) govern the Np speciation in the IL [Hbet][Tf₂N].

This spectrophotometric study demonstrates for the first time the complex redox chemistry of an actinide element in an IL and illustrates the competitive nature of water and betaine coordination. Spectroscopic data indicates water and betaine influences in both the inner- and outer-coordination spheres, adding to the complexity this system. The fact that all three valencies, Np(IV), (V), and (VI), exhibit unusual stability in [Hbet][Tf₂N] offers great opportunities for utilization in purification and separation from other actinides and fission products. Elevated temperatures can be utilized to stabilize Np(V) and hinder reduction to Np(IV), while the addition of reducing agents such as hydrazine accelerates the reduction of Np(V) to Np(IV) even when coordinated with betaine. The competitive complexation of water and betaine suggests additional exploration of water-miscible ILs with switchable phase behavior for separation technologies. The enhanced stability of Np(VI) questions the potential stabilities of other high-valent actinides, e.g. Pu(VI) and Am(VI), which could serve as the basis for novel separation technologies utilizing higher oxidation states. A prominent example is the separation of americium from trivalent lanthanides and curium, the most difficult predicament for used nuclear fuel processing.

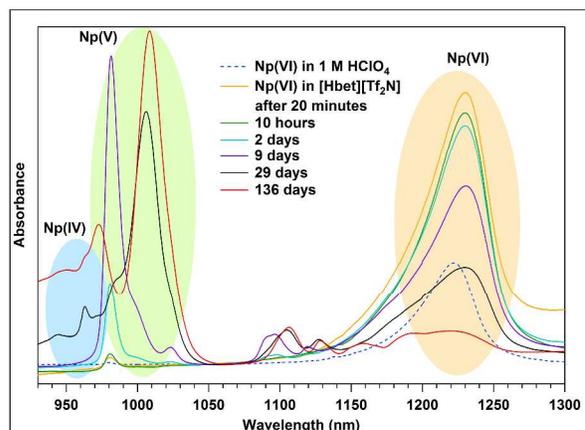


Fig. 4 Near-Infrared absorbance of 1 mM Np(VI) in acidic solution and in water-saturated [Hbet][Tf₂N].

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Notes and references

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[†] Electronic Supplementary Information (ESI) available: additional details on experimental procedures. See DOI: 10.1039/b000000x/
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Electronic Supplementary Information:

Experimental:

5 **Reagents:** Betaine Chloride (99% purity) was obtained from Acros Organics, Li(Tf₂N) was obtained from 3M Chemical Company, and all other reagents were obtained from Fisher Scientific, Inc. The ionic liquid betaine bistriflimide, [Hbet][Tf₂N], was prepared by anion metathesis of betaine chloride and Li(Tf₂N) using methods previously reported in the literature.^{7, 5b} IL purity was confirmed via ¹H-NMR. All reagent solutions were prepared gravimetrically using deionized water with a specific resistance ≥ 18.0 MΩ·cm. All IL samples were water saturated, and were prepared gravimetrically. Solution volumes were calculated using previously reported density data for [Hbet][Tf₂N].^{5b} The IL [Hbet][Tf₂N] has a melting point of 54°C and a water solubility limit of 17 wt % at 25°C.^{5b}

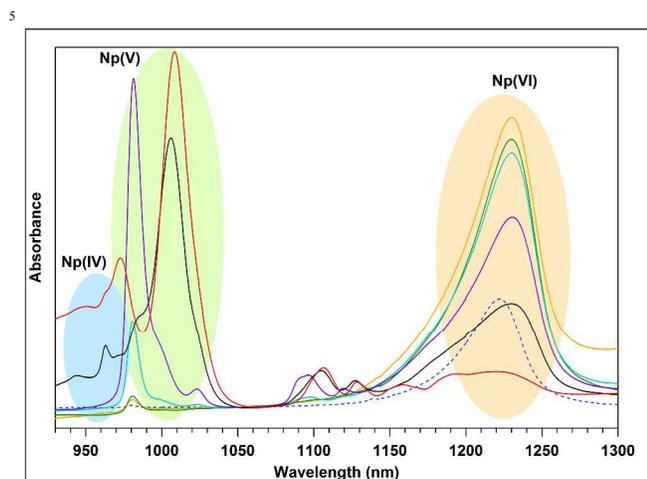
Neptunium stock solutions: Neptunium-237 is a radioactive material ($t_{1/2} = 2.1 \times 10^6$ years) and must be handled with care within appropriate laboratories. All neptunium solutions were handled and stored in a chemical fume hood equipped with a HEPA filtration system. A ²³⁷Np(V) solution was prepared by dissolving NpO₂ into 3 M HCl, followed by precipitation with 3M NaOH and subsequent redissolution in 1 M HCl. After reducing the Np(V) in 1 M HCl with an excess of hydrazine·2HCl the Np(IV) was purified by anion exchange. The purified Np(IV) was precipitated by addition of 5 M NH₄OH and the resulting precipitate was centrifuged, doubly washed with deionized water, and redissolved in 1 M HClO₄. Stock solutions of Np(V) were prepared via auto-oxidation of Np(IV) in 1 M HCl. Stock solutions of Np(VI) were prepared by oxidizing solutions of Np(IV) in 1 M HClO₄ using ozone. Solutions were analyzed by Raman spectroscopy to confirm the absence of residual ammonium or hydrazine impurities. Samples for spectrophotometric measurements Np samples were prepared by adding known aliquots of these stock solutions to water saturated [Hbet][Tf₂N].

Each of the known Np oxidation states exhibits characteristic electronic absorption bands in the region 950-1280 nm that can be used to monitor changes in the inner coordination sphere around the Np center.^{12a, 9b} Oxidation states were confirmed via UV-vis-NIR spectroscopy and previously reported molar absorptivities. Characteristic absorbance bands used for concentration determination were 960 nm for Np(IV), $\epsilon = 206 \text{ M}^{-1} \text{ cm}^{-1}$,^{12c} 980 nm for Np(V), $\epsilon = 395 \text{ M}^{-1} \text{ cm}^{-1}$,^{12b} and 1223 nm for Np(VI), $\epsilon = 395 \text{ M}^{-1} \text{ cm}^{-1}$.^{12a}

Instrumentation: Absorbance Spectra of Np solutions were measured using a Cary 5 UV-vis-NIR spectrophotometer from Varian. Raman spectra were collected on a Nicolet Magna-IR 560 ESD with a Raman accessory using a 1064 nm excitation laser. The purity of the betaine bistriflimide was examined by ¹H-NMR spectroscopy on a Bruker ARX-300 spectrometer equipped with 5- and 10-mm multinuclear probes.

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Graphical Abstract for Content Page:



In contrast to its chemistry in aqueous systems, neptunium exhibits a highly complex redox behaviour in the ionic liquid betaine bistriflimide, [Hbet][Tf₂N]. Spectroscopic studies have shown for the first time that up to three oxidation states (IV, V and VI) and up to six neptunium species can exist simultaneously. Both redox reactions and coordination of betaine with Np(IV), (V) and (VI) lead to an unprecedented stability of Np(IV) and Np(VI).

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