Effect of Temperature on the Complexation of NpO_2^+ with Benzoic Acid: Spectrophotometric and Calorimetric Studies

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Abstract

The equilibrium constants of the 1:1 NpO_2^+ /benzoate complex were determined by spectrophotometric titrations at variable temperatures ($T = 283 - 343$ K) and the ionic strength of $1.05 \text{ mol}\cdot\text{kg}^{-1}$. The enthalpy of complexation at 298 K was determined by microcalorimetric titrations. Similar to other monocarboxylates, benzoate forms a weak complex with NpO_2^+ and the complexation is strengthened as the temperature is increased. The complexation is endothermic and is entropy-driven. The enhancement of the complexation at elevated temperatures is primarily attributed to the increasingly larger entropy gain when the water molecules are released from the highly-ordered solvation spheres of NpO_2^+ and benzoate to the bulk solvent where the degree of disorder is higher at higher temperatures. The spectroscopic features of the $\text{Np(V)}/\text{benzoate}$ system, including the effect of temperature on the absorption bands, are discussed in terms of ligand field splitting and a thermal expansion mechanism.

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1 Introduction

Neptunium is a problematic element in the separation processes of used nuclear fuel reprocessing as well as in the environmental management of nuclear wastes due to its redox behavior (including “disproportionation” of the pentavalent state, Np(V)) and its transport behavior in the geological environment. One approach to safe management of high-level nuclear wastes (HLW) calls for the vitrification of HLW into durable waste forms that are disposed of in geological repositories. Engineered barrier systems are installed to isolate the waste forms from the environment, but they may gradually deteriorate and eventually lose integrity. As a result, groundwater could get into contact with the waste, dissolve and carry radionuclides into the geological environment. Among all the radionuclides, ^{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 the long half-life of ^{237}Np , it is projected that, in a proposed high-level nuclear waste (HLW) repository, ^{237}Np will become a major contributor to the total dose (as much as 67%) in 75,000 years [1]. Consequently, the migration of neptunium in the postclosure chemical environment of the repository is a great concern to long-term repository performance.

The migration behavior of Np(V) in the environment depends on its interactions with the organic and inorganic ligands that are present in the nuclear wastes and in the environment. According to the inventory of the Waste Isolation Pilot Plant repository (WIPP, in New Mexico, USA), carboxylic acids, including acetic acid, benzoic acid, and oxalic acid, exist in significant amounts in the nuclear wastes [2]. These compounds were either deliberately introduced in the separation process as complexing agents, or generated as a result of the degradation of other

organic substances. Benzoic acid, as well as a variety of aliphatic and aromatic carboxylic acids, was also identified in the low-level radioactive waste disposal sites such as Maxey Flates in Kentucky and West Valley in New York, USA [3]. The complexation of Np(V) with these ligands is expected to play an important role in determining the migration behavior of Np(V). As a result, there has been substantial interest in recent years in the studies of the complexation of Np(V) with carboxylic acids. Thermodynamic data (stability constants, enthalpy and entropy of complexation) were determined to help with the safe management of nuclear wastes.

The temperature of the HLW repository could remain significantly higher than the ambient even thousands of years after the closure of the repository, due to the radioactive decay energy. 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 carboxylate ligands at elevated temperatures. Currently, in contrast to the large volume of thermodynamic data at 298 K, data on the interactions of actinides with carboxylic acids at elevated temperatures are scarce [4-7]. Lack of reliable geochemical thermodynamic data at elevated temperatures 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 started systematic studies on the complexation of actinides (Th, U, Np and Pu) with a number of carboxylic acids at elevated temperatures. This paper summarizes the results of the complexation of Np(V) with benzoic acid at 283 – 343 K. In the literature, a value of $\log \beta (0.82 \pm 0.02)$ at $T = 298$ K and $I = 2 \text{ mol} \cdot \text{dm}^{-3} \text{ NaClO}_4$ for $\text{NpO}_2\text{L}(\text{aq})$ (L stands for the benzoate anion) was reported [8], but did not meet the criteria for critical review [9]. There have been no data for Np(V) complexation with benzoic acid at variable temperatures.

2 Experimental

2.1 Chemicals

All chemicals were reagent grade or higher. All solutions were prepared with water from a Milli-Q system. The stock solution of Np(V) in perchloric acid was prepared as follows. Solid neptunium dioxide (NpO_2) was dissolved in concentrated HCl under low heating. Concentrated HClO_4 was added to drive away the excess HCl by fuming (*Caution: extreme precautions must be taken to assure the absence of any organic matter in the container before adding concentrated HClO_4 and performing the fuming process. The presence of organic matter in the HClO_4 fuming process could lead to explosion*). The neptunium in the solution was oxidized to Np(VI) during fuming with HClO_4 . Into the pink solution of Np(VI), a small amount of NaNO_2 was added to reduce Np(VI) to Np(V), resulting in a green solution. The Np(V) was then precipitated as hydroxide with $1 \text{ mol}\cdot\text{dm}^{-3}$ NaOH. The precipitates were washed three times with distilled/deionized water to ensure the removal of excess NaOH and then dissolved with $1 \text{ mol}\cdot\text{dm}^{-3}$ HClO_4 . Absorption spectra were collected to confirm that Np(V) was the only oxidation state in the stock solution [10]. The concentration of Np(V) was determined by near-IR absorption spectroscopy, using the molar absorptivity of $395 \text{ cm}^{-1}(\text{mol}\cdot\text{dm}^{-3})^{-1}$ for NpO_2^+ at 980.4 nm in $1 \text{ mol}\cdot\text{dm}^{-3}$ HClO_4 at 298 K. A stock solution of sodium benzoate (NaL , L^- stands for the benzoate anion) was prepared by dissolving weighed amounts of solid benzoic acid (HL) in water and neutralizing it with the same equivalent of NaOH. 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.

2.2 Spectrophotometry

Spectrophotometric titrations in the near-IR region were conducted on a Varian Cary-6000i spectrophotometer to determine the stability constants of the Np(V)/benzoate complex at five temperatures: 283.15, 298.15, 313.15, 328.15 and 343.15 K. Quartz cells with 10 mm optical path but narrow width (4 mm) were used. A Peltier temperature controller was used to maintain the sample and reference cell compartments at constant temperatures. To ensure the thermal equilibrium, 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. The spectra were collected in the wavelength region from 1050 nm to 950 nm at 0.1 nm interval. The stability constants of the Np(V)/benzoate complex (on the molarity scale) at different temperatures were calculated by non-linear least-square regression using the HypSpec program [11].

2.3 Microcalorimetry

Calorimetric titrations were conducted with an isothermal microcalorimeter (ITC 4200, Calorimetry Sciences Corp) to determine the enthalpy of complexation for the Np(V)/benzoate complex at 298.15 K. The microcalorimeter uses a “twin” heat flow design to reach the 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 cm³. The titrant is delivered into the sample cell through a long and thin needle from a 250 µL syringe. The syringe is driven by a precision stepper motor that guarantees accurate delivery of the titrant. The performance of the calorimeter was tested by measuring the enthalpy of protonation of

tris(hydroxymethyl)-aminomethane (THAM). The result is $(-47.7 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15K, in excellent agreement with the literature [12].

In each titration, a benzoate solution was added stepwise through the syringe (5.0 μL per addition) into the cell that initially contained 0.900 mL Np(V) solution. n additions were made (usually $n = 40 - 50$), resulting in n experimental values of the heat generated during the titration ($Q_{\text{ex},j}$, 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 with 0.900 mL $1.0 \text{ mol} \cdot \text{dm}^{-3}$ NaClO_4 in the cell (in the absence of Np(V)) titrated with the same titrant of benzoate. 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 HypDeltaH [13] was used to analyze the data and calculate the enthalpy of complexation.

3 Results and discussion

3.1 Absorption spectra and stability constants at variable temperatures

The absorption spectra of spectrophotometric titrations at 283.15 K, 298.15 K, 328.15 K, and 343.15 K are shown in Figure 1. As the concentration of benzoate was increased, the intensity of the absorption band of free NpO_2^+ around 980 nm decreased and a “shoulder” band at about 983 - 985 nm appeared at longer wavelengths. Factor analysis of the absorption spectra by the HypSpec program indicated that there are two absorbing species of Np(V) (i.e., the free NpO_2^+ and an Np(V)/benzoate complex). Accordingly, the spectra were best-fitted with the formation of a 1:1 complex, $\text{NpO}_2\text{L}(\text{aq})$, represented by equation (1).

The stability constants of $\text{NpO}_2\text{L}(\text{aq})$ 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 benzoate at different temperatures from the literature [9] were used.

Fig. 1 Spectrophotometric titration of $\text{Np}(\text{V})$ /benzoate complexation at different temperatures. $I = 1.05 \text{ mol}\cdot\text{kg}^{-1}$ $\text{Na}(\text{ClO}_4)$. Initial solution in cuvette: 1.00 mL; $C_{\text{H}} = 5.88 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$, $C_{\text{Np}} = 5.09 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$. Titrant: 0.500 M sodium benzoate, total volume added = 0.250 mL. The spectra were normalized to C_{Np} .

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

Reaction	T K	Method	$\text{Log}_{10}\beta_{\text{M}}$	$\text{Log}_{10}\beta_{\text{m}}$	$\text{Log}_{10}\beta'$ (by SIT)	ΔH $\text{kJ}\cdot\text{mol}^{-1}$	ΔS $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
$\text{NpO}_2^+ + \text{L}^- = \text{NpO}_2\text{L}(\text{aq})$	283	sp	0.595 ± 0.018	0.58 ± 0.02	0.90 ± 0.02		
	298	sp	0.706 ± 0.012	0.69 ± 0.01	1.02 ± 0.01	$9.35 \pm 0.50^{\text{a}}$	45 ± 2
		sp, cal				$8.9 \pm 0.2^{\text{b}}$	42 ± 1
	313	sp	0.761 ± 0.012	0.74 ± 0.01	1.08 ± 0.01		
	328	sp	0.829 ± 0.009	0.81 ± 0.01	1.16 ± 0.01		
	343	sp	0.919 ± 0.009	0.90 ± 0.01	1.27 ± 0.01		

^a Calculated by van't Hoff equation using the $\log \beta_{\text{M}}$ at different temperatures (283 – 343 K).

^b Obtained by microcalorimetry.

Results from this work show that the complexation of Np(V) with benzoate is weak but strengthened as the temperature is increased. In fact, the enhancement of the complexation at higher temperatures can be identified by some subtle differences between the spectra at different temperatures. For example, at the same ratio of [benzoate]/[Np(V)], the intensity of the shoulder band at 983 - 985 nm became higher at higher temperatures (Figure 1), implying that the degree of complexation was higher when the temperature was increased.

A van't Hoff plot of $\log \beta$ as a function of $1/T$ is shown in Figure 2. The negative slope of the linear fit suggests that complexation is endothermic and the enthalpy of complexation can be assumed constant in the temperature range (283 – 343 K). From the slope of the linear fit (weighted by the uncertainties), the “average” enthalpy of complexation for the temperature range was calculated to be $(9.35 \pm 0.50) \text{ kJ} \cdot \text{mol}^{-1}$.

Fig. 2 $\log \beta$ vs. $1/T$ for the complexation of Np(V) with benzoate. Solid symbols (●): experimental data from this work ($I = 1.05 \text{ mol} \cdot \text{kg}^{-1} \text{ NaClO}_4$); solid line: linear fit, dashed lines: 95% confidence band.

3.2 Spectroscopic features and correlation with stability constants

The spectroscopic features (peak wavelength, molar absorptivity, and FWHM (Full Width at Half Maximum) of the Np(V)/benzoate system at different temperatures are shown in Table 2. Data in the literature for related monocarboxylic acids are included for comparison.

Table 2 Spectroscopic features of NpO_2^+ and its benzoate complex in solution at different temperatures

	T , K	λ (peak), Å	$\Delta\lambda$, ^a Å	ϵ , $\text{cm}^{-1}(\text{mol}\cdot\text{dm}^{-3})^{-1}$	FWHM, Å	Ref.
NpO_2^+	283.15	9809		402	65	p.w.
	298.15	9804		398	64	
	313.15	9800		396	62	
	328.15	9795		393	61	
	343.15	9790		389	60	
$\text{NpO}_2\text{L}(\text{aq})$ L = benzoate	283.15	9853	44	339	66	p.w.
	298.15	9849	45	316	70	
	313.15	9844	44	316	68	
	328.15	9840	45	310	68	
	343.15	9836	46	298	62	
L = acetate	298.15	9849	45	330	66	[8]
L = chloroacetate	298.15	9842	38	472	63	
L = dichloroacetate	298.15	9831	27	574	49	
L = bromoacetate	298.15	9839	35	405	58	
L = iodoacetate	298.15	9842	38	433	58	

^aWavelength red shift $\Delta\lambda = \lambda(\text{NpO}_2\text{L}) - \lambda(\text{NpO}_2^+)$.

Interesting trends are observed in the spectroscopic features: (1) as Np(V) forms the benzoate complex, the absorption band around 9800 Å is red-shifted by 44 – 46 Å at all temperatures. The magnitude of the shift for Np(V)/benzoate is nearly the same as that for Np(V)/acetate, but larger than other monocarboxylic acids (Table 2); (2) as the temperature is increased, the absorption bands of the free aqua NpO_2^+ ion and the $\text{NpO}_2\text{L}(\text{aq})$ complex (L = benzoate) are shifted to shorter wavelengths (“blue shift”). For the free aqua NpO_2^+ ion, the band is shifted from 9809 Å at 283 K to 9790 Å at 343 K (a shift of 19 Å); for the $\text{NpO}_2\text{L}(\text{aq})$ complex, the band is shifted from 9853 Å at 283 K to 9836 Å at 343 K (a shift of 17 Å). These trends can be discussed in terms of the perturbation of electronic energy levels upon complexation as follows.

The absorption bands of Np(V) in the near IR region originate from the intra-configuration 5f-5f transitions. The wavelengths of the absorption bands depend on the energy levels of the $5f^2$ states that are strongly influenced by the geometry and strength of the ligand field in the equatorial plane of NpO_2^+ . Surrounded by water molecules in the primary coordination sphere and ClO_4^- ions in the outer sphere, the “free” NpO_2^+ ion in aqueous solutions has a dynamically amorphous environment, namely the water molecules interacting with the ion, splitting and shifting its electronic energy levels. Determined by the centers of the absorption bands, the energy levels are split by the strong axial field of the neptunyl ($\text{O}=\text{Np}=\text{O}$) in D_∞ symmetry and a weaker equatorial field induced by the water molecules and ClO_4^- ions. The disordered structure surrounding the neptunyl ions imposes a significant inhomogeneous broadening of the free-ion spectra. When NpO_2^+ forms a complex with the ligand, well-defined new components of the ligand field are added in the equatorial plane of NpO_2^+ , thus further splitting and shifting the electronic energy levels. The scale and direction of the shift are determined by the free-ion states and the ligand field. For Np(V), ligand-field splitting of the $5f^2$ states decreases the energy gap between the ground state $^3\text{H}_4$ and the excited state near 10200 cm^{-1} ($9800\text{ \AA}$) with $^1\text{G}_4$ as the leading term of the free-ion eigenfunction. Therefore, the absorption band near $9800\text{ \AA}$ would be red-shifted when the complex forms. Based on this discussion, a correlation is expected between the magnitude of spectra red-shifts and the stability constants of Np(V) complexes with a series of ligands that are structurally related but differ in binding strength. As shown in Figure 3, a good correlation is indeed observed between $\Delta\lambda$ and $\log\beta$ for the Np(V) complexes with a series of monocarboxylic acids including benzoic acid.

Fig. 3 Correlation between the stability constants ($I = 1 - 2 \text{ M NaClO}_4$) and the magnitudes of red-shift of the near-IR absorption band of $\text{NpO}_2\text{L(aq)}$ complexes for a series of monocarboxylic acids at 298 K. $\Delta\lambda = \lambda(\text{NpO}_2\text{L}) - \lambda(\text{NpO}_2^+)$. 1 – acetate [14], 2 – benzoate (present work), 3 – iodoacetate [8], 4 – bromoacetate [8], 5 – chloroacetate [8], 6 – dichloroacetate [8].

The effect of temperature on the positions of the near-IR absorption band of Np(V) is depicted in Figure 4. For both NpO_2^+ and $\text{NpO}_2\text{L(aq)}$ ($L = \text{benzoate}$), blue shifts were observed as the temperature is increased and the magnitude of shifts have a linear dependence on temperature. The rate of shift (i.e., the slope of the linear correlation) is approximately $0.33 \text{ cm}^{-1}/\text{K}$ for NpO_2^+ and $0.29 \text{ cm}^{-1}/\text{K}$ for $\text{NpO}_2\text{L(aq)}$.

The temperature dependence of absorption bands of complexes is a general phenomenon induced by electronic coupling to the dynamics of the complex coordinate. Two mechanisms may contribute primarily to the observed shifts. The first mechanism is the thermal expansion of the complex coordinates in the solution. Bond lengths and the distance between the ion and solvent molecules increase as a function of temperature. Such expansion weakens the electrostatic field imposed on the NpO_2^+ ion. As previously discussed, an increasing ligand field decreases the energy gap between the ground state $^3\text{H}_4$ and the excited state and induces a red shift in the NpO_2^+ 9800 $\text{\AA}$ absorption band. Accordingly, a weakened ligand field is expected to

increase the energy gap and induce a blue shift. The slight difference in the rate of shift between NpO_2^+ ($0.33 \text{ cm}^{-1}/\text{K}$) and NpO_2L ($0.29 \text{ cm}^{-1}/\text{K}$) could imply that the latter has a more stable local structure and is less subjective to thermal expansion than the former. The second mechanism, well-established in solid-state spectroscopy, is the electron-phonon coupling. The temperature-dependent ion-phonon coupling induces line shift and line broadening that can be evaluated using the McCumber-Sturge model [15]. By this mechanism, the energy shift would be proportional to T^4 , a nonlinear temperature dependence, and accompanied by line broadening. Because linear temperature dependence is observed and line broadening is absent in the spectra of the $\text{Np(V)}/\text{benzoate}$ system (Table 2 and Figure 4), we conclude that the electron-phonon coupling mechanism has little contribution and the temperature-dependent blue shift is predominantly induced by the thermal expansion mechanism.

Fig. 4 Effect of temperature on the absorption bands of NpO_2^+ and $\text{NpO}_2\text{L}(\text{aq})$ (L = benzoate).

3.3 Enthalpy of Np(V) complexation with benzoate determined by calorimetry

Figure 5 (upper figure) shows a calorimetric titration of the complexation of Np(V) with benzoate at 298.15 K. The observed reaction heat includes the contributions from both the protonation of benzoate and the complexation of Np(V) with benzoate. Thus, to calculate the enthalpy of Np(V)/benzoate complexation from the reaction heat, a number of parameters, including the protonation constant and protonation enthalpy of benzoate and the stability constant of $\text{NpO}_2\text{L}(\text{aq})$, must be known. In this work, we have used the protonation constant and protonation enthalpy of benzoate previously reported [9] and the stability constant of $\text{NpO}_2\text{L}(\text{aq})$ determined by spectrophotometry in this work. The enthalpy of reaction (1) at 298.15 K was determined to be $(8.9 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$, in good agreement with the value obtained by van't Hoff plot $((9.35 \pm 0.50) \text{ kJ} \cdot \text{mol}^{-1})$. The entropy of complexation was accordingly calculated to be $42 - 45 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ (Table 1).

Fig. 5 Calorimetric titration of Np(V) benzoate complexation, $I = 1.05 \text{ mol} \cdot \text{kg}^{-1} \text{ Na}(\text{ClO}_4/\text{L})$. Upper figure: thermogram (dilution heat not corrected); lower figure: observed ($\circ$) and calculated (—) total reaction heat (right y-axis), and speciation of Np(V) (dashed lines --- , left y-axis) as a function of the titrant volume; cup solution: 0.900 mL, $C_{\text{Np}} = 1.65 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$, $C_{\text{H}} = 1.91 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$; Titrant: $0.500 \text{ mol} \cdot \text{dm}^{-3} \text{ NaL}$, 5.00 $\mu\text{L}/\text{addition}$.

Data in Table 1 show that, in the temperature range from 283 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 [16]. Dehydration of both the cation (NpO_2^+) and the anion (L^-) 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.

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

To allow the comparison at different temperatures and the use of SIT to obtain the constants to infinite dilution, the constants in molarity should be converted to the constants in molality according to equation (2),

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

where β_m and β_M are the stability constant of the $\text{NpO}_2\text{L}(\text{aq})$ complex 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 [3,4,5]. For reaction (1), $\sum_r \nu_r = -1$. ϑ 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, $\log_{10} \vartheta$ 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.

The SIT approach originated from the Brønsted-Guggenheim-Scatchard model [17-19] 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):

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

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 $D = A I_m^{1/2} / (1 + 1.5 I_m^{1/2})$, I_m is the ionic strength in molality, and ϵ is the ion interaction parameter used in the SIT method. For reaction (1), $\Delta\epsilon = \epsilon(\text{Na}^+ + \text{ClO}_4^- , \text{NpO}_2\text{L}(\text{aq})) - \epsilon(\text{Na}^+, \text{L}^-) - \epsilon(\text{NpO}_2^+, \text{ClO}_4^-)$, where L^- stands for the benzoate anion.

Values of $\Delta\epsilon$ for the Np(V)/benzoate complexation are not available. Therefore, we have elected to use the values for the Np(V)/acetate complexation from previous work [14]: $\Delta\epsilon = - (0.08 \pm 0.01) \text{ kg}\cdot\text{mol}^{-1}$ for reaction (1) at 298 K and all other temperatures. The assumption that $\Delta\epsilon$ remains constant in the temperature range of 283 – 343 K is valid because the temperature effect on the ion interaction parameters, $(\partial\epsilon/\partial T)_p$, are usually $\leq 0.005 \text{ kg}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for temperatures below 473 K [3-5]. 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 [20,21]. The calculated $\log\beta^0$ for the Np(V)/benzoate complex 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 $\Delta\epsilon$). With the values of $\log\beta^0$ and $\Delta\epsilon$ for reaction (1) at different temperatures, the stability constants of the Np(V)/benzoate complex at

these temperatures and other ionic strengths can be estimated using equation (2). Detailed discussions on the use of the SIT approach have been provided in the literature [22].

4 Summary

Np(V) forms a weak inner-sphere complex with benzoate in aqueous solutions and the complexation is enhanced at elevated temperatures. Thermodynamic parameters of complexation (ΔH and ΔS) suggest that the desolvation of participating ions (both NpO_2^+ and the benzoate anion) plays a major role in the degree of disorder and the energetics of the complexation. The complexation is entropy-driven. At higher temperatures, the entropy of complexation becomes more positive because the water molecules released from the highly ordered primary hydration spheres of NpO_2^+ and benzoate enter the bulk water that has a higher degree of disorder at higher temperatures due to thermal perturbation. As a result, the stability of $\text{NpO}_2\text{L}(\text{aq})$ increases as the temperature is increased.

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