DTN 48945 QA:NA CB 10/5/06

Complexation of Plutonium (IV) with Sulfate at Variable Temperatures

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Abstract

The complexation of plutonium(IV) with sulfate at variable temperatures has been investigated by solvent extraction method. A $NaBrO_3$ solution was used as holding oxidant to maintain the plutonium(IV) oxidation state throughout the experiments. The distribution ratio of Pu(IV) between the organic and aqueous phases was found to decrease as the concentrations of sulfate were increased. Stability constants of the 1:1 and 1:2 Pu(IV)-HSO_4^- complexes, dominant in the aqueous phase, were calculated from the effect of [HSO_4^-] on the distribution ratio. The enthalpy and entropy of complexation were calculated from the stability constants at different temperatures using the Van't Hoff equation.

Introduction

Plutonium is an important radioactive component of nuclear wastes proposed to be disposed of in high-level waste and spent nuclear fuel repositories due to its high toxicity and long half life (^{239}Pu, $t_{1/2}$ = 2.41 x 10^4 years). As a result, the migration of plutonium in the postclosure chemical environment of waste repositories is of great concern to long-term repository performance. Depending on the chemical environment in the repositories and the surrounding geologic media, plutonium could exist in oxidation states ranging from III to VII and several (e.g., Pu(III) to Pu(VI)) can exist simultaneously in significant amounts in solution. These oxidation states have drastically different chemical behavior in terms of solubility and complexation. For example, tri- and tetravalent plutonium readily form solid phases that are very insoluble when compared with penta- and hexavalent states. Moreover, tetravalent plutonium forms much stronger complexes with ligands than pentavalent plutonium. Consequently, the solubility of plutonium after disposal will depend largely on its reactions (e.g., dissolution/precipitation and complexation) with various components present in the repository. The interactions of plutonium with some inorganic ligands at elevated temperatures may be a significant factor in determining the solubility and migration of the plutonium in the nuclear waste repository. For example, sulfate is expected to be present in the water in contact with the nuclear waste packages and may affect the speciation and migration of actinides by forming complexes[1-2]. Studies of complexation of Pu(IV) with various inorganic ligands have recently reviewed[3]. Several studies of the aqueous Pu(IV) sulfate system have been conducted using spectrophotometric[4], ion exchange[5-6], solvent extraction [7-13] and potentiometric methods[14]. But all these data on the stability constants of Pu(IV) complexes with sulfate were obtained at the room temperature. Only Nash and Cleveland[13] reported their data on the stability constants of Pu(IV) complexes with HSO_4^-

at different temperatures (10, 25 and 35° C). No literature data are available in the Pu(IV)-HSO_4^- system at > 40°C temperatures. It is well known that the equilibrium constants of complexation could vary by orders of magnitude in the temperature range (25-80° C) relevant to waste repositories. In order to minimize the uncertainty in the prediction of Pu(IV) migration, it is necessary to know sufficient and reliable thermodynamic data on its complexes at elevated temperatures. Unfortunately, experimental data on the effects of temperatures in these systems are very scarce at present.

In this work, a solvent extraction method[15-18] was used to determine the stability constants of Pu(IV) complexes with sulfate anions (HSO_4^- is the dominant species in the 2.0 M of $HClO_4$ and H_2SO_4 solution) at ionic strength (I) = 2.0 and $t = 25° - 55°$ C. Thenoyltrifluoroacetone (TTA) was used as a solvent extractant and toluene as a solvent.

The complexation reaction of Pu(IV) with HSO_4^- anion under experimental conditions used in this study can be expressed as:

$$Pu^{4+} + q\,HSO_4^- = Pu\,(SO_4)_q^{4-2q} + qH^+ \qquad (1)$$

With the overall stability constant β_q defined as:

$$\beta_q = [Pu(SO_4)_q^{4-2q}]\,[H^+]^q/([\,Pu^{4+}]\,[HSO_4^-\,]^q) \qquad (2)$$

In the solvent extraction system, the distribution ratio (D) of a metal ion, M, is defined as:

$$D = \Sigma [M]_o / \Sigma [M]_a \qquad (3)$$

Assuming there is only a single organic (o) phase species, MA_n where A stands for the extractant molecule, and there are various species in the aqueous phase (a) including ML_i where L stands for the complexant ligand in the aqueous phase, the equation (3) can be written with the stability constants as expressed in the literature[15-18]:

$$D_o/D = 1 + \Sigma (\beta i / [H^+]^i) [L]^i \qquad (4)$$

where D_o is the distribution ratio in the absence of complexation in the aqueous phase. For the Pu(IV)- HSO_4^- complex system , M, L and A stand for Pu(IV), HSO_4^- anion, and the TTA anion, respectively.

Experimental

Reagents and solutions

All solutions were prepared with distilled-deionized (DDI) water and all reagents used in this work were analytical grade or higher. The stock solutions of 1.0 M H_2SO_4, 2.0 M and 4.0 M $HClO_4$ were prepared by dilution of sulfuric acid (95-98%, Aldrich) and perchloric acid, (double distilled, 70%, Aldrich) in DDI water respectively, and standardized by titration with standard NaOH (Aldrich). Sodium bromate was used as a holding oxidant to maintain plutonium as Pu(IV). A 0.05 M tetraheptylammonium chloride (THAC, Aldrich) in chloroform (Aldrich) was used to prepare the Pu(IV) stock in the 2.0 M $HClO_4$ solution.

TTA (Aldrich) was purified by vacuum sublimation at 42°C. Stock solutions of 0.5 M and 0.05 M TTA in toluene (99.8%, HPLC grade, Aldrich) were prepared by weight. The organic solutions were pre-equilibrated with dilute perchloric acid overnight to allow hydration, and stored in a dark glass bottle. All solutions except the Pu(IV) tracer solution were filtered with a 0.2 μm microfiltration system to minimize sorption of Pu(IV) by suspended particles in solution.

Preparation of stock of Pu(IV)

A Pu(IV) solution was prepared through anion exchange purification of plutonium, followed by treatment with H_2O_2. Details for the preparation of Pu(IV) in 8.0 M HNO_3 solution are given elsewhere[19]. In order to ensure that only the Pu(IV) oxidation state was present in this solution and prepare the Pu(IV) stock in 2.0 M $HClO_4$ solution, the following procedure was used: 1) The Pu(IV) in 1.0 M HNO_3 was extracted into the 0.5 M TTA in toluene, and then the Pu(IV) was back extracted into 8.0 M HNO_3 from the TTA organic phase. 2) The Pu(IV) in 8.0 M HNO_3 solution was titrated with NaOH to make freshly precipitated Pu(IV)-hydroxide. 3) The freshly precipitated Pu(IV)-hydroxide was washed several times with DDI water and dissolved by 2.0 M $HClO_4$ solution. 4) The Pu(IV) in 2.0 M $HClO_4$ was filtrated with 0.22 μm pore size to separate the colloidal Pu(IV) that was generated during the above steps. 5) The oxidation state of

Pu(IV) was confirmed spectrophotometrically on a Cary 500 UV-Vis-NIR Spectrophotometer.

To prepare Pu(IV) stock in the 2.0 M $HClO_4$ solution, the following method was also employed in this study: the Pu(IV) in 1.0 M HNO_3 was extracted into an organic phase of 0.05 M THAC in $CHCl_3$, and then the extracted Pu(IV) was directly back extracted into 2.0 M $HClO_4$ solution.

From the stock solution, a working solution of Pu(IV) was prepared in 2.0 M $HClO_4$ such that 20 μL of the solution gives an α-counting rate of ca. 19000 cpm (or 8000 cpm). The activity of ^{239}Pu in the samples was measured on a Wallac Model 1414 liquid scintillation counter (LSC).

Analysis of $\gamma-$ spectroscopy indicated that the plutonium used in this study had the following isotopic composition (as a percentage of total activity): 93.6% ^{239}Pu and 6.3% ^{240}Pu.

Temperature-controlled extraction equipment

The temperature-controlled extraction equipment used for this work has been described previously[18]. To shake the samples at the desired temperature, an aluminum reaction block with heat tape was used. The reaction block has machined holes for the selected sample vials and a specific hole for a bayonet insert. Temperature control was accomplished through a variable-voltage transformer.

A Speedfuge (HSX10K) centrifuge with a water jacket enclosed around the rotor was used to centrifuge the samples. Water from a Brinkmann RM6 Lauda temperature controlled water circulator controlled the temperature of the samples inside the centrifuge.

Two J-KEM digital temperature monitors for Type T thermocouples with a range from -200 to 250°C were used with two Type T reaction block thermocouples to monitor the temperature of reaction blocks and centrifuge during the experiments.

A temperature adjusted reaction block is used to maintain the temperature of experimental solutions, and samples.

Solvent extraction

The distribution experiments were conducted following procedure described in the literature[15-18]. A holding oxidant, sodium bromate, was used to maintain the tetravalent oxidant state of plutonium during the distribution experiments.

For each extraction experiment, 1.5 ml (or 1.0 ml) of 2.0 M $HClO_4$ and H_2SO_4 sulfuric acid and 0.01 M $NaBrO_3$, and equal volume of 0.05 M TTA in toluene was placed in a borosilicate glass vial. After addition of 20 μL ^{239}Pu(IV) tracer, the vials were inserted into the holes of the temperature-controlled reaction block and shaken for thirty minutes at the desired temperature. Preliminary kinetic studies confirmed that the extraction equilibrium was achieved within this time. The vials were centrifuged at the same temperature as the reaction block on the shaker and aliquots of 0.3 ml (or 0.4 ml) were taken from each phase to measure the α-activity by LSC using Hionic Fluor as the scintillation cocktail.

Two sets of distribution experiments were conducted at each temperature. The first set of distribution experiments, as mentioned above, at a constant concentration of 0.05 M TTA in toluene, was equilibrated with a series of aqueous solutions at 2.0 M acidity (2.0 M ionic strength) in the presence of varying HSO_4^- concentrations. The second set of experiments determined the extraction equilibrium for Pu(IV)-TTA system with varying concentrations of TTA in the absence of sulfate ions.

Precautions taken to maintain and verify the presence of Pu(IV)

Because the Pu(IV) hydrolyzes and disproportionates extensively in aqueous solutions[20], Pu(IV) could be reduced to Pu(III) during the distribution experiments using TTA[7-8,10-13]. Special precautions were taken to maintain plutonium as Pu(IV) throughout the experiments except for performing experiments in the high acidity and low concentration of Pu(IV) used. These precautions included: 1) aqueous phase contained small amounts of sodium bromate (0.01 M) as holding oxidant during the distribution experiments as mentioned above; 2) TTA was purified by vacuum sublimation at 42°C and stock solutions of 0.5 M and 0.05 M TTA in toluene were treated with 0.01 M $KBrO_3$ to remove reducing impurities in the TTA-toluene solution that could affect the results of this study; and 3) the Pu(IV) stock solution was often checked by extracting an aliquot of plutonium into 0.5 M TTA in toluene from 1.0 M HNO_3 and the extraction of > 99.9% of plutonium into 0.5 M TTA was taken as the criterion for the absence of oxidation states other than Pu(IV). In addition to these precautions, in parallel to each of the first set of experiments, the second set of experiments was conducted for each temperature as mentioned above. The second set of experiments determined the solvent extraction equilibrium for Pu(IV)-TTA system at each temperature to check the slope of about 4 from the plot of log D versus log [TTA] (see below section of Results and Discussion), and the tests were performed to confirm that plutonium was maintained as Pu(IV) during the distribution experiments. In the tests, the aqueous aliquots after 0.05 M TTA extractions were tested for Pu(IV) concentrations, as described below.

After the 0.05 M TTA extraction, a selected solution containing plutonium was immediately adjusted to 1.0 M HNO_3. The solution was then equally divided into two portions, I and II. Appropriate amounts of sodium bromate were added to portion I, but not to portion II. Both portions were equilibrated with 0.5 TTA in toluene, and the distribution ratios of plutonium were measured. If Pu(IV) was somehow reduced to Pu(III) in previous 0.05 M TTA distribution experiments, the distribution ratio obtained by this 0.5 M TTA extraction for portion I (with sodium bromate) would be higher than that for portion II (without sodium bromate). However, for all aqueous solutions tested using 0.5 M TTA extraction after 0.05 M TTA extraction, no significant difference was observed in the distribution ratios for the two portions, suggesting that no detectable degree of reduction of Pu(IV) to Pu(III) occurred during 0.05 M TTA extractions at each temperature.

Results and Discussion

Pu(IV)-TTA extraction system

For the Pu(IV)-TTA extraction system, the expected extraction equilibrium is given in equation 5:

$$Pu^{4+} + 4\ HTTA = Pu(TTA)_4 + 4\ H^+ \qquad (5)$$

With the extraction equilibrium constant K_{ex} defined as:

$$K_{ex} = ([Pu(TTA)_4]\ [H^+]^4)/([Pu^{4+}]\ [HTTA]^4) \qquad (6)$$

In Pu(IV)-TTA extraction system, the distribution ratio D is:

$$D = [Pu(TTA)_4]\ /[Pu^{4+}] \qquad (7)$$

Combining equations (6) and (7), the following equation 8 can be written as:

$$\log D = \log K_{ex} + 4 \log [HTTA] - 4 \log [H^+] \qquad (8)$$

At constant 2.0 M $HClO_4$ and a desired temperature, the slope of the log D versus log [HTTA] plots are within 3% of the theoretical slope of four. The slope data and extraction equilibrium constants are listed in Table 1. The fourth power dependence on the concentration of TTA at different temperatures confirmed that the oxidation state of Pu(IV) is unchanged during the distribution experiments. According the extraction mechanism, if Pu(IV) reduced to Pu(III) in the extraction, the slope value should be lower than the theoretical slope of 4.

The extraction constant determined from data in Table 1 is consistent with those in the literature for the extraction of Pu(IV) by TTA[13, 21-22].

Pu(IV)-HSO_4^- complexation system

A series of experiments with constant concentrations of $HClO_4$ and H_2SO_4 were conducted at an ionic strength of 2.0 M. Distribution ratios (D) of Pu(IV) between the organic and aqueous phases were found to decrease with the increase in the concentration of HSO_4^- (see Tables 2-4). The decrease in D can be attributed to the increase in concentration of Pu(IV)- HSO_4^- complexes in the aqueous phase that are not extracted by TTA. Stability constants of the 1:1 and 1:2 Pu(IV)- HSO_4^- complexes, dominant in the aqueous phase under the experimental conditions, were calculated from the effect of $[HSO_4^-]$ on the distribution ratio.

Experiments have been conducted at 25°, 40° and 55° C. A representative plot of D_o/D versus the free concentration of HSO_4^- at 55 ± 1° C is shown in Figure 1, where the points are experimental data and the solid line represents the fit for the formation of 1:1 and 1:2 complexes. From these data, the stability constants of the Pu(IV) complexes with HSO_4^- at 25 - 55° C are calculated. Because Pu(IV) is at the tracer level and the amount of Pu(IV)- HSO_4^-, complex is negligible compared to the total amount of HSO_4^-, the concentration of free HSO_4^- anion ($[HSO_4^-]_f$) can be considered equal to the total concentration of HSO_4^- anion ($[H_2PO_4^-]_T$).

The Pu(IV) hydrolyzes extensively in aqueous solutions. In this study, a lower concentration of Pu(IV) stock (1.3×10^{-5} M) in 2.0 M $HClO_4$ was used, and after two weeks a freshly Pu(IV) stock was re-prepared and re-checked to verify the oxidation state of Pu as Pu(IV). Thus, the hydrolysis reactions of Pu(IV) are not included in the calculation.

From the observation of 0.05 M TTA stoichiometries of about 4 (see Table 1) and the estimates of stability constant for the aqueous phase complexing of Pu(IV) by TTA are on the order of $K_1 = 60 \pm 15$[10,13,21], and indicating about 2% aqueous solubility for TTA in benzene. Nash and Cleveland[13] indicate that consideration of the aqueous $PuTTA^{3+}$ complex is included in the error analysis of $PuSO_4^{2+}$ stability constant. Thus, the stability constants of Pu(IV) complexes with HSO_4^- obtained from this study were not corrected.

The apparent stability constants obtained from this work are listed in Table 5 along with the literature data for comparison. There are a number of independent evaluation of the stability constants of Pu(IV)-SO_4^{2-} complexes[3]. All of the measurements are made at high ionic strength and at high acidity. The literature data on the stability constants of Pu(IV) complexes with sulfate listed in Table 5 are the best values reevaluated by the reviewers[3]. The values at 25° C from this work ($\log \beta_1 = 2.71 \pm 0.05$, $\log \beta_2 = 4.59 \pm 0.04$) are consistent with the best values, $\log \beta_1 = 2.75$ and $\log \beta_2 = 4.43$, that are recommended by reviewers[3]. The values at elevated temperatures from this work are the first experimental values to be reported. Our results show that the complexation between Pu(IV) and HSO_4^- is enhanced at higher temperatures.

Effect of temperature on stability constants

The effect of temperature on the stability constants of the Pu(IV)- HSO_4^- complexes was evaluated at the range of temperature from 25° to 55° C. By using the Van't Hoff equation, we automatically assume that the enthalpy of complexation remains constant and an "average" enthalpy of complexation for this temperature range can be calculated. From the determined stability constants listed in the Table 5, the thermodynamic parameters of ΔG^o, ΔH^o, and ΔS^o can be calculated according to equation (9) and (10):

$$\Delta G^o = - RT \ln \beta \qquad (9)$$

$$\partial \ln \beta / \partial (1/T) = - \Delta H^o/R \;;\; \Delta S^o = (\Delta H^o - \Delta G^o)/T \qquad (10)$$

The calculated thermodynamic values are listed in the Table 6. The values of ΔH^o (for 1:1 and 1:2 Pu^{4+}- HSO_4^- from this study are calculated to be 11.2 ± 1.0 (kJ/mol) and 5.1 ± 2.0 (kJ/mol), respectively.

The values of ΔH^o have been estimated from the stability constants determined in identical experiment over a range of temperatures (see Table 5) by reviewers[3] as follows:

for 1:1 Pu^{4+}- HSO_4^-, ΔH^o = -(7.1± 1.7), (2.4± 3.5), (7.2± 3.0), and (18.6± 1.2) (kJ/mol), and

for 1:2 Pu^{4+}- HSO_4^-, ΔH^o = (3.1± 1.8), (8.6± 1.4), (7.5± 2.3), and (1.5±3.4) (kJ/mol). As the reviewers[3] have no basis to eliminate any of these experimental results (see Table 5), they recommend no best value, and advise caution in the determination of fundamental thermodynamic properties from the temperature variation of stability constants in this system. Based on these estimated data obtained from revieweres[3], our values of ΔH^o obtained from temperature range between 25°C and 55°C are reasonable. The results indicate that the values of $\Delta H^{o'}$ and $\Delta S^{o'}$ are positive and relatively large, indicating that the complexation reactions are entropy-driven. The positive enthalpy reflects the dehydration energy required to form complexes and supports the interpretation of inner sphere binding for the Pu(IV) complexes with HSO_4^-. These parameters should be helpful in predicting of the effect of temperature on the complexation of Pu(IV) with HSO_4^- at elevated temperatures.

Pu(IV)-SO_4^{2-} complexation system

In nuclear waste disposal site, the high radiation field may generate a moderately acidic environment in which the effectiveness of HCO_3^- as an important inorganic ligand for Pu(IV) will be negligible, and hydrolysis will be minimized[13]. In this case (such as in the low pH range of 1-3), the complexes of Pu(IV) with SO_4^{2-} will be the dominant species in the aqueous phase in this system. Therefore, the equilibria can be considered as follows:

$$Pu^{4+} + m\, SO_4^{2-} = Pu\,(SO_4)_m^{4-2m} \qquad (11)$$

With the overall stability constant β_m^* defined as:

$$\beta_m^* = [Pu(SO_4)_m^{4-2m}] / ([Pu^{4+}]\,[SO_4^{2-}]^m) \qquad (12)$$

The log β_1 and log β_2 obtained from this study were converted to the log β_1^* and log β_2^* by adding the negative logarithm of the dissociation constant of bisulfate obtained from the literature[23] in the following manner[16]:

$$\log \beta_1^* = \log \beta_1 + \mathrm{p}K_a \qquad (13)$$

$$\log \beta_2^* = \log \beta_2 + 2\ \mathrm{p}K_a \qquad (14)$$

The calculated stability constants of Pu(IV) with SO_4^{2-} at different temperatures are listed in the Table 7, and includes the literature data. The stability constants of the 1:1 and 1:2 Pu(IV) - SO_4^{2-} complexes at 25°C and I =2.0 M are close agreement with literature data obtained from literature[3,6], but, no data are available at elevated temperatures in the literature. These stability constants are useful for help us to assess of the solubility and migration of Pu(IV) in the environmental conditions with high concentration of sulfate and at low pH range of 1-3 in the aqueous solutions. In order to obtain more accurate data, the hydrolysis constants of Pu(IV) can be used to correct the log β_1^* and log β_2^*.

Conclusions

The 1:1 and 1:2 Pu(IV)-HSO_4^- complexes were found to be the dominant species in the aqueous phase under the experimental conditions, and the stability constants of Pu(IV) complexes with HSO_4^- increased with increasing temperature, consistent with a positive enthalpy of complexation. These results have demonstrated that temperature has a significant effect on the complexation of plutonium, and it is important to conduct studies for evaluation of temperature effects to help predict the migration of actinides in the proposed repository where temperature could be higher than the ambient temperature. The stability constants of Pu(IV) complexes with SO_4^{2-} have been calculated by using the pK_a values of bisulfate and the stability constants of Pu(IV) complexes with HSO_4^- obtained from this study. These data can be used to predict the migration of Pu(IV) in the environmental conditions in the presence of high concentration of sulfate and at the lower pH values.

Acknowledgements

This work was supported by the Office of Civilian Radioactive Waste Management (OCRWM), U.S. Department of Energy. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

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Table 1. Extraction equilibrium constants of Pu(IV)-TTA reaction and TTA stoichiometries* with literature data

Temperature (°C)	Ionic strength ($HClO_4$, M)	log K_{ex}	Slope*	Reference
25	2.0	6.6		13
25	2.0	6.8		21
25	2.0	7.3		22
25	2.0	7.08 ± 0.01	4.10 ± 0.05	this work
40	2.0	6.91 ± 0.01	4.10 ± 0.10	this work
55	2.0	6.63 ± 0.01	4.07 ± 0.03	this work

* According to equation 8, the slope of log D vs. log [HTTA] plots.

Table 2. Solvent extraction data for the system of Pu(IV)-HSO_4^- - 2.0 M $HClO_4$- 0.05 M TTA/toluene at 25 ± 1°C

$[HSO_4^-]_T$, M	Activity, cpm* Org. phase	Activity, cpm* Aq. Phase	D
0	2593	881	2.94
3.00e-3	2030	1321	1.54
6.00e-3	1611	1736	0.93
1.20e-2	1124	2175	0.52
1.80e-2	831	2478	0.33
3.00e-2	453	2829	0.16
4.50e-2	275	3011	0.09
6.00e-2	176	3156	0.06

* The aliquots of 0.4 ml from both phases were taken for counting.

The activity of background: 1 cpm.

Table 3. Solvent extraction data for the system of Pu(IV)-HSO_4^- - 2.0 M $HClO_4$- 0.05 M TTA/toluene at 40 ± 1°C

$[HSO_4^-]_T$, M	Activity, cpm* Org. phase	Activity, cpm* Aq. Phase	D
0	2624	1300	2.02
2.00e-3	2103	1755	1.20
4.00e-3	1739	2048	0.85
8.00e-3	1273	2554	0.50
1.20e-2	984	2899	0.34
2.00e-2	573	3289	0.17
3.00e-2	344	3564	0.10
4.00e-2	233	3589	0.06

* The aliquots of 0.3 ml from both phases were taken for counting.

The activity of background: 1 cpm.

Table 4. Solvent extraction data for the system of Pu(IV)-HSO_4^- - 2.0 M $HClO_4$- 0.05 M TTA/toluene at 55 ± 1°C

$[HSO_4^-]_T$, M	Activity, cpm* Org. phase	Activity, cpm* Aq. Phase	D
0	2219	1709	1.30
2.00e-3	1608	2102	0.77
4.00e-3	1248	2461	0.51
8.00e-3	907	2853	0.32
1.20e-2	638	3050	0.21
2.00e-2	363	3356	0.11
3.00e-2	216	3470	0.06
4.00e-2	147	3438	0.04

* The aliquots of 0.3 ml from both phases were taken for counting.

The activity of background: 1 cpm.

Table 5. Apparent stability constants of Pu(IV) complexes with sulfate (Pu^{4+} + q HSO_4^- = Pu $(SO_4)_q^{4-2q}$ + qH^+)

Method	Ionic medium	Temp.,°C	log β_{101}	log β_{102}	Reference
dis	2.0 M ($HClO_4$)	10	(2.84 ± 0.06)[(a)]	(4.33 ± 0.05)[(a)]	8
		40	(2.72 ± 0.05)[(a)]	(4.39 ± 0.03)[(a)]	
dis	2.0 M ($HClO_4$)	25	(2.76 ± 0.03)	(4.35 ± 0.27)	9
		25	(2.68 ± 0.06)	(4.51 ± 0.27)	
ix	2.0 M ($HClO_4$)	25	(2.75 ± 0.02)	(4.43 ± 0.03)	6
dis	2.0 M ($HClO_4$)	25	(2.73 ± 0.18)	(4.66 ± 0.07)	10
		25	(2.80 ± 0.13)	(4.47 ± 0.08)	
dis	2.0 M ($HClO_4$)	25	(3.00 ± 0.17)	(4.59 ± 0.11)	11
		25	(2.95 ± 0.14)	(4.45 ± 0.11)	
dis	2.0 M ($HClO_4$)	10	(2.71 ± 0.03)[(a)]	(4.58 ± 0.01)	12
		10	(2.88 ± 0.07)[(a)]	(4.38 ± 0.05)	
dis	2.0 M ($HClO_4$)	0	(2.45 ± 0.07)[(a)]	(4.10 ± 0.09)	13
		10	(2.58 ± 0.04)[(a)]	(4.06 ± 0.07)	
		25	(2.76 ± 0.03)	(4.13 ± 0.07)	
		35	(2.85 ± 0.05)[(a)]	(4.11 ± 0.08)	
dis	2.0 M ($HClO_4$)	25	(2.71 ± 0.05)	(4.59 ± 0.04)	this work
		40	(2.79 ± 0.04)	(4.66 ± 0.04)	
		55	(2.87 ± 0.03)	(4.58 ± 0.04)	

(a) Used to calculate $\Delta_r H^o$ only (see section of *Effect of temperature on stability constants*).

Dis: Solvent extraction; Ix: Ion exchange.

Table 6. Stability constants and thermodynamic values for 1:1 and 1:2 complexes of plutonium (IV) with HSO_4^-

Temp., °C	Ionic Strength, M	log β_{101}	log β_{102}	ΔG°, kJ/mol	ΔS°, J/K mol	ΔH°, kJ/mol	Reference
For the complex formation of $PuSO_4^{2+}$							
25	2.0	2.71±0.05		-15.5	89.6	11.2	this work
40	2.0	2.79±0.04		-16.7	89.3	11.2	this work
55	2.0	2.87±0.04		-18.2	89.6	11.2	this work
For the complex formation of $Pu(SO_4)_2$							
25	2.0		4.59±0.04	-26.2	104.8	5.1	this work
40	2.0		4.66±0.04	-27.9	105.4	5.1	this work
55	2.0		4.58±0.04	-28.8	103.1	5.1	this work

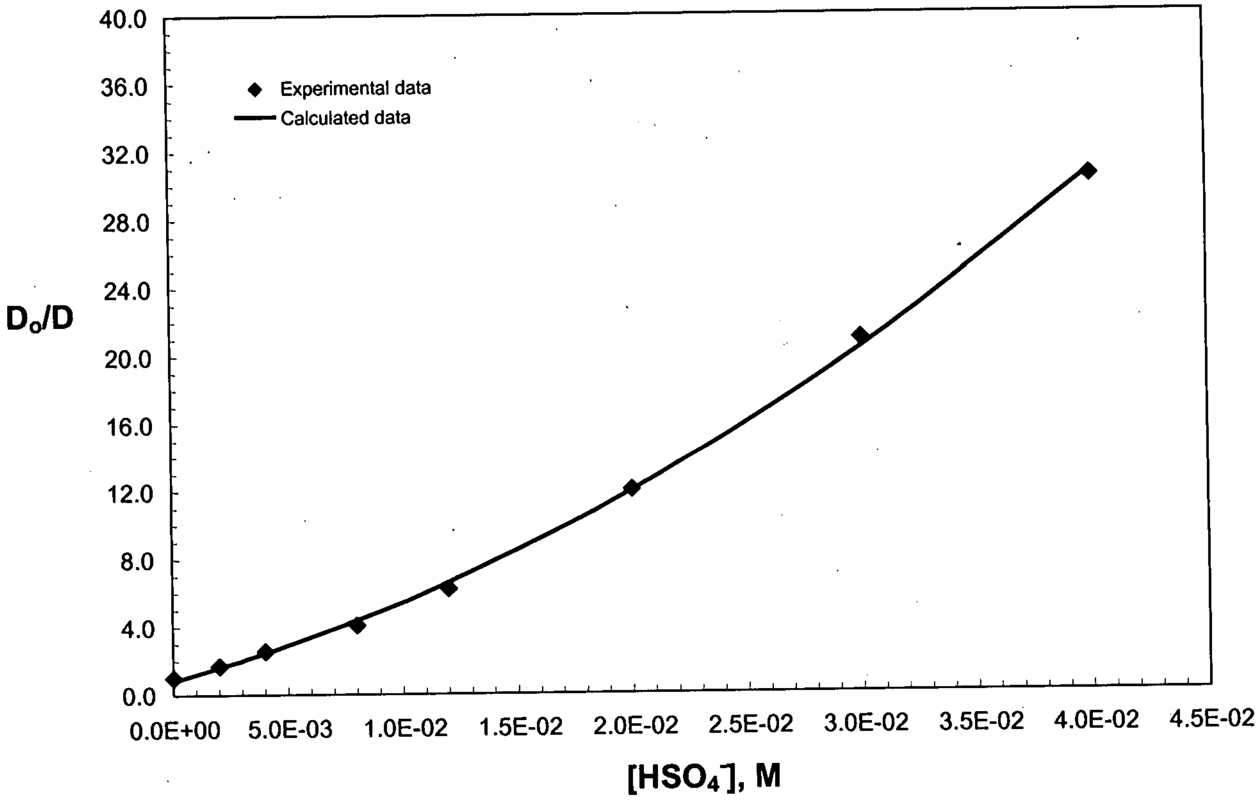
Table 7. Calculated stability constants of Pu(IV) complexes with sulfate ($Pu^{4+} + m\ SO_4^{2-} = Pu(SO_4)_m^{4-2m}$)

Temp., °C	Ionic Strength, M	pK_a (b)	log β_1	log β_2	Reference
25	2.0		3.82 (c)	6.58 (c)	[3, 6]
25	2.0	1.07	3.78 ± 0.05	6.73 ± 0.04	this work
40	2.0	1.14	3.93 ± 0.03	6.94 ± 0.04	this work
55	2.0	1.28	4.15 ± 0.03	7.14 ± 0.04	this work

(b) pK_a (- log K_a) = - log ($[SO_4^{2-}][H^+]/[HSO_4^-]$) obtained from[23].

(c) No error is given.

Figure 1. Plot of D_o/D vs. concentrations of HSO_4^- in the extraction system of Pu(IV) - 2.0 M ($HClO_4 + H_2SO_4$) - 0.05 M TTA/toluene at 55 °C.



Yuanxian Xia, Figure 1