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SPECTROPHOTOMETRIC AND CALORIMETRIC STUDIES OF Np(V) COMPLEXATION WITH SULFATE AT 10–70°C

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Sulfate, one of the inorganic constituents in the groundwater of nuclear waste repository, could affect the migration of radioactive materials by forming complexes. Spectrophotometric and microcalorimetric titrations were performed to identify the Np(V)/sulfate complex and determine the equilibrium constants and enthalpy of complexation at 10–70°C.

Results show that the complexation of Np(V) with sulfate is weak but slightly enhanced by the increase in temperature. The complexation is endothermic and becomes more endothermic with the increase in temperature. The enhanced complexation at elevated temperatures is due to the increasingly larger entropy of complexation that exceeds the increase in enthalpy, indicating that the complexation of Np(V) with sulfate is entropy-driven.

Keywords: *complexation, neptunium, sulfate, temperature effect*

Introduction

One of the approaches to safe management of high-level nuclear wastes (HLW) calls for the disposal of HLW in geological repositories. Though the engineered barrier systems are expected to last a very long time after the repository is closed, they may gradually deteriorate and eventually lose integrity. Consequently, water could contact the waste, dissolve it, and carry radionuclides out of the repository. Under the chemical environment in the vicinity of the waste form, ^{237}Np(V) is one of the most soluble radionuclides and is most likely to be carried away from the repository. Because of its long half-life and high mobility, it is projected that, in the proposed Yucca Mountain Repository, the fractional dose attributed to ^{237}Np will increase to 67% of the total dose in 75000 years [1]. As a result, the migration of Np in the postclosure chemical environment of the repository is a great concern to long-term repository performance.

Because the temperature of the HLW repository could remain significantly higher than the ambient even thousands of years after the closure of the repository, predictions of the chemical behavior of Np in the repository can not be made without reliable thermodynamic data concerning the interactions of Np with the ligands that exist in the groundwater of the repository (e.g., OH^-, F^-, SO_4^{2-}, PO_4^{3-} and CO_3^{2}) at elevated temperatures. Unfortunately, thermodynamic data on actinide complexation at elevated temperatures are scarce and highly scattered [2]. Lack of reliable geochemical thermodynamic data could lead to conservative decisions that have too big safety margins and raise the cost of the project. To help with the performance assessment of the HLW repository and fill the gap in thermodynamic data on actinide complexation at elevated temperatures, we have studied the complexation of actinides (Th, U, Np and Pu) with selected organic and inorganic ligands at elevated temperatures. This paper summarizes the results of the complexation of Np(V) with sulfate at 10–70°C.

Experimental

Chemicals

All chemicals except neptunium were reagent grade or higher. Water from a Milli-Q system was used in preparing all solutions. Details on the preparation and standardization of the Np(V) stock solution were provided elsewhere [3]. Solutions of sulfate were prepared by dissolving solid Na_2SO_4 in water. $NaClO_4$ was used as background electrolyte to maintain the ionic strength of working solutions. Due to the use of Na_2SO_4 as the titrant in the spectrophotometric and calorimetric titrations, the ionic strength of the working solutions may deviate from 1.0 mol dm^{-3}, but the concentration of sodium ion remains constant at 1.0 mol dm^{-3} (25°C).

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Methods

Spectrophotometry

Spectrophotometric titrations in the near-IR region were conducted at 10, 25, 40, 55 and 70°C on a Varian Cary-5G spectrophotometer. The temperature of the samples was maintained constant by a 1×1 Peltier temperature controller. An external constant-temperature water bath was used to pre-equilibrate the sample cells at the required temperature before they were inserted into the sample holders. 10 mm quartz cells were used. Multiple titrations with different initial concentrations of Np(V) were performed. The stability constants of the Np(V)/sulfate complex (on the molarity scale) at different temperatures were calculated by non-linear least-square regression using the Hyperquad program [4].

Microcalorimetry

Calorimetric titrations were conducted at 25, 40, 55 and 70°C with an isothermal microcalorimeter (Model ITC 4200, Calorimetry Sciences Corp.). The calorimeter is not equipped with a dry nitrogen purging system so that it is not suitable for the titrations below the room temperature due to possible water condensation inside the calorimeter. As a result, calorimetric titrations at 10°C were not performed in this study.

The microcalorimeter uses a ‘twin’ heat flow design to reach maximum sensitivity. The reaction heat is measured from the difference in the heat flows between the sample and the reference cells. The volume of the cells is about 1.2 cm^3. The titrant is delivered into the sample cell through a long and thin needle from a 100 or 250 μL syringe. The syringe is driven by a precision stepper motor that guarantees accurate delivery of the titrant. The performance of the calorimeter has been tested by measuring the enthalpy of protonation of tris(hydroxymethyl)-aminomethane (THAM). The results (in kJ mol^{-1}) are –47.7±0.3 (25°C), –46.8±0.2 (40°C), –45.8±0.5 (55°C) and –45.2±0.5 (70°C), compared well with the values in the literature: –46.0±0.3 at 45°C and –46.2±0.3 at 70°C [5], –46.81±0.02 at 35°C and –46.0±0.02 at 50°C [6].

Multiple titrations with different initial concentrations of Np(V) 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 ($Q_{\mathrm{ex,j}}$, where j=1 to n). These values were corrected for the heat of dilution of the titrant ($Q_{\mathrm{dil,j}}$), which was determined in separate runs. The net reaction heat at the j-th point ($Q_{\mathrm{r,j}}$) was obtained from the difference: $Q_{\mathrm{r,j}}=Q_{\mathrm{ex,j}}-Q_{\mathrm{dil,j}}$. The program Letagrop [7] was used to analyze the data and calculate the thermodynamic parameters.

Results and discussion

Stability constants of Np(V)/sulfate complexes at variable temperatures

The absorption spectra of two representative spectrophotometric titrations at 10 and 70°C are shown in Fig. 1. As the top plots show, the position of the absorption band of free NpO$_2^+$ at 980 nm was slightly shifted to longer wavelengths, as the concentration of sulfate was increased from 0 to 0.19 mol dm^{-3} in the titration. More significant changes in spectra were observed at higher temperatures (e.g., 70°C). The observations suggested that a rather weak Np(V)/sulfate complex formed and the complex is stronger at higher temperatures. Factor analysis of the absorption spectra by the Hyperquad program indicated that there are two absorbing species of Np(V) and the spectra were best-fitted with the formation of a 1:1 complex, NpO$_2$SO$_4^-$, represented by Eq. (1). Calculated molar absorptivity of NpO$_2^+$ and NpO$_2$SO$_4^-$ at 10 and 70°C are shown in the bottom plots of Fig. 1.

$$\mathrm{NpO_2^+ + SO_4^{2-} = NpO_2SO_4^-} \qquad (1)$$

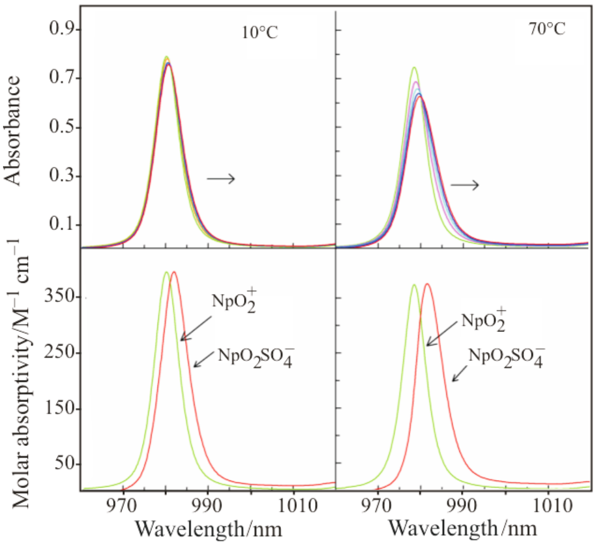

Fig. 1 Representative spectrophotometric titrations of Np(V)/sulfate complexation. I=1.0 mol dm^{-3} Na(ClO$_4$/SO$_4$). Upper figures – normalized absorption spectra. Titrant: 0.500 mol dm^{-3} Na$_2$SO$_4$. Initial solution in cuvette: 2.50 mL; 5.124·10^{-3} mol dm^{-3} NpO$_2$ClO$_4$/1·10^{-6} mol dm^{-3} HClO$_4$ (10°C), 5.00·10^{-3} mol dm^{-3} NpO$_2$ClO$_4$/1·10^{-6} mol dm^{-3} HClO$_4$ (70°C). Lower figures – calculated molar absorptivity of NpO$_2^+$ and NpO$_2$SO$_4^-$

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

Reaction	t/°C	Method	logβ I=1.0 M Na(ClO$_4$/SO$_4$)	logβ^0 I=0	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	Ref.
$NpO_2^+ + SO_4^{2-} = NpO_2SO_4^-$	10	sp	0.43±0.11	0.92±0.22			p.w.
	25	sp, cal	0.53±0.14	1.03±0.25	21±7	81±25	p.w.
				0.44±0.27	23.2±7.2	86.2±24.6	[2]
	40	sp,cal	0.56±0.04	1.09±0.15	24±5	87±17	p.w.
	55	sp, cal	0.60±0.12	1.15±0.20	34±2	115±9	p.w.
	70	sp, cal	0.62±0.08	1.21±0.18	53±5	166±18	p.w.
	25	sx	0.49±0.31				[9]
	40	sx	0.65±0.19				
	50	sx	0.73±0.16				
$H^+ + SO_4^{2-} = HSO_4^-$	25	cal	1.07±0.09		22.7±0.3	97±3	[8]
	40	cal	1.14±0.12		32±2	124±10	
	55	cal	1.28±0.09		40±5	146±18	
	70	cal	1.38±0.09		50±5	172±18	

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

The stability constants of $NpO_2SO_4^-$ at 10, 25, 40, 55 and 70°C were calculated and listed in Table 1. In the calculation, the protonation constants of sulfate at different temperatures from [8] were used. A set of stability constants for $NpO_2SO_4^-$ at 25, 40 and 50°C determined by solvent extraction in previous work [9] are also listed in Table 1 for comparison. As shown by both sets of data, the complexation of Np(V) with sulfate is weak, but becomes slightly stronger as the temperature is elevated. Assuming the enthalpies of complexation for $NpO_2SO_4^-$ are constant in the temperature range (10–70°C), the van't Hoff plot of logβ *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 $NpO_2SO_4^-$ in the temperature range (10–70°C) were calculated to be 6±3 kJ mol^{-1}. It should be noted that, a 1:2 complex, $NpO_2(SO_4)_2^{3-}$, was observed by solvent extraction in the previous work [9], but was obviously not identified by spectrophotometric titrations shown in Fig. 1.

To allow the comparison of stability constants at different temperatures, the constants in molarity units should be corrected to the constants in molality units. However, for the ionic medium of 1 mol dm^{-3} $NaClO_4$ in this work, such correction is about 0.02–0.03 logarithm unit, insignificant compared to the uncertainties associated with the experimental stability constants of $NpO_2SO_4^-$. Therefore, we elected not to convert the values in molarity into those in molality and assumed $\log\beta_M \approx \log\beta_m$ in this work.

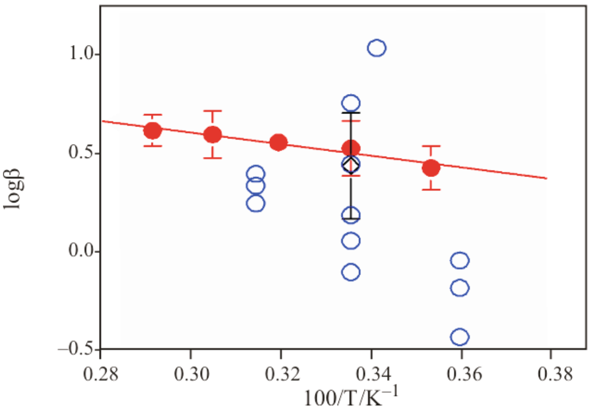

Fig. 2 logβ *vs.* 1/*T* for the complexation of Np(V) with sulfate. ● – experimental data from this work (I=1.0 mol dm^{-3} Na(ClO$_4$/SO$_4$)); ○ – experimental data in [2] at variable ionic strengths; ◇ – NEA selected value of logβ^0 [2]

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

Figure 3 shows a representative calorimetric titration of the complexation of Np(V) with sulfate at 40°C. The observed reaction heat includes the contributions from several reactions including the protonation of sulfate and the complexation of Np(V) with sulfate. Thus, to calculate the enthalpy of Np(V)/sulfate complexation from the reaction heat, a number of parameters, including the protonation constant and enthalpy of sulfate and the stability constant of

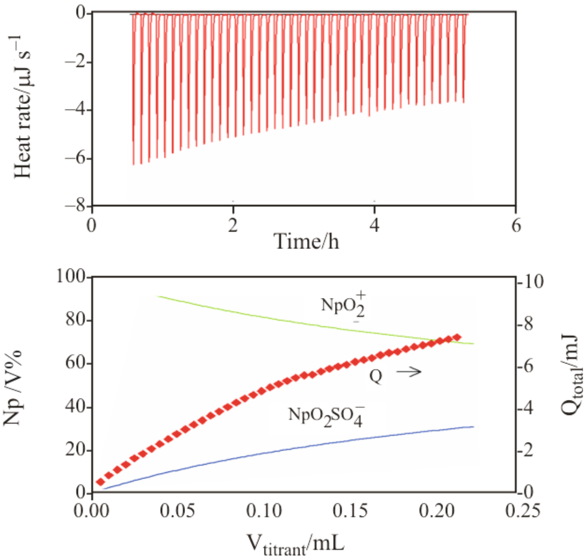

Fig. 3 Calorimetric titration of Np(V) sulfate complexation. I=1.0 mol dm^{-3} Na(ClO$_4$/SO$_4$), t=40°C. Cup: 0.900 mL C_{Np}=1.72·10^{-3} mol dm^{-3}, C_H=3·10^{-7} mol dm^{-3}; titrant: 0.500 mol dm^{-3} Na$_2$SO$_4$, 5 μL/addition

$NpO_2SO_4^-$ must be known. In this work, we have used the protonation constants and enthalpy of sulfate previously reported [8] and the stability constant of $NpO_2SO_4^-$ determined by spectrophotometry in this work. The calculated enthalpies of reaction (1) at 25, 40, 55 and 70°C are summarized in Table 1.

As shown in Table 1, the complexation of Np(V) with sulfate is endothermic and becomes increasingly endothermic at higher temperatures. Assuming linear correlations between ΔH and T, the heat capacity of reaction (1) was calculated to be 720±170 J K^{-1} mol^{-1}. It should be noted that the enthalpy of complexation at 25°C directly determined by calorimetry in this work 21±7 kJ mol^{-1} is in excellent agreement with that selected by the NEA review 23.2±7.2 kJ mol^{-1} [2], but significantly higher than that obtained by a linear fit of the data of stability constants at different temperatures. Without a satisfactory explanation for this discrepancy at present, we can just point out that extending the temperature range (e.g., 5–90°C) and increasing the number of data sets (different temperatures) of the spectrophotometric titrations may significantly reduce the uncertainty of stability constants and, possibly, decrease the discrepancy.

Data in Table 1 show that the enthalpy and entropy of reaction (1) are quite similar to the enthalpy and entropy of the protonation of sulfate ($H^+ + SO_4^{2-} = HSO_4^-$). Such similarity implies that, desolvation of SO_4^{2-} is probably the major contributor to the overall energetics (ΔH) and disorder (ΔS) in both the complexation and protonation processes. It is also interesting to compare the ΔH and ΔS of Np(V)/sulfate complexation with those of Np(V)/ fluoride complexation. The ΔH and ΔS values for the former reaction ($NpO_2^+ + SO_4^{2-} = NpO_2SO_4^-$) are both significantly larger (more positive) than those for the latter ($NpO_2^+ + F^- = NpO_2F(aq)$) [10]. This could be rationalized by assuming that the desolvation of SO_4^{2-} (–2 charge) requires more energy than the desolvation of F^- (–1 charge). In addition, SO_4^{2-} could complex metal ions in mono- and bi-dentate modes while F^- is a monodentate ligand. More water molecules would be released from the solvation spheres of bidentate SO_4^{2-} ligand and the metal ions, creating larger entropy changes upon complexation. Though we do not have structural data to ascertain the coordination mode of SO_4^{2-} in the $NpO_2SO_4^-$ complex, existence of both mono- and bi-dentate SO_4^{2-} in the complexes with UO_2^{2+} was supported by experimental data in solution and solids as well as by theoretical calculations [11].

Calculation of stability constants at variable temperatures to infinitely dilute solutions: analysis by the specific ion interaction approach (SIT)

The SIT (specific ion interaction) approach originated from the Brønsted–Guggenheim–Scatchard model [12–15] can be used to calculate the equilibrium constants at zero ionic strength from experimental data at other ionic strengths. For reaction (1), the equilibrium constant at I=0 ($\log\beta^0$) are related to $\log\beta$ at other ionic strengths by Eq. (2):

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

where $\Delta Z^2 = \{\Sigma(Z^2_{products}) - \Sigma(Z^2_{reactants})\}$, and equals –4 for reaction (1). 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 ion interaction parameters (25°C, kg mol^{-1}) used in the SIT calculation include the following: $\varepsilon(Na^+, SO_4^{2-}) = -0.12\pm0.06$ and $\varepsilon(NpO_2^+, ClO_4^-) = 0.25\pm0.05$ [2]. $\varepsilon(Na^+, NpO_2SO_4^-)$ is not available, but we assumed that it is equal to $\varepsilon(Na^+, NpO_2CO_3^-) = -0.18\pm0.15$ [2]. Therefore, $\Delta\varepsilon$ (25°C, kg mol^{-1})= $\varepsilon(Na^+, NpO_2SO_4^-) - \varepsilon(Na^+, SO_4^{2-}) - \varepsilon(NpO_2^+, ClO_4^-) = -0.31\pm0.18$. For the calculation of $\log K^0$ at temperatures other than 25°C, we used the values of A at different temperatures tabulated in [16] and 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 [17]. 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 [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 $\log\beta_M$ and the uncertainty in $\Delta\varepsilon$ at 25°C). The value of $\log\beta^0$ ($NpO_2SO_4^-$) at 25°C (1.03±0.25) is higher than and barely overlap with the value selected by the NEA review within the error limits ($\log\beta^0$=0.44±0.27) [2]. It should be noted that the NEA review selected the value based on two quite different experimental values, one of which ($\log\beta$=0.44±0.09 at 25°C and I=2 mol dm^{-3}) is in fact close to our value at I=1 mol dm^{-3}.

Conclusions

Complexation of Np(V) with sulfate anion (SO_4^{2-}) is weak and is slightly enhanced at elevated temperatures. Thermodynamic parameters of complexation (ΔH and ΔS) suggest that the desolvation of sulfate plays a major role in the energetics and disorder of the complex system. As the temperature is increased, both the enthalpy and entropy of complexation increase, making opposite contributions to the temperature effect on the Gibbs free energy (and thus on the stability of $NpO_2SO_4^-$). The stability constant of $NpO_2SO_4^-$ increases at elevated temperatures because the increase in the entropy term ($T\Delta S$) exceeds the increase in the enthalpy.

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