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Author

Tian, Guoxin

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Complexation of Np(V) with Oxalate at 283 – 343 K: Spectroscopic and Microcalorimetric Studies

Guoxin Tian^a and Linfeng Rao^{*a}

Thermodynamic parameters including the equilibrium constants and enthalpy of complexation of Np(V) with oxalate at variable temperatures ($T = 283 - 343$ K, ionic strength = $1.05 \text{ mol} \cdot \text{kg}^{-1}$ NaClO_4) were determined by spectrophotometric and microcalorimetric titrations. Results show that the complexation of Np(V) with oxalate is moderately strong and becomes weaker at higher temperatures. The complexation is exothermic and driven by both enthalpy (negative) and entropy (positive) in the temperature range from 283 K to 343 K. As the temperature is increased, both the enthalpy and entropy of complexation increase (ΔH becomes less negative and ΔS becomes more positive), having opposing effects on the complexation. Because the increase in the enthalpy (ΔH) exceeds that of the entropy term ($T\Delta S$), the complexation of Np(V) with oxalate becomes weaker at higher temperatures. The effect of temperature on the complexation is discussed in terms of the energetics of ion solvation and hydrogen bonding involved in the complexation.

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 get into contact with the waste, dissolve and carry radionuclides out of the repository. Under the chemical environment in the vicinity of the waste form, ^{237}Np (in its pentavalent state, Np(V)) is one of the most soluble radioactive elements and is most likely to be carried away from the repository. Because of its long half-life, 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 75,000 years [1]. As a result, the migration of neptunium in the postclosure chemical environment of the repository is a great concern to long-term repository performance.

The composition of nuclear wastes in the storage tanks is extremely diverse, where a number of carboxylic acids (acetic acid, oxalic acid, citric acid, EDTA, etc.) exist in large amounts. Among these, oxalic acid is one of the most important. According to the inventory of the Waste Isolation Pilot Plant repository (WIPP, in New Mexico, USA), the total amount of sodium oxalate and oxalic acid is expected to be close to 50 tons, more than the total amounts of acetate/acetic acid and citrate/citric acid [2]. In addition, oxalate is present at relatively high concentrations in several natural environments such as soil solutions, oil field sedimentary basin brines, and deposits originated from thermal degradation of complex organic matters [3]. As a result, complexation of Np(V) with oxalic acid could play important roles in determining the transport of neptunium in the repository. Thermodynamic data (stability constants, enthalpy and entropy of complexation) are needed to predict the behavior of Np(V) in the repository and surrounding environment.

Due to the radioactive decay energy, the temperature of the

HLW in the repository could rise to as high as 473 – 573 K, decrease gradually with time, and remain significantly higher than the ambient even thousands of years after the closure of the repository (about 330 - 360 K) [1]. Therefore, accurate predictions of the chemical behavior of neptunium in the repository cannot be made without reliable thermodynamic data concerning the interactions of Np(V) with the ligands including oxalate at elevated temperatures. However, a recent critical review by the Nuclear Energy Agency [4] indicates that there are no data in the literature on the complexation of Np(V) with oxalate at temperatures other than around 298 K. Lack of reliable geochemical thermodynamic data could lead to conservative decisions that have too big safety margins and raise the cost of the waste repository. Therefore, at the practical level, it is necessary to study the complexation of actinides at elevated temperatures, bridging the gap in the thermodynamic database for the performance assessment of the HLW repository.

It is equally important that, at the fundamental level, studies of the complexation of actinides at elevated temperatures could improve the fundamental understanding of the coordination chemistry of actinides as well. For example, the change in temperature perturbs the structure of the solvent media in the bulk and in the vicinity of the ions, alters its dielectric property and thus affects the energetics of the complexation [5,6]. Therefore, the trends in thermodynamic parameters over a wide range of temperature could provide insight into the nature of the actinide complex and the solvent medium effect.

Based on the interests at both the practical and fundamental levels, we have studied the thermodynamics of the complexation of actinides (Th, U, Np and Pu) with a number of organic and inorganic ligands at elevated temperatures. This paper summarizes the results of the complexation of Np(V) with oxalate at 283 – 343 K.

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 [7].

Solutions of oxalate were prepared by dissolving solid sodium oxalate (Na_2ox) in water. The ionic strength of all working solutions were maintained at $1.00 \text{ mol}\cdot\text{dm}^{-3}$ NaClO_4 (298.15 K), equivalent to $1.05 \text{ mol}\cdot\text{kg}^{-1}$ NaClO_4 for all temperatures. In this paper, all concentrations in the molarity unit are referred to 298.15 K.

Spectrophotometry

Spectrophotometric titrations in the near-IR region were conducted at 283.15, 298.15, 313.15, 328.15 and 343.15 K on a Varian Cary-6000i spectrophotometer. 10 mm quartz cells were used. The temperature of the samples was maintained constant by a Peltier temperature controller. An external constant-temperature water bath was used to pre-equilibrate the samples at the required temperature before they were placed in the sample holders. Multiple titrations with different initial concentrations of Np(V) were performed. The stability constants of the Np(V)/oxalate complex (on the molarity scale) at different temperatures were calculated by non-linear least-square regression using the Hyperquad 2000 program [8].

Microcalorimetry

Calorimetric titrations were conducted at variable temperatures (298.15 K, 313.15 K, 328.15 K and 343.15 K) with an isothermal microcalorimeter (ITC 4200, Calorimetry Sciences Corp). The full volume of the sample and reference cells is about 1.2 cm^3 . The titrant is delivered into the sample cell through a long and thin needle from a 100 μl 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 $\text{kJ}\cdot\text{mol}^{-1}$) are -47.7 ± 0.3 (298 K), -46.8 ± 0.2 (313 K), -45.8 ± 0.5 (328 K), -45.2 ± 0.5 (343 K) and -43.1 ± 0.8 (353 K), compared well with the values in the literature: -46.0 ± 0.3 (318 K) [9], -46.81 ± 0.02 (308 K) and -46.0 ± 0.02 (323 K) [10].

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 ($Q_{\text{ex},j}$, 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 [11] was used to analyze the data and calculate the thermodynamic parameters.

Results and Discussion

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

The absorption spectra of two representative

spectrophotometric titrations at 283.15 K and 343.15 K are shown in Figure 1. As the concentration of oxalate was increased, the intensity of the absorption peak of free NpO_2^+ at 980.2 nm decreased and a new peak appeared at ~ 987 nm. As the titration continued, the intensity of the peak at 987 nm would reach a maximum and start to decrease, as another new peak appeared at longer wavelength (995 nm) and increased in intensity (Figure 1). The spectral changes in the titrations at other temperatures (298.15, 313.15 and 328.15 K) are similar. Factor analysis of the absorption spectra indicated that there are three absorbing species of Np(V) (i.e., the free NpO_2^+ and two successive Np(V)/oxalate complexes). Accordingly, the spectra were best-fitted with the successive formation of 1:1 and 1:2 complexes, NpO_2ox^- and $\text{NpO}_2(\text{ox})_2^{3-}$, represented by equations (1) and (2). The successive complexation of Np^{V} with oxalate and the absorption properties (band positions and molar absorptivities) of Np(V) species are illustrated by Scheme 1.

Fig. 1 Representative spectrophotometric titrations of Np(V)/oxalate complexation. $I = 1.0 \text{ mol}\cdot\text{dm}^{-3}$ NaClO_4 . Upper figures – normalized absorption spectra at 283.15 K and 343.15 K; initial solution: 2.50 mL; $2.65 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ $\text{NpO}_2\text{ClO}_4/3 \times 10^{-7} \text{ mol}\cdot\text{dm}^{-3}$ HClO_4 ; $C_{\text{Na}_2\text{ox}} = 0 - 0.03 \text{ mol}\cdot\text{dm}^{-3}$. Titrant: $0.100 \text{ mol}\cdot\text{dm}^{-3}$ Na_2ox . Lower figures – calculated molar absorptivity of Np(V) species at 283.15 K and 343.15 K.

Scheme 1. Stepwise formation of Np(V) complexes with oxalate and the accompanying changes in symmetry and optical absorption properties (band position / molar absorptivity at 298.15 K).

The stability constants of NpO_2ox^- and $\text{NpO}_2(\text{ox})_2^{3-}$ at 283.15, 298.15, 313.15, 328.15 and 343.15 K were calculated, and listed in Table 1. In the calculation, the protonation constants of oxalate at different temperatures from the literature [12] were used.

(insert Table 1)

To allow the comparison at different temperatures, the constants in molarity should be converted to the constants in molality according to equation (3),

$$\log_{10}\beta_m = \log_{10}\beta_M + \sum_r \nu_r \log_{10} \vartheta \quad (3)$$

where β_m and β_M are the stability constants in molality and molarity, respectively, $\sum_r \nu_r$ is the sum of stoichiometric coefficients of the reaction. ν_r is positive for products and negative for reactants [4]. For reactions (1) and (2), $\sum_r \nu_r = -1$ and -2 , respectively. ϑ is the ratio of the values of molality to molarity for the specific ionic medium. For the 1.05 mol·kg⁻¹ NaClO₄ in this study, $\log_{10}\vartheta$ equals 0.02. Therefore, $\log_{10}\beta_{m,1} = \log_{10}\beta_{M,1} - 0.02$, and $\log_{10}\beta_{m,2} = \log_{10}\beta_{M,2} - 0.04$. The converted stability constants on molality are shown in Table 1.

Results from this work show that the complexation of Np(V) with oxalate is moderately strong and is weakened as the temperature is increased. The weakening of complexation with oxalate at higher temperatures is manifested by the changes in the spectra of a solution at different temperatures shown in Figure 2. The highest intensity of the spectrum at 283 K corresponds to the absorption of NpO₂(ox)₂³⁻ (at 995 nm). As the temperature is increased, the intensity at 995 nm decreases and the intensity at lower wavelengths increases. At 343 K, the highest intensity of the spectrum corresponds to the absorption of NpO₂ox⁻. Using the stability constants from this work, the distribution of Np(V) species in this solution was calculated to be 3% NpO₂⁺, 39% NpO₂ox⁻ and 58% NpO₂(ox)₂³⁻ at 283 K, and 8% NpO₂⁺, 58% NpO₂ox⁻ and 34% NpO₂(ox)₂³⁻ at 343 K, with $\pm 1\%$ as the uncertainty.

Fig. 2 Absorption spectra of a solution containing Np(V) and oxalate at different temperatures. $V = 2.90$ mL, $C_{\text{Np(V)}} = 6.02 \times 10^{-4}$ mol·dm⁻³, $C_{\text{ox}} = 3.45 \times 10^{-3}$ mol·dm⁻³, $-\log [\text{H}^+] \sim 7$. $I = 1.0$ mol·dm⁻³ NaClO₄.

The stability constants of Np(V)/oxalate complexes are plotted against $1/T$ in Figure 3. It appears that the data could be approximately fitted with straight lines. From the slopes of the linear fits (weighted by the uncertainties), the “average” enthalpies of complexation for NpO₂ox⁻ and NpO₂(ox)₂³⁻ in the temperature range (283 – 343 K) were calculated to be $-(7.0 \pm 0.9)$ and $-(19.6 \pm 1.7)$ kJ·mol⁻¹, respectively.

Fig. 3 $\log \beta$ vs. $1/T$ for the complexation of Np(V) with oxalate. Solid symbols ($\bullet$ $\log \beta_1$, $\bullet$ $\log \beta_2$): experimental data from this work ($I = 1.0$ mol·dm⁻³ NaClO₄); Open symbols ($\diamond$ $\log \beta_1$, $\circ$ $\log \beta_2$): experimental data ($I = 1.0$ mol·dm⁻³ NaClO₄ in the literature [4]; Cross: $\log \beta_1^0$ ($+$) and $\log \beta_2^0$ ($+$) at 298.15 K selected in the Nuclear Energy Agency review [4]. The error bars of $\log \beta$ from this work are ± 0.02 (not shown in the plot).

Enthalpy, entropy and heat capacity of Np(V) complexation with oxalate

Figure 4 (upper figure) shows a representative calorimetric titration of the complexation of Np(V) with oxalate at 298 K. The observed reaction heat includes the contributions from both the protonation of oxalate and the complexation of Np(V) with oxalate. Thus, to calculate the enthalpy of Np(V)/oxalate complexation from the reaction heat, a number of parameters, including the protonation constant and protonation enthalpy of oxalate and the stability constants of NpO₂ox⁻ and NpO₂(ox)₂³⁻, must be known. In this work, we have used the protonation constant and protonation enthalpy of oxalate previously reported [12] and the stability constants of NpO₂ox⁻ and NpO₂(ox)₂³⁻ determined by spectrophotometry in this work. The enthalpies of reactions (1) and (2) at different temperatures were calculated from the best-fit of the calorimetric data. The entropies of complexation were accordingly calculated from the Gibbs free energy ($\Delta G = -RT \ln \beta$) and the enthalpy ($\Delta S = (\Delta H - \Delta G)/T$). These thermodynamic parameters are listed in Table 1.

The enthalpies and entropies of complexation at different temperatures are shown in Figure 5. The data show that the enthalpy of complexation becomes less negative (exothermic) and the entropy of complexation becomes more positive at higher temperatures. This means that, as the temperature is increased, the enthalpy becomes less favourable while the entropy becomes more favourable for the complexation. Because the effect of enthalpy (ΔH) exceeds that of the entropy term ($T\Delta S$), the complexation of Np(V) with oxalate becomes weaker at higher temperatures. From the slope of a linear fit for the plot of ΔH as a function of temperature (Figure 5, upper figure), the heat capacity of complexation for reactions (1) and (2) is calculated to be (98 ± 11) and (124 ± 16) J·mol⁻¹·K⁻¹.

Fig. 4 Calorimetric titration of Np(V) oxalate complexation. $I = 1.0$ mol·dm⁻³ NaClO₄, $T = 298.15$ K. Cup: 0.900 mL $C_{\text{Np}} = 1.64 \times 10^{-3}$ mol·dm⁻³, $C_{\text{H}} = 3 \times 10^{-7}$ mol·dm⁻³, titrant: 0.050 mol·dm⁻³ Na₂Ox, 5 μ L/addition.

Fig. 5 Enthalpy and entropy of complexation at different temperatures. $I = 1.0$ mol·dm⁻³ NaClO₄.

The changes in the enthalpy and entropy of complexation caused by the increase in the temperature could be explained in terms of the energetics of dehydration involved in the complexation of NpO_2^+ with oxalate. In the complexation, dehydration of both the cation (NpO_2^+) and anion (ox^{2-}) plays the most significant roles: (1) energy is required for dehydration, contributing to the positive enthalpy; (2) energy is gained when the water molecules released from the primary hydration sphere form hydrogen bonding with the bulk water molecules, contributing to the negative enthalpy; and (3) the release of water molecules from the primary hydration sphere increases the degree of disorder, contributing to the positive entropy. For the formation of NpO_2ox^- and $\text{NpO}_2(\text{ox})_2^{3-}$, both the entropy and enthalpy of complexation become more positive as the temperature is increased. The increase of entropy with the temperature could be the consequence of a

more disordered bulk water structure at higher temperatures due to the perturbation by thermal movements. In the process of complexation, the solvating water molecules are released to an already expanded and more disordered bulk solvent [13]. As a result, the net gain in the complexation entropy is larger at higher temperatures. Meanwhile, the released water molecules would form fewer and/or weaker hydrogen bonds with the bulk water at higher temperatures due to the thermal motion, thus resulting in less favorable (more positive) enthalpy of complexation at higher temperatures.

Calculation of stability constants at variable temperatures to infinite dilution using the Specific Ion Interaction approach (SIT)

The SIT (Specific Ion Interaction Theory) approach originated from the Brønsted-Guggenheim-Scatchard model [14-16] can be used to calculate the equilibrium constants at zero ionic strength from experimental data at other ionic strengths. For reactions (1) and (2), the equilibrium constants at $I = 0$ ($\log \beta^0$) are related to $\log \beta$ at other ionic strengths by equation (4):

$$\log \beta - \Delta Z^2 \times D = \log \beta^0 - \Delta \epsilon I_m \quad (4)$$

where $\Delta Z^2 = \{\Sigma(Z_{\text{products}}^2) - \Sigma(Z_{\text{reactants}}^2)\}$, and equals -4 for reaction (1), and 0 for reaction (2). 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. At 298.15 K, $\Delta \epsilon = \epsilon(\text{Na}^+, \text{NpO}_2\text{ox}^-) - \epsilon(\text{Na}^+, \text{ox}^{2-}) - \epsilon(\text{NpO}_2^+, \text{ClO}_4^-) = -(0.3 \pm 0.1)$ kg·mol⁻¹ for reaction (1), and $\Delta \epsilon = \epsilon(\text{Na}^+, \text{NpO}_2(\text{ox})_2^{3-}) - 2\epsilon(\text{Na}^+, \text{ox}^{2-}) - \epsilon(\text{NpO}_2^+, \text{ClO}_4^-) = -(0.1 \pm 0.2)$ kg·mol⁻¹ for reaction (2) [4].

Values of $\Delta \epsilon$ at different temperatures should be known in order to calculate $\log \beta^0$ at different temperatures, but are not currently available. Therefore, we assumed that $\Delta \epsilon$ remains constant in the temperature range of 283 – 343 K and used the value of $\Delta \epsilon(298.15 \text{ K})$ for all other temperatures. The errors thus introduced are probably quite small, since the values of $(\partial \epsilon / \partial T)_p$ are usually ≤ 0.005 kg·mol⁻¹·K⁻¹ for temperatures below 473 K [4]. 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 373 K [17,18]. The calculated $\log \beta^0$ for NpO_2ox^- and $\text{NpO}_2(\text{ox})_2^{3-}$ at different temperatures are summarized in Table 1 (the error limits were obtained by propagation of the uncertainties in the experimental values of $\log \beta$ and the uncertainty in $\Delta \epsilon$). The data of $\log \beta^0$ for NpO_2ox^- and $\text{NpO}_2(\text{ox})_2^{3-}$ at 298 K from this work agree with those from the literature [4] within uncertainties limits, while the data at other temperatures from this work are the first such values reported. Detailed discussions on the use of the SIT approach have been provided in the literature [19].

Summary

Complexation of Np(V) with oxalate in aqueous solutions is moderately strong at 283 – 343 K, and is weakened at elevated temperatures. The complexation is exothermic and becomes less exothermic, while the entropy of complexation is positive

and becomes more positive when the temperature is increased from 283 to 343 K. The effect of temperature on the enthalpy and entropy of complexation can be explained by the changes in the energetics of dehydration of participating ions (NpO_2^{+} and ox^{2-}) and the hydrogen bonding in water.

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Notes and references

^a Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA. Fax: 510 486 5596; Tel: 510 486 5427; E-

mail: lrhao@lbl.gov, gtian@lbl.gov

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Table 1 Thermodynamic parameters for the complexation of Np(V) with oxalate, $I = 1.05 \text{ mol}\cdot\text{kg}^{-1} \text{ Na}(\text{ClO}_4)$. (sp – spectrophotometry, cal – calorimetry)

Reaction	T K	Method	$\log\beta_M$	$\log\beta_m$	$\text{Log}\beta^p$ (by SIT)	ΔH $\text{kJ}\cdot\text{mol}^{-1}$	ΔS $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
$\text{NpO}_2^+ + \text{ox}^{2-} =$ $\text{NpO}_2(\text{ox})^-$	283	sp, cal	3.66 ± 0.02	3.64 ± 0.02	4.13 ± 0.11		
	298	sp, cal	3.59 ± 0.02	3.57 ± 0.02	4.08 ± 0.11	-12.2 ± 0.1	27.4 ± 0.6
					3.9 ± 0.1 [4]		
	313	sp, cal	3.59 ± 0.02	3.57 ± 0.02	4.10 ± 0.11	-10.3 ± 0.1	35.4 ± 0.5
	328	sp, cal	3.54 ± 0.02	3.52 ± 0.02	4.08 ± 0.11	-8.92 ± 0.1	40.2 ± 0.5
	343	sp, cal	3.40 ± 0.02	3.38 ± 0.02	3.96 ± 0.11	-7.98 ± 0.2	41.4 ± 0.7
$\text{NpO}_2^+ + 2\text{ox}^{2-} =$ $\text{NpO}_2(\text{ox})_2^{3-}$	283	sp, cal	6.43 ± 0.02	6.39 ± 0.02	6.28 ± 0.21		
	298	sp, cal	6.27 ± 0.02	6.23 ± 0.02	6.12 ± 0.21	-25.5 ± 0.1	33.7 ± 0.9
					5.8 ± 0.2 [4]		
	313	sp, cal	6.17 ± 0.02	6.13 ± 0.02	6.02 ± 0.21	-22.8 ± 0.2	44.5 ± 0.5
	328	sp, cal	6.05 ± 0.02	6.01 ± 0.02	5.90 ± 0.21	-22.4 ± 0.2	46.8 ± 0.7
	343	sp, cal	5.74 ± 0.02	5.70 ± 0.02	5.60 ± 0.21	-17.0 ± 0.4	59.6 ± 1.3