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NEW SPECTROSCOPIC STUDIES OF PLUTONIUM (IV) NITRATE
COMPLEX FORMATION IN SOLUTION

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Abstract:

Spectrophotometric titrations of Pu(IV) with HNO₃ were conducted in a series of aqueous HClO₄ solutions ranging ionic strength from 2 to 19 mol/kg on the molality scale. The Pu f-f absorption spectra in the visible and near IR range were deconvoluted into spectra of Pu⁴⁺(aq), Pu(NO₃)³⁺ and Pu(NO₃)₂²⁺ complexes and their formation constants as functions of ionic strength. When corrected for the incomplete dissociation of nitric acid, these formation constants exhibit smooth increases with ionic strength from 5 to 19 mol/kg.

Introduction:

The complexation of Pu(IV) by NO_3^- in aqueous solution has provoked interest since shortly after the discovery of Pu because of its importance in separations techniques. Reports of experimental evidence for several nitrate complexes appear in the literature as early as 1949.¹ However, despite the number of studies that have been conducted since that time, basic questions remain about the stoichiometry of the dominant complexes at different nitrate concentrations. The number of possible complexes that had to be considered presented a challenge to both experimental and computational methods available at the time and led to incomplete and conflicting information in the literature.^{2,3,4,5,6,7,8,9} While many complexes have been reported, only the presence of $\text{Pu}(\text{NO}_3)_6^{2-}$ at nitrate concentrations above 10 M may be regarded as well established. Little is known about the solution equilibria that involve even this species.

We have undertaken a systematic study of this equilibrium system using changes in the Pu(IV) electronic absorption spectra to identify all significant Pu nitrate complexes and measure their overall formation constants under a wide range of solution conditions. In this paper we report the overall formation constants of $\text{Pu}(\text{NO}_3)_3^{3+}$ and $\text{Pu}(\text{NO}_3)_2^{2+}$ at ten different ionic strengths ranging from 2 to 19 molal. In future reports we will discuss the identification of the additional complexes and report their formation constants.

Approach:

The experimental work presented in this paper revisits a range of solution conditions that have been explored by several other researcher and uses experimental

¹J. C. HINDMAN, *The Transuranium Elements*, Pt. 1, eds. G. T. Seaborg, J. J. Katz and W. M. Manning, (New York, McGraw-Hill), 1949.

²J. C. Hindman, *The Transuranium Elements*, Pt. 1, eds. G. T. Seaborg, J. J. Katz and W. M. Manning, (New York, McGraw-Hill), 1949.

³J. C. Hindman, *The Transuranium Elements*, Pt. 1, eds. G. T. Seaborg, J. J. Katz and W. M. Manning, (New York, McGraw-Hill), 1949.

⁴J. A. Brothers, R. G. Hart, and W. G. Mathers, *J. Inorg. Nucl. Chem.* **7**, 85 (1958).

⁵J. M. Cleveland, *Coord. Chem. Rev.* **5**, 101 (1970).

⁶L. V. Lipis, B. G. Pozharskii, and V. V. Fomin, *Zhur. Sturkt. Khim.* **1**, 135 (1960).

⁷I. Grenthe and B. Noren, *Acta Chem. Scand.* **14**, 2216 (1960).

⁸T. S. Laxminarayanan, S. K. Patil, and H. D. Sharma, *J. Inorg. Nucl. Chem.* **26**, 1001 (1964).

⁹H. S. Rossotti, *Talanta* **21**, 809 (1974).

techniques that have been applied to this system before as well. The duplication and expansion of the earlier work is necessary because the correct identification and quantitative characterization of the low coordination number complexes forms the foundation of this project, and our assessment of the literature is that no existing study of those complexes is free enough of unjustified assumptions that we can safely rely on it. We are optimistic that we can improve this situation because we can employ an analysis strategy made possible by computational tools not available to earlier researchers.

In most older uses of spectroscopic methods to determine stability constants the analysis examined only one wavelength, even though spectra were collected over the full visible range, because one could not afford to carry out a laborious analysis on more data than was required to reach a unique answer. In theory one can determine the stability constants of q complexes in equilibrium with each other by measuring the absorbance at a single, carefully chosen wavelength of $2q$ solutions spanning the range of solution conditions over which significant chemical changes occur. In practice several characteristics of any real data set usually make this an unreliable approach for studying systems with multiple equilibria. Any real spectrum contains measurement errors that place a lower limit on the absorbance changes that can be reliably measured. It is difficult to choose a wavelength at which all of the complexes have molar absorptivities that are different enough from each other and from zero that the changes in the mole fractions of the complexes are observable above the measurement errors. Also, because one is usually trying to determine both the stability constant and molar absorptivity of each complex, the parameters in the model are not linearly independent. The values of β and ϵ for a given complex are likely to be highly correlated unless that complex is a major component in a significant number of the solutions in the data set, a condition that is difficult to satisfy for all of the complexes included in the model. Thus, modeling of absorbances at a single wavelength is unlikely to give accurate stability constants unless the chemical system is cooperative and fortuitous choices are made at each step of the experimental design and

execution. It is just this difficulty that has led some reviewers to dismiss spectrophotometric methods for the investigation of complex equilibria.¹⁰

Simultaneous analysis of spectra at multiple wavelengths is a more robust approach. With an increase in the number of wavelengths the modeling problem becomes more overdetermined because, while additional molar absorptivities must now be determined at these new wavelengths, no new unknown stability constants are introduced into the model. Measurement errors not correlated with solution composition have a minimal effect on the measured values of the stability constants because they are averaged out over all the wavelengths. Also, multiple-wavelength analysis eliminates the need to locate a single wavelength where all species absorb strongly but not identically. All species must still exhibit strong and distinguishable absorbances in the spectra being analyzed, but those requirements can be fulfilled at different wavelengths for each of the species.

All advances that we shall claim to have made regarding the identification of species and the determination of stability constants result in some way from the advantages of using the full range of the spectra in our analysis. The spectroscopic information collected and analyzed here is no more extensive than that collected by previous researchers whose work is referenced above. Any advances that we shall claim to make are simply the result of taking advantage of the advances in computational tools that have been made in the twenty years since the last significant work on this chemical system was published.

EXPERIMENTAL

A 10 g/l stock solution of Pu(IV) in 2.3 M nitric acid was prepared by standard anion exchange purification (Reillex HPQ resin) of an impure solution containing Pu(IV). Series of solutions for spectrophotometric titrations were prepared *in situ* in an optical flow cell apparatus by adding a known mass of the Pu stock solution to an initial sample solution containing an HNO₃/HClO₄ mixture formulated to give an initial sample Pu solution of the

¹⁰H. S. ROSSOTTI, *Talanta*, 21 (1974) 809 .

desired total ionic strength and nitrate concentration. Subsequent sample solutions in a given constant ionic strength titration series were prepared by adding weighed aliquots of another $\text{HNO}_3/\text{HClO}_4$ mixture of the same ionic strength as the initial sample. Spectra were taken subsequent to each titrant addition in a 1 cm path length flow cell using a Perkin Elmer Lambda 9 spectrophotometer. This procedure resulted in a gradual dilution of the Pu(IV) during a titration. All spectra were normalized to a Pu concentration of 1 mole/liter prior to analysis to compensate.

Modeling Absorption Spectra:

The absorption spectra of a solution containing a mixture of non-interacting complexes of Pu and nitrate can be described by:

$$A_m(\lambda) = \sum_n [\text{Pu}(\text{NO}_3)_n^{4-n}] \epsilon_n(\lambda) \quad (1)$$

where λ is a wavelength $\epsilon_n(\lambda)$ is the molar absorptivity at λ of the complex containing one Pu(IV) ion and n NO_3^- ions. The concentrations of the Pu-nitrate complexes are given by

$$[\text{Pu}(\text{NO}_3)_n^{4-n}] = [\text{Pu(IV)}] \frac{m_{\text{Pu}(\text{NO}_3)_n^{4-n}}}{m_{\text{Pu(IV)}}} = [\text{Pu(IV)}] \frac{\beta_n (m_{\text{Pu}^{4+}}) (m_{\text{NO}_3^-})^n}{1 + \sum_{n'=1}^6 \beta_{n'} (m_{\text{Pu}^{4+}}) (m_{\text{NO}_3^-})^{n'}} \quad (2)$$

where $[\text{Pu(IV)}]$ and $m_{\text{Pu(IV)}}$ are the total Pu(IV) molarities and molalities, respectively, and $\beta_{p,q}$ is the molality scale stability constant for $\text{Pu}_p(\text{NO}_3)_q^{4p-q}$. The concentration of

$\text{Pu}^{4+}(\text{aq})$ is given by

$$[\text{Pu}^{4+}] = [\text{Pu(IV)}] \frac{m_{\text{Pu}^{4+}}}{m_{\text{Pu(IV)}}} = [\text{Pu(IV)}] \frac{1}{1 + \sum_{n'=1}^6 \beta_{n'} (m_{\text{Pu}^{4+}}) (m_{\text{NO}_3^-})^{n'}} \quad (3)$$

The net molar absorptivity of Pu(IV) in a solution can be obtained by substituting Eq. 2 into Eq. 1 and rearranging to give

$$\epsilon_{net}(\lambda) = \frac{A(\lambda)}{[Pu(IV)]} = \frac{\sum_n \beta_n (m_{Pu^{4+}}) (m_{NO_3^-})^n \epsilon_n(\lambda)}{1 + \sum_{n=1}^6 \beta_n (m_{Pu^{4+}}) (m_{NO_3^-})^n} \quad (4)$$

For a series of N solutions having different nitrate molalities, the absorbance at each λ can be modeled by N equations of the form of Eq. 4, with the β 's and ϵ 's as free parameters. Alternatively, numerical differentiation of the total Pu(IV) molar absorptivity with respect to the sampled wavelength or energy x yields

$$\frac{\partial \epsilon_{net}(\lambda)}{\partial \lambda} = \frac{\sum_n \beta_n (m_{NO_3^-})^n \frac{\partial \epsilon_n(\lambda)}{\partial \lambda}}{1 + \sum_{n=1}^6 \beta_n (m_{NO_3^-})^n} \quad (5)$$

which can be used to generate models in the same way as Eq. 4 but where the free parameters now include the set of $\partial \epsilon / \partial \lambda$'s rather than ϵ 's. The differential form has advantages for fitting some data sets, as we shall see below.

If there are N spectra and M sampled wavelengths, λ , from each spectrum included in the analysis, the data set can be modeled by N x M equations of the form of either Eq. 4 or Eq. 5. If there are Q complexes, the system of equations will have (M x Q) + Q - 1 unknown parameters, Q different ϵ 's for every λ and Q - 1 β 's. The system of equations is overdetermined and can have a unique solution whenever $N \times M > (M \times Q) + Q - 1$.

The figure-of-merit function χ^2 is used as a measure of the goodness of fit for the model. It is defined as

$$\chi^2 = \sum_{i=1}^{N \times M} \left(\frac{[y_i^{observed} - y_i^{calculated}]}{\sigma_i} \right)^2 \quad (6)$$

where y_i is either $\epsilon_{Pu(IV)}$ or $\partial \epsilon_{Pu(IV)} / \partial x_m$, and σ_i is the standard deviation of the measurement of data point i . Since we do not know the distribution of measurement errors at this point, we set $\sigma_i = 1$ for all data points. The best-fit parameters for each model are determined by varying all ϵ 's and β 's to minimize χ^2 .

Results:

In earlier work we determined that titration of Pu(IV) with nitrate first produces $\text{Pu}(\text{NO}_3)^{3+}$ and then $\text{Pu}(\text{NO}_3)_2^{2+}$ as the nitrate concentration increases from 0.01 molal to 1.0 mol/kg in a series of aqueous $\text{HClO}_4/\text{HNO}_3$ solutions of constant 2.34 molal ionic strength. We build upon that work here by assuming that equilibria between these two nitrate complexes and the $\text{Pu}^{4+}(\text{aq})$ species can completely account for observed spectroscopic changes in the present titrations up to $m(\text{NO}_3^-) = 0.3$ mol/kg. The present data are modeled using the above equations with n and $n' = 1, 2$. Part of one of the titration data sets is shown below.

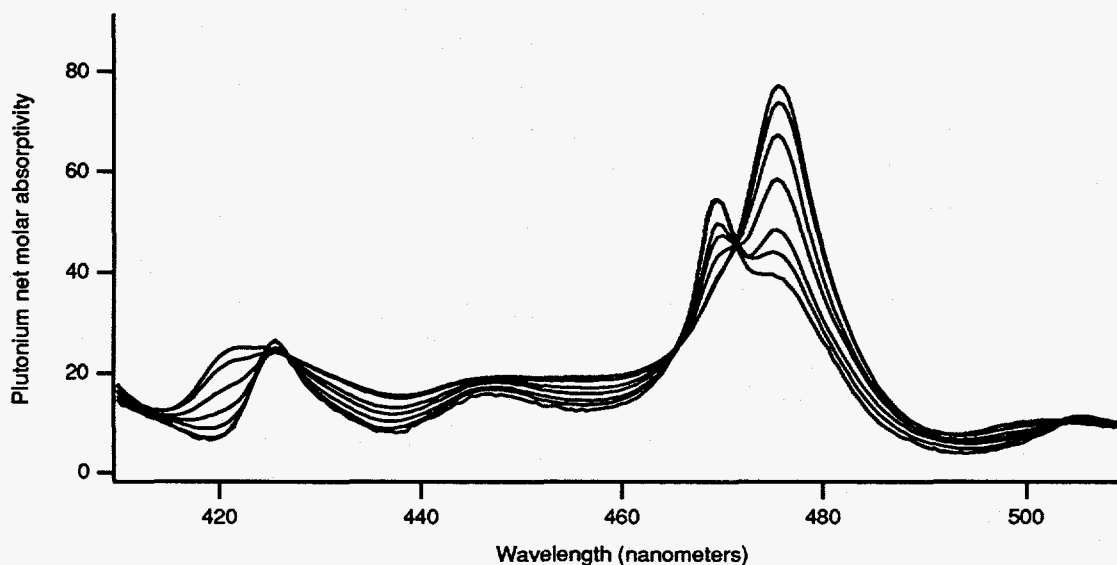


Figure 1. A subset of the spectra from the $I = 2$ mol/kg titration that were analyzed for this paper. Shading is from $m_{\text{nitrate}} = 0.01$ mol/kg (light) to $m_{\text{nitrate}} = 0.8$ mol/kg (dark).

We fit such data sets to a model of the form of Eq. 4 discussed above. The model parameters determined by the fitting procedure are the overall formation constants of $\text{Pu}(\text{NO}_3)^{3+}$ and $\text{Pu}(\text{NO}_3)_2^{2+}$, as well as the spectra of these two species and that of the $\text{Pu}^{4+}(\text{aq})$ species. The fitted spectra of the individual species are shown in Figure 2, and the formation constants are listed in Table I and shown in Figure 3.

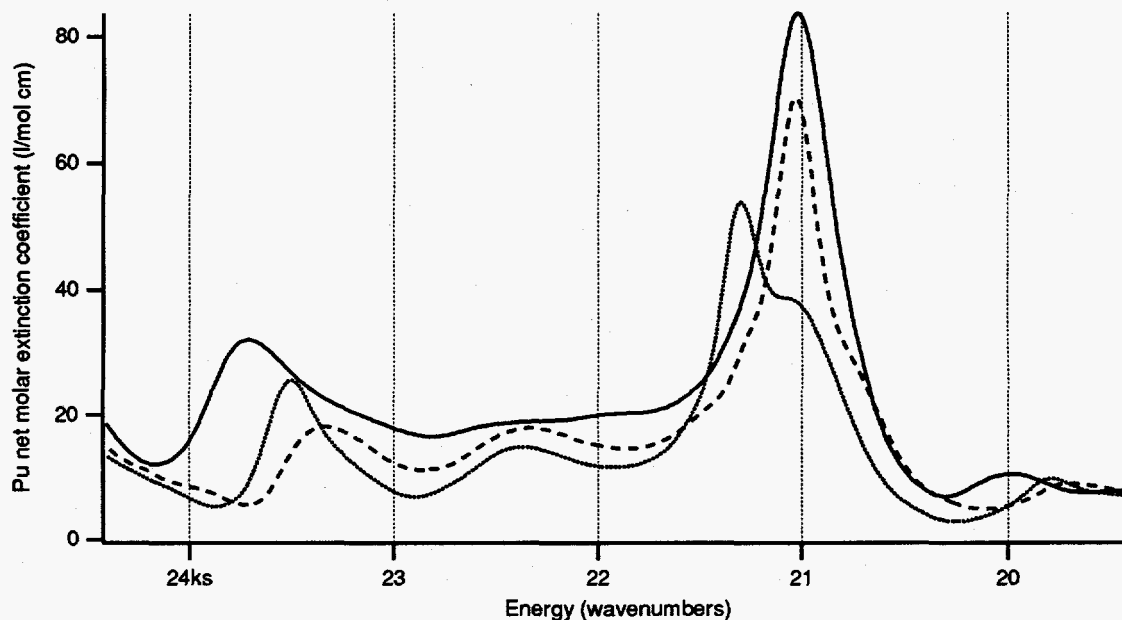


Figure 2. Spectra of $\text{Pu}^{4+}(\text{aq})$ (dotted line), $\text{Pu}(\text{NO}_3)^{3+}$ (dashed line) and $\text{Pu}(\text{NO}_3)_2^{2+}$ (solid line) as determined by our modeling of $I = 2$ mol/kg titration data.

Table I. Logarithms of the overall formation constants β_1 and β_2 for each ionic strength. Also shown are the degree of dissociation of nitric acid in a perchloric acid from the data in Ref. x, and the logarithms of the overall formation constants adjusted for the amount of free nitrate ion available to complex Pu.

I (mol/kg)	$\log \beta_1$ ((mol/kg) ⁻¹)	$\log \beta_2$ ((mol/kg) ⁻²)	α	$\log (\beta_1/\alpha)$	$\log (\beta_2/\alpha^2)$
2	0.48	1.08	0.98	0.49	1.10
5	0.72	1.63	0.89	0.78	1.74
9	1.14	2.46	0.53	1.42	3.02
11	1.29	2.90	0.32	1.78	3.88
13	1.26	2.93	0.17	2.04	4.48
15	1.27	2.91	0.083	2.35	5.07
17	1.27	2.92	0.040	2.66	5.71
19	1.30	2.93	0.020	3.00	6.33

The formation constants have been presented in two forms. The first form is the empirically determined constant assuming that the nitrate concentration available to complex

Pu(IV) is the same as the total nitrate concentration in solution. In the second form the nitrate concentrations are corrected for the less than complete dissociation of HNO_3 in the relatively concentrated perchloric acid solutions used in this study. For these dissociation corrections we use the degree of dissociation that has been measured by Sampoli *et al.*¹¹ using Raman spectroscopy.

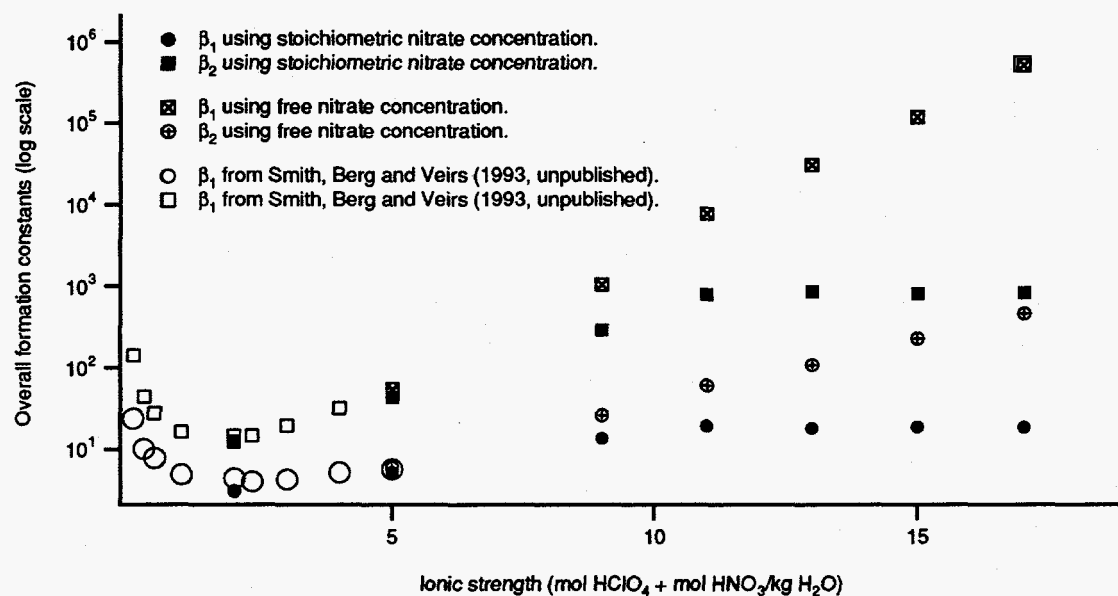


Figure 3. Overall formation constants determined in this work as a function of total ionic strength and the same formation constants corrected for the degree of dissociation of HNO_3 . Also shown are formation constants at lower ionic strengths determined by us in earlier work.

Discussion:

The results show that the formation constants pass through a minimum around 2-4 mol/kg, increase rapidly to 11 mol/kg, then remain relatively constant to very high ionic strengths. Once corrected for the degree of dissociation of HNO_3 , the formation constants exhibit smooth increases with ionic strength from below 5 mol/kg up to the upper limit of our experimental data.

¹¹ M. SAMPOLI, A. DE SANTIS, N. C. MARZIANO, F. PINNA, AND A. ZINGALES, *J. Phys. Chem.*, 89 (1985) 2864.