

Initial Hydrolysis of Plutonium(VI)*

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Plutonium(VI) / Hydrolysis / Spectroscopy

Abstract

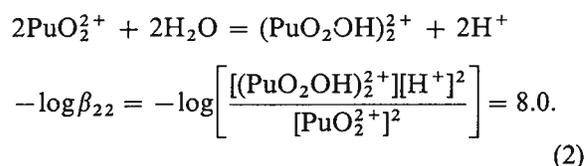
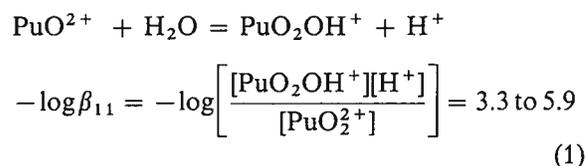
The initial hydrolysis of Pu(VI) was investigated as a function of pH, total plutonium concentration, and temperature using a combination of absorption spectrometry and laser photoacoustic spectroscopy. The initial product observed at total plutonium concentrations greater than 6×10^{-5} M in sodium perchlorate was identified as a polynuclear species and proposed to be the $(\text{PuO}_2\text{OH})_2^{2+}$ complex. The formation constant determined for the hydrolytic reaction is $5.0 \pm 1.5 \times 10^{-8}$ M, corresponding to a $-\log \beta_{22}$ value of 7.3 ± 0.2 . Varying the temperature between 10° and 45°C had essentially no effect on this hydrolytic reaction.

Introduction

The environmental chemistry of plutonium is of continuing interest because of the predominance of plutonium as a radioactive contaminant at DOE waste sites. Plutonium(VI), as PuO_2^{2+} , although often of little importance in deep geologic media, which tend to be reducing, is expected to be an important species in determining the initial near-surface chemistry of plutonium at the point of its release to the environment. This is because plutonium(VI), if stable towards reduction, is generally more soluble than Pu(IV) and is likely to be present in the more oxidizing conditions found in both near-surface groundwaters and radiois-affected zones at the source of the contamination.

Choppin and Mathur [1] have discussed the importance of hydrolysis with respect to plutonyl (as PuO_2^{2+}) migration in groundwaters. Most subsurface groundwaters have a pH that is near-neutral to slightly alkaline (pH = 5–10), where hydrolysis will compete with inorganic and organic complexants in the groundwater. An understanding of this process is, therefore, needed to predict the mobility of plutonium in the subsurface.

Plutonium(VI) hydrolysis is complex and does not proceed reversibly at high plutonium concentrations and pH [2, 3]. This has been attributed to the formation of polynuclear/polymeric species. The initial hydrolysis of Pu(VI), as reported by others, proceeds by one or both of the following reactions:



The published literature on these and other hydrolytic reactions has been reviewed by Baes and Mesmer [4] and summarized by Katz *et al.* [5]. The reported values for the formation constant of the 1:1 PuO_2OH^+ species (Reaction 1) disagree by two orders of magnitude, with the more generally accepted values being $-\log \beta_{11} = 5.6 - 5.9$. The formation of the PuO_2OH^+ species has been postulated by analogy with the uranyl system, although the formation of the UO_2OH^+ 1:1 complex is controversial [6]. For these reasons, an unqualified determination of the 1:1 hydrolysis formation constant has not been made. A more complete understanding of the initial hydrolysis of PuO_2^{2+} is important since the initial hydrolytic product generated will be the most important at the low (typically sub-nanomolar) plutonium concentrations of importance in groundwater systems.

The work reported herein is a continuation of prior efforts to apply spectroscopic methods to investigate radionuclide speciation in groundwater-relevant systems [3, 7–9]. The absorption spectrum of the Pu(VI) aquo ion, shown in Figure 1, is well established. The plutonyl cation has a favorable spectroscopy for speciation studies in that shifts in the absorption bands occur as a result of complexation [9]. In prior work [9], we had characterized changes due to hydrolysis on the absorption spectrum of plutonium(VI) in the 600–750 nm region of the spectrum. Here, we observed four spectroscopically distinct hydrolytic species with maxima occurring at 622 nm (aquo species), 632 nm, 638 nm, and 655 nm.

Based on the hydrolytic scheme proposed by others we tentatively assigned the 632 nm band, which corresponds to the initial hydrolytic species observed, to the PuO_2OH^+ (1:1) complex but noted that this was not completely consistent with our data. To further resolve the inconsistency noted, we performed more extensive studies that focused on the initial hydrolytic

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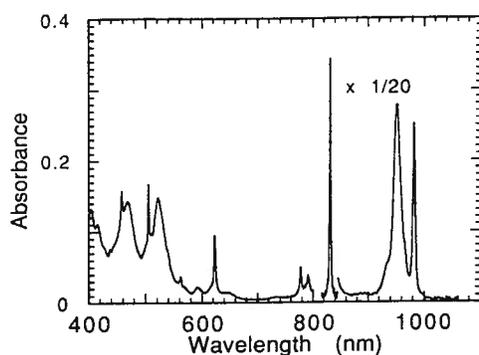


Fig. 1. Absorption spectrum of 0.12 *M* Pu(VI) in sodium perchlorate at pH = 3.

species formed. This was done using a combination of absorption spectrometry and laser photoacoustic spectroscopy (LPAS) to cover a broad range in the total plutonium concentration. The spectra obtained were deconvoluted to establish the relative concentration of the various species present and determine the associated formation constant. The initial hydrolytic species formed, owing to the low concentrations of plutonium observed in the subsurface and the near-neutral pH of most near-surface groundwaters, is of greatest interest in the environmental chemistry of the plutonyl cation.

Experimental

Preparation of Pu(VI) solutions

Sodium hydroxide (semiconductor grade) and perchloric acid (99.99%) were purchased from Aldrich Chemical Co. and used without further purification. Sodium perchlorate was prepared by neutralization of sodium carbonate (99.995 + %) with perchloric acid to avoid impurities (e.g., Fe). It was recrystallized once from triply distilled water and heated to a constant weight at 120°C to remove residual water.

Both ^{242}Pu and ^{239}Pu isotopes were obtained from Oak Ridge National Laboratory and purified by ion-exchange (Bio-Rad MP-1). The plutonium was oxidized to Pu(VI) by fuming with a small amount of concentrated perchloric acid to near dryness. The ^{242}Pu was used to minimize the formation of Pu(IV, V) as the result of autoradiolysis.

After oxidation to the VI state, the plutonium was dissolved in a known amount of triply distilled water and analyzed by absorption spectrometry to establish its oxidation-state purity. The concentration of Pu(VI) in the solution was determined from the spectrum of the aquo ion. The extinction coefficient (ϵ) was $7.5 \text{ M}^{-1} \text{ cm}^{-1}$ at 622 nm [10], which we also confirmed in our work. The pH of the solution was measured to estimate the residual perchloric acid concentration in the solution. At total plutonium concentrations above 0.01 *M*, the Pu(VI) concentration was significant relative to the desired ionic strength, and it was necessary to adjust the amount of sodium hydrox-

ide and sodium perchlorate added so that a constant ionic strength of 0.10 *M* was maintained. At lower Pu(VI) concentrations ($< 10^{-3} \text{ M}$), the Pu(VI) was added directly to 0.10 *M* sodium perchlorate.

The pH of the stock solutions prepared, as just described, was typically 3. This was measured using an Orion research model 8103 Ross combination electrode and Orion research model 901 microprocessor ionanalyzer meter. The electrode was standardized using pH = 4.01 and pH = 7.00 buffer solutions. Subsequent pH adjustments were made by adding appropriate amounts of sodium hydroxide solution to 4 ml of the Pu(VI) stock solution. This was done in a Pyrex vessel while the solution was bubbled with argon gas to minimize carbon dioxide uptake. Only upward adjustments in pH were made due to the pH hysteresis previously noted [2, 3]. The Pu(VI) solution was then transferred into a quartz optical cell (1-cm optical pathlength), which was sealed with a gas-tight Teflon cap.

The solution pH was measured before and after spectroscopic analysis. Differences between the initial pH measured and that measured after taking the spectrum were noted when the total plutonium concentration of the sample was $\sim < 10^{-4} \text{ M}$. For these solutions, the pH was also measured in the cuvette using a microcombination pH probe (MI-410, Microelectrode, Inc.) with an Orion model 501 digital ionanalyzer. When differences in pH of > 0.1 pH units were noted before and after analysis, the results were not used and a new solution was prepared.

Temperature variable LPAS and absorption spectrometers

Our single beam differential LPAS spectrometer was described in detail previously [11]. Briefly, the LPAS spectrometer consists of a Lambda Physik excimer-pumped dye laser with a piezoelectric transducer (PZT) crystal detector. The LPAS signal from the sample cell (solute and solvent) and that from the reference cell (containing only solvent) were fed to the differential amplifier, through a preamplifier with high- and low-frequency filter channel, to subtract out the LPAS signal due to the solvent. The output of the differential amplifier was sent to a boxcar integrator for signal averaging. The output of the boxcar was digitized and stored in a personal computer for later analysis.

Temperature, in both the spectrometric and LPAS studies, was varied using a flow-through cell holder. The temperature of the water was controlled to $\pm 0.2^\circ\text{C}$ with a Fisher water circulating bath. An Omega portable RTD thermometer, which was calibrated by boiling point/ice point determination, measured the temperature. Readings were within $\pm 0.5^\circ\text{C}$ of the set point on the circulating bath.

A Perkin Elmer-Hitachi model 304 absorption spectrometer fitted with a thermostated cell holder

recorded the UV-VIS absorption spectrum at variable temperature. The recorded absorption spectrum was digitized and also stored in a personal computer for analysis. A fixed slit width of 0.3 nm was used throughout.

Data analysis

The recorded absorption and LPAS spectra were analyzed to (1) identify the spectrum corresponding to each Pu(VI) species and (2) determine the concentration of the Pu(VI) hydrolytic species in the sample as a function of pH.

The contribution of each hydrolytic species to the overall absorption spectrum was determined by spectral stripping using a spectral subtraction computer program [12]. The spectrum of the aquo ion (622 nm band) was determined at low pH (usually pH = 3) where no hydrolysis was present. This was subtracted from the spectra obtained at increasingly higher pH until the 632 nm band was clearly evident. From this information, the extinction coefficient (in terms of plutonium concentration) of the 632 nm band was determined, and the band shape was identified. This procedure was applied to spectra obtained at higher pH until the band at 638 nm was also clearly identifiable. There was no evidence that any of the three bands changed shape as the pH of the system increased.

Once these "library" spectra were obtained, each observed spectrum was deconvoluted by adding the component spectra until a match with the observed spectrum was obtained. Figure 2 gives an example spectrum, along with the component "library" spectra obtained for the 622, 632, and 638 nm species.

Although all the spectra obtained were deconvoluted into the component spectra, we relied primarily on the decrease in the aquo ion concentration to determine the formation constant of the first hydrolytic species (at 632 nm). There is less uncertainty associated with the spectral characteristics of the aquo species since the 622 nm band is well separated from the other absorption bands, and the signal intensity is always greater. In determining the magnitude of the formation constant, we utilized spectra with, based on spectral deconvolution, only two species present.

The total plutonium concentration in our solutions was determined from the absorption of the Pu(VI) aquo ion at 622 nm ($\epsilon = 7.5 \text{ M}^{-1} \text{ cm}^{-1}$) prior to adjusting pH. For LPAS spectra, the signal intensity was related to Pu(VI) concentration by a proportionality constant that was a function of the operating conditions of the laser system. Hence, we report relative LPAS units. The operating conditions of the LPAS system were kept the same for each series of solutions at the same total plutonium concentration but were changed to optimize the signal when the total concentration was changed. The LPAS signal intensity was normalized to the laser pulse energy and was proportional to the Pu(VI) concentration when tempera-

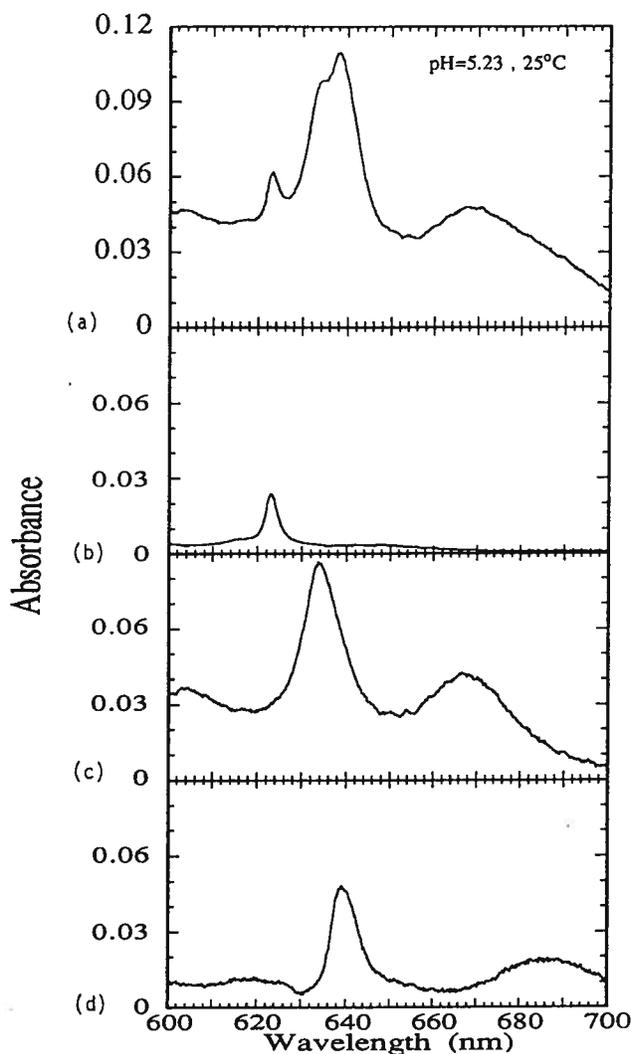
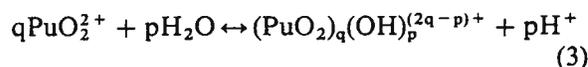


Fig. 2. Spectrum (a) of 0.012 M Pu(VI) in sodium perchlorate at pH = 5.23 and temperature = 25°C showing the component absorption bands for (b) the aquo ion at 622 nm, (c) the first hydrolysis product at 632 nm, and (d) the second hydrolysis product at 638 nm.

ture was held constant [9]. The spectra obtained at higher pH were deconvoluted in the same manner as the spectrometric data.

The generalized reaction for the hydrolysis of Pu(VI) is:



and the stability constant β_{pq} is defined as

$$\beta_{pq} = \frac{[(\text{PuO}_2)_q(\text{OH})_p^{(2q-p)+}][\text{H}^+]^p}{[\text{PuO}_2^{2+}]^q} \quad (4)$$

The total Pu(VI) concentration in the sample solution is given by

$$[\text{PuO}_2^{2+}]_t = [\text{PuO}_2^{2+}] + \sum_{q,p} q[(\text{PuO}_2)_q(\text{OH})_p^{(2q-p)+}] \quad (5)$$

here the subscript t denotes the total Pu(VI) concen-

tration. For a single value of q and p , the elimination of $[(\text{PuO}_2)_q(\text{OH})_p]^{(2q-p)+}$ from Eqs. (4) and (5) leads to the following:

$$[\text{H}^+]^p = \beta_{pq} \frac{q[\text{PuO}_2^{2+}]^q}{\{[\text{PuO}_2^{2+}]_t - [\text{PuO}_2^{2+}]\}} \quad (6)$$

The stability constant, when only two species are present, is the slope obtained when

$$[\text{H}^+]^p \text{ vs. } q[\text{PuO}_2^{2+}] / \{[\text{PuO}_2^{2+}]_t - [\text{PuO}_2^{2+}]\} \quad (7)$$

is plotted for a particular set of (p, q) . Since the initial hydrolysis of Pu(VI) was being emphasized, only (p, q) values of (1,1) and (2,2) were investigated. Analysis was limited to spectra where only the 622 nm and 632 nm bands were present.

Quantitative application of photoacoustic spectroscopy to temperature-variable studies

There are few reported studies that utilize photoacoustic spectroscopy to obtain quantitative measurements for aqueous systems and, in particular, actinide-containing aqueous systems. This is primarily because of the difficulty in establishing a reproducible signal baseline from sample to sample and day to day. We have, however, accomplished this at variable temperature by improving our overall methodology. The contribution of the acoustic signal due to the presence of particulates was minimized by allowing 16–24 h settling times after solution preparation. Less than 2% assembly/reassembly signal variation was present when the absorbance of interest was greater than that of water. Low dye laser pulse repetition (typically 10 Hz) was used to minimize long-term drift in the beam position due to the heating of the laser dye. When the absorbance of interest was < 50% that of water, it was not possible to decouple the PZT sensor to a satisfactory level of reproducibility. At these low plutonium concentrations, solution adjustments and changes were made in the LPAS cell without decoupling the PZT sensor to maintain signal reproducibility. Even with this approach, shifts in the absolute system response were occasionally observed.

The photoacoustic signal obtained, for directly comparable experimental configurations, was proportional to the concentration of the Pu(VI) species present in solution. A linear power dependence was observed [9] for the 622 nm (aquo) and 638 nm (second hydrolysis product) bands up to laser energies of 10 mJ/pulse.

Two important observations were made when the LPAS and spectrometric data were compared. First, at a fixed temperature, the band shapes obtained at 622 nm, 632 nm, and 638 nm are identical for each technique. This suggests that these bands represent the same hydrolytic species. Second, the relative extinction coefficients of the various absorption bands present are clearly not the same in the LPAS and spectrometric

spectra. The relative extinction coefficient at 632 nm and 638 nm is twice and three times as high, respectively, for the spectrometric data. We do not, at this time, have a defensible explanation for this result although a number of possibilities exist.

When temperature is varied, two additional factors need to be considered. First, the band shape of the Pu(VI) aquo ion (at 622 nm) varies with temperature. The extinction coefficients and bandwidths observed in the 10–45°C temperature range are tabulated in Table 1. Increased temperature resulted in a broadening of the band at a rate of $0.4 \pm 0.08 \text{ cm}^{-1} \text{ per } ^\circ\text{C}$ and a decrease in the molar absorptivity of $0.22 \pm 0.002 \text{ M}^{-1} \text{ cm}^{-1} \text{ per } ^\circ\text{C}$.

Second, the photoacoustic signal will also vary with temperature due to change in the acoustic properties of the solvent. The actual signal obtained will reflect both this change and the effect of temperature on the absorption spectrum. The LPAS signal increase observed for the Pu(VI) aquo ion are also listed in Table 1. Our results are in good agreement with the theoretical signal enhancement with increased temperature predicted by the equation of Tam and Patel [13]:

$$\text{LPAS signal} \propto \frac{BV_s^2}{C_p}$$

where B is the compressibility of the solvent, V_s is the velocity of sound in the solvent, and C_p is the isobaric heat capacity of the solvent.

Results and discussion

Auto-reduction of Pu(VI) in perchlorate media

In an aqueous medium that is both low in ionic strength and noncomplexing, autoradiolysis reduces Pu(VI) to Pu(V). At high total plutonium concentrations, the Pu(V) may build up in concentration to where its disproportionation to Pu(IV, VI) becomes important. The presence of Pu(IV and V) was of concern in this study because the various oxidation states of plutonium have very different tendencies toward hydrolysis, and spectral overlap between the Pu(VI) species of interest and absorption due to the other oxidation states could complicate data interpretation.

The oxidation-state stability of $^{242}\text{Pu(VI)}$ was determined by spectroscopically monitoring the buildup of Pu(IV) ($\epsilon = 34.4 \text{ M}^{-1} \text{ cm}^{-1}$ at 655 nm) and Pu(V) ($\epsilon = 19.3 \text{ M}^{-1} \text{ cm}^{-1}$ at 569 nm). The total activity of the ^{242}Pu used was, based on alpha scintillation counting, twice as high as predicted for the same concentration of the pure isotope. This was largely due to the presence of other plutonium isotopes as impurities (< 0.1 mol%) in the plutonium stock.

At a total plutonium concentration of 0.012 M, Pu(V) was radiolytically generated at a rate of 1.2% per week, corresponding to a decrease in the average oxidation state of 0.0017/day. Correspondingly,

Table 1. Effect of temperature on the band shape and LPAS signal for the Pu(VI) aquo ion absorption at 622 nm

Temperature (°C)	Absorption spectrometry			LPAS			
	$\Delta\lambda$ (nm)	Band width (cm^{-1})	Molar extinction coefficient ($\text{M}^{-1} \text{cm}^{-1}$)	$\Delta\lambda$ (nm)	Band width (cm^{-1})	Relative signal intensity <small>(at $\lambda = 622 \text{ nm}$)</small>	Relative* BV_2^2/C_p
10	-0.1	96	7.8				
15	0	99	7.8	-0.1	102	0.6	0.6
25	0	105	7.5	0	105	1.0	1.0
35	0.1	104	7.2				
45	0.1	112	7.1	0.1	113	1.6	1.6

* Predicted relative enhancement based on the theory of Tam and Patel [12].

G[Pu(V)] was 3.5 ± 0.3 molec/100 eV. There was no spectroscopic evidence of Pu(IV) formation after monitoring the solution for two weeks.

The extent of auto-reduction observed was consistent with previous work done with ^{239}Pu in acid media. A decrease in the average oxidation state of 0.014/day (G[Pu(V)] = 3.2 molec/100 eV) has been reported [14–16] and shown to be relatively insensitive to the presence of air and perchlorate concentration for $>1 \text{ M}$ acid. Our data extend these results to lower dose rates because of the lower isotopic activity of ^{242}Pu , and to higher pH (our sample pH was 3). To minimize oxidation-state impurities, experiments with ^{242}Pu were limited to 2 weeks, and experiments with ^{239}Pu were limited to <6 hours. The estimated oxidation state impurities under these conditions are $<2.5\%$ and $<0.4\%$, respectively.

Absorption and LPAS spectra as a function of pH at 25°C

The hydrolysis of Pu(VI) at 25°C was investigated as a function of total plutonium concentration and pH, with emphasis on the initial hydrolytic species observed. Spectrometric data were obtained at total plutonium concentrations of 0.028 and 0.012 M; LPAS was utilized to obtain data at lower plutonium concentrations, 1.6×10^{-4} and $6.9 \times 10^{-5} \text{ M}$. All solutions were at a total ionic strength of 0.10 M (sodium perchlorate and plutonium as the Pu(VI) aquo ion). The total plutonium concentration, solution pH, aquo ion concentration, and optical densities corresponding to the deconvoluted 622, 632, and 638 nm absorption bands are given in Table 2 for the spectrometric data and in Table 3 for the LPAS data.

Visible absorption spectra as a function of pH are shown in Figure 3 for 0.012 M Pu. Increasing pH resulted in a decrease in the absorption at 622 nm with a corresponding increase in the absorbance at 632 nm and 638 nm. As indicated in Table 2, the first spectral evidence for hydrolysis occurred at pH = 3.80 for absorbance at 632 nm. The second hydrolysis product (638 nm band) was not evident until pH = 4.93. This product becomes the predominant species at pH =

5.46. A similar trend was noted at $[\text{Pu}] = 0.028 \text{ M}$, except that the amount of hydrolyzed species present was approximately 10% greater at a given pH.

The LPAS spectra at $[\text{Pu}] = 1.6 \times 10^{-4} \text{ M}$ are shown as a function of pH in Figure 4. A similar sequence of band formations, as just described for the spectrometric data, was noted. As indicated in Table 3, the onset of hydrolysis was evident at pH = 4.89 and pH = 5.27 for $[\text{Pu}] = 1.6 \times 10^{-4}$ and $6.9 \times 10^{-5} \text{ M}$, respectively. The 638 nm species became predominant at pH = 6.36 at the lower plutonium concentration.

Figure 5 shows the distribution of the aquo ion, the first hydrolysis complex, and the second hydrolysis complex as a function of pH. These data correspond to total plutonium concentrations of 0.012 M, $1.6 \times 10^{-4} \text{ M}$, and $6.9 \times 10^{-5} \text{ M}$ and represent the relative concentration, in terms of plutonium content, of each species as obtained from the deconvoluted spectra. The 632 nm species is initially the predominant hydrolysis product at the higher plutonium concentrations; however, at lower concentrations, hydrolysis proceeds essentially directly to the 638 nm species.

Identity of the 632 nm species

At all plutonium concentrations investigated, the first hydrolytic species that we could distinguish spectrally occurred at 632 nm. Since we covered the range of total plutonium concentrations used by other investigators, this species is probably the first major hydrolytic species that they observed. Based on the data presented by others and comparisons with the hydrolytic scheme proposed for the uranyl system, this species is either PuO_2OH^+ (1:1 complex), its dimer (2:2 complex), or a mixture of both.

We had initially [9] assigned the 632 nm band to the 1:1 complex, based on the predictions of others that this species would be the predominant initial species at the plutonium concentrations used in our studies. We, however, also noted that our spectra were not completely consistent with that assignment. It is now our conclusion that the species represented by the 632 nm band is polynuclear and most likely the 2:2 complex. This conclusion is based on three findings.

Table 2. Spectrometric data for Pu(VI) hydrolysis at 25°C. Optical densities are obtained after deconvolution of the absorption spectra

Total Pu conc. (<i>M</i>)	pH ^a	Aquo ion conc. (<i>M</i>)	Optical density (OD) ^b		
			@ 622 nm	@ 632 nm	@ 638 nm
0.028	3.57	0.028	0.211	ND	ND
	4.28	0.0254	0.184	0.043	ND
	4.37	0.0239	0.180	0.053	ND
	4.47	0.0226	0.170	0.070	ND
0.0125	3.65	0.0125	0.094	ND	ND
	3.80	0.0122	0.092	0.005	ND
	4.21	0.0106	0.080	0.014	ND
	4.43	0.0096	0.072	0.025	ND
	4.78	0.0072	0.054	0.064	ND
	4.93	0.0055	0.041	0.078	0.009
	5.23	0.0029	0.022	0.078	0.052
	5.46	0.0012	0.009	0.051	0.143

^a Uncertainty is ± 0.02 pH units.

^b Uncertainty in the deconvoluted absorption data is ± 0.002 OD units.

ND = not detected.

Table 3. LPAS data for Pu(VI) hydrolysis at 25°C. Relative LPAS signal obtained after deconvolution of the LPAS spectra.

Total Pu conc. (<i>M</i>)	pH ^a	Aquo ion conc. (<i>M</i>)	Relative LPAS signal ^b		
			@ 622 nm	@ 632 nm	@ 638 nm
1.6×10^{-4}	2.6	1.6×10^{-4}	0.105	ND	ND
	4.89	1.54×10^{-4}	0.101	0.0035	ND
	5.26	1.34×10^{-4}	0.088	0.014	ND
	5.50	1.02×10^{-4}	0.067	0.034	ND
	5.60	1.14×10^{-4}	0.075	0.031	ND
	5.90	7.2×10^{-5}	0.047	0.060	0.003
	6.40	1.7×10^{-5}	0.011	0.044	0.029
6.9×10^{-5}	3.3	6.90×10^{-5}	0.103	ND	ND
	4.8	6.69×10^{-5}	0.0998	ND	ND
	4.95	6.53×10^{-5}	0.0975	ND	ND
	5.27	5.93×10^{-5}	0.0885	0.012	ND
	5.58	4.70×10^{-5}	0.0702	0.023	ND
	5.80	5.17×10^{-5}	0.0771	0.035	ND
	5.96	1.98×10^{-5}	0.0296	0.034	0.007
	6.36	1.15×10^{-5}	0.0172	0.025	0.047

^a Uncertainty is ± 0.02 pH units.

^b Uncertainty is ± 0.002 relative units. Note that system gain is adjusted when total solution concentration is changed.

ND = not detected.

First, we found no evidence for a change in the band shape of the deconvoluted spectrum as the total concentration of plutonium and pH changed. The absorption band centered at 632 nm, which is the first hydrolysis product observed at all plutonium concentrations, was analyzed for evidence of a change in band shape, indicating that more than one complex may be present. Figure 6 shows the 632 nm band obtained at [Pu]=0.012 *M* (pH=4.78) and the normalized LPAS spectrum obtained at [Pu]= 1.6×10^{-4} *M* (pH=5.60). These spectra are identical within the uncertainty of the data. We estimate, based on experimental uncertainty, that 3% of the plutonyl could be present as the 1:1 complex at pH=5.27, corresponding to a $-\log \beta_{11} \geq 6.7$.

The second, and perhaps most convincing, argument for the 632 nm band as a polynuclear species is that the onset of hydrolysis is a function of the total plutonium concentration. As indicated by Figures 3 and 4, the pH at which hydrolysis was evident increased as the plutonium concentration decreased. This can only be explained if the 632 nm band represents a predominantly polynuclear species. This effect is not small, as evident in the spectra taken at the same pH but differing total plutonium concentrations shown in Figure 7. If the 632 nm band could be interpreted as a 1:1 complex, the [aquo ion]/[632 nm species] would not change with total plutonium concentration at a fixed pH.

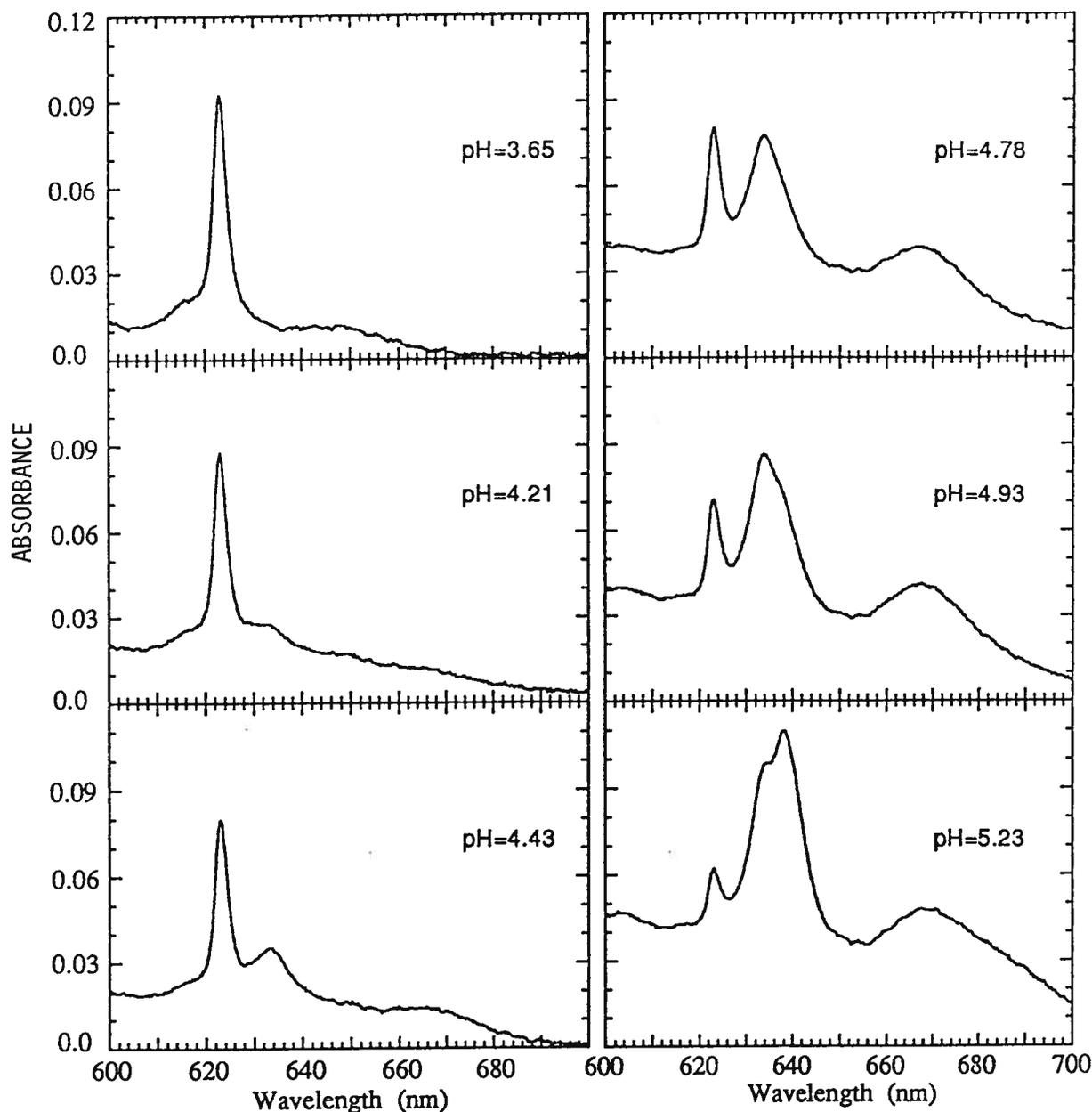


Fig. 3. Absorption spectra for 0.012 *M* Pu(VI) in sodium perchlorate at 25°C as a function of pH.

The third argument that supports the assignment of the 632 nm band to the 2:2 complex is that reaction 2 is most consistent with the formation constant determinations. The species distribution data, at all concentrations investigated, were analyzed assuming both a 1:1 and 2:2 hydrolysis complex. These results are summarized in Table 4. As is evident from these data, although reasonable linearity was obtained for each plutonium concentration and type of analysis, the magnitude of the formation constant as a function of total plutonium concentration changed when a 1:1 complex was assumed. The determination of β_{22} for the highest plutonium concentration had high uncertainty because only three data points were used. The three lowest plutonium concentrations have β_{22} values that are within experimental error. The β_{22} plot

obtained at $[\text{Pu}]_i = 6.9 \times 10^{-5} \text{ M}$ was linear, as shown in Figure 8. The formation constant derived from the slope is $5.0 \pm 1.5 \times 10^{-8} \text{ M}$, corresponding to a $-\log \beta_{22}$ value of 7.3 ± 0.2 .

Comparison of our results to the literature

The hydrolysis of Pu(VI) has been previously investigated by potentiometry [17–19], absorption spectrometry [2, 20, 21], Raman spectroscopy [10], and solubility studies of plutonium [22]. Earlier work [18–21] concluded that the initial hydrolytic product was the PuO_2OH^+ complex and reported formation constants for this complex that ranged between $4.68 \times 10^{-4} \text{ M}$ and $1.07 \times 10^{-6} \text{ M}$, with the latter

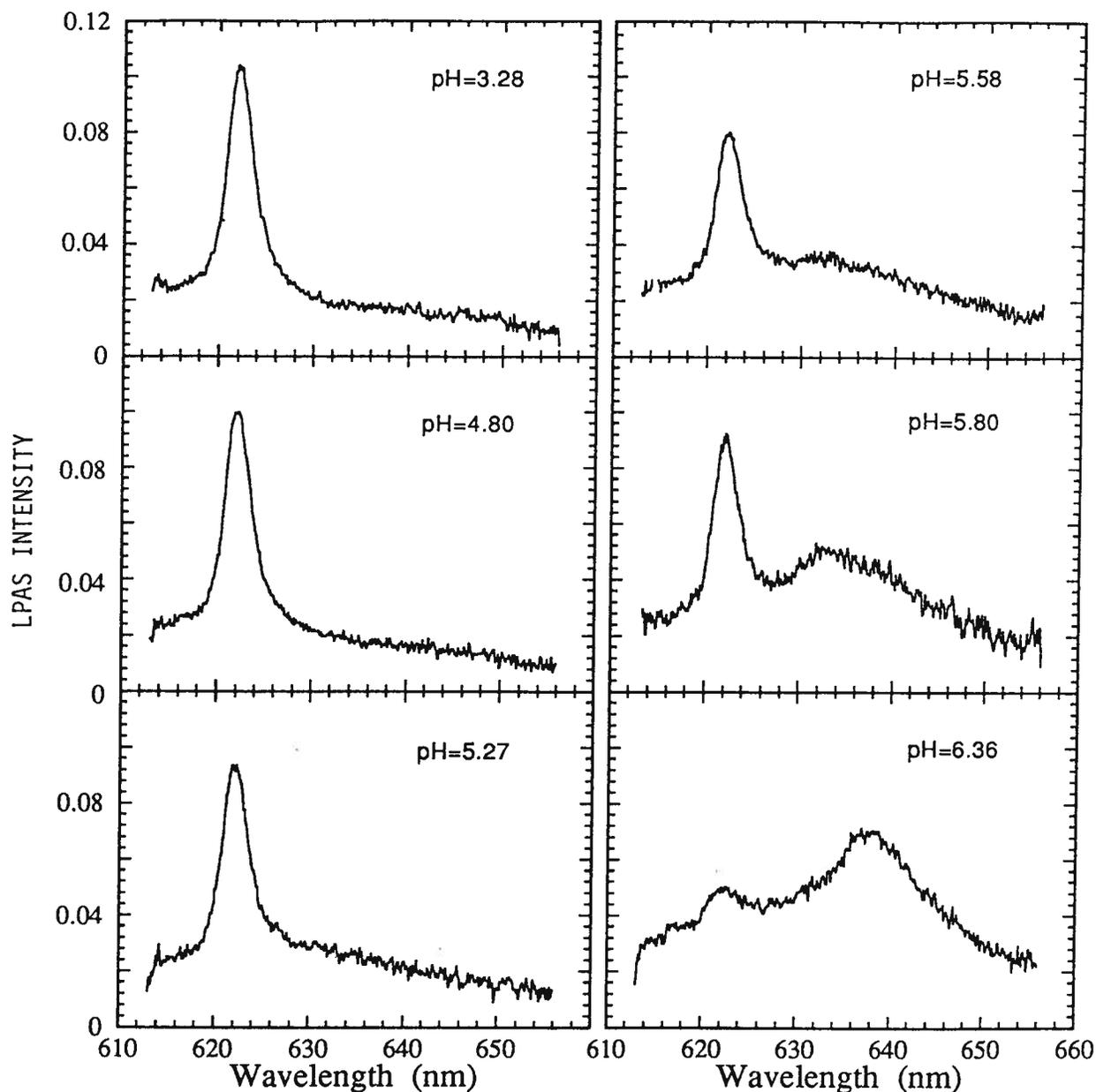


Fig. 4. Laser photoacoustic spectra for $6.9 \times 10^{-5} M$ Pu(VI) in sodium perchlorate at $25^\circ C$ as a function of pH.

value being the more favored. Our data indicate that the formation constant for this complex is smaller than $3 \times 10^{-7} M$, corresponding to a $-\log \beta_{11}$ value of ≥ 6.7 .

Schedin [17] was the first to suggest that the 2:2 complex is an important hydrolytic species. It is clearly the predominant initial hydrolytic species at plutonium concentrations greater than $0.001 M$. The 2:2 complex has also been identified as an important initial hydrolytic species by Raman spectroscopy [10] at high plutonium concentrations. This is consistent with what we observed spectroscopically in our high-concentration data. The formation of the 2:2 complex, although never predominant, is the first spectrally observable hydrolytic product at the lowest concentration that we investigated ($6.9 \times 10^{-5} M$).

The magnitude of the formation constant that we determined for the 2:2 complex was a factor of five to ten greater than that reported by indirect methods. We believe this is, in part, due to important differences in our experimental approach other than our utilization of spectroscopic methods. Whereas potentiometric titrations are relatively short (typical equilibration times are < 1 min), we used equilibration times of 16–24 hours for each pH adjustment. Re-analysis of our $0.012 M$ solutions, where only the 622 and 632 nm bands were evident, showed that no slow change in the extent of hydrolysis occurred between 1 and 7 days. We, however, noted pH drift over a period of a few hours, for even the 632 nm species, at the lowest plutonium concentration. These observations, along with results reported by others [2, 23], suggest that

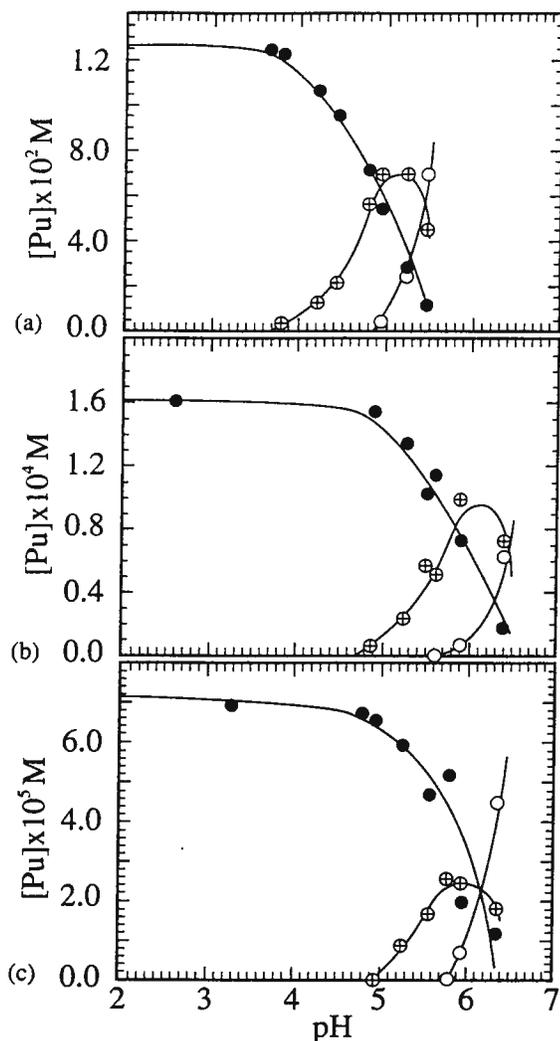


Fig. 5. Distribution of aquo ion (●), initial hydrolysis complex (⊕), and second hydrolysis complex (○) as a function of pH at plutonium concentration of (a) $1.2 \times 10^{-2} \text{ M}$, (b) $1.6 \times 10^{-4} \text{ M}$, and (c) $6.9 \times 10^{-5} \text{ M}$.

hydrolysis kinetics is likely an important consideration for the formation of the 2:2 complex.

Our data do not agree with predictions [1], based on existing Pu(VI) hydrolysis data, concerning the importance of polynuclear vs. mononuclear species. In the plutonyl system, all the species that we directly identified, both the 632 and 638 nm bands, were polynuclear. The 638 nm species, once formed, does not dehydrolyze reversibly and takes at least weeks to completely dehydrolyze. We previously [3] suggested that this indicates the possible presence of polymerization, which may be affected by solution aging. Our data show that monomeric species are not important at concentrations as low as 10^{-4} M . Plutonyl appears to have a tendency toward the formation of polynuclear species that is comparable to the uranyl (UO_2^{2+}) species.

We were not able to observe an absorption band that could be directly attributed to the 1:1 complex for the plutonyl system. Since we have shown that the band formation in the 600–700 nm region of the

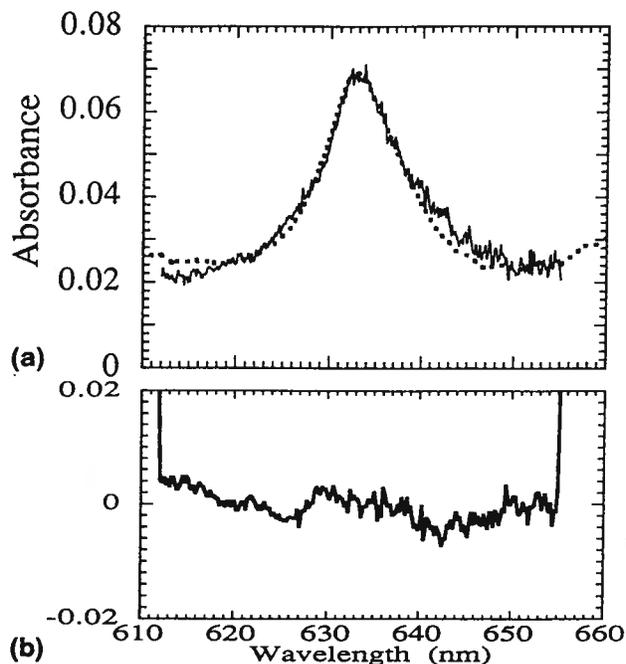


Fig. 6. Comparison of the 632 nm absorption band obtained at 25°C for 0.012 M Pu(VI), $\text{pH} = 4.78$, and $1.6 \times 10^{-4} \text{ M}$ Pu(VI), $\text{pH} = 5.60$. (a) Superposition of the high (solid line) and low (dashed line) concentration spectrum and (b) difference obtained when the normalized spectra are subtracted.

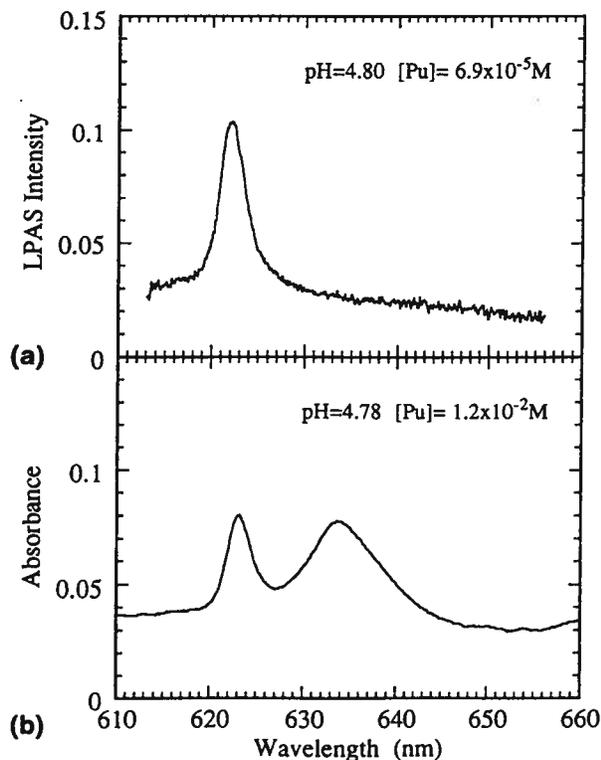


Fig. 7. Comparison of the Pu(VI) spectra obtained at $\text{pH} = 4.8$ for (a) $6.9 \times 10^{-5} \text{ M}$ and (b) $1.2 \times 10^{-2} \text{ M}$ plutonium solutions.

Pu(VI) spectrum is related to that observed in the more commonly investigated 800–900 nm region [9], we do not believe that any of the absorption bands

Table 4. Formation constants as a function of total plutonium concentration. Correlation values obtained are shown in parenthesis

Total plutonium concentration (M)	$-\log\beta_{11}$ value ^a	$-\log\beta_{22}$ value ^a
0.028	5.2 ± 0.3 (0.98)	8.0 ± 0.4 (0.96)
0.012	5.4 ± 0.2 (0.96)	7.5 ± 0.1 (1.00)
1.4×10^{-4}	6.2 ± 0.2 (0.93)	7.5 ± 0.2 (0.91)
6.9×10^{-5}	6.3 ± 0.1 (0.98)	7.3 ± 0.1 (1.00)

^a 3σ error limits corresponding to $>95\%$ confidence interval.

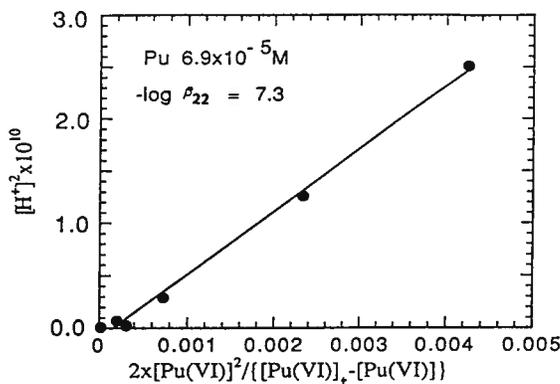


Fig. 8. Plot of $[H^+]^2$ vs. $2[PuO_2^{2+}]^2 / \{[PuO_2^{2+}]_t - [PuO_2^{2+}]\}$ observed at $25^\circ C$ and $[Pu(VI)] = 6.9 \times 10^{-5} M$.

reported in the literature in the longer wavelength region correspond to the 1:1 complex. We recognize, however, that at a low enough total plutonium concentration, this species should exist. Nevertheless, the formation constants for the 1:1 complex reported in the literature are not consistent with our observations. This yet unobserved complex, along with the 638 nm complex, is the most likely hydrolytic species to be of environmental significance and should be the focus of environmental studies.

Effect of temperature on the formation of $(PuO_2OH)_2^{2+}$

The effect of temperature on the initial hydrolysis of Pu(VI), which we have proposed to involve the formation of the $(PuO_2OH)_2^{2+}$ complex, was determined between $10^\circ C$ and $45^\circ C$ using both LPAS and absorption spectrometry. Essentially no effect of temperature was noted. The absorption spectra as a function of temperature are shown in Figure 9 for $0.012 M$ Pu(VI) at $pH = 4.78$. At this pH, approximately 50% of the Pu(VI) was hydrolyzed. The LPAS spectra as a function of temperature are shown in Figure 10; these data are for $5.0 \times 10^{-4} M$ Pu(VI) at $pH = 5.37$. The spectra recorded at $15^\circ C$ and $45^\circ C$ were corrected for the temperature enhancement of the LPAS signal, as previously discussed. We assumed that the effect of temperature on the molar extinction coefficient for the 632 nm band was similar to that of the aquo ion.

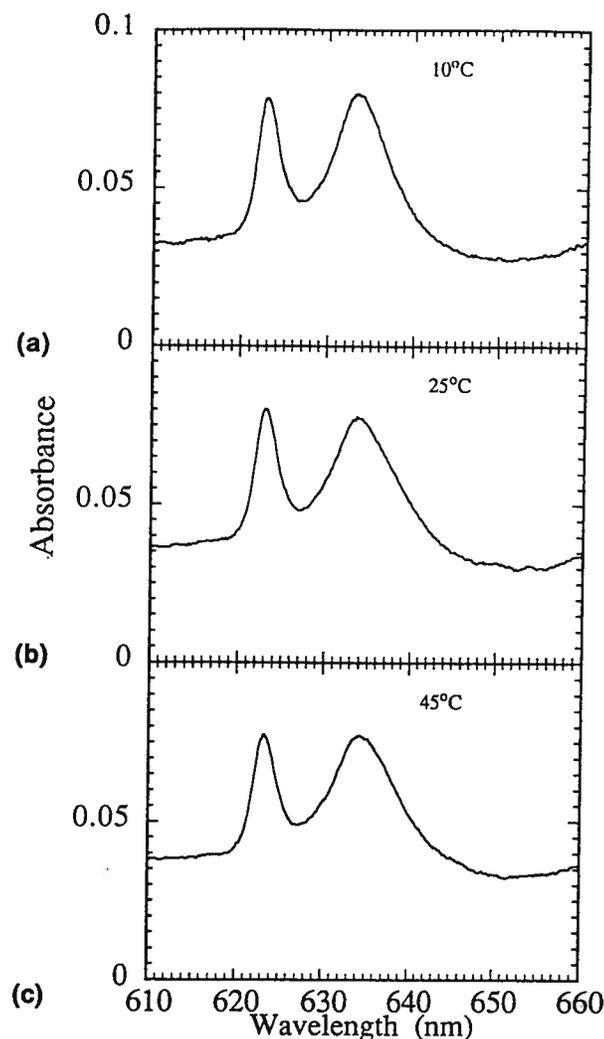


Fig. 9. Absorption spectra of $0.012 M$ Pu(VI) for $pH = 4.78$ ($21^\circ C$) at (a) $10^\circ C$, (b) $25^\circ C$, and (c) $45^\circ C$.

Both the LPAS and spectrometric data show that the effect of temperature on the extent of Pu(VI) hydrolysis is small and close to the experimental limitations of the spectroscopic methodology utilized. This temperature dependence is not in agreement with the predictions, based on estimates of thermodynamic data, made by Lemire and Tremaine [24]. For the temperature range that we investigated, increased temperature should have increased hydrolysis by a factor of ten.

To estimate the reaction enthalpy for the formation of $(PuO_2OH)_2^{2+}$, the effect of temperature on the formation constant was determined for the LPAS and spectrometric data. The results are presented in Figure 11, along with the results by Lemire and Tremaine [24]. The slope of the plots, which corresponds to the enthalpy of reaction, obtained from LPAS and absorption data was 215 ± 1.0 and 564 ± 500 , respectively. Although the small effect of temperature and the relatively narrow temperature range investigated do not permit a precise determination of the temperature dependence, it is important

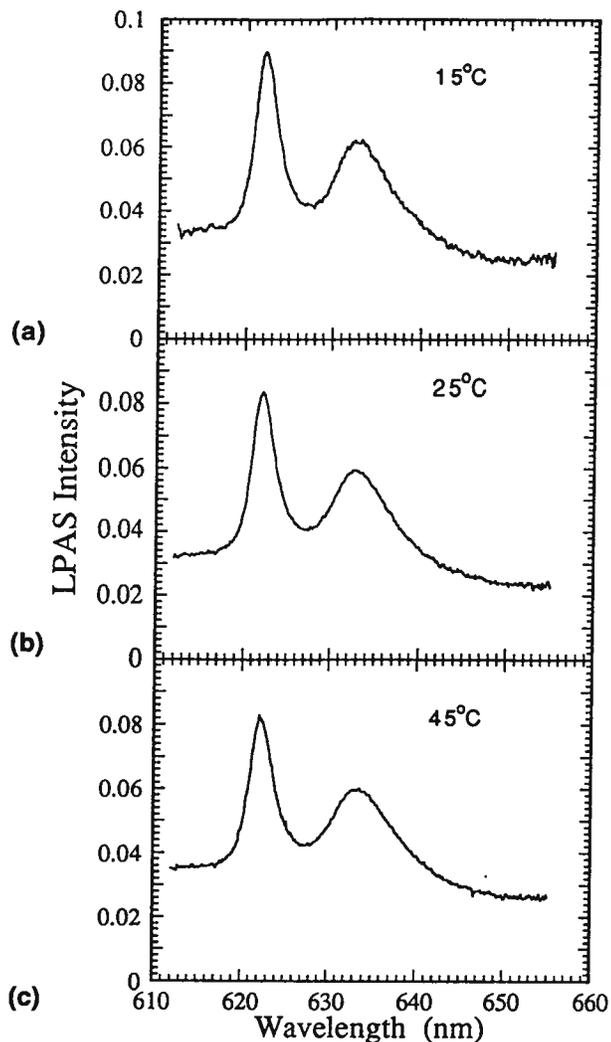


Fig. 10. LPAS spectra of $5.0 \times 10^{-4} M$ Pu(VI) for pH = 5.37 (21°C) at (a) 15°C, (b) 25°C, and (c) 45°C.

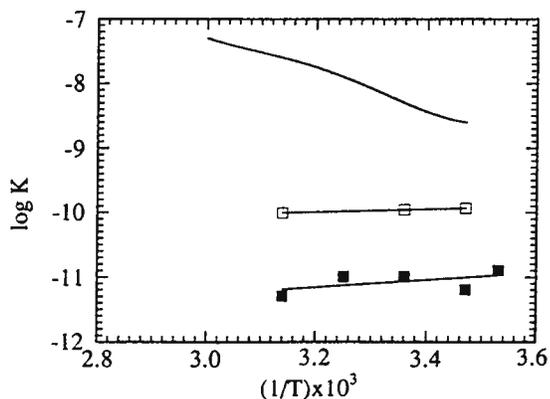


Fig. 11. Relative change in $\log(K)$ as a function of $1/T$. LPAS data obtained at $5 \times 10^{-4} M$ (\square) and absorption data at $0.012 M$ (\blacksquare). Solid line represents theoretical predictions from Lemire and Tremaine [24].

to note that our results suggest an exothermic rather than endothermic hydrolysis reaction. The similarity in temperature dependence of the formation constant that was observed at high and low Pu(VI) concen-

trations is additional evidence that the same species is being observed.

The enthalpy and the entropy corresponding to the formation of $(PuO_2OH)_2^{2+}$ species were estimated from the absorption and LPAS data. Acknowledging the limited nature of our data, we estimate a value of $\Delta H = -11 \pm 10$ kJ/mol and -4.0 ± 0.1 kJ/mol from the UV-VIS and LPAS data, respectively. The corresponding $\Delta S = 170 \pm 30$ J/molK. The enthalpy and the entropy calculated using literature values for the 2:2 complex are $\Delta H = 59$ kJ/mol and $\Delta S = 357$ J/molK. Further temperature-dependent data are needed with other Pu(VI) species, as well as the hydrolytic species, to resolve these discrepancies.

Conclusions

The initial hydrolytic species observed spectroscopically at plutonium concentrations $\geq 6.9 \times 10^{-5} M$ was a polynuclear species, which we believe to be the $(PuO_2OH)_2^{2+}$ hydrolytic complex. The formation constant for the hydrolytic reaction is $5.0 \pm 1.5 \times 10^{-8} M$. The effect of temperature on the relative concentration of the aquo and $(PuO_2OH)_2^{2+}$ complex is small and at or near the detection limits of the methodology utilized. We have estimated a $\Delta H = -11 \pm 10$ kJ/mol and $\Delta S = 170 \pm 30$ J/molK for this hydrolytic reaction.

Our conclusions do not agree with most existing literature in three respects. First, we have concluded that polynuclear hydrolytic species are more important than predicted by existing data. We have proposed that this discrepancy is, in part, due to slow hydrolysis kinetics that have not been fully recognized in other work reported. This effect needs to be investigated further using other experimental methods. Second, we have seen no spectroscopic evidence for the formation of the PuO_2OH^+ hydrolytic species and suggest that the formation constant for this reaction is $< 3 \times 10^{-7} M$. Third, we have measured a much smaller effect of temperature than is predicted by current theoretical estimates. As we are the first to report temperature-effect data for the Pu(VI) hydrolytic system, we believe that further work is needed to validate our results and extend them to other systems before a definitive explanation for this can be given.

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