

STABILITY CONSTANTS OF NP(V) COMPLEXES WITH FLUORIDE  
AND SULFATE AT VARIABLE TEMPERATURES

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## ABSTRACT

A solvent extraction method was used to determine the stability constants of Np(V) complexes with fluoride and sulfate in 1.0 M NaClO<sub>4</sub> from 25°C to 60°C. The distribution ratio of Np(V) between the organic and aqueous phases was found to decrease as the concentrations of fluoride and sulfate were increased. Stability constants of the 1:1 Np(V)-fluoride complexes and the 1:1 Np(V)-sulfate and 1:2 Np(V)-sulfate complexes, dominant in the aqueous phase under the experimental conditions, were calculated from the effect of [F<sup>-</sup>] and [SO<sub>4</sub><sup>2-</sup>] on the distribution ratio. The enthalpy and entropy of complexation were calculated from the stability constants at different temperatures by using the Van't Hoff equation.

*Key words:* Neptunium (V) / Fluoride / Sulfate/ Complexation / Stability constants / Solvent extraction

## INTRODUCTION

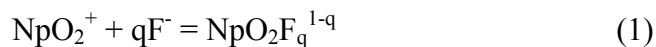
Neptunium is an important radioactive component of nuclear wastes disposed of in low-level and high-level waste repositories because of its high toxicity and very long half life ( $^{237}\text{Np}$ ,  $t_{1/2} = 2.14 \times 10^6$  years) as well as its high abundance in nuclear waste. The fractional dose attributed to  $^{237}\text{Np}$  will reach 67% at 75,000 years.<sup>1</sup> As a result, the migration of neptunium 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, neptunium could exist in multiple oxidation states in nature (e.g., III, IV, V and VI). Np(V) is the most stable oxidation state under environmental and waste conditions. The solubility of neptunium after disposal will depend largely on its reactions (e.g., solubility and complexation) with various components present in the repository. The interactions of actinides with some inorganic ligands at elevated temperatures may be a significant factor in determining the solubility and migration of the actinides in the nuclear waste repository. For example, fluoride and sulfate are expected to be present in the water in contact with the nuclear waste packages and affect the speciation of actinides by forming complexes. The Np(V) complexes with fluoride and sulfate at elevated temperatures may play an important role in the migration

behavior of Np(V). Studies of complexation of Np(V) with various inorganic ligands have recently been reviewed.<sup>2</sup> Fluoride complexation has been studied in near-neutral solutions by several authors using spectrophotometric,<sup>3</sup> solvent extraction,<sup>4-6</sup> and potentiometric<sup>7</sup> methods. But all these data on the stability constants of Np(V) complexes with fluoride were obtained from room temperature. Five experimental studies describing the Np(V) sulfate complexes<sup>4, 6, 8-10</sup> have been published. Much data have been obtained from studies at room temperature, but only Halperin and Olliver<sup>10</sup> reported their data on the stability constants obtained at temperatures of 5, 25, and 45°C. 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. To minimize uncertainty in the prediction of Np(V) 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<sup>11-14</sup> was used to determine the stability constants of Np(V) complexes with fluoride and sulfate anions in 1.0 M NaClO<sub>4</sub> solutions at the various temperatures ranging from 25°C to 60°C. Di-(2-ethylhexyl) phosphoric acid (HDEHP) was used as a solvent extractant and heptane as a solvent.

The complex reaction of Np(V) with fluoride and sulfate under

experimental conditions used in this study can be expressed as:



with the overall stability constant  $\beta_q$  defined as:

$$\beta_q = (\text{NpO}_2\text{F}_q^{1-q})/[(\text{NpO}_2^+) (\text{F}^-)^q] \quad (3)$$

$$\beta_q = [\text{NpO}_2(\text{SO}_4)_q^{1-2q}]/[(\text{NpO}_2^+) (\text{SO}_4^{2-})^q] \quad (4)$$

In the solvent extraction system, the distribution ratio (D) is defined as:

$$D = \Sigma (M)_o / \Sigma (M)_a \quad (5)$$

Assuming only a single organic (o) phase species,  $\text{MA}_n$ , and the various species in the aqueous phase (a), Equation (5) can be written with the stability constants as:<sup>11-12</sup>

$$D_o/D = 1 + \Sigma \beta_i(L)^i \quad (6)$$

For the Np(V)-fluoride and Np(V)-sulfate complex systems at a fixed pcH (see Equation 7), Np(V) stands for M, fluoride and sulfate anions are L, A is the HDEHP anion, and  $D_o$  is the distribution ratio in the absence of complexation.

## EXPERIMENTAL

### Reagents and Solutions

All reagents used in this work were analytical grade or higher. The stock solutions of 1.0 M and 0.1 M sodium fluoride (Aldrich) and sodium sulfate (Sigma) were prepared by dissolving appropriate amounts of these reagents in deionized water, respectively. The stock solution of fluoride was analyzed by a fluoride combination ion selective electrode (Accumet). Sodium perchlorate (Aldrich) was used for ionic strength adjustment without further purification. Perchloric acid (Aldrich) and NaOH (1.0 N standard, Aldrich) were used to adjust pH. Sodium bromate (Aldrich) and NaNO<sub>2</sub> (Aldrich) were used for oxidizing and reducing neptunium, respectively, during the preparation of the stock solution of NpO<sub>2</sub><sup>+</sup>. Di-(2-ethylhexyl) phosphoric acid, HDEHP (Alfa Aesar), was not further purified, and the stock solutions of 0.1 M and 0.01 M HDEHP in heptane (anhydrous, Sigma-Aldrich) were prepared. The organic solutions were pre-equilibrated with the aqueous stock solution of 1.0 M NaClO<sub>4</sub> and stored in a dark glass bottle. All solutions except Np(V) tracer solution used in the experiments were filtered with a 0.2- $\mu$ m microfiltration system to minimize the sorption of Np(V) by suspended particles in solution.

An Np(V) solution was prepared using the procedure described in the literature.<sup>15</sup> A small amount of solid NaBrO<sub>3</sub> was added to a solution of neptunium in 1.0 M HClO<sub>4</sub>, and the solution was warmed to facilitate the oxidation of neptunium to Np(VI). Then a small amount of NaNO<sub>2</sub> was added to this solution, causing a change in color from pink to green

indicating the reduction of  $\text{NpO}_2^{2+}$  to  $\text{NpO}_2^+$ . Finally, the  $\text{NpO}_2^+$  species was precipitated by adding 1.0 M NaOH to the solution. The  $\text{NpO}_2(\text{OH})$  precipitate was washed several times with deionized water and dissolved with 0.1 M  $\text{HClO}_4$ . The oxidation state was confirmed spectrophotometrically by a Cary 500 Scan ultraviolet visible near infrared spectrophotometer and showed that Np was present as  $\text{NpO}_2^+$ . A stock solution of Np(V) was prepared from this in a solution of 0.06 N  $\text{HClO}_4$  such that 10  $\mu\text{l}$  of the solution gives ca. 15,600 cpm. A Wallac (Model 1414) liquid scintillation counter (LSC) was used to measure  $^{237}\text{Np}$ .

#### Temperature-Controlled Extraction Equipment

To shake the samples at the desired temperature, a reaction block with the heat tape or a block heater was used. The reaction block was strapped onto a Lab-line orbital shaker at an approximately  $45^\circ$  angle to facilitate the mixing of the two phases. The temperature was controlled with the block heater's temperature control or through a variable transformer output unit when using the heat tape.

The reaction blocks are aluminum blocks that have been dimensioned to fit pre-purchased dry block heaters. Each of the blocks has machined holes for the selected sample tubes and a specific hole for a bayonet insert.

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 the reaction blocks and centrifuge during the experiment. The thermocouples have armored cable to withstand constant shaking and a quick-release spring-loaded bayonet style connector. Both of the thermocouples were cross calibrated with each of the monitors.

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.

Temperature adjusted reaction blocks were used to maintain the temperature of experimental solutions, samples, and pH buffers.

#### Determination of H<sup>+</sup> Concentrations

A Corning 355 pH meter was used with a combination of glass electrodes (Ross Orion) to measure the change in pH. Because pH was measured in sodium perchlorate solution, the inner solution (3 M KCl) of the glass electrode was replaced with saturated NaCl solution to avoid erratic electrode performance. The electrode was calibrated with 4.00 ± 0.01 and 7.00 ± 0.01 pH buffer standard solutions at the same temperature as the reaction block. The pH meter readings (pH<sub>m</sub>) were converted to a



hydrogen concentration ( $\text{pcH} = -\log [\text{H}^+]$ ) using the following calibration equation proposed by Irving et al.:<sup>16</sup>

$$\text{pcH} = \text{pH}_m + b \quad (7)$$

where  $b$  is the correction factor of an electrode, depending on the solution composition, such as  $b = 0.27$  in 1.0 M  $\text{NaClO}_4$  solution.<sup>11</sup>

### Solvent Extraction

The distribution experiments were conducted following the procedure described in the literature.<sup>11-12</sup> For each extraction experiment, 2.0 ml of aqueous solution was adjusted to the appropriate pcH having the desired amounts of fluoride/sulfate, and an equal volume of 0.01 M HDEHP in heptane was placed in a borosilicate glass vial. After adding 10  $\mu\text{l}$   $^{237}\text{Np(V)}$  tracer, the vials were inserted into the holes of the temperature-controlled reaction block and shaken for 3 hours at the desired temperature. Kinetic studies confirmed that the extraction equilibrium was attained in less than 1 hour.<sup>11</sup> The vials were centrifuged at the same temperature as the reaction block on the shaker, and the aliquots of 0.5 ml were taken from both phases to measure the  $\alpha$ -activity in Opti Fluor cocktail by LSC. The remaining aqueous phase was used for pH measurement at the same temperature as the reaction block on the shaker.

## RESULTS AND DISCUSSION

### Np(V)-Fluoride Complexation

A series of experiments with constant pcH were conducted at an ionic strength of 1.0 M NaClO<sub>4</sub>, and distribution ratios (D) of Np(V) in organic and aqueous phases were found to decrease with increased fluoride concentration (for a complete set of the extraction data, see Appendix A Table A1-A4). The decrease in D can be attributed to the increase in concentration of Np(V)-fluoride complexes in the aqueous phase, which are not extracted by HDEHP. Stability constants of the 1:1 Np(V)-fluoride complexes, dominant in the aqueous phase under the experimental conditions, were calculated from the effect of [F<sup>-</sup>] on the distribution ratio.

A typical fit curve showing the function of D<sub>o</sub>/D versus fluoride anion concentration is shown in Figure 1 in which the points are experimental data and the solid line represents 1:1 complexes that provide the first stability constant. In the pcH range used in this work, the free fluoride anion concentration (F<sup>-</sup>]<sub>f</sub>) can be considered as the total concentration of fluoride ([F<sup>-</sup>]<sub>T</sub>). The first stability constant (β<sub>1</sub>) can be calculated as a slope of the linear regression between D<sub>o</sub>/D and [F<sup>-</sup>]<sub>T</sub> (see Figure 1).

In the extraction experiments, the pH/pcH values measured after extraction sometimes varied slightly. The minor corrections to the D

values for this pcH fluctuation were made by the following relationship:

$$\log D = \log D_{\text{exp}} + n (\text{pcH}_{\text{avg}} - \text{pcH}) \quad (8)$$

where n is the experimental slope of the log  $D_{\text{exp}}$  dependence on pcH in the absence of ligand for the certain  $\text{NaClO}_4$  ionic strength solution (1.0 M) at the required temperature (see Appendix A Tables A1-A7). The  $\text{pcH}_{\text{avg}}$  is an average value of pcH measured for each sample.

Literature data indicate that the hydrolysis of Np(V) is insignificant when  $\text{pcH} < 7$  in the temperature range of 10–85°C.<sup>17</sup> The experiments in this study were conducted at  $\text{pcH} \sim 5$ . As a result, the hydrolysis reactions of Np(V) are not included in the calculation.

The apparent stability constants are listed in Table 1 along with the literature values for comparison. The first stability constant of the Np(V)-fluoride complex at room temperature that was obtained from our experiments is consistent with the literature values. Our results show that the stability constants of the 1:1 Np(V)-fluoride complexes were enhanced with increasing temperature.

#### Np(V)-Sulfate Complexation

Similar to the Np(V)-fluoride system, a series of experiments with constant pcH and temperature were conducted at ionic strength of 1.0 M ( $\text{NaClO}_4 + \text{Na}_2\text{SO}_4$ ). The distribution ratio of Np(V) between the organic

and aqueous phases was found to decrease as the concentration of sulfate was increased (for a complete set of the extraction data. see Appendix A Table A5-A7). Stability constants of the 1:1 Np(V)-sulfate and 1:2 Np(V)-sulfate complexes, dominant in the aqueous phase under the experimental conditions, were calculated from the effect of  $[\text{SO}_4^{2-}]$  on the distribution ratio.

A typical fit curve showing function of  $D_o/D$  versus free sulfate anion concentration ( $[\text{SO}_4^{2-}]_f$ ) is shown in Figure 2 in which the points are experimental data. The curve is a polynomial fit including both the first stability constant ( $\beta_1$ ) and the second stability constant ( $\beta_2$ ), and the solid line only represents 1:1 complexes that provide  $\beta_1$ . The stability constants,  $\beta_1$  and  $\beta_2$ , were obtained in the ionic strength of 1.0 M ( $\text{NaClO}_4 + \text{Na}_2\text{SO}_4$ ) by analyzing such curves. The minor corrections to the D values for this pH fluctuation were made using the same method as the system of Np(V)-fluoride. It should be noted that the sulfate was completely dissociated to  $\text{SO}_4^{2-}$  at  $\text{pH} > 3$ ; thus, in the pH range used in this work, the free sulfate anion concentration  $[\text{SO}_4^{2-}]_f$  can be replaced by the total concentration of sulfate (see Figure 2).

The first apparent stability constants of Np(V) complexes with sulfate are listed in Table 2, including the literature values for comparison. Our measured stability constants for the 1:1 Np(V)-sulfate complex do not compare well with any literature value, but our value does fall within the

overall spread of these literature values. Halperin and Oliver's results<sup>10</sup> indicated that in sulfate concentrations of up to 0.3 M, there is no evidence for Np(V) complexes higher than the monosulfate. The results from our experiments show that there is a formation of 1: 2 complexes of Np(V)-sulfate complex at sulfate concentrations lower than 0.3 M (see Figure 2). The stability constant for 1:2 Np(V)-sulfate complex was calculated to be  $1.60 \pm 0.11$  at 40° C and  $1.82 \pm 0.07$  at 50° C. The sulfate complexation of Np(V) is relatively weak, but increases with increasing temperature.

#### Effect of Temperature on Stability Constants

The effect of temperature on the stability constants was evaluated at the range of temperature from 25°C to 60°C for Np(V)-F<sup>-</sup> complexes and from 25°C to 50°C for Np(V)-SO<sub>4</sub><sup>2-</sup> complexes, respectively. Halperin and Oliver<sup>10</sup> have pointed out that although the thermodynamic values of free energy, enthalpy, and entropy cannot be evaluated from the concentration dependent stability constants, the effective values for these thermodynamic quantities can be calculated by using Van't Hoff equation. To distinguish these calculated values from the true thermodynamic values, they will be hereafter referred to as prime free energy ( $\Delta G^{\circ'}$ ), prime enthalpy ( $\Delta H^{\circ'}$ ), and prime entropy ( $\Delta S^{\circ'}$ ), respectively. From the determined stability constants listed in Tables 1 and 2, the corresponding

values of  $\Delta G^{\circ}$  defined according to Equation (9) for each value at a fixed temperature were calculated:

$$\Delta G^{\circ} = - RT \ln \beta \quad (9)$$

The values of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  at 25°C were calculated by using the Van't Hoff equation:

$$\partial \ln \beta / \partial (1/T) = - \Delta H^{\circ} / R ; \quad \Delta S^{\circ} = (\Delta H^{\circ} - \Delta G^{\circ}) / T \quad (10)$$

These calculated values are listed in Table 3. The small values of  $\Delta G^{\circ}$  reflect the low values of the stability constant. The Np(V)-fluoride complexes are stronger than those with Np(V)-sulfate complexes. The results indicate that the values of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  are positive and relatively large.  $\text{NpO}_2^+$  should be classified as a hard acceptor<sup>10</sup> using the nomenclature and criteria of Person and Ahrland<sup>18-20</sup> whereas  $\text{F}^-$  and  $\text{SO}_4^{2-}$  have been classified as hard donors.<sup>20</sup> Ahrland<sup>20</sup> has pointed out that inner complexes are generally entropy controlled. The gain in enthalpy supports the interpretation of inner sphere binding for the Np(V) complexes with fluoride and sulfate.<sup>10</sup>

## CONCLUSION

A solvent extraction method was used to determine the stability constants of the Np(V)-fluoride and -sulfate complexes in 1.0 M ionic strength at various temperatures. The 1:1 Np(V)-fluoride complex was

found to be dominant in the aqueous phase under the experimental conditions, and the values of the stability constants increased with increasing temperature. The sulfate complexes of  $\text{NpO}_2^+$  are relatively weak, and their respective stability constants are relatively small, but they show an enhancement with increasing temperature. The values of enthalpy and entropy of complexation calculated by Equation (10) are relatively large positive values that are consistent with the inner sphere complexing.<sup>10, 20</sup> The 1:2 Np(V)-sulfate complex was found to form under the experimental conditions (sulfate concentrations from 0.03 to 0.21 M). The values obtained in these experiments show that both Np(V)-fluoride and sulfate complexes may be important in the migration behavior of Np(V) in nuclear waste given elevated surface temperatures and high fluoride/sulfate concentrations.

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## APPENDIX A: SOLVENT EXTRACTION DATA TABLES