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### Title

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# Spectrophotometric and Calorimetric Studies of Np(V) Complexation with Acetate at Variable Temperatures ( $T = 283 - 343$ K)

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**Abstract** Spectrophotometric titrations were performed to identify the Np(V)/acetate complex and determine the equilibrium constants at variable temperatures ( $T = 283 - 343$  K) and at the ionic strength of  $1.05 \text{ mol}\cdot\text{kg}^{-1}$ . The enthalpy of complexation at corresponding temperatures was determined by microcalorimetric titrations. Results show that the complexation of Np(V) with acetate is weak but strengthened as the temperature is increased. The complexation is endothermic and is entropy-driven. The enhancement of the complexation at elevated temperatures is primarily due to the increasingly larger entropy gain when the solvent molecules are released from the highly-ordered solvation spheres of  $\text{NpO}_2^+$  and acetate to the bulk solvent where the degree of disorder is higher at higher temperatures.

**Key Words** Neptunium · Acetate · Complexation · Temperature effect

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## 1 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,  $^{237}\text{Np}$  (in its pentavalent state,  $\text{Np(V)}$ ) 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  $^{237}\text{Np}$  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.

According to the inventory of the Waste Isolation Pilot Plant repository (WIPP, in New Mexico, USA), a number of carboxylic acids (acetic acid, oxalic acid, citric acid, etc.) exist in large amounts in the nuclear wastes [2]. Therefore, complexation of  $\text{Np(V)}$  with carboxylate ligands is expected to 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  $\text{Np(V)}$  in the repository and surrounding environment.

Due to the radioactive decay energy, the temperature of the HLW repository could remain significantly higher than the ambient even thousands of years after the closure of the repository. Therefore, accurate predictions of the chemical behavior of neptunium in the repository cannot be made without reliable thermodynamic data concerning the interactions of  $\text{Np(V)}$  with the carboxylate ligands at elevated temperatures. Currently, thermodynamic data on the

complexation of Np(V), and actinides in general, at elevated temperatures are scarce [3,4,5,6]. 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. To help with the performance assessment of the HLW repository and bridge the gap in thermodynamic data on actinide complexation at elevated temperatures, we have studied 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 acetate at 283 – 343 K.

## **2 Experimental**

### 2.1 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 acetate were prepared by dissolving solid sodium acetate (NaAc) in water. The ionic strength of all working solutions were maintained at  $1.00 \text{ mol}\cdot\text{dm}^{-3} \text{ NaClO}_4$  (298.15 K), equivalent to  $1.05 \text{ mol}\cdot\text{kg}^{-1} \text{ NaClO}_4$  for all temperatures. In this paper, all concentrations in the molarity unit are referred to 298.15 K.

### 2.2 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-5G 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)/acetate

complex (on the molarity scale) at different temperatures were calculated by non-linear least-square regression using the Hyperquad 2000 program [8].

### 2.3 Microcalorimetry

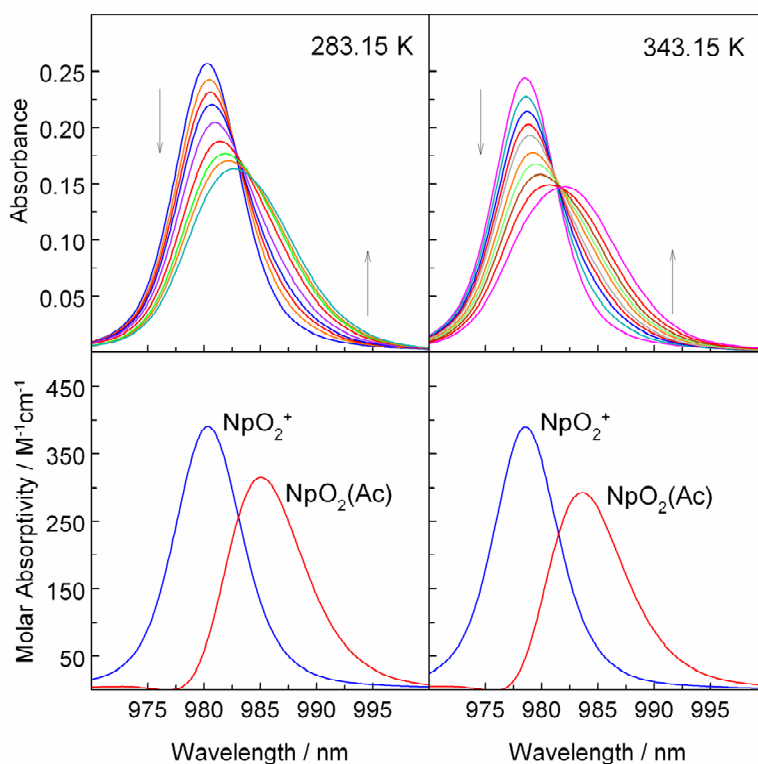
Calorimetric titrations were conducted at variable temperatures (298.15 K, 313.15 K, 328.15 K and 343.15 K) with an isothermal microcalorimeter (ITC 4200, Calorimetry Sciences Corp). The full volume of the sample and reference cells is about 1.2 cm<sup>3</sup>. The titrant is delivered into the sample cell through a long and thin needle from a 100  $\mu$ l or 250  $\mu$ l 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<sup>-1</sup>) are  $-47.7 \pm 0.3$  (298 K),  $-46.8 \pm 0.2$  (313 K),  $-45.8 \pm 0.5$  (328 K),  $-45.2 \pm 0.5$  (343 K) and  $-43.1 \pm 0.8$  (353 K), compared well with the values in the literature:  $-46.0 \pm 0.3$  (318 K) and  $-46.2 \pm 0.3$  (343 K) [9],  $-46.81 \pm 0.02$  (308 K) and  $-46.0 \pm 0.02$  (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.

## 3 Results and discussion

### 3.1 Stability constants of the Np(V)/acetate complex 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 acetate was increased, the intensity of the absorption band of free  $\text{NpO}_2^+$  at 980.2 nm decreased and a “shoulder” appeared at longer wavelengths. 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 by the Hyperquad program indicated that there are two absorbing species of Np(V) (i.e., the free  $\text{NpO}_2^+$  and an Np(V)/acetate complex). Accordingly, the spectra were best-fitted with the formation of a 1:1 complex,  $\text{NpO}_2\text{Ac}(\text{aq})$ , represented by equation (1).



**Fig. 1** Representative spectrophotometric titrations of Np(V)/acetate complexation.  $I = 1.05 \text{ mol}\cdot\text{kg}^{-1} \text{ Na}(\text{ClO}_4/\text{Ac})$ . Upper figures: normalized absorption spectra collected in the titration at 283 K and 343 K. Titrant:  $C_{\text{H}} = 0.100 \text{ mol}\cdot\text{dm}^{-3}$ ,  $C_{\text{acetate}} = 1.00 \text{ mol}\cdot\text{dm}^{-3}$ , total volume added = 0.950 mL (283 K) and 0.750 mL (343 K). Initial solution in cuvette: 2.50 mL;  $C_{\text{H}} = 3 \times 10^{-7} \text{ mol}\cdot\text{dm}^{-3}$ ,  $C_{\text{Np}} = 6.644 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$  (283 K) and  $6.304 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$  (343 K). Lower figures: calculated molar absorptivity of  $\text{NpO}_2^+$ , and  $\text{NpO}_2\text{Ac}(\text{aq})$  at 283 and 343 K.

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

Reaction	$t$ °C	Method	$\log\beta_M$	$\log\beta_m$	$\text{Log}\beta^0$ (by SIT)	$\Delta H$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta S$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	Ref.
$\text{NpO}_2^+ + \text{Ac}^- = \text{NpO}_2(\text{Ac})(\text{aq})$	10	sp, cal	$0.68 \pm 0.02$	$0.66 \pm 0.02$	$0.98 \pm 0.02$			p.w.
	25	sp, cal	$0.74 \pm 0.04$	$0.72 \pm 0.04$	$1.05 \pm 0.04$	$18.1 \pm 1.8$	$75 \pm 6$	
					$1.27 \pm 0.02^a$			
	40	sp, cal	$0.79 \pm 0.03$	$0.77 \pm 0.03$	$1.11 \pm 0.03$	$20.8 \pm 0.8$	$81 \pm 3$	
	55	sp, cal	$0.86 \pm 0.03$	$0.84 \pm 0.03$	$1.19 \pm 0.03$	$25.5 \pm 1.8$	$94 \pm 6$	
	70	sp, cal	$0.99 \pm 0.05$	$0.97 \pm 0.05$	$1.34 \pm 0.05$	$27.6 \pm 3.9$	$99 \pm 11$	
$\text{H}^+ + \text{Ac}^- = \text{H}(\text{Ac})(\text{aq})$	10	pot	$4.58 \pm 0.02^b$			-3.09	$77 \pm 1$	[12]
	25	pot, cal	$4.59 \pm 0.02$			$-1.63 \pm 0.09$	$83 \pm 1$	
	40	pot	$4.62 \pm 0.02^b$			-0.16	$88 \pm 1$	
	55		$4.65 \pm 0.02$			$1.29 \pm 0.03$	$94 \pm 1$	
	70		$4.72 \pm 0.02$			$2.79 \pm 0.16$	$99 \pm 1$	

<sup>a</sup>The value is obtained by SIT using the stability constants at  $I = 0 - 3 \text{ mol}\cdot\text{kg}^{-1}$  in the literature. See Section 3.3.

<sup>b</sup>The values are obtained by interpolation or extrapolation of the data at 298.15, 308.15, 318.15, 328.15 and 343.15 K in ref.[12]



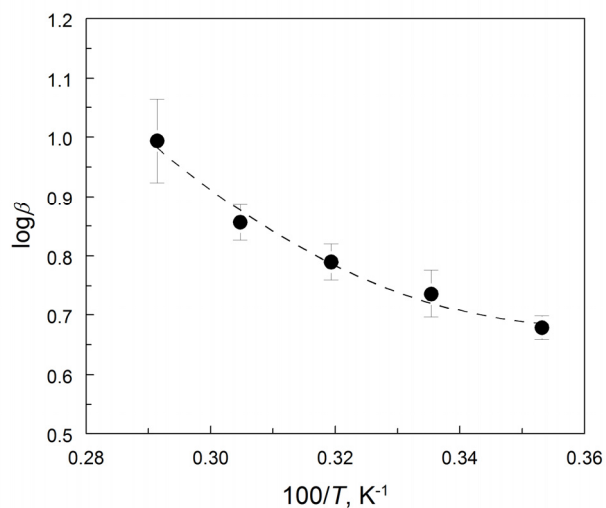
The stability constants of  $\text{NpO}_2\text{Ac}(\text{aq})$  at 283.15, 298.15, 313.15, 328.15 and 343.15 K were calculated, and listed in Table 1. In the calculation, the protonation constants of acetate at different temperatures from the literature [12] were used.

To allow the comparison at different temperatures, the constants in molarity should be converted to the constants in molality according to equation (2),

$$\log_{10}\beta_m = \log_{10}\beta_M + \sum_r \nu_r \log_{10} \mathcal{G} \quad (2)$$

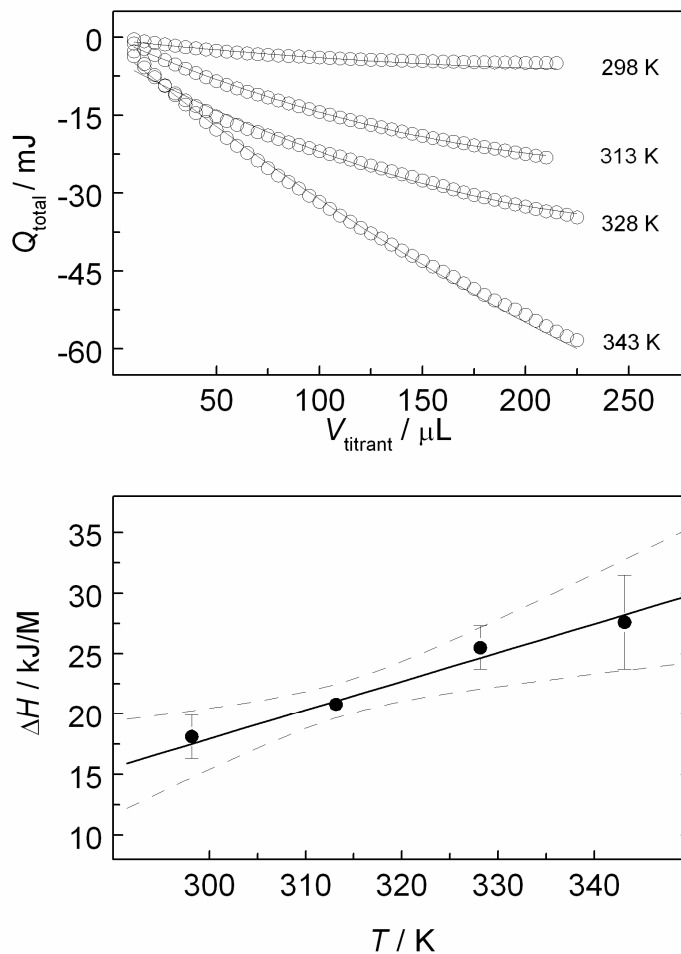
where  $\beta_m$  and  $\beta_M$  are the stability constant of the  $\text{NpO}_2\text{Ac}(\text{aq})$  complex in molality and molarity, respectively,  $\sum_r \nu_r$  is the sum of stoichiometric coefficients of the reaction.  $\nu_r$  is positive for products and negative for reactants [3,4,5]. For reaction (1),  $\sum_r \nu_r = -1$ .  $\mathcal{G}$  is the ratio of the values of molality to molarity for the specific ionic medium. For the  $1.05 \text{ mol}\cdot\text{kg}^{-1}$   $\text{NaClO}_4$  in this study,  $\log_{10}\mathcal{G}$  equals 0.02. Therefore,  $\log_{10}\beta_m = \log_{10}\beta_M - 0.02$ . The converted stability constants on molality are shown in Table 1. Results from this work show that the complexation of Np(V) with acetate is weak but strengthened as the temperature is increased.

A plot of  $\log\beta$  as a function of  $1/T$  (Figure 2) indicates: i) that the enthalpy of complexation is positive because  $d \log\beta/d (1/T) < 0$ , ii) that the enthalpy of complexation does not remain constant because the best-fit of the data is a second-order polynomial, instead of a linear function, and iii) that the enthalpy of complexation should become increasingly more positive as the temperature is increased because  $d \log\beta/d (1/T)$  becomes larger at higher temperatures. These observations are further elaborated with the results of enthalpy directly determined by calorimetry at different temperatures.



**Fig. 2**  $\log\beta$  vs.  $1/T$  for the complexation of Np(V) with acetate. Solid symbols (●): experimental data from this work ( $I = 1.05 \text{ mol}\cdot\text{kg}^{-1}$   $\text{Na}(\text{ClO}_4/\text{Ac})$ ); dashed line (----): polynomial fit.





**Fig. 3** Calorimetric titration of Np(V) acetate complexation,  $I = 1.05 \text{ mol}\cdot\text{kg}^{-1} \text{ Na}(\text{ClO}_4/\text{Ac})$ . Upper figure: observed ( $\circ$ ) and calculated ( $\text{—}$ ) total reaction heat as a function of the titrant volume; cup solution:  $0.900 \text{ mL}$ ,  $C_{\text{Np}} = 1.67 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ ,  $C_{\text{H}} = 1.93 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ ; Titrant:  $1.00 \text{ mol}\cdot\text{dm}^{-3} \text{ NaAc}$ ,  $5.00 \mu\text{L}/\text{addition}$ . Lower figure: enthalpy of complexation as a function of temperature, solid line ( $\text{—}$ ): linear fit weighted with the uncertainties of  $\Delta H$ , dashed line ( $\text{---}$ ): 95% confidence band.

### 3.2 Enthalpy of Np(V) complexation with acetate determined by calorimetry

Figure 3 (upper figure) shows representative calorimetric titrations of the complexation of Np(V) with acetate at different temperatures (298 - 343 K). Multiple titrations were conducted at each temperature, but only one titration is shown for each temperature for clarity. The observed reaction heat includes the contributions from both the protonation of acetate and the

complexation of Np(V) with acetate. Thus, to calculate the enthalpy of Np(V)/acetate complexation from the reaction heat, a number of parameters, including the protonation constant and protonation enthalpy of acetate and the stability constant of  $\text{NpO}_2\text{Ac}(\text{aq})$ , must be known. In this work, we have used the protonation constant and protonation enthalpy of acetate previously reported [12] and the stability constant of  $\text{NpO}_2\text{Ac}(\text{aq})$  determined by spectrophotometry in this work. The enthalpy of reaction (1) at different temperatures was calculated from the best-fit of the calorimetric data, and is listed in Table 1.

As the enthalpy data determined by calorimetry at different temperatures show, the complexation of Np(V) with acetate (reaction 1) is endothermic at 298 K and becomes more endothermic at higher temperatures. The enthalpy data are in good agreement with the observations that  $d \log\beta/d (1/T) < 0$  (therefore  $\Delta H > 0$ ) and  $d \log\beta/d (1/T)$  becomes larger at higher temperatures (therefore  $d \Delta H /dT > 0$ ), shown in Figure 2 and described in Section 3.1. From the slope of a linear fit for the plot of  $\Delta H$  as a function of temperature (Figure 3, lower figure), the heat capacity of complexation for  $\text{NpO}_2(\text{Ac})(\text{aq})$  is calculated to be  $238 \pm 71 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ .

Data in Table 1 show that, in the temperature range from 298 K to 343 K, both the enthalpy and entropy of complexation are positive. The complexation is entropy-driven, characteristic of "hard acid" and "hard base" interactions and inner-sphere complexation [13]. Dehydration of both the cation ( $\text{NpO}_2^+$ ) and anion ( $\text{Ac}^-$ ) plays the most significant roles in the complexation: the energy required for dehydration contributing to the positive enthalpy and the number of water molecules released from the hydration spheres contributing to the positive entropy. For the formation of  $\text{NpO}_2\text{Ac}(\text{aq})$ , both the enthalpy and entropy of complexation increases 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 [14]. 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 enthalpy of complexation at higher temperatures. It is because the increase in the entropy term ( $T\Delta S$ ) slightly exceeds the increase in the enthalpy that the complexation is moderately enhanced at higher temperatures.

The coordination mode of acetate in the Np(V)/acetate complex in aqueous solutions remains a question to be answered. In the absence of structural characterization of the Np(V)/acetate complex in solution, discussions can be made based on the thermodynamic and structural data of the U(VI)/acetate complexes in the literature. A previous study using thermodynamic measurements and EXAFS characterization has shown that acetate could coordinate with  $\text{UO}_2^{2+}$  via the equatorial plane in either monodentate or bidentate modes [12]. In the 1:1 U(VI)/acetate complex, the acetate is bidentate and replaces two water molecules from the primary coordination sphere of  $\text{UO}_2^{2+}$ . The magnitude of the entropy of complexation is directly related to the number of water molecules replaced by acetate. For the 1:1 U(VI)/acetate complex, the entropy of complexation is  $86 - 102 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  in the temperature range from 298 K to 343 K [12]. In comparison, the entropy of complexation for the 1:1 Np(V)/acetate complex is  $75 - 99 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  in the same temperature range from this work. The similarity in the magnitude of the entropy of complexation between the Np(V)/acetate and U(VI)/acetate complexes suggests that the acetate ion probably coordinates to  $\text{NpO}_2^+$  in a bidentate mode in aqueous solutions.

### 3.3 Calculation of stability constants at variable temperatures to infinite dilution: Analysis by the Specific Ion Interaction approach (SIT)

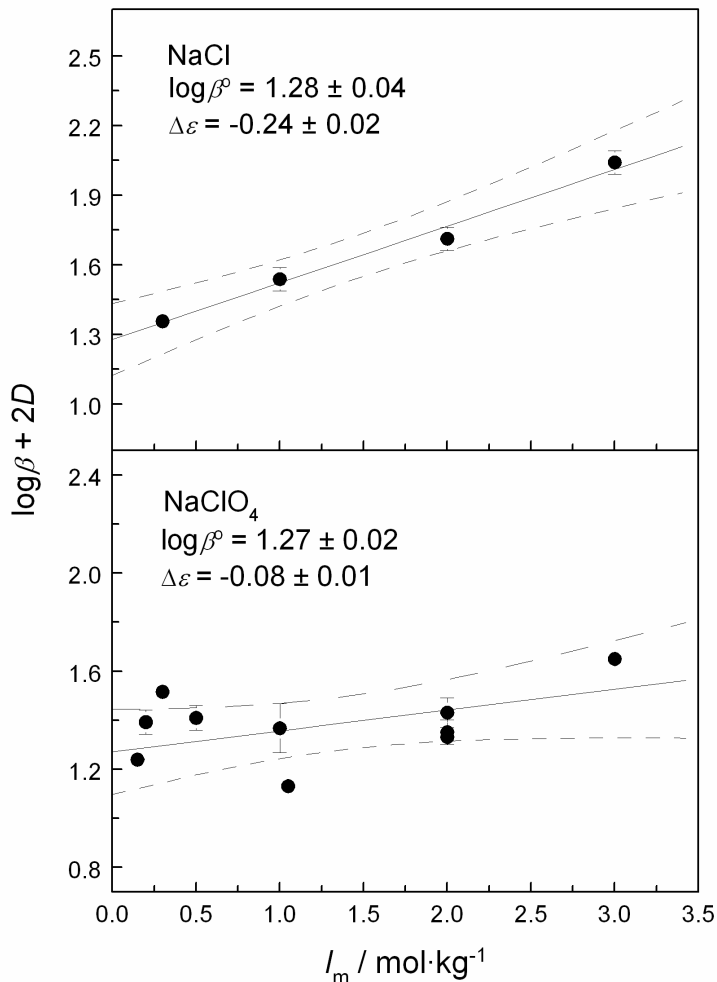
The SIT (Specific Ion Interaction) approach originated from the Brønsted-Guggenheim-Scatchard model [15-17] can be used to calculate the equilibrium constants at zero ionic strength from experimental data at other ionic strengths. For reaction (1), the equilibrium constant at  $I = 0$  ( $\log\beta^0$ ) are related to  $\log\beta$  at other ionic strengths by equation (3):

$$\log\beta - \Delta Z^2 \times D = \log\beta^0 - \Delta\varepsilon I_m \quad (3)$$

where  $\Delta Z^2 = \{\Sigma(Z_{\text{products}}^2) - \Sigma(Z_{\text{reactants}}^2)\}$ , and equals -2 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  $\varepsilon$  is the ion interaction parameter used in the SIT method. For reaction (1),  $\Delta\varepsilon = \varepsilon(\text{Na}^+ + \text{ClO}_4^-) - \varepsilon(\text{Na}^+, \text{Ac}^-) - \varepsilon(\text{NpO}_2^+, \text{ClO}_4^-)$ .

Values of  $\Delta\varepsilon$  at different temperatures should be known in order to calculate  $\log\beta^0$  at different temperatures, but are not currently available. Therefore, we have taken the following two-step approach: (1) Using the data in the literature on the stability constants of  $\text{NpO}_2\text{Ac}(\text{aq})$  at different ionic strength ( $I = 0.15 - 3.0 \text{ mol}\cdot\text{kg}^{-1} \text{ NaClO}_4$ ) [18,19],  $\Delta\varepsilon(298.15 \text{ K})$  of reaction (1) was calculated to be  $-(0.08 \pm 0.01) \text{ kg}\cdot\text{mol}^{-1}$  by an SIT plot (Figure 4); (2) assuming that  $\Delta\varepsilon$  remains constant in the temperature range of 283 – 343 K, the value of  $\Delta\varepsilon(298.15 \text{ K})$  was used for all other temperatures. The errors thus introduced are probably quite small, since the values of  $(\partial\varepsilon/\partial T)_p$  are usually  $\leq 0.005 \text{ kg}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  for temperatures below 473 K [3,4,5]. 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 373 K [23,24]. The calculated  $\log\beta^\circ$  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  $\Delta\varepsilon$ ).



**Fig. 4** SIT plots for the reaction  $\text{NpO}_2^+ + \text{Ac}^- = \text{NpO}_2\text{Ac}(\text{aq})$  in  $\text{NaClO}_4$  (lower) and  $\text{NaCl}$  (upper) at 298 K. (●): Experimental data [18-21]; solid line (—): weighted (by uncertainty) linear fit; dashed lines (----): 95% confidence band. The upper figure for the  $\text{NaCl}$  system is just for comparison since the  $\text{NaCl}$  system is not directly related to this work.

#### 4 Summary

Complexation of Np(V) with acetate is weak and is enhanced at elevated temperatures. Thermodynamic parameters of complexation ( $\Delta H$  and  $\Delta S$ ) suggest that the desolvation of participating ions (both  $\text{NpO}_2^+$  and  $\text{Ac}^-$ ) plays a major role in the degree of disorder and the energetics of the complexation. As the temperature is increased, the stability constant of  $\text{NpO}_2\text{Ac}(\text{aq})$  increases because the increase in the entropy term ( $T\Delta S$ ) exceeds that of the enthalpy.

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## Figure Captions

**Fig. 1** Representative spectrophotometric titrations of Np(V)/acetate complexation.  $I = 1.05 \text{ mol}\cdot\text{kg}^{-1}$  Na(ClO<sub>4</sub>/Ac). Upper figures: normalized absorption spectra collected in the titration at 283 K and 343 K. Titrant:  $C_{\text{H}} = 0.100 \text{ mol}\cdot\text{dm}^{-3}$ ,  $C_{\text{acetate}} = 1.00 \text{ mol}\cdot\text{dm}^{-3}$ , total volume added = 0.950 mL (283 K) and 0.750 mL (343 K). Initial solution in cuvette: 2.50 mL;  $C_{\text{H}} = 3 \times 10^{-7} \text{ mol}\cdot\text{dm}^{-3}$ ,  $C_{\text{Np}} = 6.644 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$  (283 K) and  $6.304 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$  (343 K). Lower figures: calculated molar absorptivity of NpO<sub>2</sub><sup>+</sup>, and NpO<sub>2</sub>Ac(aq) at 283 and 343 K.

**Fig. 2**  $\log\beta$  vs.  $1/T$  for the complexation of Np(V) with acetate. Solid symbols (●): experimental data from this work ( $I = 1.05 \text{ mol}\cdot\text{kg}^{-1}$  Na(ClO<sub>4</sub>/Ac)); dashed line (-----): polynomial fit.

**Fig. 3** Calorimetric titration of Np(V) acetate complexation,  $I = 1.05 \text{ mol}\cdot\text{kg}^{-1}$  Na(ClO<sub>4</sub>/Ac). Upper figure: observed (○) and calculated (—) total reaction heat as a function of the titrant volume; cup solution: 0.900 mL,  $C_{\text{Np}} = 1.67 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ ,  $C_{\text{H}} = 1.93 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ ; Titrant:  $1.00 \text{ mol}\cdot\text{dm}^{-3}$  NaAc, 5.00 μL/addition. Lower figure: enthalpy of complexation as a function of temperature, solid line (—): linear fit weighted with the uncertainties of  $\Delta H$ , dashed line (-----): 95% confidence band.

**Fig. 4** SIT plots for the reaction  $\text{NpO}_2^+ + \text{Ac}^- = \text{NpO}_2\text{Ac}(\text{aq})$  in NaClO<sub>4</sub> (lower) and NaCl (upper) at 298 K. (●): Experimental data [18-21]; solid line (—): weighted (by uncertainty) linear fit; dashed lines (-----): 95% confidence band. The upper figure for the NaCl system is just for comparison since the NaCl system is not directly related to this work.