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THE COMPLEXATION BEHAVIOR OF NEPTUNIUM AND PLUTONIUM WITH NITRILOTRIACETIC ACID

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Abstract

The first stability constant of NpO_2^+ with nitrilotriacetic acid (NTA) was determined at four ionic strengths (0.5, 1.0, 2.0, 3.0 M) using spectrophotometry. Nonlinear least-squares data fitting identified the complex as NpO_2NTA^{2-}. The Specific Ion Interaction Theory (S.I.T.) approximation method was used to determine the stability constants at infinite dilution. First results on Pu^{4+} and PuO_2^{2+} complexation with NTA are reported. The stability constant for the $Pu(NTA)^+$ complex at $I = 0.1$ M strength is given. From results for PuO_2^{2+} complexation with NTA ($I = 1$ M) at $pH < 3$, the stability constant was derived for PuO_2NTA^-. At $pH > 3$, NTA partially reduced PuO_2^{2+} to PuO_2^+.

History

The U.S. Department of Energy (DOE) has initiated efforts to identify, assess, prevent, and remediate possible environmental impacts of wastes at DOE operated nuclear production sites (1, 2). The inventories are large, and the wastes generated come from the large-scale production of plutonium, which includes fabrication, irridiation, and subsequent chemical processing of nuclear fuel.

The production chronology is determined by three major reprocessing strategies: the Bismuth Phosphate Process (3), the Hexone Process (4), and the Tributyl Phosphate Process (5). The Bismuth Phosphate Process was first used in the pilot plant at the Clinton Works (later the Oak Ridge National Laboratory) and was then transferred to the first industrial plutonium production plant at Hanford, Washington. Used until 1951, this process depended upon differences in coprecipitation behavior of Pu^{4+} and PuO_2^{2+} with $BiPO_4$ to separate plutonium from uranium and fission products. Pu^{4+} was precipitated with $BiPO_4$, while uranium and fission products remained in solution. Then the precipitate was dissolved, the Pu^{4+} oxidized to PuO_2^{2+}, and the precipitation repeated. The plutonium remained in solution while the impurities precipitated. Six such precipitation and dissolution cycles were carried out, followed by two lanthanum fluoride precipitations for further product refining and concentration. The yield was about 90%. The major disadvantages of this process were the discontinuous operation mode, relatively large losses of plutonium (5%), and very large waste streams, because the uranium was not separated from the fission products. This led to the development of the Hexone Process, which allowed continuous mode operations and simultaneous recovery of uranium and plutonium. It was used at the Hanford Redox Plant between 1951 and 1960. The Hexone Process, also known as the Redox Process, used the commercial solvent hexone (methyl isobutyl ketone) as the extraction agent. Hexone extracts Pu^{4+}, PuO_2^{2+}, and UO_2^{2+}, but it does not extract Pu^{3+}. Alternating oxidation and reduction steps were used to separate plutonium from uranium. The disadvantage of this process was the chemical instability of hexone, which required the use of large quantities of aluminum nitrate as a "salting agent." This resulted in large radioactive waste streams which could not be further concentrated for waste minimization. These shortcomings were recognized early on and led to the development of the Purex Process (Plutonium Uranium Reduction Extraction Process), which uses tributyl phosphate as the extractant and does not require a "salting agent." It was first employed in 1954 at the Savannah River Plant, Aiken, South Carolina. A second production plant followed in 1956 at Hanford, Washington.

The wastes generated by these processes and associated operations, such as decontamination and decommissioning, were discharged into disposal pits and ponds or directly into the soil (soil column technique). Furthermore, decommissioned equipment was disposed of in landfills, and numerous decommissioned contaminated buildings exist.

The chemical nature of the waste is manifold and consists of synthetic inorganic and organic materials. They include both nonradioactive and radioactive organic and inorganic compounds in liquid or solid form. The wastes present in the subsurface represent a large source for potential environmental release via groundwater transport. There is a great need to identify, assess, prevent, and remediate possible environmental impacts. The contaminant migration rate through the subsurface is controlled by many physical and chemical processes. Profound knowledge of many thermochemical parameters, such as solubility, complexation, and speciation of possible waste compounds, is essential to predict accurately their concentrations and release rates for risk assessment and remedial action studies. Existing thermodynamic data bases that are being used as input for predictive transport modeling are either incomplete or completely lack data on most mixed organic-radionuclide waste complexes and compounds.

Project Orientation

We initiated a study to provide fundamental knowledge on the basic chemical processes that occur between radionuclides and synthetic organics present in mixed organic-radionuclide wastes at DOE sites. This knowledge will increase understanding and allow more accurate predictions of the processes that control contaminant mobilization and movement in the subsurface.

We are studying thermodynamic complexation constants, solution speciation, and the solubility of complexes and compounds that can form between radionuclides and organic constituents of mixed organic radionuclide wastes. The study focuses on the reactions of neptunium and plutonium with organic facilitators. Facilitators are organic compounds that interact with the radionuclides and modify their geochemical behavior; for example, aliphatic and aromatic organic acids, chelating agents and fragments, solvents, and diluents (6). Chelator fragments are generated in the waste by degradation of the chelating agents, which can degrade through radiolytic, thermal, or chemical influence. The fragments may be as important in complexing and mobilizing waste radionuclides of mixed organic wastes as the chelating agents themselves. Because many of the wastes were stored over long times (up to 45 years), the concentration of the degradation products can exceed the concentration of the initially present chelating agents.

Very little information is available in the literature on the thermodynamic solution properties of actinide ions with organic facilitators. Table I lists a survey of available complexation data for the most prominent ions of neptunium and plutonium with the chelators nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA), the chelator fragment iminodiacetic acid (IDA), the aliphatic organic glycollic acid, and the aromatic organic benzoic acid (7–11). The data are given as complex stability constants β_n. Three important facts can be concluded from Table I.

First, no data whatsoever are available for many of the listed actinide-organic complexes. This clearly shows the urgency to produce these data in order to increase our understanding and predictive capabilities for these metal organic contaminant systems.

Second, the available data given in Table I are inconsistent for several complexes. For example, two different values of $10^{-25.6}$ and $10^{-17.66}$ are given for the stability constant of the 1:1 Pu^{4+}-EDTA complex. The difference between these two values of about eight orders of magnitude is very significant and unacceptable, because no meaningful predictions about the solution behavior of plutonium-EDTA complexes can be made from such uncertain data. Even a much smaller discrepancy of data, as it exists for the PuO_2^{2+}-EDTA complex ($\log\beta_1(0.1) = 14.6$ and 16.4), still presents a significant and unacceptable uncertainty, representing a factor of 63 in complexing strength.

Third, most of the data are only available for a very limited range of ionic strength conditions. Stability constants, however, are very dependent on the ionic strength of the solution in which the metal organic complex is formed. For example, the stability constant for the 1:1 neptunyl(V)–EDTA complex decreases from $10^{10.77}$ to $10^{7.33}$ when the ionic strength changes from the hypothetical state of infinite dilution (zero) to a concentration of 0.1 M; this is a decrease of about 2754-fold. The available limited information on the ionic strength dependence of the stability constants poses an important problem for the modeling effort of "real world" contamination. In real contaminant scenarios, the ionic strength of contaminant solutions can vary over a wide range (up to several moles per liter) due to the presence of salts and other co-contaminants. The stability constants for the metal-organic complexes, however, are at best available up to 1 M; many other data are known only for very dilute concentrations of 0.1 M. This makes it very difficult to perform accurate modeling calculations for predicting contaminant concentrations and speciation. Commonly, data on complex stability, determined at a certain ionic strength, is extrapolated to the ionic strength of the system to be modeled. This can lead to wrong constants as input for the modeling calculations, because the extrapolation often cannot approximate the actual conditions. Therefore, the model mispredicts solution and species concentrations. Having complex stability constants available for a range of different ionic strengths improves the accuracy of predicting contaminant and species concentrations at contaminated sites, because the constants can be used directly without the extrapolation process.

Additionally, we are using the Specific Ion Interaction Theory (S.I.T.) for these data. The S.I.T. is an approximation method to obtain fairly accurate estimates for stability constants at infinite dilution and an ion interaction parameter from stability constants determined at ionic strengths up to 3 M (12–15). The Nuclear Energy Agency (NEA) of the Organization of Economic Cooperation and Development (OECD) has accepted the S.I.T. method for their expert review of thermodynamic solution data, and they have published guidelines on the application of this method (16). We have successfully used this method to determine stability constants for the carbonate systems of Am^{3+} (17) and NpO_2^+ (18). We are interested if this method can also be applied to metal-organic co-contaminant complex systems.

In this paper, we are describing first efforts to determine the complex formation constants of NpO_2^+, Pu^{4+}, and PuO_2^{2+} with nitrilotriacetic acid. The spectrophotometric measurements are conducted as a function of pH and ionic strength, ranging from 1 to 7 and from 0.5 M to 3 M, respectively.

Experimental Approach

The spectrophotometric investigations are based on the fact that the neptunium and plutonium ions show relatively strong light absorption in the wavelength range from 400 to 1000 nm. The formation of actinide-organic complexes causes gradual shifts of the absorption maxima to higher wavelengths. At sufficiently small concentrations of organic complexing agent, the shifted absorption peak(s) consist(s) of two absorption bands: one from the uncomplexed actinide ion and (at least) one second band from the organic-actinide complex. We study the peak shifts as a function of the concentration of the organic ion and determine the formation constants using the peak-fitting program SQUAD (19). SQUAD calculates the best values for the stability constants and molar absorptivities of the assumed model by using a nonlinear least-squares approach.

We used a portable computer-controlled spectrophotometer (Guided Wave Inc., model 260) that has remote sensing capability through fiber optics. Details of the instrument are described elsewhere (17).

The pH was measured with a pH meter (Orion Research Inc., model 321) and a semimicro Ross combination electrode (Orion Research Inc., model 810300). The 3 M KCl electrolyte of the reference electrode was replaced by carbonate-free 3 M NaCl to avoid precipitation of insoluble $KClO_4$ at the reference junction. The electrode's response is calibrated in concentrations (not activity) of hydrogen ion ($pcH = -\log[H^+]$). The calibration is performed at each ionic strength by titrating standardized $HClO_4$ (GFS Chemicals) with standardized carbonate free NaOH (J.T. Baker Inc.); both were adjusted to the proper ionic strength with $NaClO_4$ (GFS Chemicals). $NaClO_4$ was also used for all other ionic strength adjustments.

The neptunium and plutonium stock solutions were prepared from $^{237}NpO_2$ and $^{239}PuO_2$, respectively. After purification through anion-exchange chromatography, the solutions were converted to perchlorate by repeated fuming with $HClO_4$ to near dryness and dissolution of the residue in $HClO_4$. Electrochemical oxidation state adjustments at a platinum electrode yielded NpO_2^+, Pu^{4+}, and PuO_2^{2+} solutions. Neptunium and plutonium concentrations were determined from acidified aliquots by counting the 29.38 keV photon and the uranium *L* X-rays (20) with a germanium detector (LBL design), respectively. The maximum calculated error in the measured concentrations was below 4% (2σ).

Nitrilotriacetic acid (Baker Analyzed, J. T. Baker Inc.) was used without further purification. All measurements were performed under argon with carbonate-free solutions at 23 ± 1.5°C.

Results and Discussion

Neptunium(V)

The absorption band of uncomplexed NpO_2^+ possesses a well-established maximum at 980.0 nm with a molar absorptivity of 395 M^{-1} cm^{-1} (21). The addition of NTA and the gradual increase in pH from about 1 to 9 resulted in a decrease of the 980 nm band, and a new band appears at 990.2, coming from the neptunyl(V)–NTA complex formation. Figure 1 shows thirteen spectra of neptunium(V) (each 3.4×10^{-3} M) with different NTA^{3-} concentrations ($0–3 \times 10^{-6}$ M). The analytical NTA concentration was 5.8×10^{-3} M; the change in NTA^{3-} concentration was obtained by varying the pH from 2.37 to 6.79. The ionic strength was held constant at 2 M. The spectra are representative for the results from additional measurements at ionic strengths of 0.5, 1.0, and 3.0 M. The data analysis using the nonlinear least-squares fitting routine SQUAD requires the assumption of an equilibrium model to calculate the best values for the stability constants. The calculated standard deviation in the absorbance data provides an overall measure of the fit of the model to the data. The data were analyzed using either NTA^{3-} or $HNTA^{2-}$ or H_2NTA^- as the complexing ligand that can form a 1:1 complex with NpO_2^+. The isosbestic point of the spectra indicates that only two independent species are involved in the equilibrium: free and complexed neptunium(V). This assumes, however, that no higher complexes (e.g., 1:2) have the same molar absorptivities as the 1:1 complex. The NTA protonation constants used with the fitting routine are shown in Table II; they were determined by an associated study (22). Excellent fits were obtained with NTA^{3-} for all four different ionic strength solutions. Using $HNTA^{2-}$ as the ligand, the fits were poor for the 1, 2, and 3 M solutions with standard deviations up to a hundred times higher than those for NTA^{3-} calculations. No convergence was reached for the 0.5 M solution. The fitting did not improve when only the data in the more acidic range from pH 2.4 to 5 were used, where the $HNTA^{2-}$ species is prevalent. We also did not obtain convergence with the H_2NTA^- complexation model. From these results we conclude that NTA^{3-} is the complexing ion. The complex stability constants for $NpO_2\,NTA^{2-}$ are listed in Table III. Also included are the result for infinite dilution and the respective interaction parameter ε; both were determined with the S.I.T. approximation method.

The S.I.T. describes the activity coefficient in two terms: the Debye-Hückel term, which describes the electrostatic long-range interactions in dilute solution, and the ion-specific nonelectrostatic short-range interaction, which shows little or no variation for many ions up to 3 M. The activity coefficient γ_j of an ion with the charge z_j in a solution of ionic strength I can be expressed as

$$\log\gamma_j = -z_j^2 D + \sum_k \varepsilon(j,k)\, I_m \qquad [1]$$

where $D = 0.5109\sqrt{I}/(1 + 1.5\sqrt{I})$ is the Debye-Hückel term at 25°C and $\varepsilon(j,k)$ is the interaction coefficient of ion j with ion k; the summation extends over all ions k present in solution with the molality m_k. The interaction coefficients ε are zero for ions of the same charge sign and for uncharged species. Introducing Eq. 1 into the expression for the stability constant β and rearranging gives

$$\log\beta(I) - \Delta z^2 D = \log\beta(0) - \Delta\varepsilon I_m \qquad [2]$$

where $\Delta\varepsilon$ and Δz^2 are the differences in the interaction coefficient and the squared ionic charges, respectively. For the equilibrium

$$NpO_2^+ + NTA^{3-} = NpO_2NTA^{2-} \qquad [3]$$

the S.I.T. expression is

$$\log\beta_{101}(I) + 6D = \log\beta_{101}^0 - \Delta\varepsilon\, I_m \qquad [4]$$

with $\Delta z^2 = z^2_{NpO_2NTA^{2-}} - z^2_{NpO_2^+} - z^2_{NTA^{3-}} = -6$

and $\Delta\varepsilon = \varepsilon(NpO_2NTA^{2-}, Na^+) - \varepsilon(NpO_2^+, ClO_4^-) - \varepsilon(Na^+, NTA^{3-})$. From the plot of $\log\beta_{101}(I) + 6D$ against the ionic strength I (in mole/kg), we obtain the formation constant

$\log\beta^0_{101}$ at infinite dilution as the intercept and $\Delta\varepsilon$ as the slope. The data for this plot are also listed in Table III. The $1/\sigma^2$ weighted regression lines for the S.I.T. plots yield $\log\beta^0_{101} = 6.93 \pm 0.01$, with $\Delta\varepsilon = -0.22 \pm 0.01$. The interaction parameter $\varepsilon(NpO_2NTA^{2-}, Na^+) = 0.02 \pm 0.14$ was calculated from $\Delta\varepsilon$ and published values for $\varepsilon(NpO_2^+, ClO_4^-) = 0.25 \pm 0.05$ (16), and $\varepsilon(NTA^-, Na^+) = -0.01 \pm 0.05$ (16).

The degree of linearity of the S.I.T. plots indicates the range of validity for this approximation method. The regression line for $NpO_2(NTA)^{2-}$ fits quite well (R = 0.9934) and lends confidence to the derived β^0_{101} value. Several literature values are available for the stability constants of the neptunium(V)–NTA system at 0.1, 0.5, and 1.0 M ionic strengths. They are summarized in Table IV. Our value at I = 1.0 is somewhat larger than the value derived by Stöber (24). The value of Rizkalla et al. (25) appears too high in light of our results at I = 0.1 M and 0.5 M and of those obtained by Eberle and Wede (23) at I = 0.1 M. The good agreement of our extrapolated stability constant at infinite dilution, $\log\beta^0_{101} = 6.93 \pm 0.01$, with Eberle and Wede's value at I = 0.1 M, $\log\beta_{101} = 6.80 \pm 0.10$, lends confidence to the validity of the S.I.T. approximation for this system. Including the additional literature values at I = 0.1 M and 1.0 M in the S.I.T. treatment gives $\log\beta^0_{101} = 6.91 \pm 0.01$ (R = 0.9846).

All authors agree that the complex formed is NpO_2NTA^{2-}. Eberle and Wede and Rizkalla et al. also report the existence of a NpO_2HNTA^- complex, but they show no conclusive evidence for the coexistence of this specie with NpO_2NTA^{2-}.

Plutonium

We performed preliminary scoping studies of NTA complexation with Pu^{4+} and PuO_2^{2+}.

Plutonium(IV)

Figure 2 shows five absorption spectra of Pu^{4+} (each 1.5×10^{-3} M) with different NTA^{3-} concentrations ($0 - 3.1 \times 10^{-14}$) at 0.1 M ionic strength. The NTA concentration was gradually varied from 0 to 9.1×10^{-4} M while the pH was held constant at 1.1. Measurements cannot be performed at higher pH because the Pu^{4+} ion will form Pu(IV) colloids and Pu(IV) polymer precipitate. Pu^{4+} hydrolysis was considered in the calculation using the published value for the first hydrolysis constant ($Pu^{4+} + H_2O = PuOH^{3+} + H^+$, $\log Q_{11} = -1.53$) (26). Nonlinear least-squares fitting of the spectra yielded good fits for $PuNTA^+$ and $PuHNTA^{2+}$ with $\log\beta_{101} = 12.86 \pm 0.03$ and $\log\beta_{111} = 13.83 \pm 0.04$, respectively. No convergence was reached with higher protonated ligands. No data on Pu^{4+}–NTA complexation are available from the literature. Data on the oxidation state analogue Th^{4+} show the formation of $ThNTA^+$ and not $ThHNTA^{2+}$. The published values for $\log\beta_{101}$ are (1) 12.4 (I = 0.1 M KNO_3, 20°C) (27), (2) 13.15 (I = 0.1 M $NaClO_4$, 25°C) (28), and (3) 16.9 (I = 0.1 M $NaClO_4$, 20°C) (29). Our value agrees well with the values of Courtney et al. and of Skorik et al. In light of these results, Bottari and Anderegg's value, determined from potentiometric measurements, appears to be too high. We are currently studying the Pu^{4+} complexation with NTA as a function of ionic strength, varying from 0.5 to 3.0 M.

Plutonium(VI)

We studied PuO_2^{2+} complexation with NTA at 1.0 M ionic strength in the pH range from about 1 to 6. The PuO_2^{2+} and the analytical NTA concentrations were held constant for all experiments at 1.5×10^{-3} M and 2.5×10^{-3} M, respectively. Depending on the pH, different results were obtained.

From pH 1.92 to 2.55, the PuO_2^{2+} absorption band at 830 nm decreased with increasing NTA concentration and an absorption band at 842 nm increased. The spectra are shown in Figure 3. The data treatment by SQUAD indicated that complexation by either NTA^{3-} or $HNTA^{2-}$ may have occurred. The data fitted the model for PuO_2NTA^- or PuO_2HNTA complexing to give the stability constants $\log\beta_{101} = 9.84 \pm 0.02$ or $\log\beta_{111} = 11.76 \pm 0.01$, respectively. Starý and Prásilová report for the analogous UO_2^{2+} the formation of the UO_2NTA^- complex (30). They derived $\log\beta_{101} = 9.56 \pm 0.03$ and 9.41 ± 0.04 from extraction and ion-exchange data, respectively. No evidence was found for the formation of the protonated complex. We therefore propose PuO_2NTA^- as the predominant complex in our solution.

At pH 3.25, three absorption bands were present, as shown in Figure 4: one at 830.0 nm from the uncomplexed PuO_2^{2+}, a second at 840.6 nm indicating PuO_2^{2+}–NTA complexation, and a third at 569.0 nm representing uncomplexed PuO_2^{+}. Part of the PuO_2^{2+} was reduced by NTA to PuO_2^{+}. Figure 5 shows the spectra of the same solution after 15, 30, 45, 60, and 75 minutes. Both peaks decreased with time, and the PuO_2^{+} peak at 569 nm increased (not shown). The pH also increased with time, from pH 3.25 to pH 3.47 after 75 minutes. When we changed the pH from 3.47 to pH 5.95, the band at 830 nm disappeared, the PuO_2^{2+} – NTA complexation peak increased significantly, and the PuO_2^{+} peak showed no further change. We are continuing to study this phenomenon in order to determine the conditions, kinetics, and mechanisms for the reduction of PuO_2^{2+} by NTA.

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Table I. Survey of available complex formation constants for selected actinide-organic species (7–11).

	NpO_2^+	Pu^{4+}	PuO_2^+	PuO_2^{2+}
NTA	$\beta_1(.1) = 6.80$ $\beta_1(1.) = 5.85$ $\beta_2(1.) = 6.77$	N/A	$\beta_1(.1) = 6.31$	N/A
IDA	$\beta_1(.1) = 6.27$ $\beta_1(1.) = 5.50$ $\beta_2(.1) = 6.79$	N/A	$\beta_1(.1) = 6.18$	N/A
EDTA	$\beta(0) = 10.77$ $\beta_1(.05) = 9.70$ $\beta_1(.1) = 7.33$	$\beta_1(.1) = 25.6$ $\beta_1(.1) = 17.66$	$\beta_1(0) = 10.89$ $\beta_1(0.5) = 10.17$ $\beta_1(.1) = 12.9$	$\beta_1(.1) = 14.6$ $\beta_1(.1) = 16.4$
Glycollic Acid	$\beta_1(0) = 1.90$ $\beta_1(.1) = 1.51$ $\beta_1(.2) = 1.60$ $\beta_1(1.) = 1.39$ $\beta_2(1.) = 1.68$	N/A	N/A	$\beta_1(.1) = 2.43$ $\beta_2(.1) = 3.79$
Benzoic Acid	$\beta_1(1.) = 0.80$ $\beta_2(1.) = 0.17$	N/A	N/A	N/A

$\beta_1(.1) = 5.85$ means $\log\beta$, at 0.1 M ionic strength.

Table II. Protonation constants for NTA at 25°C and various ionic strengths (22).

I(M)	pK_1*	pK_2**	pK_3***
0.5	8.99	2.35	1.87
1	8.96	2.37	1.85
2	9.08	2.46	1.78
3	9.35	2.64	1.96

$^{*}K_1 = \frac{[HNTA^{2-}]}{[H^+]\,[NTA^{3-}]}$; $^{**}K_2 = \frac{[H_2NTA^-]}{[HNTA^{2-}]\,[H^+]}$; $^{***}K_3 = \frac{[H_3NTA]}{[H_2NTA^-]\,[H^+]}$

Table III. Stability constants at various ionic strengths for the NpO_2^+ - NTA system and parameters for S.I.T. plots.

I_m	D	$\log\beta_{101}(I)$	$\log\beta_{101}(I) + 6D$
0.5128	0.1764	5.949 ± 0.010	7.008 ± 0.012
1.0499	0.2064	5.966 ± 0.010	7.204 ± 0.012
2.207	0.2351	5.995 ± 0.002	7.406 ± 0.003
3.4956	0.2511	6.175 ± 0.010	7.681 ±0.013

$\log\beta_{101}\ \{NpO_2NTA^{2-}\} = 6.93 \pm 0.01$

$\varepsilon\{NpO_2NTA^{2-}, Na\} = 0.02 \pm 0.07$

Table IV. Stability constants for NpO_2^+ complexation with NTA.

Method	*I*(M)	$\log\beta_{101}$	$\log\beta_{111}$	Reference
Spectrophotometry	0	6.91± 0.01	–	this work
	0.5	5.95 ± 0.01	–	
	1.0	5.97 ± 0.01	–	
	2.0	6.00 ± 0.01	–	
	3.0	6.18 ± 0.01	–	
Spectrophotometry	0.1	6.80 ± 0.10	1.77 ± 0.37	Eberle and Wede (23)
Spectrophotometry	1.0	5.85 ± 0.01	–	Stöber (24)
pH titration	0.5	7.51 ± 0.03	13.46 ± 0.05	Rizkalla et al. (25)

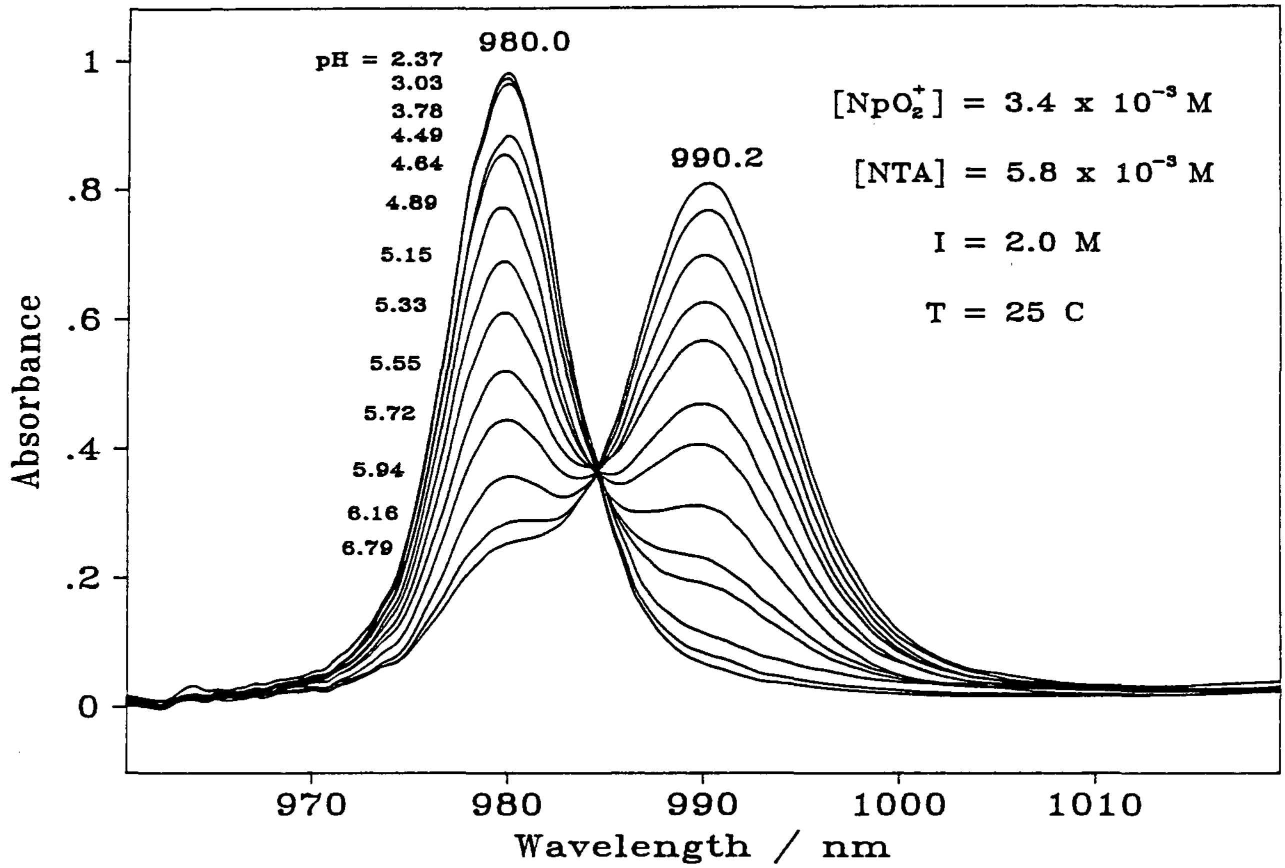

Figure 1. Absorption spectra of neptunium(V)–NTA solutions; $[NpO_2^+] = 3.4 \times 10^{-3}$ M, [NTA] = 5.8×10^{-3} M, pH = 2.37 – 6.79, I = 2 M.

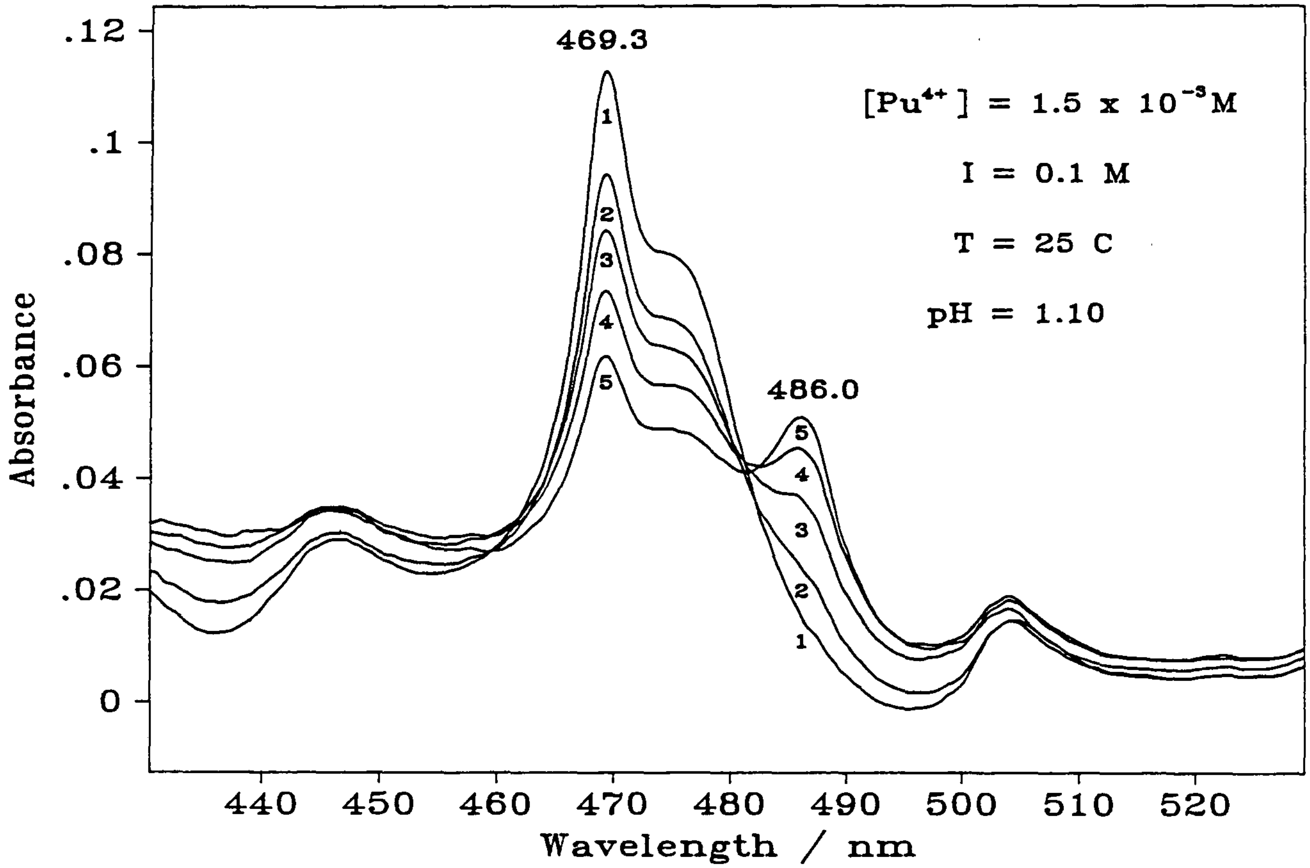

Figure 2. Absorption spectra of plutonium(IV)–NTA solutions; $[Pu^{4+}] = 1.5 \times 10^{-3}$ M; the NTA concentrations are (1) 0 M, (2) 2.4×10^{-4} M, (3) 4.8×10^{-4} M, (4) 7.0×10^{-4} M, and (5) 9.1×10^{-4} M.

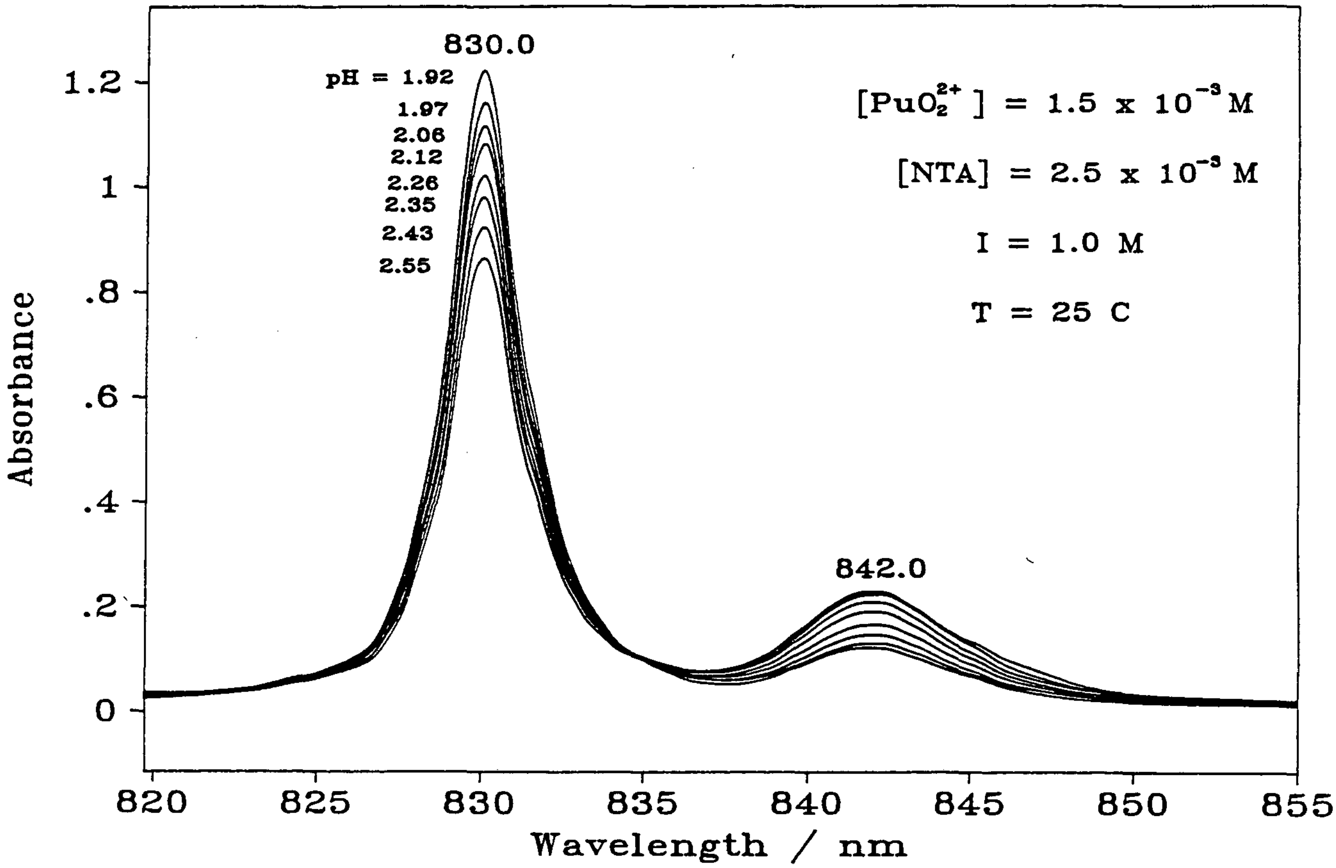

Figure 3. Absorption spectra of plutonium(VI)–NTA solutions; [PuO_2^{2+}] = 1.5 × 10^{-3} M, [NTA] = 2.5 × 10^{-3} M.

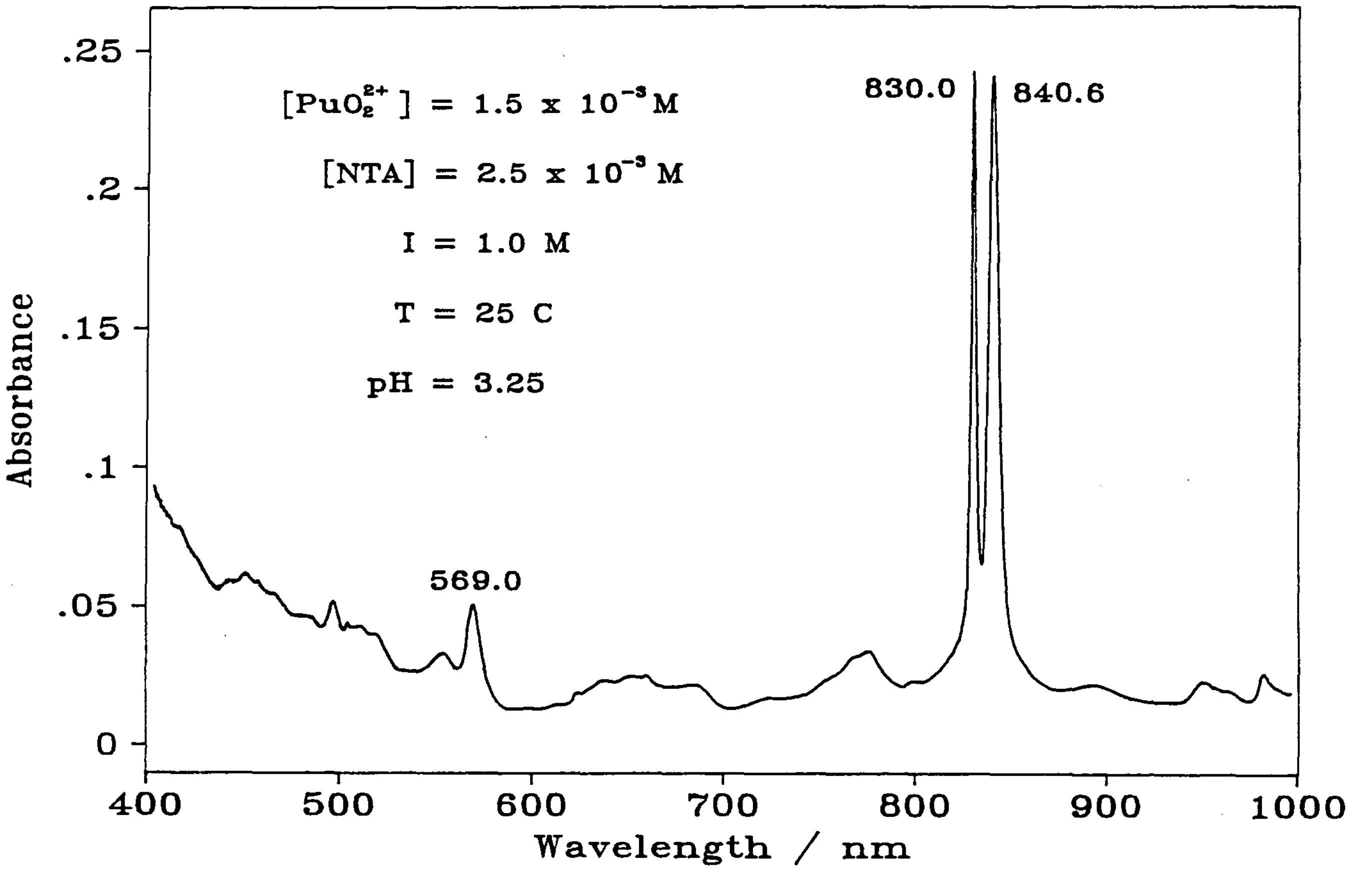

Figure 4. Absorption spectra of plutonium(VI)–NTA solution immediately after the addition of NTA; $[PuO_2^{2+}] = 1.5 \times 10^{-3}$ M, $[NTA] = 2.5 \times 10^{-3}$ M, pH = 3.25, I = 1.0 M.

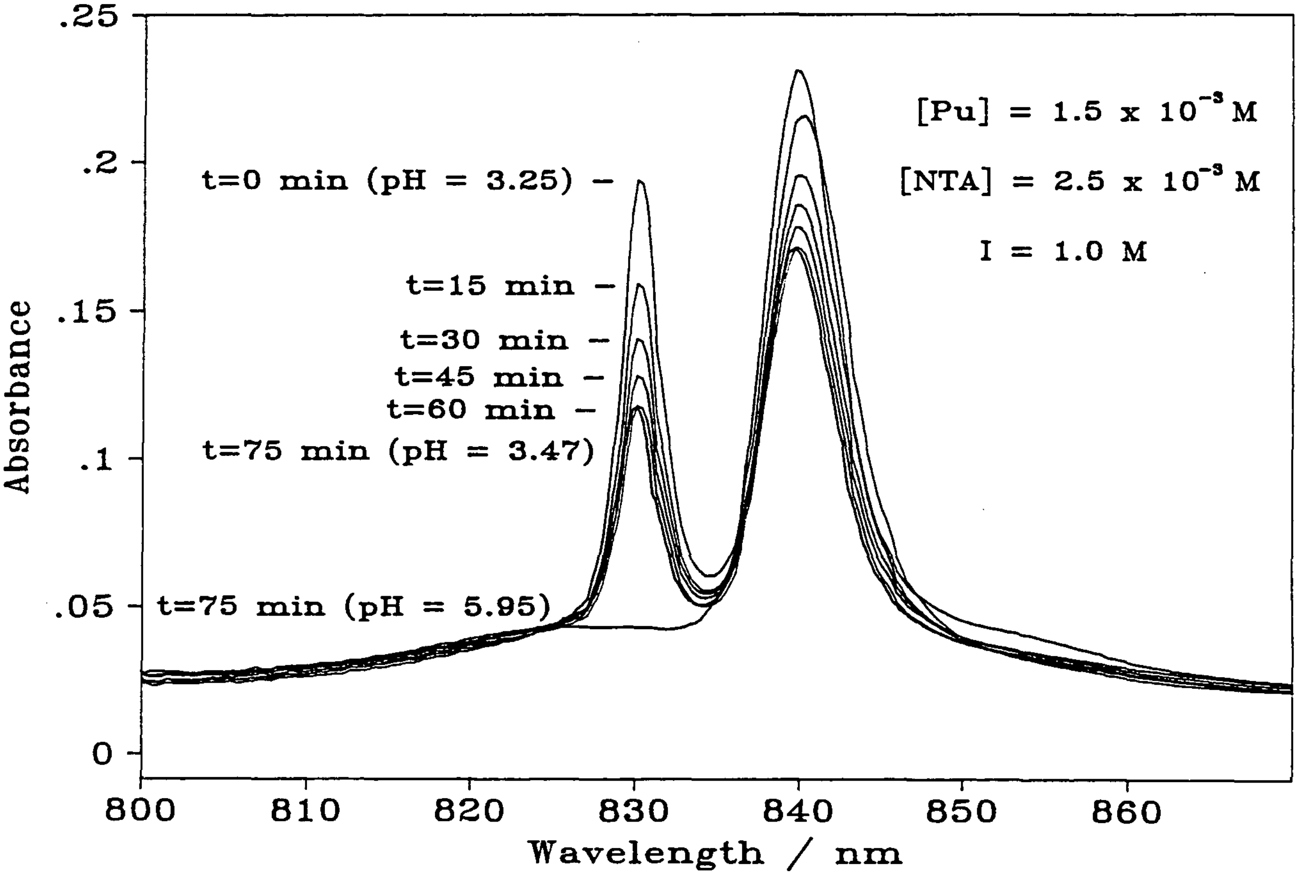

Figure 5. Absorption spectra of plutonium(VI)–NTA as a function of time; $[PuO_2^{2+}] = 1.5 \times 10^{-3}$ M, [NTA] = 2.5×10^{-3} M, pH = 3.25 and 5.95, I = 1.0 M.

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