Complexation of Plutonium(IV) with Fluoride at Variable Temperatures

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Abstract

Complexation of Pu(IV) with fluoride was studied by solvent extraction at 25, 40 and 55°C in 2.2 mol·kg^{-1} $HClO_4$. The distribution ratio of Pu(IV) between the organic and aqueous phases decreased as the concentration of fluoride was increased due to the formation of Pu(IV)-F complexes in the aqueous phase. Two complexes, PuF^{3+} and PuF_2^{2+}, were identified under the conditions in this work and their stability constants at 25, 40 and 55°C and I = 2.2 mol·kg^{-1} $HClO_4$ were determined from the distribution data. The Specific Ion Interaction approach (SIT) was used to extrapolate the constants to the state of infinite dilution. Data from this work indicate that the complexation of Pu(IV) with fluoride is endothermic and entropy-driven. The complexation becomes stronger at higher temperatures.

Key Words: Plutonium (IV) / Fluoride / Complexation / Stability constants / Temperature effect / Solvent extraction

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1. Introduction

Due to its high toxicity and the long half life of some of its isotopes (e.g., $t_{1/2}(^{239}Pu) = 2.41 \times 10^4$ years), the migration of plutonium in the post-closure chemical environment of waste repositories is of great concern to long-term repository performance. The post-closure chemical environment in the repository for high-level nuclear wastes is expected to be at elevated temperatures for many years due to the radiation energy [1]. Under oxic conditions that are likely to encounter in some geological repositories, plutonium is most likely to be in the tetravalent state, Pu(IV). Compared with other oxidation states (e.g., hexa-, penta and tri-valent), Pu(IV) has a higher tendency for hydrolysis that leads to the formation of colloids and precipitates, as well as a stronger ability to form complexes with many ligands that are present in the repository and the surrounding environment. Therefore, the interactions of plutonium with various ligands play an important role in determining the migration of plutonium in the environment. Thermodynamic data on the complexation of Pu(IV), especially the data at elevated temperatures, are needed in order to predict the migration behavior of plutonium. Fluoride is one of the inorganic ligands that have been found in the groundwater of the repository. Previous studies have shown that it forms fairly strong complexes with Pu(IV) and stability constants of the complexes at or below 25°C have been reported [2-10]. However, there are no data on the complexation of Pu(IV) with fluoride at temperatures above 25°C.

In this work, a distribution method with solvent extraction was used to determine the stability constants of Pu(IV) complexes with fluoride in 2.2 $mol \cdot kg^{-1}$ $HClO_4$ at 25, 40 and 55°C. The stability constants were extrapolated to the state of infinite dilution by the Specific Ion Interaction approach (SIT). The enthalpies of complexation were calculated from the temperature

dependency of the stability constants. The energetics of complexation (enthalpy and entropy) is discussed in terms of the effect of the dehydration of Pu^{4+} and F^- ions. .

2. Experimental

2.1 Chemicals

All chemicals used in this work were of analytical grade or higher. All solutions were prepared with distilled-deionized water. Stock solutions of HF and $HClO_4$ were prepared by appropriate dilutions of hydrofluoric acid (48%, Aldrich) and perchloric acid (double distilled, 70%, Aldrich), respectively, and standardized by titrations with NaOH (Aldrich). Thenoyltrifluoroacetone (TTA, Aldrich) was purified by vacuum sublimation at 42°C. Stock solutions of 0.5 and 0.05 mol·dm^{-3} TTA in toluene (99.8%, HPLC grade, Aldrich) were prepared by dissolving weighted amounts of TTA in toluene. Prior to use, the TTA-toluene solutions were pre-equilibrated with aqueous solutions of dilute perchloric acid overnight and stored in dark glass bottles. All stock solutions were filtered with a 0.2 μm microfiltration system.

The ionic strength of all working solutions is maintained at 2.0 mol·dm^{-3} $HClO_4$ at 25°C, corresponding to 2.2 mol·kg^{-1} at variable temperatures. In this paper, all concentrations in molarity are referred to 25°C.

2.2 Preparation of Pu(IV) solution

A Pu(IV) solution in 8 mol·dm^{-3} HNO_3 was obtained from the stock of Pacific Northwest National Laboratory [11]. Analysis by γ–spectroscopy has shown that it contains 93.6% ^{239}Pu and 6.3% ^{240}Pu (as percentages of total activity).

To prepare a Pu(IV) solution in 2.0 mol·dm^{-3} $HClO_4$ for this study and ensure that Pu(IV) is the only oxidation state in solution, a multi-step procedure as follows was taken. 1) The Pu(IV) in 1.0 mol·dm^{-3} HNO_3 was extracted into 0.5 mol·dm^{-3} TTA-toluene, and then back extracted into 8.0 mol·dm^{-3} HNO_3. 2) The Pu(IV) in 8.0 mol·dm^{-3} HNO_3 was titrated with NaOH to obtain freshly precipitated Pu(IV)-hydroxide. 3) The fresh Pu(IV)-hydroxide precipitate was washed several times with water and dissolved in 2.0 mol·dm^{-3} $HClO_4$. 4) The Pu(IV) in 2.0 mol·dm^{-3} $HClO_4$ was filtered with a 0.2 μm filter to separate any colloidal Pu(IV) that might have formed in previous processes. 5) The oxidation state of Pu(IV) was confirmed by optical spectroscopy on a Cary 500 UV-Vis-NIR Spectrometer. Details of the above procedure have been described previously [12]. In addition, the oxidation state of Pu in the stock solution was checked by validation extraction experiments. Extraction of higher than 99.9% of Pu by 0.5 mol·dm^{-3} TTA-toluene from 1.0 M HNO_3 was taken as the criterion for the absence of oxidation states other than Pu(IV).

A working solution of Pu(IV) in 2.0 mol·dm^{-3} $HClO_4$ was prepared so that an aliquot of 20 μL has an α-counting rate of about 8000 cpm. The activity of Pu(IV) in solution samples was measured on a Wallac Model 1414 liquid scintillation counter (LSC) using Hionic Fluor as the scintillation solution.

2.3 Distribution experiments

Solvent extraction experiments were conducted following the procedures described in the literature [13]. An orbital shaker equipped with a constant-temperature aluminum block and a water-jacketed centrifuge (Speedfuge, HSX10K) were used to conduct the extraction

experiments at desired temperatures. Details of the shaker and centrifuge and the mechanism for temperature control are described elsewhere [13].

In the distribution experiments for the determination of the stability constants of Pu(IV)-F complexes, each plastic vial contains 1.0 ml aqueous solution (different amounts of HF, 2.0 $mol \cdot dm^{-3}$ $HClO_4$ and 0.01 $mol \cdot dm^{-3}$ $NaBrO_3$) and 1.0 ml 0.05 $mol \cdot dm^{-3}$ TTA-toluene. After the addition of 20 μL Pu(IV) tracer into each vial ($[Pu]_{aq} \approx 2.5$ $\mu mol \cdot dm^{-3}$), the vials were placed on the orbital shaker and shaken for one hour at the desired temperature. Preliminary kinetic studies confirmed that the extraction equilibrium was achieved within this time. The vials were then centrifuged and aliquots of 0.3 – 0.4 ml were taken from each phase for α-counting by LSC.

Earlier studies indicate that Pu(IV) could be reduced to Pu(III) during the distribution experiments using TTA [5-7, 14-16]. Therefore, special measures that proved to be successful in previous studies [12] were taken in this study to maintain plutonium as Pu(IV) throughout the experiments. The measures included: 1) using small amounts of sodium bromate (0.01 $mol \cdot dm^{-3}$) as holding oxidant in the aqueous phase; and 2) purifying TTA by vacuum sublimation and, prior to use, treating the TTA-toluene solution with 0.01 $mol \cdot dm^{-3}$ $KBrO_3$ to remove any reducing impurities.

2.4 Validation experiments to verify the oxidation state of Pu(IV)

Two validation experiments were conducted to verify the oxidation state of Pu(IV). The first validation experiment was conducted in parallel with the above-mentioned distribution experiments, but with varying concentrations of TTA and in the absence of HF. The distribution ratio (R) of Pu was determined as a function of [TTA]. The stoichiometry of the extracted

Pu(IV)-TTA species in the organic phase was obtained by a slope analysis of the plot of log *R* vs. log [TTA]. A stoichiometry of $Pu(TTA)_4$(org) would confirm the presence of Pu(IV) in the extraction.

The second validation experiment was conducted after the above-mentioned distribution experiments. After the distribution experiments, an aliquot of the aqueous solution containing Pu was immediately adjusted to 1.0 mol·dm^{-3} HNO_3 and equally divided into portions I and II. A small amount of sodium bromate was added to portion I, but not to portion II. Both portions were equilibrated with 0.5 mol·dm^{-3} TTA-toluene and the distribution ratios of plutonium were measured. If Pu(IV) was somehow reduced to Pu(III) in previous extraction experiments, the distribution ratio obtained in this validation experiment for portion I (with sodium bromate) would be higher than that for portion II (without sodium bromate). For all aqueous solutions tested by this validation experiment, no significant difference was observed in the distribution ratios between the two portions, suggesting that no detectable degree of reduction of Pu(IV) to Pu(III) occurred during the distribution experiments.

2.5 Data Analysis

The extraction equilibrium of the Pu(IV)-TTA system can be expressed by equation 1:

$$Pu^{4+}_{(aq)} + 4\ HTTA_{(org)} = Pu(TTA)_{4(org)} + 4\ H^{+}_{(aq)} \quad (1)$$

The distribution ratio, $R = [Pu]_{org}/[Pu]_{aq}$, where $[Pu]_{org}$ and $[Pu]_{aq}$ are the total concentrations of Pu in the organic and aqueous phases, respectively. In the absence of fluoride,

$$R = R^{o} = [Pu(TTA)_4]_{org}/[Pu^{4+}]_{aq}. \quad (2)$$

In the presence of fluoride, Pu(IV) forms complexes in the aqueous phase and the complexation

reactions in strongly acidic solutions (2.0 mol·dm^{-3} $HClO_4$) are expressed as:

$$Pu^{4+} + q\ HF = PuF_q^{(4-q)+} + q\ H^+ \quad (3)$$

The equilibrium constants, $*\beta_q$, are defined as:

$$*\beta_q = [PuF_q^{(4-q)+}][H^+]^q/([Pu^{4+}][HF]^q) \quad (4)$$

The distribution ratio in the presence of fluoride,

$$R = [Pu(TTA)_4]_{org}/\Sigma[PuF_q^{(4-q)+}]_{aq}$$

$$= [Pu(TTA)_4]_{org}/\{[Pu^{4+}]_{aq}(1+ \Sigma(*\beta_q/[H^+]^q)[HF]^q)\}$$

$$= R^o/(1+ \Sigma(*\beta_q/[H^+]^q)[HF]^q) \quad (5)$$

Equation 5 can be re-arranged as:

$$R^o/R - 1 = \Sigma(*\beta_q/[H^+]^q)[HF]^q) \quad (6)$$

In equation 6, $[H^+]$ and [HF] are known and $(R^o/R - 1)$ are experimental data obtained by the distribution experiments. Therefore, values of $*\beta_q$ can be determined by fitting the data according to equation 6.

3. Results and Discussion

3.1 Stoichiometry of extracted Pu(IV)-TTA complex

The equilibrium constant of equation 1, K_{ex}, is defined as:

$$K_{ex} = ([Pu(TTA)_4]_{org}[H^+]_{aq}^4)/([Pu^{4+}]_{aq}[HTTA]_{org}^4) \quad (7)$$

Combining equations 7 and 2 and taking the logarithm result in equation 8:

$$\log R^o = \log K_{ex} + 4 \log [HTTA]_{org} - 4 \log [H^+]_{aq} \quad (8)$$

This means that, if the Pu is in the tetravalent Pu(IV), the slope of log R vs. log [HTTA] should be 4 and the extracted Pu species is $Pu(TTA)_4$. In this work, the slope of log R vs. log [HTTA]

was found to be 4.07 – 4.10 at three different temperatures (25, 40 and 55°C, I = 2.2 mol·kg^{-1} $HClO_4$). These results indicated that the extraction mechanism was the same at different temperatures and that the oxidation state of Pu(IV) remained unchanged during the extraction experiments. The equilibrium constant of equation 1, K_{ex}, was determined to be 7.08 ± 0.01 (25°C), 6.91 ± 0.01 (40°C), and 6.63 ± 0.01 (55°C), in fairly good agreement with the values at 25°C in the literature [14-16].

3.2. Equilibrium constants for ($Pu^{4+} + q\ HF = PuF_q^{(4-q)+} + q\ H^+$) at I = 2.2 mol·kg^{-1} ($HClO_4$) and t = 25, 40 and 55°C

The results of distribution experiments are shown in Figure 1 as the plot of (R^o/R – 1) vs. [HF]. The curves are best-fitted with second-order polynomials, suggesting the formation of two consecutive complexes of Pu(IV) with fluoride (i.e., q = 1 and 2 in equation 6), PuF^{3+} and PuF_2^{2+}. The equilibrium constants at different temperatures, $*\beta_1$ and $*\beta_2$, were obtained from the best fit and listed in Table 1. To compare the constants at different temperatures, the constants obtained in molarity should be converted to those in molality according to the methods described in the literature [2]. However, such conversion is unnecessary for the reactions represented by equation 3, because the sum of the stoichiometric coefficients of the reaction is zero and the equilibrium constants in molarity and molality for equation 3 are identical. Table 1 shows that the values of log $*\beta_1$ and log $*\beta_2$ at 25°C from this work are in good agreement with those at 25°C from the literature. Values at 40 and 55°C from this work are the first such values at temperatures above 25°C.

3.3. Calculation of equilibrium constants for (Pu^{4+} + q HF = $PuF_q^{(4-q)+}$ + q H^+) to the state of infinite dilute: Analysis by the Specific Ion Interaction approach (SIT)

The SIT approach is originated from the Brϕnsted-Guggenheim-Scatchard model [17-19] and used to calculate the equilibrium constants at zero ionic strength [2]. For reactions (Pu^{4+} + q HF = $PuF_q^{(4-q)+}$ + q H^+) where q = 1 and 2, the equilibrium constants at I = 0 (log $*\beta^o$) are related to log $*\beta$ at other ionic strengths by the following equations:

$$\log *\beta_1 + 6\,D = \log *\beta_1^{\,o} - \Delta\varepsilon_1 I_m \qquad (9a)$$

$$\log *\beta_2 + 10\,D = \log *\beta_2^{\,o} - \Delta\varepsilon_2 I_m \qquad (9b)$$

where D is the Debye-Huckel term used in the SIT method and $D = AI_m^{1/2}/(1 + 1.5I_m^{1/2})$, I_m is the ionic strength in molality, and ε is the ion interaction parameter used in the SIT method [2]. The values of $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ at 25°C are –(0.12 ± 0.09) and –(0.18 ± 0.15) kg·mol^{-1}, respectively [2]. For the calculation of log $*\beta^o$ at temperatures other than 25°C, we have adopted the following approaches: (1) using the values of A at different temperatures tabulated in the literature [2]; and (2) using the value of $\Delta\varepsilon$ at 25°C for all temperatures, because the values at other temperatures were not known and the errors thus introduced are probably quite small, since the values of $(\partial\varepsilon/\partial T)_p$ are usually ≤ 0.005 kg·mol^{-1}·K^{-1} for temperatures below 200°C [2]. Besides, the values of $(\partial\varepsilon/\partial T)_p$ for the reactants and products may balance out each other so that $\Delta\varepsilon$ for many reactions remains approximately constant up to 100°C [20,21]. The calculated values of log $*\beta_1^{\,o}$ and log $*\beta_2^{\,o}$ are summarized in Table 1 (the error limits were obtained by propagation of the uncertainties in the experimental values of log $*\beta$ and the uncertainties in $\Delta\varepsilon$ at 25°C). The value of log $*\beta_1^{\,o}$ at 25°C from this work (5.68 ± 0.21) is in excellent agreement with that selected by

NEA (5.66 ± 0.10) [2]. However, the value of log $*\beta_2^o$ at 25°C from this work (9.55 ± 0.33) is higher than that selected by NEA (9.38 ± 0.10) [2], though the two values overlap within the error limits. It should be noted that the NEA value of log $*\beta_2^o$ (9.38 ± 0.10) was calculated from the average of four experimental log $*\beta_2$ values, two of which (7.62, 7.61) are nearly identical to the value from this work (7.60) while the other two values (7.46 and 7.35) are significantly lower.

3.4. Stability constants of $PuF_q^{(4-q)+}$ at infinite dilution

The complexation reactions between Pu(IV) and fluoride and the stability constants of the complxes are expressed in equations 10a and 10b:

$$Pu^{4+} + F^- = PuF^{3+} \qquad \beta_1 = [PuF^{3+}]/([Pu^{4+}][F^-]) \qquad (10a)$$

$$Pu^{4+} + 2\ F^- = PuF_2^{2+} \qquad \beta_2 = [PuF_2^{2+}]/([Pu^{4+}][F^-]^2) \qquad (10b)$$

Using the equilibrium constants for reactions ($Pu^{4+} + q\ HF = PuF_q^{(4-q)+} + q\ H^+$), $*\beta_q$, in conjunction with the protonation constants of HF ($H^+ + F^- = HF(aq)$), K_{HF}, the stability constants of Pu(IV)-F complexes, β_q, can be calculated as follows:

$$\log \beta_1^o = \log *\beta_1^o + \log K^o_{HF} \qquad (11a)$$

$$\log \beta_2^o = \log *\beta_2^o + 2 \log K^o_{HF} \qquad (11b)$$

The value of log K^o_{HF} at 25°C is available in the literature and the value of log K^o_{HF} at other temperatures can be calculated with the van't Hoff equation and the value of $\Delta_r H^o(H^+ + F^- = HF(aq))$ at 25°C [2]. Using these values (see Table 2) and the values of log $*\beta_1^o$ and log $*\beta_2^o$ from this work (Table 1), values of log β_1^o and log β_2^o at 25, 40 and 55°C were calculated and listed in Table 2. Again, the stability constants at 40 and 55°C from this work are the first such data for

temperatures above 25°C.

3.5 Enthalpy of complexation and the effect of temperature on the complexation

As shown in Table 2, the stability constants of PuF^{3+} and PuF_2^{2+} increase as the temperature is increased from 25 to 55°C. The stability constants are plotted as a function of $1/T$ in Figure 2 and the data are fitted very well with straight lines. From the slopes of the lines, the enthalpies of complexation for PuF^{3+} and PuF_2^{2+} were calculated to be (9.4 ± 5.0) kJ·mol^{-1} and (15.0 ± 8.0) kJ·mol^{-1}, respectively. From the enthalpy and Gibbs free energy of complexation, the entropies of complexation were accordingly calculated (Table 2). The values of enthalpy and entropy of complexation for PuF^{3+} at 25°C from this work are in excellent agreement with those recommended by NEA, while the values for PuF_2^{2+} from this work overlap with those recommended by NEA within the uncertainty limits [2].

Thermodynamic parameters in Table 2 indicate that the complexation of Pu(IV) with fluoride is endothermic and entropy-driven. This is typical of the formation of inner-sphere complexes and is not surprising because both Pu^{4+} and F^- ions are strongly hydrated and a significant amount of energy is expected to spend on dehydrating the ions, resulting in unfavorable enthalpy. Meanwhile, the dehydration of both the cation and anion and the re-arrangement of the water structure in the vicinity of the complex (PuF^{3+} and PuF_2^{2+}) as well as in the bulk create a high degree of disorder, resulting in large positive entropy.

Summary

The stability constants of PuF^{3+} and PuF_2^{2+} at 25, 40 and 55°C (I = 2.2 mol·kg^{-1} $HClO_4$) were

determined by distribution method and corresponding constants at $I = 0$ were obtained using the Specific Ion Interaction approach. The enthalpies of complexation were calculated from the van't Hoff plot of the stability constants at variable temperatures. The positive enthalpy and entropy of complexation are the result of the dehydration of both Pu^{4+} and F^- ions accompanying the formation of inner-sphere PuF^{3+} and PuF_2^{2+} complexes.

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References

1. *Yucca Mountain Science and Engineering Report Rev.I*, DOE/RW- 0539-1, Office of Civilian Radioactive Waste Management: North Las Vegas, NV (2002).
2. Lemire, R. J., Fuger, J., Nitsche, H., Potter, P., Rand, M. H., Rydberg, J., Spahiu, K., Sullivan, J. C., Ullman, W. G., Vitorge, P., Wanner, H., *Chemical Thermodynamics of Neptunium and Plutonium.* Edited by OECD Nuclear Energy Agency, Data Bank, *Chemical Thermodynamics 4*, Elsevier, New York (2001).
3. Krylov, V. N., Komarov, E. V., Sov. Radiochem., 11, 94 (1969).

4. Krylov, V. N., Komarov, E. V., Sov. Radiochem., 11, 237 (1969).
5. Bagawde, S. V., Ramakrishna, V. V., Patil, S. K., J. Inorg. Nucl. Chem.,38, 2085 (1976).
6. Bagawde, S. V., Ramakrishna, V. V., Patil, S. K., J. Inorg. Nucl. Chem., 38 , 1339 (1976).
7. Bagawde, S. V., Ramakrishna, V. V., Patil, S. K.., Radiochem. Radioanal. Lett., 31, 65 (1977).
8. Nash, K. I., Cleveland, J. M., Raiochim. Acta.36, 129 (1984).
9. Chitnis, R. T., Talnikar, S. G., Bhogale, R. G., Patil, S. K., J. Radioanal. Chem.50, 53 (1979).
10. Sawant, R. M., Chaudhuri, N. K., Patil, S. K., J. Radioanal. Nucl. Chem.,143, 295 (1990).
11. Xia, Y., Friese, J. I., Moore, D. A., Rao, L., J. Radioanal. Nucl. Chem, 268, 445 (2006).
12. Xia, Y., Friese, J. I., Moore, D. A., Bachelor, P. P., Rao, L., J. Radioanal. Nucl. Chem. in press, 274, 1 (2007).
13. Rai, D., Radiochim. Acta 35, 97 (1984).
14. Poskanzer, A. M., Foreman, B. M., J. Inorg. Nucl. Chem., 16, 323 (1961).
15. Ramakrishna, V. V., Patil, S. K., Prakas Hara B., Sepn. Sci. Techn., 14, 571 (1979).
16. Nash, K. L., Cleveland, J. M., Radiochim. Acta 33,105 (1983).
17. a) J. N. Brϕnsted, *J. Am. Chem. Soc*. 44 (1922) 877; (b) J. N. Brϕnsted, *J. Am. Chem. Soc*. 44 (1922) 938.
18. E. A. Guggenheim, *Philos. Mag*. 57 (seventh series) (1935) 588.
19. G. Scatchard, *Chem. Rev*. 19 (1936) 309.
20. A. V. Plyasunov, I. Grenthe, *Geochim. Cosmochim. Acta*, 58 (1994) 3561.

21. A. Skerencak, P.J. Panak, W. Hauser, V. Neck, R. Klenze, P. Lindqvist-Reis, Th. Fanghänel, "TRLFS study on the complexation of Cm(III) with nitrate in the temperature range from 5 to 200°C," *Radiochim. Acta*, in press.

Table 1 Equilibrium constants for the complexation of Pu(IV) with fluoride. I = 2.2 mol·kg^{-1} $HClO_4$. Legends: dis - solvent extraction, cix - ion exchange, p.w. – present work.

Reaction	t °C	Method	log $*\beta$	log $*\beta^o$ (I = 0)	Ref.
$Pu^{4+} + HF \leftrightarrows PuF^{3+} + H^+$	25	dis	4.54 ± 0.07	5.68 ± 0.21	p.w.
				5.66 ± 0.10	2
	40	dis	4.50 ± 0.03	5.67 ± 0.20	p.w.
	55	dis	4.41 ± 0.03	5.63 ± 0.20	p.w.
	25	cix	4.45 ± 0.30		3
	25	cix	4.65 ± 0.40		4
	25	dis	4.64 ± 0.15		5
	25	dis	4.64 ± 0.20		6
	10	dis	4.70		7
	25	dis	4.47 ± 0.20		8
	15		4.50		
	7.5		4.51		
	1		4.52		
	25		4.36 ± 0.20[a]		
$Pu^{4+} + 2HF \leftrightarrows PuF_2^{2+} + 2H^+$	25	dis	7.60 ± 0.04	9.55 ± 0.33	p.w.
				9.38 ± 0.19	2
	40	dis	7.45 ± 0.04	9.46 ± 0.33	p.w.
	55	dis	7.31 ± 0.04	9.39 ± 0.33	p.w.
	25	dis	7.62 ± 0.30		5
	25	dis	7.61 ± 0.40		6
	10	dis	7.65		7
	25	dis	7.46 ± 0.20		8
	15		7.54		
	7.5		7.58		
	1		7.69		
	25		7.35 ± 0.20[a]		

[a] I = 2.0 mol·dm^{-3} (H/Na)ClO_4

Table 2. Thermodynamic parameters for the complexation of Pu(IV) with fluoride at $I = 0$.

Reaction	t °C	log β^o	$\Delta_r G^o$ kJ·mol^{-1}	$\Delta_r H^o$ kJ·mol^{-1}	$\Delta_r S^o$ J·mol^{-1}·K^{-1}	Ref.
$Pu^{4+} + F^- \leftrightarrows PuF^{3+}$	25	8.86 ± 0.21	-(50.56 ± 1.20)	9.4 ± 5.0	201 ± 17	p.w.
		8.840 ± 0.100	-(50.459 ± 0.571)	9.100 ± 2.200	199.762 ± 7.623	2
	40	8.95 ± 0.20				p.w.
	55	9.01 ± 0.20				p.w.
$Pu^{4+} + 2F^- \leftrightarrows PuF_2^{2+}$	25	15.91 ± 0.21	-(90.80 ± 1.20)	15.0 ± 8.0	355 ± 27	p.w.
		15.700 ± 0.200	-(89.616 ± 1.142)	11.000 ± 5.000	337.469 ± 17.202	2
	40	16.02 ± 0.20				p.w.
	55	16.15 ± 0.20				p.w.
$H^+ + F^- \leftrightarrows HF(aq)$	25	3.180 ± 0.020	-(18.152 ± 0.114)	12.200 ± 0.300	101.800 ± 1.077	2
	40	3.28 ± 0.02[a]				
	55	3.38 ± 0.02[a]				

[a]Calculated from the values of log β^o and $\Delta_r H^o$ at 25°C [2] using the van't Hoff equation.

Figure Captions

Figure 1 Distribution data at difference temperatures. (◆) 25°C, (■) 40°C, (●) 55°C.

Figure 2 log β^0 vs. 1/T. The dashed lines represent the 95% confidence band.

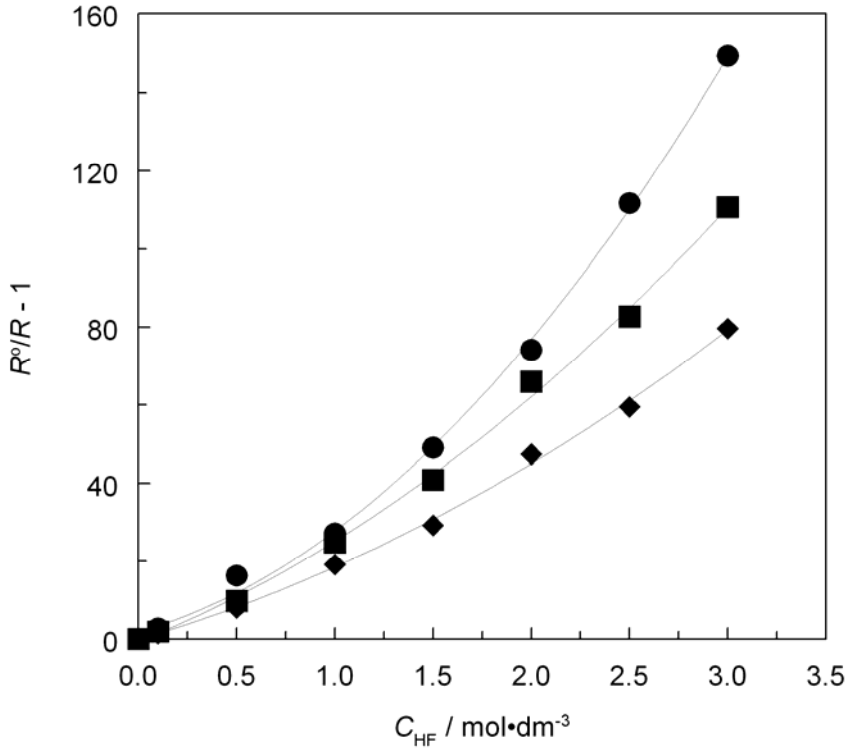

Figure 1 Distribution data at difference temperatures. (◆) 25°C, (■) 40°C, (●) 55°C.

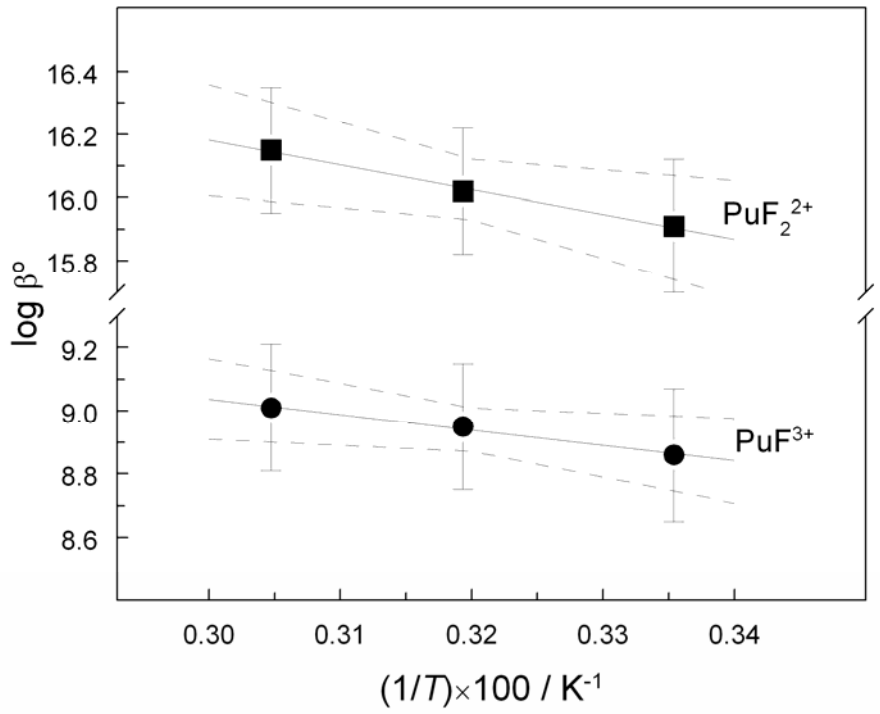

Figure 2 log β^{o} vs. 1/T. The dashed lines represent the 95% confidence band.