Np(VII) Coordination in Solution: A Spectroelectrochemcial Study

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The solution coordination environment of Np(VII) remains uncertain despite numerous studies since its discovery by Krot and Gelman in 1967.[1] Interest in the heptavalent Np ion is driven both by the incomplete understanding of fundamental bonding interactions and Np's technological importance in treating nuclear waste. Np(VII) is a highly oxidizing ion that is slowly reduced in strongly alkaline and rapidly reduced in acidic solutions. Its speciation has been reported as the linear dioxo moiety, O=Np=O in solution, that is coordinated equatorially to oxo or hydroxo anions or waters.[2,3] In contrast, Np(VII) has also been reported as a tetraoxo-coordinated ion $NpO_4(OH)_2^{2-}$ from NMR experiments in solution[4] and in the solid state.[5]

We have taken advantage of the unique opportunity afforded by the Actinide Facility to perform electrochemistry and ozonolysis of highly basic Np solutions while the sample is in the x-ray beam. This *in situ* spectroelectrochemistry permits data collection as the Np solution is held under the electrochemical control necessary to stabilize a phase-pure solution of Np(VII).

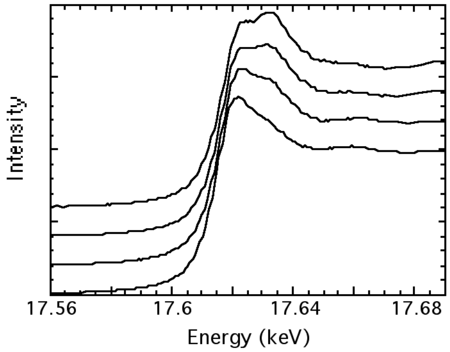

FIG. 1. In situ Np L3 XANES from (top) fully oxidized Np(VII) and (bottom) Np(VI) are compared with spectra representing a mixture of both oxidation states.

The preparative details of the starting Np(V) hydroxide solution and the electrochemistry are outlined elsewhere.[6] The Np solution was transferred in a purpose-built electrochemical cell[7] from the Chemistry Division to the BESSRC-CAT 12-BM-B bending magnet beamline within 30 minutes of solution preparation. Np(V) was oxidized, first to Np(VI) and then to Np(VII), by continuously sparging with ozone while simultaneously applying an oxidizing potential. After several hours the ozone was stopped and XAFS data collected on the fully oxidized sample, which was held under a +500 mV potential during data collection. The applied potential was subsequently varied and data obtained after bulk electrolysis at a variety of applied potentials.

Representative Np L_3-edge XANES spectra, obtained at various applied potentials, are shown in Fig. 1. The Np(VI) spectrum exhibits the shoulder feature characteristic of the actinyl moiety. In contrast, the spectrum from Np(VII) has a broader, doubled white line, thereby suggesting a change in the coordination environment from the simple O=Np=O configuration known for Np(VI). The difference in coordination environments between Np(VI) and Np(VII) is confirmed and quantified by analyses of the EXAFS data shown in Fig. 2. A tetraoxo coordination environment is determined for Np(VII), with 4 O at 1.87(1) Å and 2 O at 2.24(4) Å.

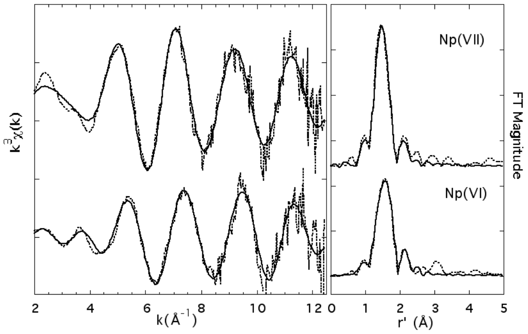

FIG. 2. Left: The k3 weighted EXAFS of Np(VII) (top) and Np(VI) (bottom) and Right: their Fourier transforms before phase correction, depicted as solid lines, are compared with their fits, which are shown as dotted lines.

The necessity of in-beam electrochemical control is clear from our results. We have obtained XAFS spectra from single-species solutions of both Np(VI) and Np(VII). The tetraoxo Np(VII) coordination determined here is different from the previously reported coordination of Np(VII) determined from *ex situ* EXAFS experiments and also from other high-valent actinides or transition metals in solution. An insight into the stabilization of this unusual coordination environment has been obtained from calculations based on density functional theory methodology that include relativistic effects. The calculated coordination compares well with our EXAFS results. The calculated bond angles, not available from EXAFS analyses, are 169.83° for trans O-Np-O ligands and 89.11° for adjacent ligands. The lowest energy configuration with no calculated imaginary frequencies has D_{2d} symmetry.

Combining our XAFS results with DFT calculations, we conclude that Np(VII) has a tetraoxo first-coordination sphere that is slightly distorted from square planar. This unusual coordination appears to result from a competition for ligand electron density among the Np d- and f-orbitals of various symmetries with increasing nuclear charge stabilizing 5f with respect to 6d orbitals.

Acknowledgments

The authors acknowledge the infrastructure support from the Actinide Facility and the BESSRC CAT. This work is supported by the U.S. DOE, BES – Chemical Sciences, and the APS is supported by the U.S. DOE, BES – Material Sciences, all under contract W-31-109-ENG-38. The authors also acknowledge the Ohio Supercomputer Center for a grant of computer time.

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