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CONF-9706138--2

Title:

PLUTONIUM (IV) COMPLEXATION BY NITRATE
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FROM 2 TO 19 MOLAL

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Submitted to:

Proceedings paper to be presented at the
Nuclear Energy Agency Workshop on
Long-lived Radionuclide Chemistry in
Nuclear Waste Treatment, June 18-20,
1997, Villeneuve-les-Avignon, France.

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PLUTONIUM (IV) COMPLEXATION BY NITRATE IN ACID SOLUTIONS OF IONIC STRENGTHS FROM 2 TO 19 MOLAL

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Abstract

Titration of Pu(IV) with HNO_3 in a series of aqueous HClO_4 solutions ranging in ionic strength from 2 to 19 molal were followed using absorption spectrophotometry. The Pu 5f-5f spectra in the visible and near IR range change with complex formation. At each ionic strength, a series of spectra were obtained by varying nitrate concentration. Each series was deconvoluted into spectra of $\text{Pu}^{4+}(\text{aq})$, $\text{Pu}(\text{NO}_3)^{3+}$ and $\text{Pu}(\text{NO}_3)_2^{2+}$ complexes, and simultaneously their formation constants were determined. When corrected for the incomplete dissociation of nitric acid, the ionic strength dependence of each formation constant can be described by two parameters, β^0 and $\Delta\epsilon$ using the formulae of specific ion interaction theory. The difficulties with extending this analysis to higher nitrate coordination numbers are discussed.

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} 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 $\text{Pu}(\text{NO}_3)^{3+}$ and $\text{Pu}(\text{NO}_3)_2^{2+}$ at ten different ionic strengths ranging from 2 to 19 molal. We also briefly discuss the evidence for higher complexes in our data set, and outline the difficulties in extending this method of analysis to quantitative measurement of their formation constants.

A brief overview of the existing literature is necessary to explain why we are revisiting a system that has been studied so extensively. Hindman published the first description of the nitrate complexes of Pu(IV) present in nitric acid solutions in 1949.⁸ By analyzing spectra he concluded that in 2.0 M $[\text{H}^+]$ solutions $\text{Pu}(\text{NO}_3)_6^{2-}$ was the dominant Pu species when $[\text{NO}_3^-] = 13\text{M}$ and $\text{Pu}(\text{NO}_3)^{3+}$ was the dominant species below $[\text{NO}_3^-] = 4.6\text{M}$. He measured a stability constant for $\text{Pu}(\text{NO}_3)^{3+}$ of $\beta_1 = 2.9 \pm 0.6$ by following the change in absorbance with acid concentration (0–2M) at a single wavelength. His conclusion that only a single Pu nitrate complex was formed from 0–4.6M $[\text{NO}_3^-]$ depended on the assumption that all species would have different molar absorptivities at the single wavelength he used in his analysis. We shall show that it is much more likely that there are two important nitrate complexes formed even in solutions below 1M $[\text{NO}_3^-]$, and that Hindman's analysis missed this possibility because of a near coincidence in the molar absorptivities of two of the complexes at the single wavelength that was used. As a result, while he arrived at what we will show to be a reasonable value for β_1 , his results lead to an incorrect assignment of the dominant species below 4.6M $[\text{NO}_3^-]$ as $\text{Pu}(\text{NO}_3)^{3+}$ and hence to an incorrect assignment of the absorption spectrum under those solution conditions.

Rabideau and Lemons used electrochemical methods to determine $\beta_1 = 3.48$.⁹ Like Hindman, they assumed only one nitrate complex was formed in their samples, but their solution conditions did not range as high in $[\text{NO}_3^-]$ so the neglect of the possible second complex is less important. However, the validity of their results is questionable because they depend on the unsupported assumption that complexation of Pu(III) by nitrate was not significant in the solutions they studied.¹⁰

Lipis *et al.* analyzed absorption spectra and concluded that $\text{Pu}(\text{NO}_3)^{3+}$, $\text{Pu}(\text{NO}_3)_2^{2+}$, $\text{Pu}(\text{NO}_3)_3^+$, and $\text{Pu}(\text{NO}_3)_4$ all exist in significant amounts below $[\text{NO}_3^-] =$

6M.¹¹ They identified complexes by plotting the dependence of the maximum absorbance in a given wavelength interval as a function of $[\text{NO}_3^-]$ and assigning each of the extrema to a region of dominance of a different $\text{Pu}(\text{NO}_3)_q$ complex. However, their assumptions in making these assignments are questionable because they do not take into account the effect of shifts in peak positions between complexes. Minima in peak molar absorptivities could equally well be produced by mixtures of two complexes with absorption maxima of the similar intensity but at slightly shifted wavelengths.

Grenthe and Noren¹² used a cation exchange method to calculate stability constants for $\text{Pu}(\text{NO}_3)^{3+}$, $\text{Pu}(\text{NO}_3)_2^{2+}$, and $\text{Pu}(\text{NO}_3)_3^+$ at $I=4$ M based on the dependence on $[\text{NO}_3^-]$ of the total Pu sorption on the resin. Their calculation assumes that each of these complexes is formed in significant amounts as $[\text{NO}_3^-]$ increases, and it relies on several approximations to deal with the additional unknown parameters that characterize the equilibria between a complex in solution and sorbed onto the resin. It is difficult to assess the reliability of their β determinations without testing their assumptions and mathematical approximations, which go considerably beyond those made in the papers they reference.

Laxminarayanan *et al.* calculated values for β_1 through β_4 from extraction data obtained at $I=1.02$, 1.9 and 4.7 mol/kg.¹³ Their values were dependent upon which of several computational methods were used, probably due to the different approximations inherent in each. Danesi *et al.* used a different extractant and a different computational method to determine β_1 and β_2 at $I=4$ mol/kg and $I=6$ mol/kg. Their measurements are in agreement with some of those Laxminarayanan. Like the ion exchange measurements, the results of the solvent extraction studies are subject to question because they make several untested assumptions about the chemistry in each phase.

All of these measurements of stability constants involve the fitting of a set of experimental data by a model that presupposes the identities of the important chemical species in solution and includes, at minimum, the equilibrium constants for the reactions between them as adjustable parameters. None of the experimental techniques that were used gave direct information about the structure or stoichiometry of any of the $\text{Pu}(\text{IV})$ species that were present in solution. Relative nitrate coordination numbers for any two sequentially-formed species could be assigned by determining what power of $[\text{NO}_3^-]$ best described functionality of the equilibrium between them. But in order to assign the absolute nitrate coordination numbers, all of these techniques required that the nitrate coordination number of at least one of the major Pu complexes be known or assumed. The absolute nitrate coordination numbers for the other species could then be determined by tying their measured relative coordination numbers to the absolute coordination number of the one known species. The obvious known reference point in this system is Pu^{4+} in a solution with only non-coordinating anions, ClO_4^- being the most common choice, and no nitrate.

For a multicomponent equilibrium where the nitrate coordination number is known to range as high as six, this method of analysis presents problems because any analysis of the species with high coordination number is critically dependent on the reliability of the analyses of the species with lower coordination. Any error in the nitrate coordination number of one of the first species to be formed will propagate directly into the measured coordination numbers of all higher complexes. Since we do not believe that the literature provides solid assignments of the lowest nitrate complexes, our first order of business is to clarify the identities of these complexes and measure their stability constants. The scope of

this paper includes that effort and the determination of the stability constants for the first two complexes at one ionic strength. Subsequent papers will address identification of higher complexes and measurements of stability constants at different ionic strengths.

The experimental work presented in this paper revisits a range of solution conditions that have been explored by several of the papers cited above. The replication and expansion of the earlier work is necessary because the correct identification and quantitative characterization of the initial nitrate 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.¹⁴

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 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 HNO₃/HClO₄ 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:

$$A_m(\lambda) = \sum_n [Pu(NO_3)_n] \epsilon_n(\lambda) \quad (1)$$

where λ is a wavelength $\epsilon_n(\lambda)$ is the molar absorptivity at λ of the complex containing one Pu(IV) ion and n NO₃⁻ ions. In a series of solutions of constant ionic strength but varying m_{nitrate} , the concentrations of the Pu-nitrate complexes are given by

$$[Pu(NO_3)_n] = [Pu(IV)] \frac{m_{Pu(NO_3)_n}}{m_{Pu(IV)}} = [Pu(IV)] \frac{\beta_n (m_{Pu^{4+}}) (m_{NO_3^-})^n}{1 + \sum_{n'=1}^6 \beta_{n'} (m_{Pu^{4+}}) (m_{NO_3^-})^{n'}} \quad (2)$$

where $[Pu(IV)]$ and $m_{Pu(IV)}$ are the total Pu(IV) molarities and molalities, respectively, and β_n is the apparent molality scale stability constant for $Pu(NO_3)_n$ at the ionic strength of the series solutions. The ionic strength dependences of the activity coefficients of reactants and products are contained within the apparent β 's. The concentration of Pu⁴⁺(aq) is given by

$$[Pu^{4+}] = [Pu(IV)] \frac{m_{Pu^{4+}}}{m_{Pu(IV)}} = [Pu(IV)] \frac{1}{1 + \sum_{n'=1}^6 \beta_{n'} (m_{Pu^{4+}}) (m_{NO_3^-})^{n'}} \quad (3)$$

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 $N \times M$ equations of the form of either Eq. 4 or Eq. 5. If there are Q complexes, the system of equations will have $(M \times Q) + Q - 1$ 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.

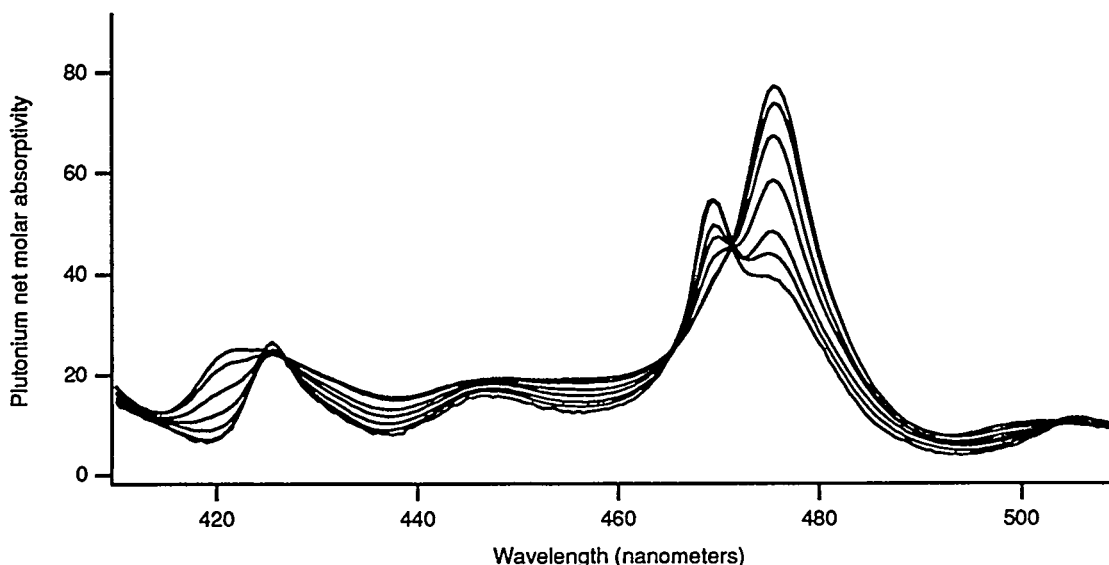


Figure 1. A subset of the spectra from the $I = 2$ mol/kg titration that were analyzed for this paper. Shading is from $m_{\text{nitrate}} = 0.01$ mol/kg (light) to $m_{\text{nitrate}} = 0.8$ mol/kg (dark).

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 spectra of the individual species from the fit at 2 molal ionic strength are shown in Figure 2. The formation constants are listed in Table I and shown in Figure 3.

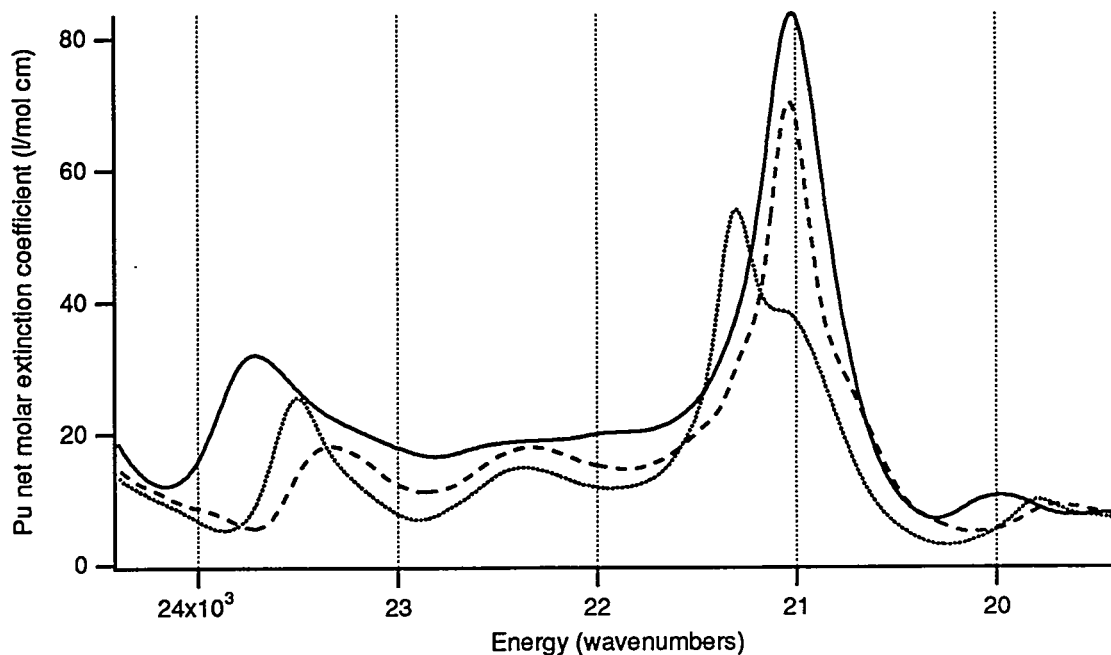


Figure 2. Spectra of $\text{Pu}^{4+}(\text{aq})$ (dotted line), $\text{Pu}(\text{NO}_3)^{3+}$ (dashed line) and $\text{Pu}(\text{NO}_3)_2^{2+}$ (solid line) as determined by our modeling of $I = 2 \text{ mol/kg}$ titration data.

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.*¹⁵ using Raman spectroscopy.

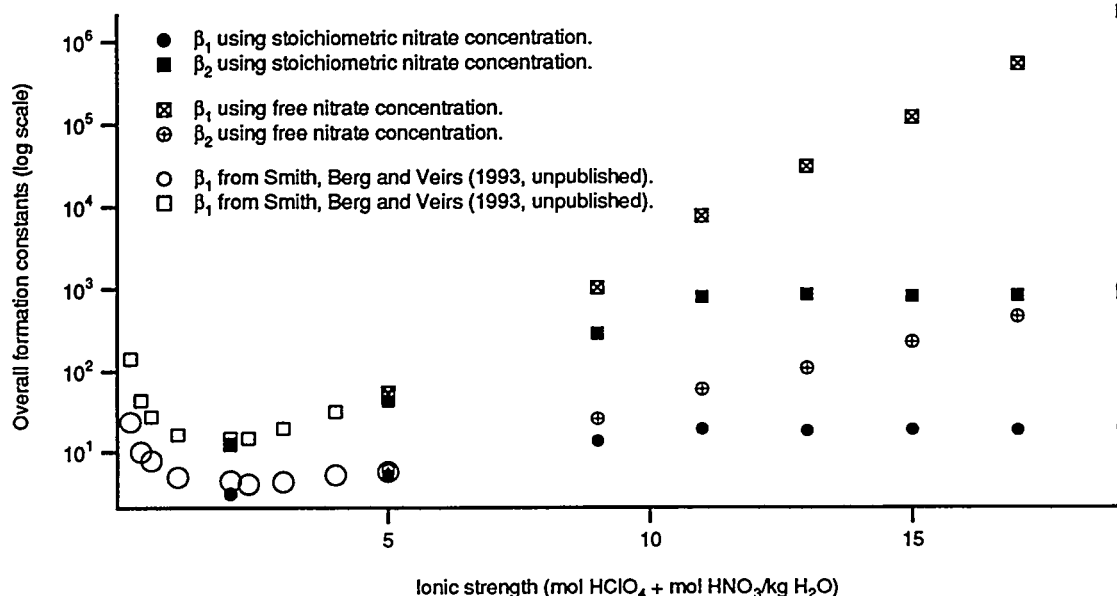


Figure 3. Overall formation constants determined in this work as a function of total ionic strength and the same formation constants corrected for the degree of dissociation of HNO_3 . Also shown are formation constants at lower ionic strengths determined by us in earlier work.

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. This increase is linear on a log scale from $I = 5$ mol/kg to the upper limit of our data, as is evident in Fig. 3. This linearity suggests that compact representation of the data set using specific ion interaction theory is possible.¹⁶ In this formalism in a 1-1 electrolyte, the ionic strength dependences of the formation constants for the first two plutonium nitrate complexes are given by

$$\log(\beta_1) + 8D = \log(\beta_1^0) - \Delta\epsilon I \quad (7)$$

and by

$$\log(\beta_2) + 14D = \log(\beta_2^0) - \Delta\epsilon I \quad (8)$$

where D is the Debye-Huckel term

$$D = \frac{0.5091\sqrt{I}}{1 + 1.5\sqrt{I}}$$

and $\Delta\epsilon$ is the sum of ion interaction terms for the products with oppositely charged components of the electrolyte minus ion interaction terms for the reactants with oppositely charged components of the electrolyte

$$\Delta\epsilon = \epsilon(Pu(NO_3)_3^{3+}, ClO_4^-) - \epsilon(Pu^{4+}, ClO_4^-) - \epsilon(H^+, NO_3^-) \text{ for } \beta_1$$

and

$$\Delta\epsilon = \epsilon(Pu(NO_3)_2^{2+}, ClO_4^-) - \epsilon(Pu^{4+}, ClO_4^-) - 2\epsilon(H^+, NO_3^-) \text{ for } \beta_2$$

The results of least squares fits of Equations 7 and 8 to the empirical formation constants corrected for association of HNO_3 are shown in Figure 4.

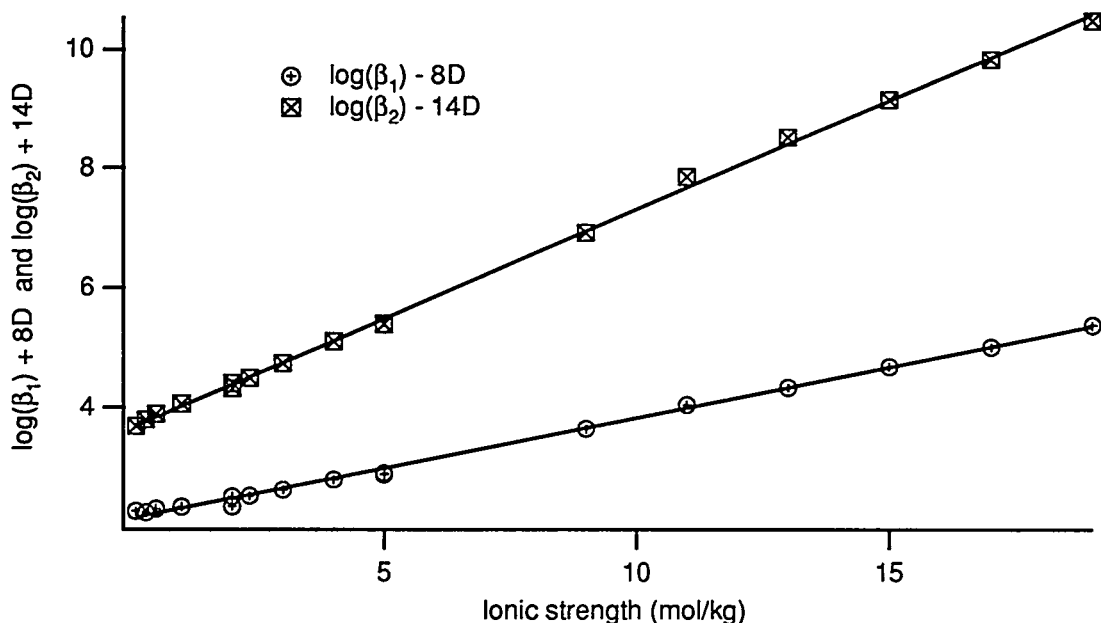


Figure 4: Experimentally determined formation constants for the first two Pu(IV) nitrate complexes corrected for ionic strength and plotted in the forms of Eqns. 7 and 8. Linear least squares fits of these data to Eqns. 7 and 8 are also shown as solid lines.

The best fit parameters for β_1 are $\log(\beta_1^0) = 2.12$, $\Delta\epsilon = 0.17$, and for β_2 are $\log(\beta_2^0) = 3.66$, $\Delta\epsilon = 0.36$. No systematic deviations from these linear functions are noted either at the high or low ranges of ionic strength, despite the fact these fits apply the specific ion interaction model to far higher ionic strength than is common.

The series of solution sample spectra that were analyzed above to determine the formation constants of the first two Pu(IV) nitrate complexes also contain clear evidence for the formation of at least two additional nitrate complexes. These complexes have been discussed in previously published work prior to collection of this data set.¹⁷ However, quantitative analysis of the solution equilibria to confirm the earlier assignments and to determine formation constants of the higher complexes is more difficult than the same analysis for the first two complexes.

The central difficulty in analyzing the higher formation constants is that these complexes form over a range of nitrate concentrations over which significant effects on the activities of all solution constituents can be expected even in a series of solutions with constant ionic strength. Because nitrate is a relatively weak ligand, some complexes are not formed until nitrate concentrations reach a large fraction of the total ionic strength. Under these conditions, the activity coefficients of the nitrate ion, the perchlorate ion, water, and each of the plutonium species could change considerably within a series of solutions of constant ionic strength beginning with pure perchloric acid and ending with pure nitric acid. This effect can be seen clearly in the much more complete ionization of nitric acid in pure nitric acid than as a trace constituent in perchloric acid of the same concentration.¹⁸

Conclusions:

We have determined the overall formation constants for the first two nitrate complexes of Pu(IV) in perchloric acid solutions ranging from moderate to high ionic strengths by modeling the changes in the visible-NIR absorption spectra of the Pu 5f-5f transitions as being due to discrete changes in the inner sphere coordination of Pu as a function of nitrate concentration. The formation constants increase with ionic strength only up to about 10 mol/kg and then remain relatively constant. However, if the effects of incomplete dissociation of nitric acid in the more concentrated samples are taken into account by correcting the equilibrium expression so that only free NO_3^- rather than total nitrate is used to calculate formation constants, then the formation constants increase linearly with ionic strength above 5 mol/kg, and can be modeled quite well by equations of the form used in specific ion interaction theory.

Acknowledgement:

Funding for this effort was made possible through the Nuclear Materials Stabilization Task Group, EM-66 of the U. S. Department of Energy under Contract W-7405-ENG-36.

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