Characterization of the nitrate complexes of Pu(IV) using absorption spectroscopy, ^{15}N NMR, and EXAFS

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Abstract

The nitrate complexes of Pu(IV) are studied in solutions containing nitrate at concentrations up to 13 molar (M) using absorption spectroscopy, ^{15}N nuclear magnetic resonance (NMR), and extended X-ray absorption fine structure (EXAFS). Four major nitrato complexes are observed and identified as $Pu(NO_3)^{3+}$, $Pu(NO_3)_2^{2+}$, $Pu(NO_3)_4$, and $Pu(NO_3)_6^{2-}$. The $Pu(NO_3)_3^{1+}$ and $Pu(NO_3)_5^{1-}$ complexes are not observed here and an upper limit of 0.10 can be set on the fraction for each of these species.

1. Introduction

The nitrate complexes of Pu(IV) in aqueous solutions were first studied in detail by Hindman [1] using absorption spectroscopy. Hindman used intensity variations in the absorption spectra at 476 nm to study the dominant species at 2 M nitric acid. The method used to assign the nitrate complex was very sensitive to the absolute magnitude of the molar absorptivity at 476 nm for both the hydrated Pu(IV) ion and the complex. Hindman adjusted the molar absorptivity of the complex by successive approximation to ensure that the absorption data fitted the model for the mononitrato complex and derived a value for the mononitrato stability constant of $\beta_1 = 2.9$. Hindman also identified two other major complexes: a hexanitrato complex that dominates at 13 M nitric acid and a species that appears near 8 M nitric acid, which he did not assign.

Numerous authors have determined stability constants for the mononitrato, dinitrato, and higher complexes of Pu(IV) at various ionic strengths and temperatures using extraction techniques [2–5]. A complete set of stability constants referenced to zero ionic strength has been compiled from the literature and used to model the distribution of species in ground water [6]. At 1.9 molal (m) ionic strength, values for the stability constants of $\beta_1 = 4.1$ and $\beta_2 = 6.5$ have been reported [5]. Using these values at 2.0 mol kg^{-1} nitric acid leads to a species distribution for the aquo, mononitrato, and dinitrato complexes of 0.03, 0.23, and 0.74. Three species should contribute to the absorption spectra studied by Hindman.

Modern instrumentation has made it possible for us to repeat the earlier absorption spectroscopy work in more detail and to reexamine the conclusions regarding the major nitrate complexes present in solution. Our work shows that two species are associated with the peak in the absorption spectra at 476 nm: the mononitrato and dinitrato species. We confirm that the hexanitrato species dominates at 13 M nitric acid (major absorption peak at 491 nm) and assign the species that appears at 8 M nitric acid to the tetranitrato species (major absorption peak at 483 nm).

2. Experimental

A stock solution of 70 g l^{-1} Pu(IV) in 7 M nitric acid was used in most cases. Carefully measured aliquots were added to solutions containing appropriate amounts of perchloric acid, nitric acid, and sodium nitrate so as to obtain the desired ionic strength and nitrate concentration. In some cases a stock solution of 100 g l^{-1} Pu(III) in 3 M perchloric acid was used, and the oxidation state of the plutonium in the resulting solution was adjusted electrochemically. In all cases, the oxidation state was monitored by absorption spectroscopy.

Absorption spectroscopy was done on a Perkin-Elmer Lambda 9 spectrometer using a 0.4 nm step size and a 0.4 nm slit width over the 400–900 nm range in most cases. Variable temperature, multinuclear magnetic resonance (NMR) was done on a Varian 300 MHz instrument. Extended X-ray absorption fine structure (EXAFS) experiments were performed at the Stanford Synchrotron Radiation Laboratory.

Absorption spectra of solutions containing more than one nitrato complex are analyzed to obtain the fraction of each species using SQUAD [7]. The observed spectra are assumed to be composed of (a) absorbances from various complexes that add linearly and (b) a constant background (this could arise, for instance, from irreproducible alignment of the cuvettes). The background term for each spectrum was removed by setting the mean values of the absorbance equal for all spectra.

3. Results and discussion

The absorption spectra of Pu(IV) in 6 M perchloric acid, and 1, 8 and 13 M nitric acid are shown in Fig. 1. The region between 450 and 500 nm shows the most systematic changes, with identifiable peaks at 469, 476, 483 and 491 nm dominating, respectively, in the four solutions. Similar absorption spectra taken at small increments in nitrate concentration show that these absorption features rise and fall in intensity and do not shift in position as the nitrate concentration increases. This behavior suggests that at least four separate Pu(IV) species exist in these solutions.

The species associated with the 469 nm peak has been previously assigned to hydrated Pu(IV) [8, 9]. Pu(IV) in solutions of perchloric acid ranging from 0.1 M to 7 M acid have identical spectra, consistent with the noncomplexing nature of the perchlorate anion. Thus, in 6 M perchloric acid the Pu(IV) is not complexed with perchlorate and the spectrum can only arise from hydrated Pu(IV).
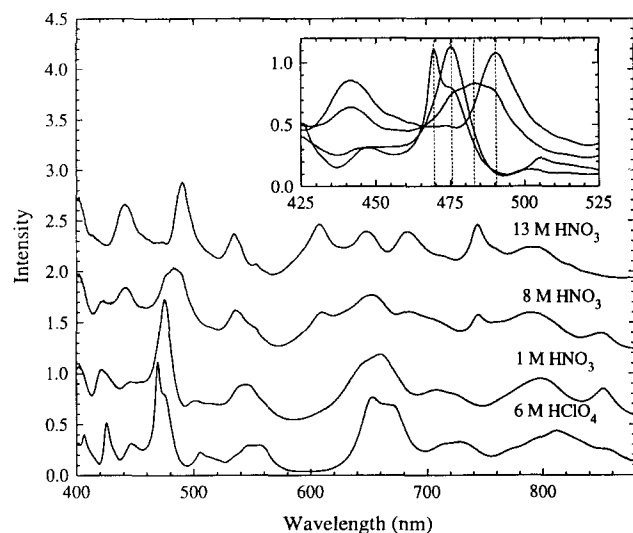
The hexanitrato complex is readily assigned to the species associated with the 491 nm peak in the absorption spectrum. The absorption spectrum of $TBA_2Pu(NO_3)_6$ (bistetrabutylammonium plutonium hexanitrate) solid is virtually identical with the spectrum of Pu(IV) in 13 M nitric acid [10]. The structure of the salts of plutonium hexanitrate derived from X-ray diffraction studies shows that the Pu is 12-coordinated to the oxygens of the six nitrates (each nitrate is bidentate) with the associated cations lying outside the inner coordination sphere [11]. Thus, the spectrum in 13 M nitric acid is due to hexanitrato complex with all of the nitrates complexed bidentate.

The species associated with the absorption feature at 476 nm are assigned by studying the nitrate dependence of absorption spectra at a constant ionic strength of 2.34 m. Sixteen solutions were studied with nitrate concentrations ranging from 0.000 to 0.718 m and Pu(IV) concentration of 0.00364 m. The fall of the 469 nm absorption feature of the aquo species and the rise of the 476 nm absorption feature with increasing nitrate concentration can be seen in Fig. 2. It is reasonable to conclude that two species give rise to the changes observed. However, closer examination of the region where all of these spectra cross reveals that there is not a true isobestic point, as would be expected if only two species were present. Instead, we observe two near-isobestic points. The first, at 472.3 nm, holds reasonably well up to $[NO_3^-] = 0.22$ m. The second begins to appear at $[NO_3^-] = 0.31$ m. These details are shown in the inset of Fig. 2, where the spectra are displayed over a wavelength range of 468–475 nm and an absorbance range of 0.10–0.18; the two vertical lines are at 471.2 and 472.3 nm. These observations suggest that at least three species are present in the range of nitrate concentration studied here.

The behaviour of the peaks at 420 and 425 nm also suggests three species are present. At 425 nm the peak height decreases monotonically for most of the spectra and stops changing for the last five spectra, whereas the peak at 420 nm shows little change in intensity for the first few spectra and large changes in intensity for the last five spectra. Qualitatively, this behaviour can be explained as follows. The molar absorptivity of the aquo and mononitrato species is similar at 420 nm and different at 425 nm while the molar absorptivity of the mononitrato and dinitrato species is different at 420 nm and similar at 425 nm. At low nitrate concentration the mononitrato concentration grows at the expense of the aquo species concentration; therefore, little change is observed at 420 nm while substantial changes are observed at 425 nm. At the higher nitrate concentrations the dinitrato species concentration starts to increase at the expense of the mononitrato species concentration; therefore, substantial changes are ob-

Fig. 1. Absorption spectra of Pu(IV) at a concentration of 4.8 g l^{-1} in 6 M perchloric acid, and 1, 8, and 13 M nitric acid. The spectra, obtained with 1 cm pathlength, are offset for clarity; the intensity scale is absorbance. The vertical dotted lines are at 469, 476, 483 and 491 nm.
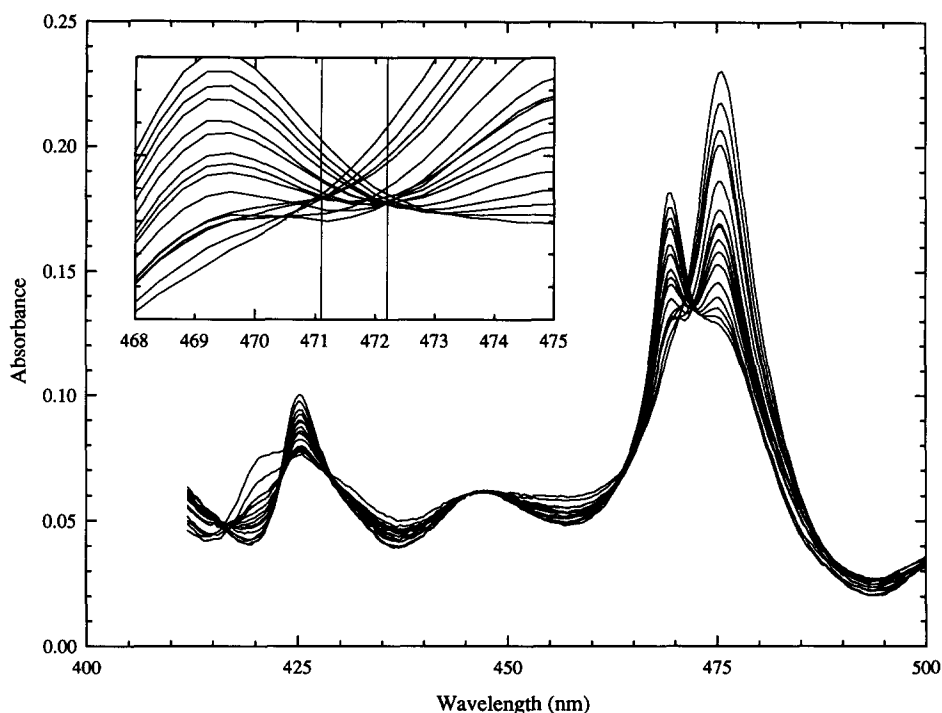
Fig. 2. The absorption spectra of Pu(IV) at 2.34 mol kg^{-1} ionic strength as a function of increasing nitrate concentration. The inset expands the 468–475 nm region to show more clearly the isobestic points near 471.2 and 472.3 nm.

served at 420 nm and little change is observed at 425 nm. Both the mononitrato and dinitrato species have their maximum molar absorptivity at 476 nm: hence the behavior of the absorption at that wavelength resembles the behavior one would expect for a single species. Mathematically, a fit of the spectra to two species yields a substantially larger goodness-of-fit

$$GOF = \sum_{j=1}^{m} \sum_{i=1}^{N} (A_{obs} - A_{calc})^2$$

where m is the number of spectra and N is the number of wavelengths, $GOF = 3400$, than a fit to three species, $GOF = 1960$ (a perfect fit would yield $GOF = 0$). Therefore, we conclude that three species are observed in this nitrate concentration range and they are the aquo, mononitrato, and dinitrato species.

With respect to the species associated with the 483 nm peak in the absorption spectrum, identification using absorption spectroscopy alone is difficult. NMR experiments were used to study the nitrate complexes more directly. Thorium was used as a surrogate for plutonium because Th(IV) also forms hexanitrato anionic complexes, and the crystal structures of thorium tetranitrato and hexanitrato salts are isomorphic with the crystal structures of the plutonium tetranitrato and hexanitrato salts [11]. A series of ^{15}N NMR spectra was obtained in a solvent of deuterated acetone and CFCl$_3$ at -100 °C. As the nitrate-to-thorium ratio

increased, new NMR peaks appeared and grew as previous ones diminished (see Fig. 3).

The assignment of each peak to a specific nitrato complex was made by the dependence of the integrated intensities on the nitrate-to-thorium ratio shown in Fig. 4. First, the order of the appearance of the peaks with increasing nitrate-to-thorium ratio gives the order of the complexes with increasing number of nitrates. Second, because the thorium concentration is constant, the intensities are directly related to the number of
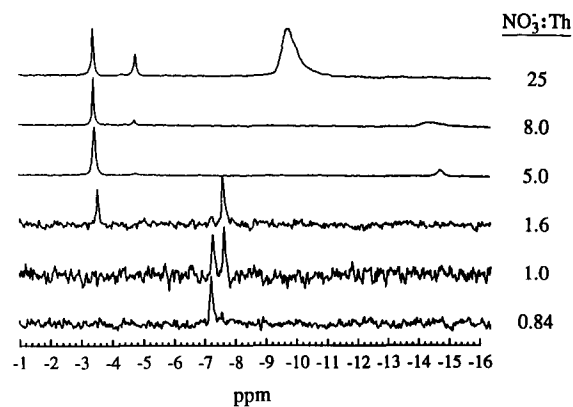

Fig. 3. NMR spectra of ^{15}N-labeled NO$_3^-$ shows the presence of four thorium nitrato complexes with shifts at -7.2, -7.6, -3.4, and -4.8 ppm. Free nitrate first appears at a nitrate-to-thorium ratio of 5.0 at -14.8 ppm and shifts to -9.6 ppm as the ionic strength of the solution increases.
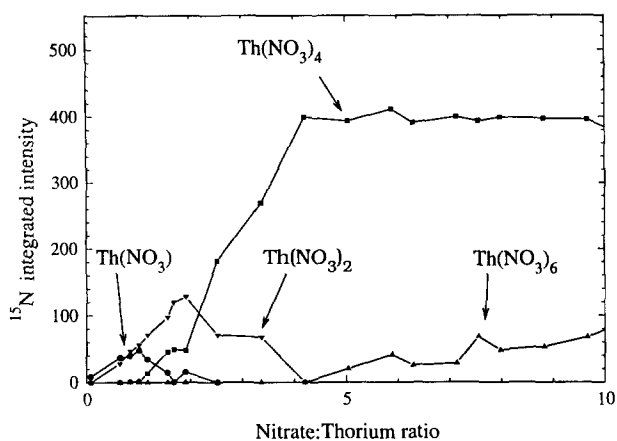
Fig. 4. The integrated intensity of the four ^{15}N NMR peaks shown in Fig. 4 versus the nitrate-to-thorium ratio. The changes in the intensities lead to an unambiguous assignment as shown.
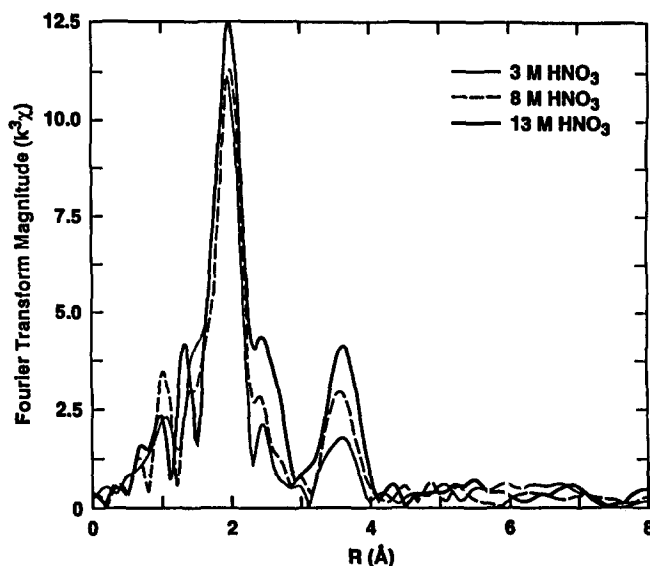

Fig. 5. Radial distribution function from EXAFS data for Pu(IV) in 3, 8, and 13 M nitric acid. The magnitude of the Fourier transform of the raw data is shown. The x-axis origin is arbitrary.

nitrates associated with each complex. Four nitrato complexes were observed; these were assigned to $Th(NO_3)^{3+}$, $Th(NO_3)_2^{+2}$, $Th(NO_3)_4$, and $Th(NO_3)_6^{-2}$ (no peaks due to the tri- and pentanitrato complexes were observed). The slow rise of the hexanitrato complex is due to competition with the water accompanying the nitrate (the nitric acid reagent always had water present). To eliminate this effect, anhydrous samples of thorium nitrate were prepared by adding stoichiometric amounts of TBAN (tetrabutyl ammonium nitrate) to $Th(NO_3)_4$ salts dissolved in CD_3CN. At nitrate-to-thorium ratios of 4, 5 and 6, the ratio of the tetranitrato peak to the hexanitrato peak was observed to be 1.0:0.0, 0.5:0.5, and 0.0:1.0 respectively.

When the analogous anhydrous experiment was carried out for plutonium, no ^{15}N peak was observed at a ratio of 4:1, but a peak was observed at -96.5 ppm at both 5:1 and 6:1 ratios, the latter being twice as strong as the former. The lack of any observable ^{15}N signal for the plutonium tetranitrato species may be due to changes in the electronic structure of the plutonium caused by the complexing ligands. Such behavior has been observed in cobalt [12]. The tetranitrato species may be more paramagnetic, thereby strongly perturbing the ^{15}N signal. This could result in a broadening of the signal to the extent that it would be lost in the noise. Taken together, these observations suggest that the tri- and pentanitrato complexes for plutonium may not exist to any appreciable extent and that the species associated with the 483 nm peak in the plutonium absorption spectrum arises from the tetranitrato species.

EXAFS spectra of Pu(IV) were obtained in nitric acid solutions of 3, 8 and 13 M. Pu concentration was 0.025 M in all cases. Initial results (not corrected for the phase shifts associated with nitrogen and oxygen) are shown in Fig. 5. Three peaks representing the inner coordination sphere dominate the spectra (oscillations

preceding the largest peak are artifacts). Beyond the third peak there is no structure, i.e. no order exists beyond the first coordination sphere, as expected for an ion in solution. Preliminary analysis indicates that the first peak arises from the oxygens closest to the Pu cation, the second peak occurs at a distance of 0.5 Å from the first peak, and the third peak occurs at a distance of 1.2 Å from the second peak. These distances are consistent with a bidentate nitrate anion. The nitrogen in nitrate is at 0.45 Å beyond the bridging oxygens and the lone oxygen in nitrate is at 1.20 Å from the central nitrogen [10].

The intensities of peaks occurring at the same distance and assigned to the same element can be compared to obtain the ratios of the number of atoms. Intensities of peaks that occur at different distances, even if assigned to the same element, cannot be directly compared without a detailed analysis (currently under way). The intensity of the third peak arises from the apical oxygen of a nitrate species and can be used to count the number of nitrates bound to Pu. The observed intensities are in a ratio of 6:4.4:2.6. Using the distribution of Pu nitrato species obtained from absorption spectra, the expected ratio would be 6:4.3:2.5. The intensity of the second peak is due mainly to the nitrogens in the complexed nitrates; they follow the ratio of the intensities of the third peak. The intensities of the first peak represent the number of closest oxygens. In the 13 M solution the inner coordination sphere consists of six bidentate nitrates with 12 closest oxygens. Taking the peak height of the 13 M spectrum as representing 12 oxygens, the average number of oxygens closest to the plutonium in both the 8 M and 3 M solutions is 11.

This implies that the hydration number is 7 for the dinitrato species and 3 for the tetranitrato species. Solid plutonium tetranitrate pentahydrate has three waters in the inner coordination sphere [11]. Thus, for the tetranitrato species, the solid and the solvated ion appear to have the same number of waters in the inner coordination sphere.

4. Summary

Four spectroscopically distinct Pu(IV) nitrato species are observed in absorption spectra of nitrate containing solutions of Pu(IV). Identification of these three species as the mononitrato, dinitrato, tetranitrato, and hexanitrato complexes of Pu(IV) provides a consistent interpretation of experimental data from three distinct experimental methods. The structure of the nitrate complexes was found to be similar to solid plutonium nitrate compounds with the nitrates bound bidentate.

Acknowledgments

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