

COMPLEXATION OF NEPTUNIUM(V) WITH FLUORIDE IN AQUEOUS SOLUTIONS AT ELEVATED TEMPERATURES

G. Tian¹, L. Rao^{1*}, Y. Xia² and J. I. Friese²

¹Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

²Pacific Northwest National Laboratory, Richland, WA 99352, USA

Complexation of neptunium(V) with fluoride in aqueous solutions at elevated temperatures was studied by spectrophotometry and microcalorimetry. Two successive complexes, $\text{NpO}_2\text{F}(\text{aq})$ and NpO_2F_2^- , were identified by spectrophotometry in the temperature range of 10–70°C. Thermodynamic parameters, including the equilibrium constants and enthalpy of complexation between $\text{Np}(\text{V})$ and fluoride at 10–70°C were determined. Results show that the complexation of $\text{Np}(\text{V})$ with fluoride is endothermic and that the complexation is enhanced by the increase in temperature – a two-fold increase in the stability constants of $\text{NpO}_2\text{F}(\text{aq})$ and more than five-fold increase in the stability constants of NpO_2F_2^- as the temperature is increased from 10 to 70°C.

Keywords: complexation, fluoride, neptunium, temperature effect

Introduction

Over the past several decades, the production and testing of nuclear weapons in the U.S. have created significant amounts of high-level nuclear wastes (HLW) that are currently stored in underground tanks across the U.S. DOE (Department of Energy) sites. Eventually, the HLW will be made into the waste form and disposed of in geological repositories for HLW. Among the radioactive materials, neptunium is of great concern in the post-closure chemical environment in the repository because of the long half-life of ^{237}Np ($2.14 \cdot 10^6$ years) and the high mobility of $\text{Np}(\text{V})$, the most stable oxidation state of neptunium. It is estimated that ^{237}Np , together with ^{129}I and ^{99}Tc , will be the major contributors to the potential total annual dose from the repository beyond 10000 years [1].

Due to the high radiation energy released from the HLW, the postclosure repository is expected to remain at elevated temperatures for thousands of years [1]. If the waste package is breached and becomes in contact with groundwater, neptunium, as well as other radioactive materials will be in aqueous solutions at elevated temperatures. Interactions of radioactive materials with the chemical components in groundwater play an important role in determining their migration in the repository. To predict the migration behavior of neptunium, it is necessary to have sufficient and reliable thermodynamic data on its complexation with the ligands that are present in the groundwater of the repository (e.g., OH^- , F^- , SO_4^{2-} , PO_4^{3-} and CO_3^{2-}) at elevated temperatures. However,

such data are scarce and scattered for 25°C, and nearly nonexistent for elevated temperatures [2]. To provide reliable thermodynamic data, we have conducted investigations of the complexation of actinides, including thorium, uranium, neptunium and plutonium, at elevated temperatures. Thermodynamic parameters, including formation constants, enthalpy and heat capacity of complexation are experimentally determined. This paper summarizes the results of the complexation of $\text{Np}(\text{V})$ with fluoride in aqueous solutions at 10–70°C studied by spectrophotometry and microcalorimetry.

Experimental

Chemicals

Milli-Q water was used in preparing all solutions. All chemicals except neptunium were reagent grade or higher. $\text{Np}(\text{V})$ stock solution was prepared based on procedures in the literature [3]. The oxidation state of $\text{Np}(\text{V})$ was confirmed by the characteristic absorption peak in the near IR region and the concentration of $\text{Np}(\text{V})$ was determined by the absorbance at 980 nm using the molar absorption coefficient of $395 \text{ M}^{-1} \text{ cm}^{-1}$. Gran's potentiometric method [4] was used to determine the concentration of free acid in the $\text{Np}(\text{V})$ stock solution. Solutions of fluoride were prepared by dissolving solid NaF in water. The ionic strength of all working solutions in this study was maintained at 1.0 M (25°C) by adding appropriate amounts of sodium perchlorate as the background electrolyte.

* Author for correspondence: Lrao@lbl.gov

Methods

Spectrophotometry

Spectrophotometric titrations covering the wavelength region of 950–1050 nm (0.2 nm step) were conducted on a Varian Cary-5G spectrophotometer equipped with sample holders that were maintained at constant temperatures by a 1×1 Peltier controller. 10 mm quartz cells were used. Before being inserted into the sample holders, the sealed cells were immersed in an external constant-temperature water bath to be pre-equilibrated at the required temperature. This procedure successfully prevented condensation of water on the top of the cells during the spectrophotometric measurements at high temperatures. The sample holders are also equipped with magnetic stirrers so that thorough mixing of the titrant was achieved while the cells were sealed to minimize water evaporation during the titration. Multiple titrations with different concentrations of Np(V) were performed. Usually 10–15 additions were made, thus generating a set of 10–15 spectra in each titration. The stability constants of the Np(V)/fluoride complex (on the molarity scale) at different temperatures were calculated by non-linear least-square regression using the Hyperquad program [5].

To allow the comparison of stability constants at different temperatures, the constants in molar units should be converted to the constants in molal units. According to the method in the literature [6], the equilibrium constant of a reaction in molality (K_m) is related to that in molarity (K_M) by Eq. (1).

$$\log K_m = \log K_M + \sum_r \nu_r \log \vartheta \quad (1)$$

where $\sum_r \nu_r$ is the stoichiometric coefficient of the reaction (ν_r is positive for products and negative for reactants) and is equal to -1 for the formation of the 1:1 complex ($\text{NpO}_2^+ + \text{F}^- = \text{NpO}_2\text{F}(\text{aq})$), and -2 for the formation of the 1:2 complex ($\text{NpO}_2^+ + 2\text{F}^- = \text{NpO}_2\text{F}_2^-$). Therefore,

$$\log \beta_m(\text{NpO}_2\text{F}) = \log \beta_M(\text{NpO}_2\text{F}) - \log \vartheta \quad (2)$$

$$\log \beta_m(\text{NpO}_2\text{F}_2^-) = \log \beta_M(\text{NpO}_2\text{F}_2^-) - 2 \log \vartheta \quad (3)$$

where ϑ is the ratio of the values of molality to molarity for the specific ionic medium and varies for different media and concentrations. For the mixed ionic media of $1.0 \text{ mol dm}^{-3} \text{ Na}(\text{ClO}_4/\text{NO}_3)$ used in this work, $\log \vartheta$ ranges from 0.014 to 0.021 [6]. Because the corrections are smaller than the uncertainties of the experimental values of $\log \beta_M(\text{NpO}_2\text{F})$ and $\log \beta_M(\text{NpO}_2\text{F}_2^-)$, we have elected not to convert the values in molarity into those in molality and assumed $\log \beta_M \approx \log \beta_m$ in this work.

Microcalorimetry

The enthalpies of complexation of Np(V) with fluoride at 25, 40, 55 and 70°C were determined by microcalorimetric titrations conducted on an isothermal microcalorimeter (Model ITC 4200, Calorimetry Science Corp.). The performance of the calorimeter has been tested by measuring the enthalpy of protonation of tris(hydroxymethyl)-amino-methane (THAM). The result was $-47.7 \pm 0.2 \text{ kJ mol}^{-1}$ at 25°C, in excellent agreement with the value in the literature [7]. Details of the microcalorimeter are provided elsewhere [7].

In the titrations of the complexation of Np(V) with fluoride, a Np(V) solution of 0.90 cm^3 (at 25°C) was placed in the titration vessel and titrated with solutions of 1.0 M NaF in increments of $5 \mu\text{L}$. Multiple titrations were conducted at each temperature. For each titration, n additions were made (usually $n=40-50$), resulting in n experimental values of the heat generated in the reaction cell ($Q_{\text{ex},j}$, where $j=1$ to n). These values were corrected for the heat of dilution of the titrant ($Q_{\text{dil},j}$), which was determined in separate runs. The net reaction heat at the j^{th} point ($Q_{\text{r},j}$) was obtained from the difference: $Q_{\text{r},j} = Q_{\text{ex},j} - Q_{\text{dil},j}$. The program Letagrop [8] was used to analyze the data and calculate the thermodynamic parameters.

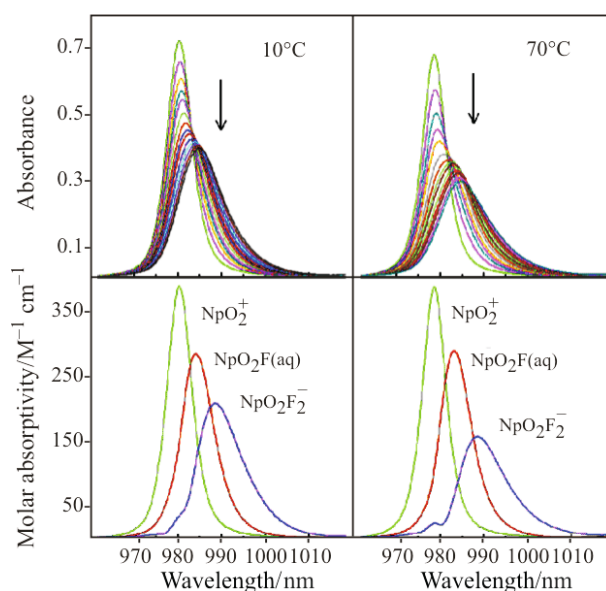
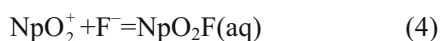


Fig. 1 Representative spectrophotometric titrations of Np(V)/fluoride complexation. $I=1.0 \text{ mol dm}^{-3} \text{ Na}(\text{ClO}_4/\text{F})$. Upper figures – normalized absorption spectra collected in the titration at 10 and 70°C. Lower figures – calculated molar absorptivity of NpO_2^+ , $\text{NpO}_2\text{F}(\text{aq})$ and NpO_2F_2^- at 10 and 70°C

Results and discussion

Stability constants of Np(V)/fluoride complexes at elevated temperatures

Figure 1 shows the absorption spectra of two representative spectrophotometric titrations at 10 and 70°C. As the top figures show, the absorption band of free NpO_2^+ decreased as the concentration of fluoride was increased in the titration. New absorption features at longer wavelengths appeared, suggesting the formation of Np(V)/fluoride complexes. Factor analysis of the absorption spectra by the HyperQuad program indicated that there are three absorbing species of Np(V) and the spectra were best-fitted with successive formation of 1:1 and 1:2 complexes represented by Eqs. (4) and (5). Calculated molar absorptivity of NpO_2^+ , $\text{NpO}_2\text{F}(\text{aq})$ and NpO_2F_2^- at 10 and 70°C are shown in the lower figures of Fig. 1.



The stability constants of $\text{NpO}_2\text{F}(\text{aq})$ and NpO_2F_2^- at 10, 25, 40, 55 and 70°C were calculated and listed in Table 1. The uncertainties of $\log \beta_M$ in the table are ‘composite’ values obtained by taking into consideration the statistic deviations of repetitive titrations at each temperature. The ‘composite’ uncertainties are about 2–4 times larger than the standard deviations calculated by the Hyperquad program. The latter are usually quite small (± 0.01 to 0.02) and probably unrealistic. For the calculation of the stability

constants of $\text{NpO}_2\text{F}(\text{aq})$ and NpO_2F_2^- , the protonation constant of fluoride at different temperatures from the literature [10] was used. Data in Table 1 indicate that the complexation of Np(V) with fluoride is moderately strong and becomes stronger as the temperature is elevated. In Table 1, the stability constants of $\text{NpO}_2\text{F}(\text{aq})$ from previous work by solvent extraction [9] are also shown for comparison. It should be noted that, values of $\log \beta_1$ from previous work are about 0.2–0.3 logarithm units higher than those from this work. The discrepancy probably results from the difference in the models for fitting the experimental data. The solvent extraction data were fitted with the formation of only 1:1 complex [9], while the spectrophotometric data in this work clearly showed the formation of both 1:1 and 1:2 complexes and the data were fitted accordingly.

Assuming the enthalpies of complexation for $\text{NpO}_2\text{F}(\text{aq})$ and NpO_2F_2^- are constant in the temperature range (10–70°C), the van’t Hoff plot of $\log \beta$ vs. $1/T$ is shown in Fig. 2. From the slopes of the linear fit (weighted by the uncertainties), the ‘average’ enthalpies of complexation for $\text{NpO}_2\text{F}(\text{aq})$ and NpO_2F_2^- in the temperature range (10–70°C) were calculated to be (7.9 ± 1.9) and (21.5 ± 3.6) kJ mol^{-1} , respectively.

Enthalpy of complexation between Np(V) and fluoride at elevated temperatures

A representative calorimetric titration of the complexation of Np(V) with fluoride at 25°C is shown in

Table 1 Thermodynamic parameters for the complexation of Np(V) with fluoride

Reaction	$T/^\circ\text{C}$	Method	$\log \beta$ $I=1.0 \text{ M}$ $\text{Na}(\text{ClO}_4/\text{F})$	$\log \beta_0$ $I=0$	ΔH kJ mol^{-1}	ΔS $\text{J K}^{-1} \text{ mol}^{-1}$	Ref.
$\text{NpO}_2^+ + \text{F}^- = \text{NpO}_2\text{F}(\text{aq})$	10	sp	1.19 ± 0.05	1.32 ± 0.12			p.w.
	25	sp, cal	1.25 ± 0.05	1.39 ± 0.12	8.1 ± 1.0	51 ± 5	
	40	sp, cal	1.36 ± 0.05	1.51 ± 0.12	8.8 ± 0.6	54 ± 4	
	55	sp, cal	1.39 ± 0.05	1.55 ± 0.12	10.2 ± 0.5	58 ± 4	
	70	sp, cal	1.44 ± 0.05	1.62 ± 0.12	11.2 ± 2.6	60 ± 11	
	25	sx	1.42 ± 0.10				[9]
	35	sx	1.63 ± 0.03				
	50	sx	1.77 ± 0.04				
	60	sx	1.80 ± 0.03				
$\text{NpO}_2^+ + 2\text{F}^- = \text{NpO}_2\text{F}_2^-$	10	sp, cal	1.37 ± 0.10	1.50 ± 0.15			p.w.
	25	sp, cal	1.77 ± 0.09	1.92 ± 0.14	14.2 ± 3.1	82 ± 12	
	40	sp, cal	1.99 ± 0.10	2.15 ± 0.15	18.6 ± 1.6	98 ± 7	
	55	sp, cal	2.04 ± 0.08	2.21 ± 0.13	36.0 ± 1.4	149 ± 7	
	70	sp, cal	2.11 ± 0.09	2.30 ± 0.14	40.8 ± 8.8	159 ± 32	

sp – spectrophotometry, cal – calorimetry, sx – solvent extraction; p.w. – present work

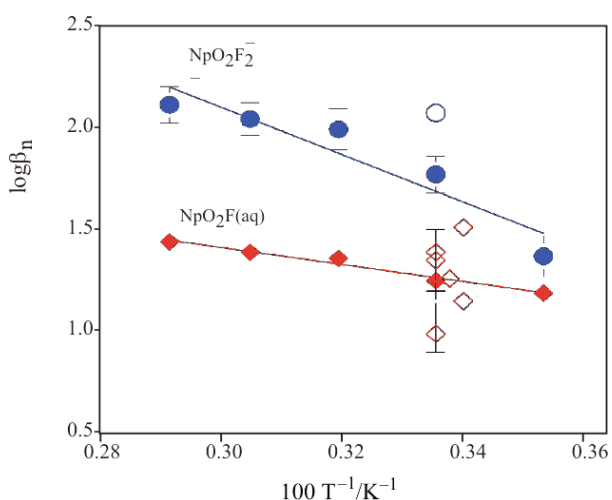


Fig. 2 $\log\beta$ vs. $1/T$ for the complexation of Np(V) with fluoride. Solid symbols (\blacklozenge – $\log\beta_1$, \bullet – $\log\beta_2$): experimental data from this work ($I=1.0 \text{ mol dm}^{-3} \text{ Na(ClO}_4\text{/F)}$); Open symbols (\diamond – $\log\beta_1$, \circ – $\log\beta_2$): experimental data in the literature [2]; Cross (+): NEA selected value of $\log\beta_1^0$ [2]. The error bars of $\log\beta_1$ from this work are ± 0.05 (not shown in the plot)

fluoride, the concentrations of reactants (Np(V), F^- and proton), and the enthalpy of complexation as well as the stability constants of the Np(V)/ F^- complexes that form in the titration. To calculate the enthalpy of Np(V)/ F^- complexation from the reaction heat, the other parameters should be known. In this work, we have used the protonation constants and enthalpy of fluoride previously reported [10]. The calculated enthalpies of Np(V)/ F^- complexation are summarized in Table 1. It should be noted that the ‘average’ enthalpies of complexation calculated from the van’t Hoff plot are near or within the range of the enthalpies of complexation for 10–70°C directly measured by calorimetry.

As shown by the enthalpy of complexation at different temperatures in Table 1, the complexation of Np(V) with fluoride is endothermic and becomes increasingly endothermic at higher temperatures. Assuming linear correlations between ΔH and T , the heat capacities of complexation for $\text{NpO}_2\text{F(aq)}$ and NpO_2F_2^- were calculated to be 76 ± 30 and $860 \pm 100 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively.

Calculation of stability constants at variable temperatures to infinitely dilute solutions

Analysis by the specific ion interaction approach (SIT)

As preferred in common compilations of thermodynamic data, the standard state is defined as the infinite dilute solution, with pure water as the solvent. The SIT (specific ion interaction) approach originated from the Brønsted–Guggenheim–Scatchard model [11–14] has been used to calculate the equilibrium constants at zero ionic strength. For reactions (4) and (5), the equilibrium constants at $I=0$ ($\log\beta^0$) are related to $\log\beta$ at other ionic strengths by the following equation:

$$\log\beta - \Delta Z^2 \cdot D = \log\beta^0 - \Delta \varepsilon I_m \quad (6)$$

where $\Delta Z^2 = \{\sum(Z_{\text{products}}^2) - \sum(Z_{\text{reactants}}^2)\}$, and equals -2 for both reactions (4) and (5) respectively. D is the Debye–Huckel term used in the SIT method and $D = A I_m^{1/2} / (1 + 1.5 I_m^{1/2})$, I_m is the ionic strength in molality, and ε is the ion interaction parameter used in the SIT method [6]. The ion interaction parameters (25°C, kg mol^{-1}) used in this work include the following: $\varepsilon(\text{Na}^+, \text{F}^-) = 0.02 \pm 0.02$ and $\varepsilon(\text{NpO}_2^+, \text{ClO}_4^-) = 0.25 \pm 0.05$ [6]. $\varepsilon(\text{Na}^+, \text{NpO}_2\text{F}_2^-)$ is not available, but we assumed that it is equal to $\varepsilon(\text{Na}^+, \text{NpO}_2(\text{OH})_2^-) = -0.01 \pm 0.07$ [6]. Therefore, $\Delta \varepsilon(25^\circ\text{C}, \text{kg mol}^{-1}) = \varepsilon(\text{Na}^+, \text{F}^-) - \varepsilon(\text{NpO}_2^+, \text{ClO}_4^-) = -0.27 \pm 0.10$ for reaction (4), and $\Delta \varepsilon(25^\circ\text{C}, \text{kg mol}^{-1}) = -0.28 \pm 0.10$ for reaction (5). For the calculation of $\log\beta^0$ at temperatures other than 25°C, we have adopted the following approaches:

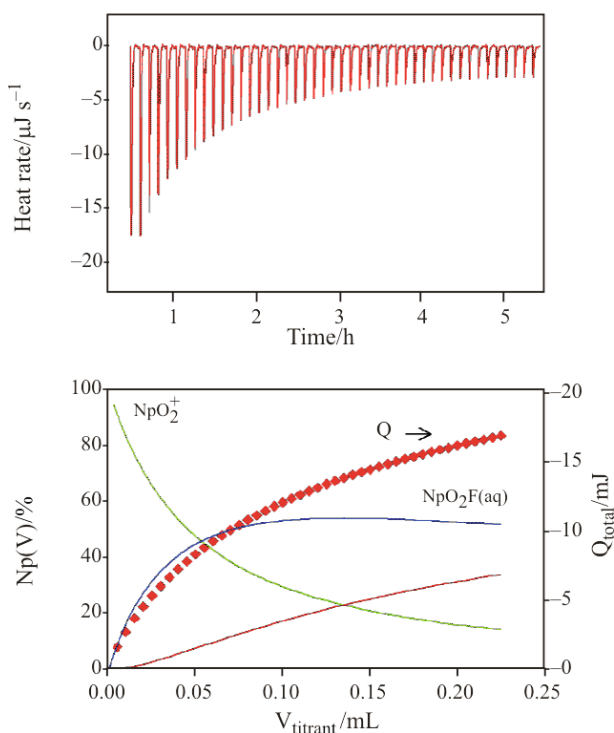


Fig. 3 Calorimetric titration of Np(V) fluoride complexation. $I=1.0 \text{ mol dm}^{-3} \text{ Na(ClO}_4\text{/F)}$, $t=25^\circ\text{C}$. Cup: 0.900 mL $C_{\text{Np}}=1.78 \cdot 10^{-3} \text{ mol dm}^{-3}$, $C_{\text{H}}=3 \cdot 10^{-7} \text{ mol dm}^{-3}$; titrant: $1.0 \text{ mol dm}^{-3} \text{ NaF}$, 5 μL /addition

Fig. 3, as the reaction heat and Np(V) speciation vs. the volume of titrant. The observed reaction heat is a function of a number of parameters, including the equilibrium constant and enthalpy of protonation of

(1) using $\log\beta_M^0$ (molarity) in Table 1 as $\log\beta_m^0$ (molality) without correction because the correction is smaller than the magnitude of uncertainties as discussed in previous sections; (2) using the values of A at different temperatures tabulated in the literature [15]; and (3) using the value of $\Delta\epsilon$ 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 $(\partial\epsilon/\partial T)_p$ are usually $\leq 0.005 \text{ kg mol}^{-1} \text{ K}^{-1}$ for temperatures below 200°C [6]. Besides, the values of $(\partial\epsilon/\partial T)_p$ for the reactants and products may balance out each other so that $\Delta\epsilon$ for many reactions remains approximately constant up to 100°C [16]. The calculated $\log\beta^0$ are summarized in Table 1 (the error limits were obtained by propagation of the uncertainties in the experimental values of $\log K_M$ and the uncertainty in $\Delta\epsilon$ at 25°C). The value of $\log\beta^0$ ($\text{NpO}_2\text{F}(\text{aq})$) at 25°C (1.39 ± 0.12) is slightly higher but comparable to that selected by the NEA review within the error limits ($\log\beta^0 = 1.20 \pm 0.30$) [2].

Conclusions

In contrast to the previous study by the solvent extraction technique, two successive $\text{Np}(\text{V})/\text{F}$ complexes were identified in aqueous solutions in the temperature range of 10–70°C by spectrophotometry. The stability constants of $\text{NpO}_2\text{F}(\text{aq})$ and NpO_2F_2^- increased by 2 to 5 times as the temperature is increased from 10 to 70°C. Thermodynamic parameters such as the enthalpy and entropy of complexation indicate that the complexation of $\text{Np}(\text{V})$ with fluoride is entropy driven. As the temperature is increased, both the enthalpy and entropy of complexation increase. The favorable contribution from the entropy term exceeds the unfavorable contribution from the enthalpy term, resulting in the enhancement of complexation at higher temperatures.

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