Neptunium Redox Speciation

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Neptunium (Np, Z = 93) is a radioactive, manmade element that is produced as a byproduct in nuclear reactors. It is considered to be the most problematic of the 5f (actinide) elements for waste storage because of its high solubility in groundwater. Predicting the fate and transport of Np under environmentally relevant conditions is difficult because of its complicated chemistry, especially its redox and sorption behaviors. In aqueous solution, Np can exhibit oxidation states from III to VII, inclusive. The relative stabilities of which are strongly affected by pH and the presence of complexing ligands.

Although the formal potentials of the Np^{3+}/Np^{4+} and Np^{5+}/Np^{6+} redox couples are well known, there are comparatively few reports on the solution coordination behavior of Np as a function of oxidation state. The Np coordination environment, in terms of bond lengths and the number of inner-sphere aquo ions about Np, is open to question. We have systematically probed the aqueous coordination chemistry of Np as a function of oxidation state.[1] The system examined herein—a dilute solution of Np in 1 M $HClO_4$—was chosen for this study in order to avoid complicating effects of hydrolysis, disproportionation, complexation, and precipitation. We used electrochemical techniques to stabilize a single Np redox state and *in situ* extended x-ray absorption fine structure (EXAFS) to probe the Np coordination. The experiments were complemented with results from density functional theory (DFT) calculations and geometric modeling.

A single solution of neptunium was used to extract metrical information about the Np coordination environment, in terms of hydration numbers (n) and Np-O interatomic distances. Four aquo ions—$Np^{3+}\cdot nH_2O$, $Np^{4+}\cdot n'H_2O$, $[Np^{5+}O_2]^{+}\cdot n''H_2O$, and $[Np^{6+}O_2]^{2+}\cdot n'''H_2O$—were electrolytically prepared and precisely maintained by use of constant potential bulk electrolysis (with coulometry) throughout the simultaneous EXAFS data acquisition at the BESSRC-CAT beamline 12-BM-B at the APS. The *in situ* preparation of the individual valence states—one at a time—in a single solution eliminates potential interferences and sources of artifacts that might arise from use of 4 separate solutions in 4 separate cells on 4 separate occasions. We have recently demonstrated that *in situ* Np x-ray absorption near-edge structure (XANES) spectroelectrochemistry on the same system provides a novel means to determine the formal potentials of the reversible Np^{3+}/Np^{4+} and Np^{5+}/Np^{6+} redox couples.[2]

The data in Fig. 1 show that the EXAFS response for all four of the hydrated cations is sensitive to variations of Np-O interatomic distances with Np oxidation state. The *in situ* EXAFS for the Np^{3+}/Np^{4+} redox states is distinct from the Np^{5+}/Np^{6+} states. For the Np^{3+} and Np^{4+} aquo ions, the experiments revealed a contraction of the average Np-O bond lengths from 2.48(2) to 2.37(2) Å, respectively. The analyses suggest that there are 9 water molecules in the first or inner hydration sphere about Np^{3+} in $[Np(OH_2)_9]^{3+}$ and Np^{4+} in $[Np(OH_2)_9]^{4+}$. The DFT calculations reveal 8–9 water molecules coordinated to Np^{3+}, supporting the EXAFS results. Simple geometric modeling supports a coordination number of 8 for both trivalent and tetravalent Np. For the Np^{5+} and Np^{6+} aquo ions, the EXAFS revealed bond length contractions. The average interatomic distances for the *trans*-dioxygen atoms in $[NpO_2]^{+}$ and $[NpO_2]^{2+}$ decreased from 1.80(2) Å for Np^{5+} to 1.73(2) Å for Np^{6+}. The average interatomic distances to the oxygen atoms of the coordinated H_2O molecules decreased from 2.44(3) Å to 2.36(3) Å, respectively. The oxygen coordination numbers were identical, suggesting that 5 water molecules are bound to Np^{5+} in $[NpO_2(OH_2)_5]^{+}$ and to Np^{6+} in $[NpO_2(OH_2)_5]^{2+}$.

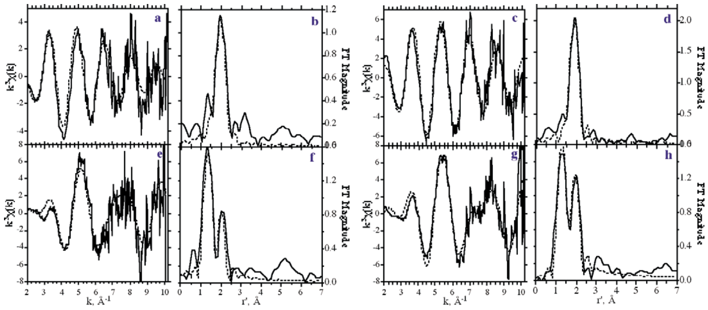

FIG. 1. Neptunium L_2–edge $k^3\chi(k)$ EXAFS and Fourier transform data without phase shift correction for (a, b) $Np^{3+}\cdot nH_2O$, (c, d) $Np^{4+}\cdot n'H_2O$, (e, f) $[Np^{5+}O_2]^{+}\cdot n''H_2O$, and (g, h) $[Np^{6+}O_2]^{2+}\cdot n'''H_2O$. Experimental data are shown as solid lines; the fits are dashed lines.

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