

	Experiment title: Redox behavior of neptunium species in solution	Experiment number: 20-01-696
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Report:

Stability and coordination of Np(VI) and Np(V) acetate complexes in aqueous solution was studied by using UV-Vis-NIR and EXAFS spectroscopy [1]. In the Np(VI) acetate system, the formation of $\text{Np}^{\text{VI}}\text{O}_2(\text{AcO})^+$, $\text{Np}^{\text{VI}}\text{O}_2(\text{AcO})_2(\text{aq})$, and $\text{Np}^{\text{VI}}\text{O}_2(\text{AcO})_3^-$ were detected (Fig. 1). Both methods resulted in the comparable stability constants ($\log K_1 = 2.98 \pm 0.01$, $\log \beta_2 = 4.60 \pm 0.01$, $\log \beta_3 = 6.34 \pm 0.01$ from UV-Vis-NIR; $\log K_1 = 2.87 \pm 0.03$, $\log \beta_2 = 4.20 \pm 0.06$, $\log \beta_3 = 6.00 \pm 0.01$ from XAFS at $I = 0.30 \text{ M}$ $(\text{H},\text{NH}_4)\text{ClO}_4$).

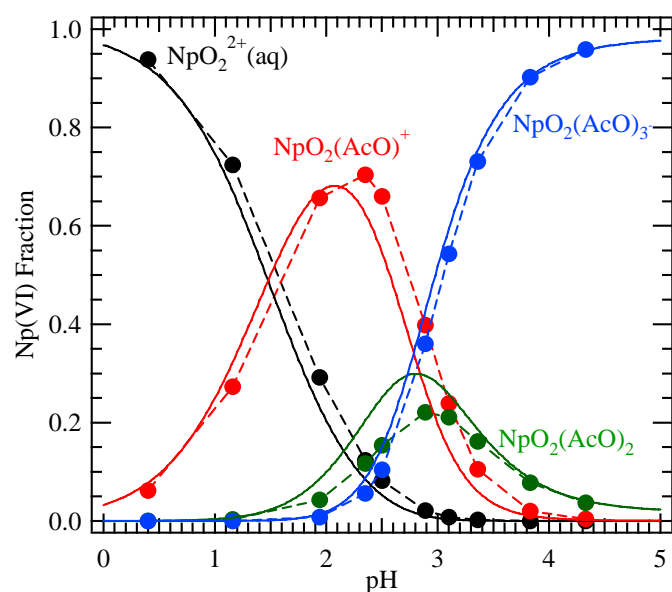


Figure 1. Species distribution of Np(VI) acetates derived from UV-Vis-NIR (solid lines) and XAFS (solid circles with dashed lines) spectroscopy at 0.015 M Np(VI) and 1 M AcOH in $I = 0.3 \text{ M}$.

The extracted EXAFS spectra of $\text{Np}^{\text{VI}}\text{O}_2^{2+}(\text{aq})$, $\text{Np}^{\text{VI}}\text{O}_2(\text{AcO})^+$, and $\text{Np}^{\text{VI}}\text{O}_2(\text{AcO})_3^-$ (Fig. 2) provided the structural data consistent with their stoichiometry, being well-explained by a bidentate coordination of acetate ($\text{Np}-\text{O}_{\text{ax}}$: 1.76-1.77 Å, $\text{Np}-\text{O}_{\text{eq}}$: 2.43-2.47 Å, $\text{Np}-\text{C}_\text{c}$: 2.87 Å, $\text{Np}-\text{C}_\text{i}$: 4.38 Å).

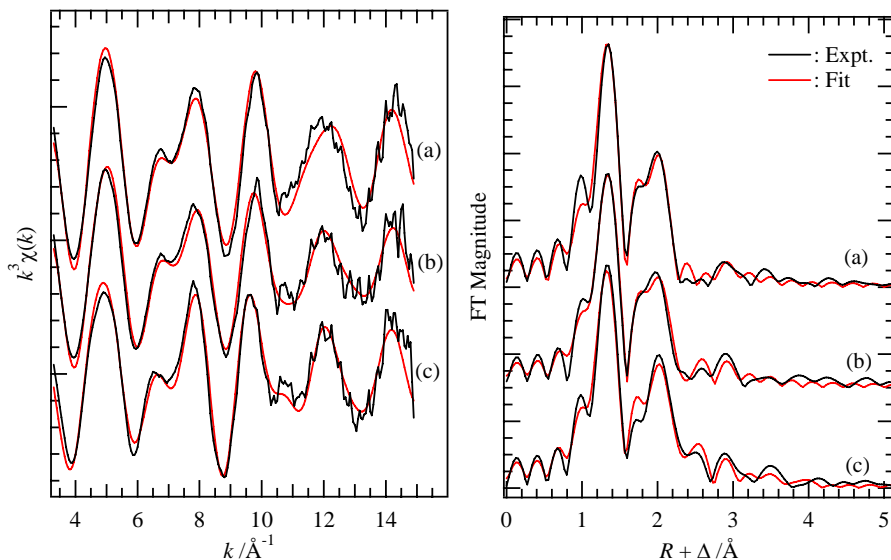


Figure 2. k^3 -weighted Np L_{III}-edge EXAFS spectra (left) and their Fourier transforms (right) of individual Np(VI) species: $\text{Np}^{\text{VI}}\text{O}_2^{2+}(\text{aq})$ (a), $\text{Np}^{\text{VI}}\text{O}_2(\text{AcO})^+$ (b), $\text{Np}^{\text{VI}}\text{O}_2(\text{AcO})_3^-$ (c).

Also, Np(V) forms complexes with acetate in 3 steps. The stability constants of $\text{Np}^{\text{V}}\text{O}_2(\text{AcO})(\text{aq})$, $\text{Np}^{\text{V}}\text{O}_2(\text{AcO})_2^-$, and $\text{Np}^{\text{V}}\text{O}_2(\text{AcO})_3^{2-}$ were determined by UV-Vis-NIR titration to $\log K_1 = 1.93 \pm 0.01$, $\log \beta_2 = 3.11 \pm 0.01$, $\log \beta_3 = 3.56 \pm 0.01$ at $I = 0.30 \text{ M}$ (H, NH_4) ClO_4 . The present result is corroborated by the structural information from EXAFS ($\text{Np}-\text{O}_{\text{ax}}$: 1.83-1.85 Å, $\text{Np}-\text{O}_{\text{eq}}$: 2.51 Å, $\text{Np}-\text{C}_\text{c}$: 2.90-2.93 Å) and electrochemical behavior of the Np(V/VI) redox couple in the presence of AcOH as a function of pH.

Reference

[1] Takao, K., Takao, S., Scheinost, A.C., Bernhard, G., Hennig, C.

Complex formation and molecular structure of neptunyl(VI) and -(V) acetates

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