

ST # 47079 QA:NA 3/6/06

## Thermodynamics of Neptunium(V) Fluoride and Sulfate at Elevated Temperatures

Linfeng Rao,<sup>1</sup> Guoxin Tian,<sup>1</sup> Yuanxian Xia<sup>2</sup> and Judah I. Friese<sup>2</sup><sup>1</sup>Lawrence Berkeley National Laboratory, Berkeley, CA 94720<sup>2</sup>Pacific Northwest National Laboratory, Richland, WA 99352

**Abstract** – Complexation of neptunium(V) with fluoride and sulfate at elevated temperatures was studied by microcalorimetry. Thermodynamic parameters, including the equilibrium constants and enthalpy of protonation of fluoride and sulfate, and the enthalpy of complexation between Np(V) and fluoride and sulfate at 25 – 70°C were determined. Results show that the complexation of Np(V) with fluoride and sulfate is endothermic and that the complexation is enhanced by the increase in temperature – a three-fold increase in the stability constants of  $\text{NpO}_2\text{F}(\text{aq})$  and  $\text{NpO}_2\text{SO}_4^-$  as the temperature is increased from 25 to 70°C.

## I. INTRODUCTION

Neptunium is one of the radionuclides of concern in the post-closure chemical environment in the proposed Yucca Mountain repository because of its mobility and long half-life ( $2.14 \times 10^6$  years). It is likely that  $^{237}\text{Np}$ ,  $^{129}\text{I}$  and  $^{99}\text{Tc}$  will be the major contributors to the potential total annual dose from the repository beyond 10,000 years [1].

The postclosure chemical environment is expected to be at near neutral pH, slightly oxidizing, and at elevated temperatures for thousands of years [1]. Np(V) is expected to be the most stable oxidation state under these conditions. Its complexation with inorganic ligands that could be present, such as  $\text{OH}^-$ ,  $\text{F}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{CO}_3^{2-}$ , plays an important role in determining its migration in the repository. To predict the migration behavior of neptunium, it is necessary to have sufficient and reliable thermodynamic data on its complexation at elevated temperatures. However, such data are scarce and scattered for 25°C, and nonexistent for elevated temperatures [2]. To provide reliable thermodynamic data, we have started investigations of the complexation of actinides 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 Np(V) with fluoride and sulfate at 25 – 70°C.

## II. EXPERIMENTAL

## II.A. Chemicals

All chemicals were reagent grade or higher. Water from a Milli-Q system was used in preparations of all the solutions. The stock solution of Np(V) in perchloric acid was prepared based on procedures previously reported [3]. The oxidation state of Np(V) was confirmed by the

characteristic absorption peak in the near IR region and the concentration of Np(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 perchloric acid in the Np(V) stock solution. Solutions of fluoride and sulfate were prepared by dissolving solid NaF or  $\text{Na}_2\text{SO}_4$  in water. The ionic strength of all the working solutions in this study was maintained at 1.0 M (25°C) by adding appropriate amounts of sodium perchlorate as the background electrolyte.

## II.B. Microcalorimetry

Calorimetric titrations were performed at 25, 40, 55 and 70°C to determine the equilibrium constants and the enthalpy of protonation of fluoride and sulfate, and the enthalpy of complexation of Np(V) with fluoride and sulfate. The titrations were 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)-aminomethane (THAM). The result was  $-(47.7 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$  at 25°C, in excellent agreement with the value in the literature [3]. Details of the microcalorimeter are provided elsewhere [5].

In the titrations of the protonation of fluoride and sulfate, the initial cell solutions ( $\sim 0.90 \text{ cm}^3$  at 25°C) containing fluoride or sulfate were titrated with  $\text{HClO}_4$  in increments of 5  $\mu\text{l}$ . In the titrations of the complexation of Np(V), the initial cell solutions ( $\sim 0.90 \text{ cm}^3$  at 25°C) containing Np(V) were titrated with solutions of fluoride or sulfate in increments of 5  $\mu\text{l}$ . Multiple titrations were conducted for each ligand 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 ( $Q_{r,j}$ ) was obtained from the difference:  $Q_{r,j} = Q_{ex,j} - Q_{dil,j}$ . The program Letagrop [6] was used to analyze the data and calculate the thermodynamic parameters.

### III. RESULTS AND DISCUSSION

#### III.A. Protonation of Fluoride and Sulfate at Elevated Temperatures

Prior to the determination of the thermodynamic parameters of neptunium complexation with fluoride and sulfate at elevated temperatures, the protonation constants and enthalpy of protonation of the ligands at these temperatures must be known or, if not available, must be determined. The frequently used potentiometry with a glass electrode is not suitable for such studies because of two reasons: 1) corrosion of the glass electrode by HF, especially at elevated temperatures, precludes the use of glass pH electrodes; 2) the  $pK_a$  of  $HSO_4^-$  ( $\sim 1$ ) is too low to be accurately measured by acid-base potentiometry. On the other hand, titration calorimetry is ideal for such measurements. Because the experimentally observed heat depends on the enthalpy of reaction as well as the changes in speciation during the titration, it is possible to obtain the equilibrium constant(s) and the enthalpy of protonation simultaneously by fitting the reaction heat.

Figure 1 shows the reaction heat of protonation of fluoride determined by calorimetry at different temperatures. Negative values of heat indicate that the overall reaction is endothermic. From the data of multiple calorimetric titrations at each temperature, the equilibrium constants and enthalpy of protonation of fluoride and sulfate at 25–70°C are calculated and shown in Figure 2 and Table 1. The trends can be summarized as follows: 1) protonation constants of fluoride and sulfate increase as the temperature is elevated; 2) protonation of fluoride and sulfate is endothermic and becomes more endothermic at higher temperatures. From the linear correlation between the enthalpy and temperature (Figure 2), the heat capacity of protonation of fluoride and sulfate was calculated to be  $(96 \pm 13) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  and  $(599 \pm 16) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ , respectively. It is worth noting that, as Table 1 shows, the equilibrium constant and the enthalpy of protonation of sulfate at 25°C and  $I = 1.0 \text{ M NaClO}_4$  from this work are similar to the calculated values by Dickson et al. at 25°C and  $I = 1.0 \text{ m NaCl}$  [7].

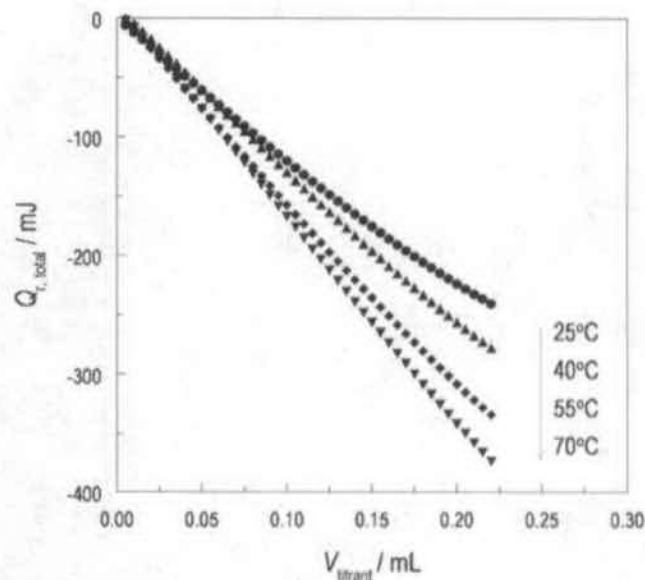


Fig. 1. Calorimetric titrations of the protonation of fluoride at different temperatures. Initial cup solution: 0.90 mL,  $C_{NaF} = 0.0333 \text{ M}$ , titrant: 0.1032 M  $\text{HClO}_4$ , 5  $\mu\text{L}/\text{addition}$ ;  $I = 1 \text{ M NaClO}_4$ .

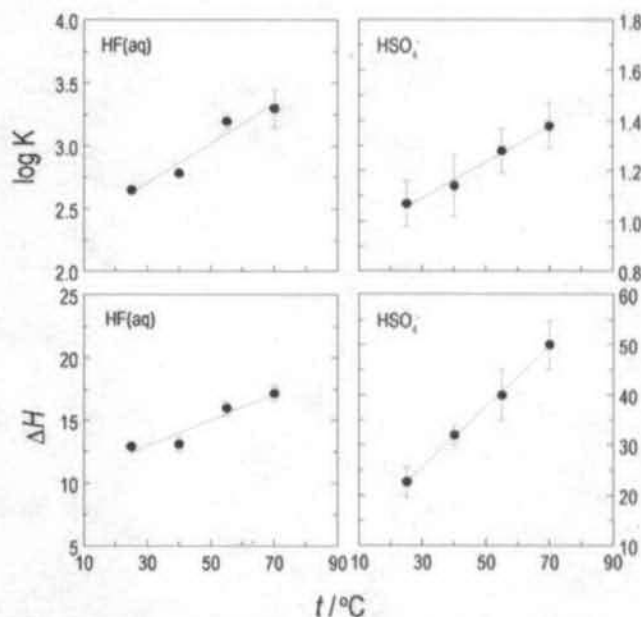


Fig. 2. Effect of temperature on the protonation constant and enthalpy (in  $\text{kJ} \cdot \text{mol}^{-1}$ ) of fluoride and sulfate.  $I = 1 \text{ M NaClO}_4$ .

TABLE 1. Thermodynamic parameters for the protonation and complexation of fluoride and sulfate with Np(V),  $t = 25^\circ\text{C}$ .

Reaction	$t$ $^\circ\text{C}$	$\log_{10}K$ $I = 1.0 \text{ M}$ $\text{NaClO}_4$	$\log_{10}K^0$ $I = 0$	$\Delta H$ $\text{kJ}\cdot\text{mol}^{-1}$
$\text{H}^+ + \text{F}^- = \text{HF}(\text{aq})$	25	$2.65 \pm 0.03$	2.87	$12.9 \pm 0.3$
	40	$2.78 \pm 0.03$	3.01	$13.1 \pm 0.6$
	55	$3.20 \pm 0.06$	3.44	$16.0 \pm 0.6$
	70	$3.30 \pm 0.15$	3.55	$17.2 \pm 0.6$
$\text{H}^+ + \text{SO}_4^{2-} = \text{HSO}_4^-$	25	$1.07 \pm 0.09$	1.84	$22.7 \pm 3.0$
		$1.06 \pm 0.02^a$		$19.9 \pm 0.8^a$
	40	$1.14 \pm 0.12$	1.92	$32.0 \pm 2.0$
	55	$1.28 \pm 0.09$	2.08	$40.0 \pm 5.0$
	70	$1.38 \pm 0.09$	2.21	$50.0 \pm 5.0$
$\text{NpO}_2^+ + \text{F}^- = \text{NpO}_2\text{F}(\text{aq})$	24	$1.42 \pm 0.10$		
	25	$1.47 \pm 0.10^b$	1.58	$18.0 \pm 0.3$
	35	$1.63 \pm 0.03$		
	40	$1.63 \pm 0.10^b$	1.75	$12.2 \pm 0.6$
	51	$1.77 \pm 0.04$		
	55	$1.78 \pm 0.10^b$	1.91	$9.4 \pm 0.8$
	60	$1.80 \pm 0.03$		
	70	$1.94 \pm 0.10^b$	2.08	$8.2 \pm 1.2$
$\text{NpO}_2^+ + \text{SO}_4^{2-} = \text{NpO}_2\text{SO}_4^-$	25	$0.49 \pm 0.31$	0.97	$23.1 \pm 2.5$
	40	$0.65 \pm 0.19$	1.14	$20.0 \pm 1.6$
	50	$0.73 \pm 0.16$		
	55	$0.78 \pm 0.20^b$	1.29	$25.1 \pm 0.3$
	70	$0.93 \pm 0.20^b$	1.47	$30.4 \pm 1.3$

<sup>a</sup> From Ref.[7],  $I = 1.0 \text{ m NaCl}$ .

<sup>b</sup> Extrapolated or interpolated stability constants of  $\text{NpO}_2\text{F}(\text{aq})$  and  $\text{NpO}_2\text{SO}_4^-$  from data in Ref.[8]. The error limits ( $3\sigma$ ) of the stability constants have been enlarged by two times to account for the uncertainties that might have been introduced by the interpolation or extrapolation.

### III.B. Complexation of Np(V) with Fluoride and Sulfate at Elevated Temperatures

A representative calorimetric titration of the complexation of Np(V) with fluoride is shown in Figure 3, as the total reaction heat and Np(V) speciation vs. the volume of titrant.

As previously discussed, the observed reaction heat is a function of a number of parameters, including the equilibrium constant and enthalpy of protonation of the ligands (fluoride and sulfate), the concentrations of reactants (Np(V), ligands and proton), and the enthalpy of complexation as well as the stability constants of the complexes that form in the titration. To calculate the enthalpy of complexation from the reaction heat, the other parameters should be known. In this work, we have used the protonation constants and enthalpy of fluoride and sulfate determined by calorimetry and the stability constants of  $\text{NpO}_2\text{F}(\text{aq})$  and  $\text{NpO}_2\text{SO}_4^-$  from ref [8]. Because some of the stability constants of  $\text{NpO}_2\text{F}(\text{aq})$  and  $\text{NpO}_2\text{SO}_4^-$  were determined in a slightly different temperature range ( $24 - 60^\circ\text{C}$ ) [8], interpolation and extrapolation were performed to obtain the stability constants at 25, 40, 55 and  $70^\circ\text{C}$ . These constants and the enthalpy of complexation are shown in Figure 4, and summarized in Table 1 together with the parameters obtained for the protonation of fluoride and sulfate.

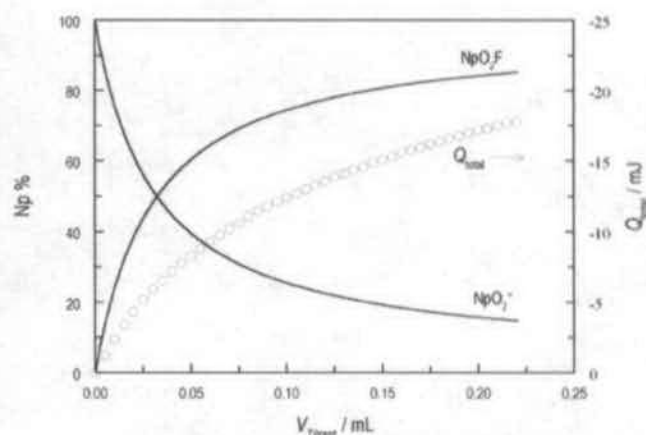


Fig. 3. Calorimetric titration of Np(V) fluoride complexation ( $I = 1.0 \text{ M NaClO}_4$ ,  $t = 25^\circ\text{C}$ ). Cup: 0.900 mL  $C_{\text{Np}} = 1.78 \times 10^{-3} \text{ M}$ ,  $C_{\text{H}} = 3 \times 10^{-7} \text{ M}$ ; titrant: 1 M NaF, 5  $\mu\text{L}/\text{addition}$ .

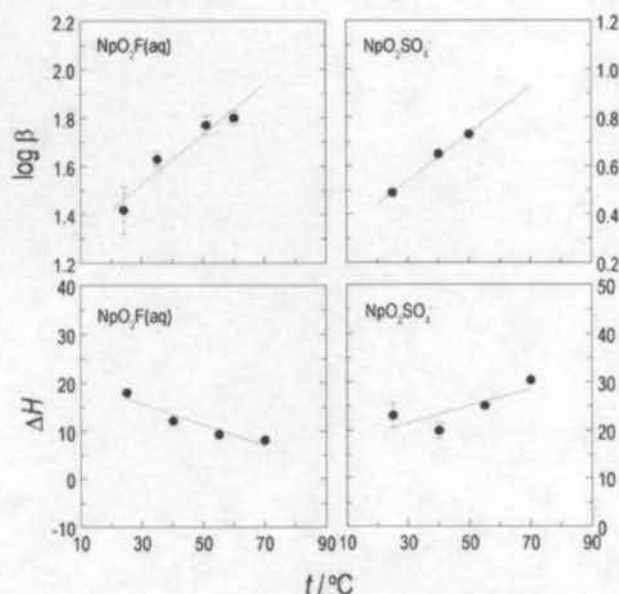


Fig. 4. Effect of temperature on the stability constants of  $\text{NpO}_2\text{F(aq)}$  and  $\text{NpO}_2\text{SO}_4^-$  [8] and the enthalpy of complexation (in  $\text{kJ}\cdot\text{mol}^{-1}$ ).  $I = 1 \text{ M NaClO}_4$ .

Data in Figure 4 indicate that the complexation of  $\text{Np(V)}$  with fluoride and sulfate is enhanced at higher temperatures. The stability constants of the complexes,  $\text{NpO}_2\text{F(aq)}$  and  $\text{NpO}_2\text{SO}_4^-$  increase by about 3 times as the temperature is elevated from 25 to 70°C. The enthalpies of complexation for  $\text{NpO}_2\text{F(aq)}$  and  $\text{NpO}_2\text{SO}_4^-$  are both endothermic, but the trends with the change in temperature are opposite. As the temperature is increased, the enthalpy of complexation for  $\text{NpO}_2\text{F(aq)}$  decreases while that for  $\text{NpO}_2\text{SO}_4^-$  increases. Assuming linear correlations between  $\Delta H$  and  $t$ , the heat capacity of complexation for  $\text{NpO}_2\text{F(aq)}$  and  $\text{NpO}_2\text{SO}_4^-$  was calculated to be  $(-267 \pm 20) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  and  $(244 \pm 51) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , respectively.

It is desirable to extrapolate the equilibrium constants at  $I = 1.0 \text{ M}$  to the values in an infinite dilute solution ( $I = 0$ ). We have used the SIT (Specific Ion Interaction) approach described in the literature [9] to calculate the equilibrium constants at  $I = 0$ . For the reactions shown in Table 1, the equilibrium constants at  $I = 0$  ( $\log K^0$ ) are related to  $\log K$  at other ionic strengths by the following equation:

$$\log K - \Delta Z^2 \times D = \log K^0 - \Delta \epsilon f_m \quad (1)$$

where  $\Delta Z^2 = \{\sum(Z_{\text{products}}^2) - \sum(Z_{\text{reactants}}^2)\}$ ,  $D$  is the Debye-Huckel term used in the SIT method and  $D = A I_m^{1/2} / (1 + 1.5 A I_m^{1/2})$ ,  $I_m$  is the ionic strength in molality, and  $\epsilon$  is the ion interaction parameter used in the SIT method [9]. The

interaction parameters at 25°C (in  $\text{kg mol}^{-1}$ ), taken from Ref.[9], include the following:  $\epsilon(\text{H}^+, \text{ClO}_4^-) = 0.14 \pm 0.02$ ,  $\epsilon(\text{Na}^+, \text{F}^-) = 0.02 \pm 0.02$ ,  $\epsilon(\text{Na}^+, \text{SO}_4^{2-}) = -0.12 \pm 0.02$ ,  $\epsilon(\text{Na}^+, \text{HSO}_4^-) = -0.01 \pm 0.02$  and  $\epsilon(\text{NpO}_2^+, \text{ClO}_4^-) = 0.25 \pm 0.05$ .  $\epsilon(\text{Na}^+, \text{NpO}_2\text{SO}_4^-)$  is not available, but we assumed that it is equal to  $\epsilon(\text{Na}^+, \text{NpO}_2\text{CO}_3^-) = -0.18 \pm 0.15 \text{ kg mol}^{-1}$  [9]. For the calculation of  $\log K^0$  at temperatures other than 25°C, the Debye-Huckel term in Eq. (1) was calculated with the values of  $A$  at different temperatures [9] and the ion interaction parameters at 25°C were used because the values at other temperatures were not known. Using the interaction parameters at 25°C may introduce some errors into the  $\log K^0$  at other temperatures. However, the errors are probably 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 [9]. Besides, the values of  $(\partial \epsilon / \partial T)_p$  for the reactants and products may balance out each other so that the  $\Delta \epsilon$  for many reactions remains approximately constant up to 100°C [10]. The calculated values of  $\log K^0$  at different temperatures are listed in Table 1.

## ACKNOWLEDGMENTS

This work was supported by the Director, OST&I Program, Office of Civilian Radioactive Waste Management, U. S. Department of Energy, under Contract No. DE-AC02-05CH11231 at Lawrence Berkeley National Laboratory.

## REFERENCES

- [1] OCRWM; "Yucca Mountain Science and Engineering Report Rev.1", DOE/RW-0539-1, Office of Civilian Radioactive Waste Management: North Las Vegas, NV. 2002.
- [2] R. Guillaumont, T. Fanghanel, J. Fuger, I. Grenthe, V. Neck, D. A. Palmer, M. H. Rand; "Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium", (Mompéan, F. J., Illemassene, M., Domenech-Orti, C., Ben Said, K., eds.), Amsterdam: Elsevier B.V., 2003.
- [3] L. Rao, T. G. Srinivasan, A. Yu. Garnov, P. Zanonato, P. Di Bernardo, A. Bismondo; Hydrolysis of Neptunium(V) at Variable Temperatures (10 - 85 °C), *Geochim. Cosmochim. Acta*, **68**, 4821-4830 (2004).
- [4] G. Gran; *Analyst*, **77**, 661 (1952).
- [5] P. Zanonato, P. Di Bernardo, A. Bismondo, G. Liu, X. Chen, L. Rao; Hydrolysis of Uranium(VI) at Variable Temperatures (10 - 85 °C), *J. Am. Chem. Soc.* **126**, 5515-5522 (2004).
- [6] R. Arnek; *Arkiv Kemi*, **32**, 81 (1970).

- [7] A. G. Dickson, D. J. Wesolowski, D. A. Palmer, R. E. Mesmer; Dissociation constant of Bisulfate Ion in Aqueous Sodium Chloride Solutions to 250°C. *J. Phys. Chem.*, **94**, 7978-7985 (1990).
- [8] Y. Xia, J. I. Friese, D. A. Moore, L. Rao; Stability Constants of Np(V) Complexes with Fluoride and Sulfate at Variable Temperatures. *J. Radioanal. Nucl. Chem.*, **268**, 3 (2006).
- [9] W. Hummel, G. Anderegg, I. Puigdomènech, L. Rao, O. Tochiyama; "Chemical Thermodynamics of Compounds and Complexes of: U, Np, Pu, Am, Tc, Zr, Ni and Se with Selected Organic Ligands", (Mompéan, F. J.; Illemassene, M.; Perrone, J. eds.), Amsterdam: Elsevier B.V. (2005).
- [10] A. V. Plyasunov, I. Grenthe; *Geochim. Cosmochim. Acta*, **58**, 3561-3582 (1994).