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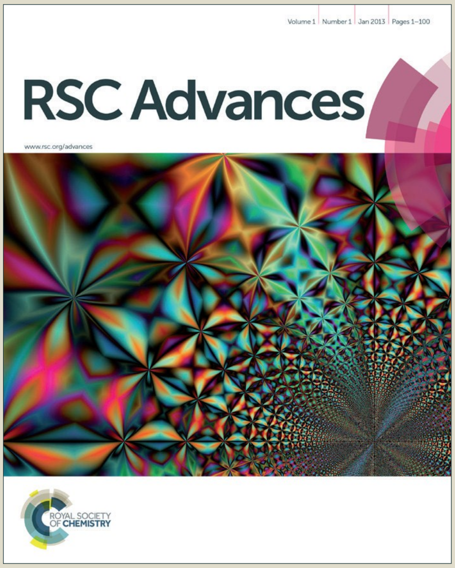

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Effect of Temperature on the Thermodynamic and Spectroscopic Properties of Np(V) Complexes with Picolinate

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Abstract

Picolinate is a well-known chelating agent and is present in the contaminated lands and nuclear wastes. Thermodynamic parameters of the complexation of picolinate with Np(V) at elevated temperatures are needed to help predict the migration behavior of Np(V) in the nuclear waste repository where the temperature could be high. In this work, the equilibrium constants of picolinate protonation and its complexation with Np(V) were determined at $T = 283 - 343$ K and $I = 1.0$ mol·dm^{-3} $NaClO_4$ by potentiometry and spectrophotometry, respectively. Both the protonation and the complexation constants decrease with the increase of temperature, indicating the reactions are exothermic. The enthalpies of protonation and complexation were both found to be negative and moderately large at $T = 298$ K and $I = 1.0$ mol·dm^{-3} $NaClO_4$ by titration calorimetry. The effect of temperature on the spectroscopic features of Np(V) is interpreted in terms of thermal expansion of the complex coordinates that results in blue shifts of the Np(V) absorption band at higher temperatures.

Key Words Temperature effect, Complexation, Neptunium, Picolinic acid.

1 Introduction

The migration of radionuclides in nuclear waste geological repositories and contaminated lands is of great concern in the waste management and performance assessment of waste repositories. As expected, the engineered barrier systems that are installed in the repository to isolate the waste forms from the environment may gradually deteriorate and eventually lose integrity. As a result, ground water could get into contact with the waste, dissolve and carry radionuclides into the surrounding geological environment.

Neptunium is one of the most concerned radioactive elements due to its chemical behavior and transport characteristics in the environment. Among all the radionuclides, ^{237}Np (in its pentavalent state, Np(V)) is one of the most soluble radioactive elements and most likely to be carried away from the repository. Because of its long half-life, 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 pathways of radionuclides need to be characterized at a predictive level so that management decisions can be made with high certainty. The migration behavior of radionuclides in the environment depends on their interactions with the organic and inorganic ligands that are present in the nuclear wastes and in the environment. Many organic complexants, either deliberately introduced into the wastes for separation or decontamination purposes, or generated as a result of the degradation of other organic substances, were present in nuclear wastes. For example, the concentration of picolinic acid in cement-solidified decontamination waste from Fizt Patrick Nuclear Power Station (NY, USA) was determined to be at least 2.2%

(by mass).[2] Picolinate was also recognized as one of the 10 categories of complexing agents that have significant availability and stability within the timeframes and the zones of a deep geological waste repository.[3-5] As a result, complexation of picolinic acid with Np(V) could play an important role in determining the migration behavior of Np(V).

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. Reliable thermodynamic data at elevated temperatures for the interactions of Np(V) with organic ligands are thus needed in order to accurately predict the chemical behavior of neptunium in the repository. There have been several thermodynamic studies for the Np(V) picolinate complexation,[6-9] but all were performed at or near 298 K. To our best knowledge, no thermodynamic data at higher temperatures are available. Besides, large discrepancies exist among the reported values at 298 K, with the stability constants of 1:1 (ML) and 1:2 (ML_2) Np(V) picolinate complexes differing by 3.5 and 10 times, respectively.[6-8] The data of enthalpy for the complexation are even scarcer, with only one value for the ML complex measured by calorimetry.[9] In the present work, potentiometry, spectrophotometry, and calorimetry were used to determine the thermodynamic data for the protonation of picolinate and its complexation with Np(V) at 283 – 343 K in 1.0 $mol \cdot dm^{-3}$ $NaClO_4$. The effect of temperature on the complexation and the spectroscopic features of Np(V) is discussed.

2 Experimental

2.1 Chemicals and solutions

All chemicals were reagent grade or higher. The stock solution of Np(V) in perchloric acid was prepared with the procedures including a few steps: (1) NpO_2 solid was dissolved in concentrated

HCl under low heating followed by addition of concentrated $HClO_4$ to drive away the excess HCl and oxidize neptunium to Np(VI) by fuming; (2) to the resulting Np(VI) solution (pink), a small quantity of solid $NaNO_2$ was added to reduce Np(VI) to Np(V) (a green solution) and then 1 $mol\cdot dm^{-3}$ NaOH was slowly added to precipitate the Np(V) as hydroxide, and (3) the Np(V) precipitates were washed three times with deionized water to remove excess NaOH, and then dissolved with 1 $mol\cdot dm^{-3}$ $HClO_4$. The presence and purity of Np(V) was confirmed by near-IR absorption spectra. The concentration of Np(V) in the stock was determined by using the molar absorptivity of 395 $cm^{-1}(mol\cdot dm^{-3})^{-1}$ for NpO_2^+ at 980.4 nm in 1 $mol\cdot dm^{-3}$ $HClO_4$ at 298 K.[10] The free acid concentration in the Np(V) stock was determined by Gran titrations.[11]

The stock solution of picolinate was prepared by dissolving a weighed quantity of solid picolinic acid into water followed by adding a known amount of NaOH. Deionized water (18.2 MΩ, Mili-Q water system) was used for the preparation of all solutions. The ionic strength of all working solutions were maintained at 1.00 $mol\cdot dm^{-3}$ $NaClO_4$. All concentrations in the molarity unit are referred to 298 K.

2.2 Potentiometry

The protonation constants of picolinate were determined by potentiometric titrations at five temperatures: 283, 298, 313, 328 and 343 K. The titrations were conducted in a specifically-designed thermostatic vessel with water-jacketed cell and lid maintained at the desired temperatures by water circulating from a constant temperature bath.

The electromotive force (EMF, in millivolts) was measured by a pH meter (Model 713, Metrohm) equipped with a combination pH electrode (6.0259.100 Unitrode, Metrohm). The original 3.0 $mol\cdot dm^{-3}$ KCl salt bridge solution of the electrode was replaced with a 1.0 $mol\cdot dm^{-3}$ NaCl solution to avoid formation of insoluble $KClO_4$ in the electrode joint sleeve that is in contact with the working solution. The *EMF* in the acidic and basic regions can be expressed by Eq. 1 and 2.

$$EMF = E^\circ + RT/F \ln[H^+] + \gamma_H[H^+] \quad (1)$$

$$EMF = E^\circ + RT/F \ln(K_w/[OH^-]) + \gamma_{OH}[OH^-] \quad (2)$$

where R is the gas constant, F is the Faraday constant, T is the temperature in K, and $[H^+]$ and $[OH^-]$ are the concentrations of hydrogen and hydroxide ions, respectively. $K_w = [H^+][OH^-]$. The last terms are the electrode junction potentials ($\Delta E_{j,H+}$ or $\Delta E_{j,OH-}$) for the hydrogen ion (Eq.1) or the hydroxide ion (Eq.2), assumed to be proportional to the concentration of the hydrogen or hydroxide ions. To correct the junction potential, the electrode was calibrated by an acid/base titration with standard $HClO_4$ and NaOH solutions to obtain the electrode parameters of E°, γ_H, and γ_{OH}. These parameters were used for the calculation of hydrogen ion concentrations from the measured *EMF* in the subsequent titration.

Multiple titrations with different concentrations of picolinic acid were conducted at each temperature. The protonation constants at different temperatures were calculated using the program *Hyperquad* 2008.[12]

2.3 Spectrophotometry

The stability constants of the Np(V)/picolinate complexes were determined with spectrophotometry at five temperatures: 283, 298, 313, 328 and 343 K. Absorption spectra of Np(V) were collected on a Varian Cary-6000i spectrophotometer using quartz cells with 10 mm optical path but narrow width (4 mm). The temperature of the sample and reference cells was maintained at constant temperatures by a Peltier temperature controller. 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 holder. The spectra were collected in the wavelength region from 1015 nm to 960 nm at 0.1 nm interval. This absorption band is hypersensitive to the change in the coordination sphere of Np(V) in solution[13] so that the formation of Np(V) complexes could be resolved from the band variations during a spectrophotometric titration. The stability constants of the Np(V)/picolinate complexes (on the molarity scale) at different temperatures were calculated by non-linear least-square regression using the HypSpec program.[12, 14]

2.4 Microcalorimetry

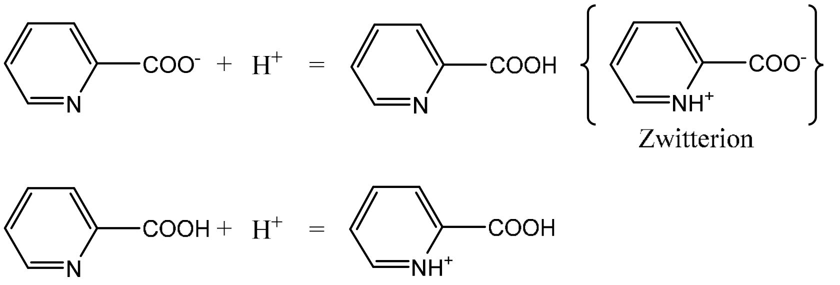
An isothermal microcalorimeter (ITC 4200, Calorimetry Sciences Corp) was used to conduct calorimetric titrations for determination of the enthalpy of complexation for the Np(V)/picolinate complexes at 298 K. The performance of the calorimeter was tested by measuring the enthalpy of protonation of tris(hydroxymethyl)-aminomethane (THAM). The value, (–47.7 ± 0.3) $kJ\cdot mol^{-1}$, was obtained at 298 K and is in excellent agreement with the literature.[15]

The cell was initially set up with 0.900 mL Np(V) solution for a titration. After a thermal equilibrium was reached, a working solution of picolinic acid was added stepwise to the cell through a 250 μL syringe (5.0 μL per addition). In each titration, n additions were made (usually n = 40 - 50), resulting in n experimental values of the heat generated during the titration ($Q_{ex,j}$, where j = 1 to n). These values were corrected for the dilution heat of the titrant ($Q_{dil,j}$). The value of dilution heat was determined in separate runs with 0.900 mL 1.0 $mol\cdot dm^{-3}$ $NaClO_4$ in the cell (in the absence of Np(V)) titrated with the same titrant of picolinic acid. The net reaction heat at the j-th point ($Q_{r,j}$) was obtained from the difference: $Q_{r,j} = Q_{ex,j} - Q_{dil,j}$. The program HypDeltaH[16] was used to analyze the data and calculate the enthalpy of complexation.

3 Results

3.1 Equilibrium constants of the protonation of picolinate at 283 – 343 K

The stepwise protonation of picolinate is described by reactions (3) and (4). It is known that the second stepwise protonation constant is very low (log K_{H2} = 0.95[17] at 298 K and I = 1.0 mol·dm^{-3}) so that reaction (4) is negligible in solutions with pH above 3. Because the experiments for the complexation of Np(V) with picolinate at different temperatures were conducted in a pH region from 3.2 to 6.0, it was not necessary to include the second stepwise protonation in the data analysis. Besides, potentiometry with a pH electrode is not an ideal technique for the accurate determination of such low protonation constants that requires using strongly acidic solutions (≥ 0.1 mol·dm^{-3} H^{+}). Therefore, no attempts were made to determine the second protonation constant at different temperatures in this work. Details of representative protonation titrations by potentiometry are provided in Supporting Information (Table S1, Fig. S1). The obtained first stepwise protonation constants of picolinate at 283, 298, 313, 328, and 343 K are listed in Table 1.



(3)

(4)

Table 1 Thermodynamic parameters for the protonation and complexation with Np(V) of picolinate, I = 1.00 mol·dm^{-3} NaClO$_4$, HL – picolinic acid; methods: pot - potentiometry, sp - spectrophotometry, cal – calorimetry.

	T, K	Method	Log K (molarity)	ΔG kJ·mol^{-1}	ΔH kJ·mol^{-1}	ΔS J·K^{-1}·mol^{-1}
$H^+ + L^- = HL(aq)$	283	pot	5.48 ± 0.04	-(29.7 ± 0.2)		

	298	pot	5.38 ± 0.02	-(30.7 ± 0.1)	-(11.7 ± 1.3)[a]	63.8 ± 4.4
		cal			-(13.9 ± 0.6)	56.3 ± 2.0
	313	pot	5.29 ± 0.02	-(31.7 ± 0.1)		
	328	pot	5.20 ± 0.03	-(32.7 ± 0.2)		
	343	pot	5.10 ± 0.03	-(33.5 ± 0.2)		
$NpO_2^+ + L^- = NpO_2L(aq)$	283	sp	3.96 ± 0.01	-(21.5 ± 0.1)		
	298	sp	3.78 ± 0.01	-(21.6 ± 0.1)	-(15.7 ± 2.5)[a]	19.8 ± 8.4
		cal			-(9.2 ± 1.0)	41.6 ± 3.4
	313	sp	3.64 ± 0.01	-(21.8 ± 0.1)		
	328	sp	3.54 ± 0.01	-(22.2 ± 0.1)		
	343	sp	3.45 ± 0.01	-22.7 ± 0.1		
$NpO_2L(aq) + L^- = NpO_2L_2^-$	283	sp	2.91 ± 0.02	-(15.8 ± 0.1)		
	298	sp	2.80 ± 0.02	-(16.0 ± 0.1)	-(13.7 ± 1.3)[a]	8.0 ± 4.4
		cal			-(10.1 ± 1.2)	19.8 ± 4.0
	313	sp	2.69 ± 0.02	-(16.1 ± 0.1)		
	328	sp	2.57 ± 0.02	-(16.1 ± 0.1)		
	343	sp	2.47 ± 0.02	-(16.2 ± 0.1)		

[a] Calculated by van't Hoff equation using the log *K* at different temperatures (283 – 343 K).

3.2 Equilibrium constants of the complexation of picolinate with Np(V) at 283 – 343 K

Two representative spectrophotometric titrations at 298 and 328 K are shown in Figure 1. The spectra changes at other temperatures are similar. As is shown in the upper graphs, with the addition of picolinic acid, the intensity of the absorption band of free NpO_2^+ around 980 nm decreased and a new band appeared at 985 nm. As more picolinic acid was added, the intensity of the 985 nm band reached the maximum and then started to decrease with concomitant increase of a new band at 993 nm. Factor analysis of the absorption spectra by the HypSpec program indicated that there are three absorbing species of Np(V) including the free NpO_2^+ in the solutions. The best fit was achieved with a model including successive formation of two Np(V)/picolinate complexes as shown by reactions (5) and (6) with stepwise equilibrium constants of K_{ML} and K_{ML2}:

$$NpO_2^+ + L^- = NpO_2L(aq) \qquad K_{ML} \qquad (5)$$

$$NpO_2L(aq) + L^- = NpO_2L_2^- \qquad K_{ML2} \qquad (6)$$

where L^- represents picolinate. In the calculation, the protonation constants of picolinate at different temperatures from the potentiometric titrations were used. The resolved molar absorbance of individual Np(V) species was depicted in the lower graphs of Figure 1. Two representative spectrum deconvoluted results from the 298K titration were provided in the supporting information (Fig. S2). To further validate the above complexation pattern, a slope analysis was conducted on the 298 K spectrophotometric titration and an observation of the two linear fitting lines (slope = 1.00) excellently demonstrated the stepwise formation of ML and ML_2 complexes in the titration solution (c.f., Fig. S3 in the supporting information). Table 1 summarizes the calculated values of K_{ML} and K_{ML2} at five temperatures (283, 298, 313, 328 and 343 K).

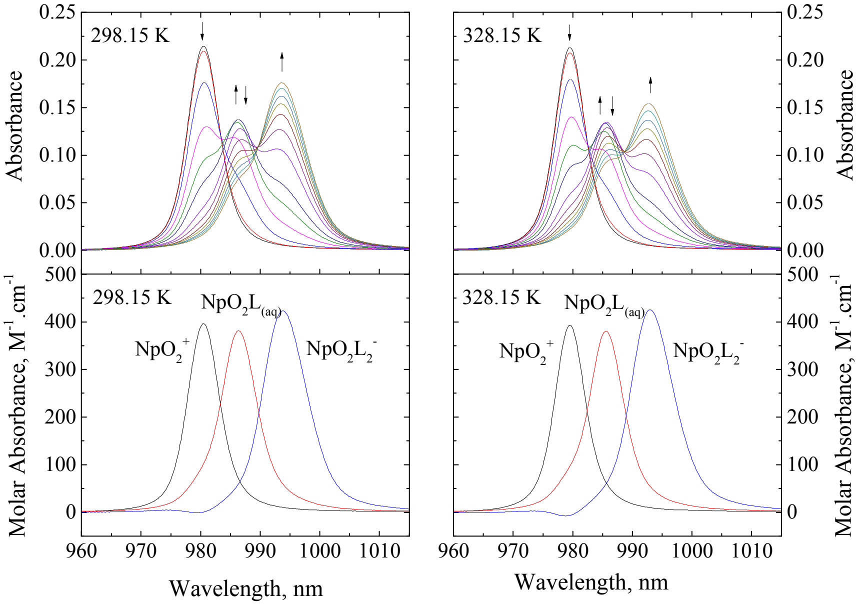


Fig. 1 Spectrophotometric titrations of Np(V)/picolinate complexation at T = 298 and 328 K. Initial solution in cuvette: 1.00 mL, $C_H = 6.22 \times 10^{-4}$ mol·dm^{-3}, $C_{Np} = 5.38 \times 10^{-4}$ mol·dm^{-3}. Titrant: $C_L = 3.96 \times 10^{-2}$ mol·dm^{-3}, $C_H = 3.82 \times 10^{-3}$ mol·dm^{-3}, total volume added = 0.200 mL.

(upper figure) absorption spectra (normalized to C_{Np}); (lower figure) molar absorptivity of Np(V) species.

3.3 Van't Hoff plots of the equilibrium constants of protonation and complexation

As shown in Table 1, the protonation constants of picolinate (log K_H) and the stability constants of the Np(V)/picolinate complexes (log K_{ML} and log K_{ML2}) all decrease with the increase of temperature. Van't Hoff plots of log K as a function of $1/T$ are shown in Figure 2. The linearity of the plots suggests that the enthalpies of protonation and complexation can be assumed constant in the temperature range from 283 K to 343 K. Also, the positive slopes indicate that the protonation and complexation are both exothermic. The "average" enthalpies of protonation and complexation in the temperature range of 283 – 343 K were calculated to be: $\Delta H_H = -(11.7 \pm 1.3)$ kJ·mol^{-1} (for reaction (3)), $\Delta H_{ML} = -(15.7 \pm 2.5)$ kJ·mol^{-1} (for reaction (5)), and $\Delta H_{ML2} = -(13.7 \pm 1.3)$ kJ·mol^{-1} (for reaction (6)).

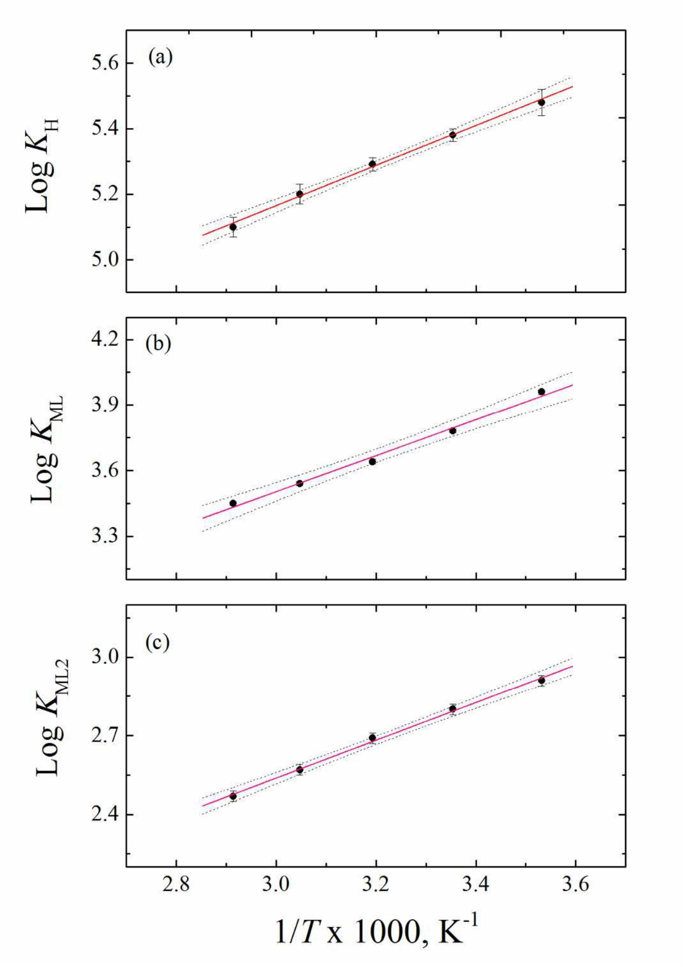


Fig. 2 Van't Hoff plots (log K vs. $1/T$). (●) experimental data, (—) linear fit, (---) 95% confidence bands. (a) protonation of picolinate, (b) stepwise 1:1 Np(V) picolinate complex, (c) stepwise 1:2 Np(V)/picolinate complex.

3.4 Enthalpy of protonation and complexation of picolinate with Np(V) by calorimetry

Details of the calorimetric titrations for the protonation are provided in Supporting Information (Table S2 and Fig. S4). The enthalpy of protonation (reaction (3)) was determined by calorimetry to be -(13.9 ± 0.6) $kJ\cdot mol^{-1}$, very close to the value calculated by the van't Hoff plot (-(11.7 ± 1.3) $kJ\cdot mol^{-1}$). The negative and moderately large enthalpy of protonation of picolinate is in distinctive contrast to the near-zero enthalpies of protonation of monocarboxylates such as acetate (0.10 $kJ\cdot mol^{-1}$) or benzoate (-0.11 $kJ\cdot mol^{-1}$),[17] suggesting that the first protonation occurs indeed on the pyridine nitrogen to form the zwitterion as shown in reaction (3). Energetically, the exothermic enthalpy of protonation results from the fact that the nitrogen atom is less hydrated than the carboxylate oxygen atom so that less dehydration energy is required upon protonation.

A representative calorimetric titration for the complexation of Np(V) with picolinate is shown in Figure 3. The data were well fitted and the stepwise enthalpies of complexation at 298 K were determined to be: ΔH_{ML} = -(9.2 ± 1.0) kJ·mol^{-1} (for reaction (5)), and ΔH_{ML2} = -(10.1 ± 1.2) kJ·mol^{-1} (for reaction (6)). These values, differing from those average enthalpies obtained by Van't Hoff plots by a few kilojoules per mole, are believed to be more accurate and more representative of the enthalpies at 298 K because they were directly measured by calorimetry at the constant temperature (298 K). The calorimetrically measured ΔH_{ML} is in excellent agreement with the value of -(9.9 ± 0.6) kJ.mol^{-1} in the literature.[9] The value of ΔH_{ML2} (-(10.1 ± 1.2) kJ·mol^{-1}) is the first such a value determined by calorimetry. In the analysis of the calorimetric data, the stability constants of Np(V)/picolinate complexes from spectrophotometry were used in conjunction with the protonation constant from potentiometry and the protonation enthalpy from calorimetry in this study.

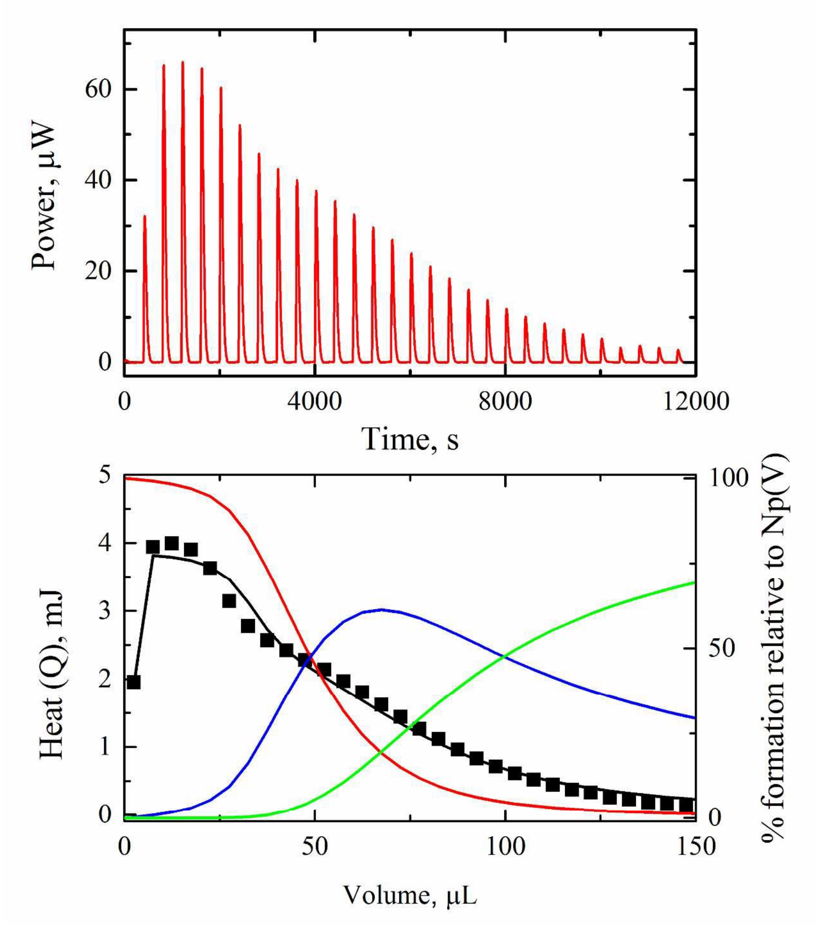


Fig. 3 Calorimetric titration of Np(V) picolinate complexation. Upper figure: thermogram (dilution heat not corrected); lower figure: observed (■) and calculated (—) total reaction heat (left y-axis), and speciation of Np(V) (color solid lines, right y-axis) as a function of the titrant volume; cup solution: 0.900 mL, $C_{Np} = 1.49 \times 10^{-3}$ mol·dm^{-3}, $C_H = 1.72 \times 10^{-3}$ mol·dm^{-3}; Titrant: $C_L = 6.07 \times 10^{-2}$ mol·dm^{-3}, $C_H = 5.85 \times 10^{-3}$ mol·dm^{-3}, 5.00 μL/addition.

4 Discussion

4.1 Comparison with related carboxylate ligands

The complexation of Np(V) with picolinate differs from that with other related monocarboxylate ligands (e.g., acetate and benzoate) in three aspects: (1) the Np(V)/picolinate complex (log K_{ML} = 3.78, from this work) is three orders of magnitude stronger than those of acetate (log K_{ML} = 0.83[17, 18]) and benzoate (log K_{ML} = 0.71[19]); (2) the complexation of Np(V) with picolinate is driven by both enthalpy and entropy, while the complexation with simple carboxylates (acetate and benzoate) is driven exclusively by entropy; and (3) due to the difference in the enthalpy of complexation (exothermic for Np(V)/picolinate but endothermic for Np(V)/acetate or Np(V)/benzoate), an increase in temperature weakens the complexation of Np(V) with picolinate but strengthens that with acetate or benzoate. As shown by the speciation plot at two temperatures (283 K and 343 K) in Figure 4, in the acidity region (-log[H^+] = 1 – 3) where the equilibrium between NpO_2^+ and $NpO_2L(aq)$ is dominant (reaction (5)), the formation of the $NpO_2L(aq)$ complex decreases by a few percent as the temperature is increased from 283 K to 343 K. Similarly, in the acidity region (-log[H^+] = 3 - 5) where the equilibrium between $NpO_2L(aq)$ and $NpO_2L_2^-$ is dominant (reaction (6)), an increase in temperature from 283 K to 343 K results in a decrease in the formation of the $NpO_2L_2^-$ complex.

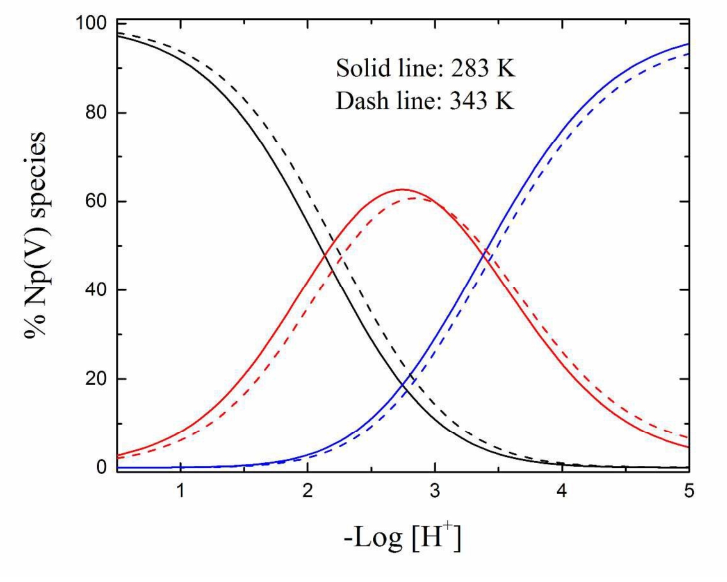


Fig. 4 Speciation of Np(V)/picolinate as a function of acidity (-log [H^+]) at 283 and 343 K. Black lines: NpO_2^+; red lines: $NpO_2L(aq)$ (L = picolinate); blue lines: $NpO_2L_2^-$. C_L/C_{Np} = 3; I = 1.0 mol·dm^{-3} $NaClO_4$. (This figure was made from the calculated speciation data by the simulation program HySS2009(Alderighi, 1999 #27) under the assumed solution conditions and the selected data points were listed in Table S3 in the supporting information)

4.2 Spectroscopic features of Np(V) and the effect of temperature

The spectroscopic properties of the Np(V)/picolinate system at different temperatures are summarized in Table 2. Two trends in the spectroscopic properties are noteworthy: (1) When the Np(V)/picolinate complexes form, the absorption band of free NpO_2^+ at 9800 Å is red-shifted by ~ 60 Å for the $NpO_2L(aq)$ complex, and by ~ 70 Å for the $NpO_2L_2^-$ complex. The magnitude of the red-shifts for Np(V)/picolinate complexes is larger than those for the Np(V)/benzoate or Np(V)/acetate complexes (Table 2); (2) As the temperature is increased from 283 K to 343 K, the absorption bands of individual Np(V) species are slightly narrowed and shifted to shorter wavelengths ("blue shift"). The magnitude of the blue shift for the free aqua NpO_2^+ ion (18 Å) is larger than those for the NpO_2^+/picolinate complexes (15-16 Å). The temperature dependence of the blue shift of individual Np(V) species is depicted in Figure 5.

Table 2 Spectroscopic features of NpO_2^+ and its picolinate complexes in solution at different temperatures (p.w. – present work)

	T K	λ (peak) Å	$\Delta\lambda^a$ Å	ε $cm^{-1}(mol\cdot dm^{-3})^{-1}$	FWHM Å	Ref.
			NpO_2^+			
	283	9809		404	65	p.w.
	298	9805		397	64	
	313	9800		393	63	
	328	9795		393	61	
	343	9791		392	60	
			$NpO_2L(aq)$			
L^- = picolinate	283	9867	58	385	75	p.w.
	298	9863	58	382	74	
	313	9859	59	383	72	
	328	9856	61	381	71	
	343	9852	61	378	70	
L^- = acetate	298	9849	44	316	70	[20]
L^- = benzoate	298	9849	45	330	66	[19]
			$NpO_2L_2^-$			
L^- = picolinate	283	9942	75	438	89	p.w.
	298	9939	76	423	88	
	313	9934	75	421	86	
	328	9930	74	425	85	
	343	9926	74	437	84	

[a] Wavelength red shift $\Delta\lambda = \lambda(NpO_2L) - \lambda(NpO_2^+)$ or $\lambda(NpO_2L_2^-) - \lambda(NpO_2L)$.

Trend (1) indicates that, at a constant temperature, the absorption bands of Np(V) are red-shifted upon complexation with ligands. This trend is known for the complexation of Np(V) with many ligands and can be discussed in terms of the perturbation of electronic energy levels upon complexation as previously described in the literature.[19] The absorption bands of Np(V) in the near-IR region originate from the intra-configuration $5f^2$ transitions. The positions of the absorption bands depend on the energy levels of the $5f^2$ states that are strongly influenced by the ion-ligand complexation and the ligand-field splitting. The ligand-field splitting of the $5f^2$ states reduces the energy gap between the ground state $^3H_4$ and the excited state with $^1G_4$ as the leading term of the free-ion eigenfunction. As a result, the absorption band of free aqua NpO_2^+ at 9800 Å would be red-shifted when the Np(V)/picolinate complexes form. Known as the Nephelauxetic effect, the magnitude of the red shift of the absorption bands is proportional to the electronegativity of the ligating atom and the coordination number.[21] Based on this, a correlation is expected between the stability constants of Np(V) complexes and the magnitude of spectra red-shifts. This correlation was shown for the complexation of Np(V) with a series of monocarboxylic acids including benzoic acid and acetic acid.[19] In the present study, the spectra red shifts for the Np(V)/picolinate complexes are larger than those for the Np(V) complexes with benzoic acid or acetic acid, because picolinate is a stronger bidentate ligand with a larger Nephelauxetic effect.

Trend (2) shows that, for individual species of Np(V), the increase in the temperature induces blue shifts of the absorption bands and makes the bands narrower. This trend can be explained by the mechanism of thermal expansion[22-24] of the complex coordinates in the solution. As discussed previously,[19] the dependence of the positions of optical absorption bands of complexes on temperature is a general phenomenon that could be induced by electronic coupling to the dynamics of the complex coordinates. Primarily, there are two mechanisms contributing to the observed shifts: (1) the mechanism of electron-phonon coupling; and (2) the mechanism of thermal expansion of the complex coordinates in the solution.

Mechanism (1), a well-established mechanism in solid-state spectroscopy, dictates that the temperature-dependence of the energy shift induced by electron-phonon coupling would be nonlinear (proportional to the fourth power of T) and should be accompanied by line broadening. This is contradictory to the observed linear temperature dependence (Figure 5) and line narrowing (Table 2) for the Np(V)/picolinate system. Obviously, mechanism (1) has little contribution to the observed temperature-dependent blue shifts observed in the present study.

In contrast, mechanism (2) should dominate in solutions because thermal expansion of complex coordinates in solutions is more significant than that in solids. Bond lengths and the distance between the ion and solvent molecules increase as a function of temperature. In the Np(V) complexes, thermal expansion occurs in both the equatorial Np-ligand coordinates and the axial O=Np=O bond length, weakening the electrostatic field imposed on the 5f electrons in NpO_2^+, resulting in the increase in the energy gap between the ground state ($^3H_4$) and the excited state ($^1G_4$), and inducing a blue shift. This mechanism would predict that the magnitude of the blue shifts should depend on the stability of the locate structure of the complexes. In other words, a stronger complex could have a more stable local structure less subjective to thermal expansion so that the temperature-induced blue shift would be smaller. Such prediction has previously been found to agree with the data for the Np(V)/benzoate system. In that system, smaller blue shifts were observed for the Np(V)/benzoate complex (0.29 cm^{-1}/K) than the free aquo NpO_2^+ ion (0.32 cm^{-1}/K) because the structural coordinates of the former is expected to be less subjective to thermal expansion than that of the latter.[19] The prediction by mechanism (2) is again validated by the results on the Np(V)/picolinate complexation from the present study. As shown in Figure 5, the blue shift rate for the Np(V)/picolinate complex (0.25 cm^{-1}/K) is even smaller than that for the Np(V)/benzoate complex because the more stable Np(V)/picolinate complex (log $\beta_1 = 3.78$ at 298 K) is expected to be less subjective to structural thermal expansion than the Np(V)/benzoate complex (log $\beta_1 = 0.71$ at 298 K). In brief, mechanism (2) is the most probable mechanism responsible for the blue shift dependence of the Np(V) absorption bands on the temperature.

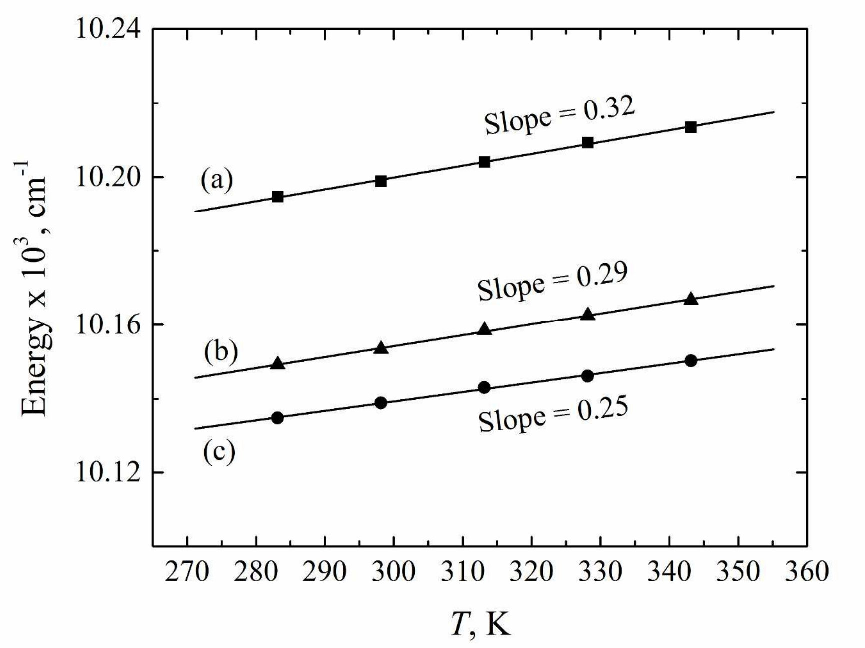


Fig. 5 Effect of temperature on the absorption bands of Np(V) species. Np(V) species: a – NpO_2^+; b – $NpO_2L(aq)$ (L = benzoate); c – $NpO_2L(aq)$ (L = picolinate).

5 Conclusions

Np(V) forms two moderately strong chelating complexes with picolinate (1:1 and 1:2) under the present experimental conditions (pH: 3.2 - 6.0, $I = 1.0$ mol·dm^{-3} $NaClO_4$ and $T = 283$ - 343 K). The complexation, driven by both enthalpy and entropy, becomes weaker at higher temperatures.

The spectroscopic features of the absorption bands of Np(V) in the near IR region are affected by the change in temperature. Blue shifts of the bands for all the Np(V) species, including the free NpO_2^+ ion and the Np(V)/picolinate complexes, were observed when the temperature was increased from 283 K to 343 K. Such effect can be satisfactorily explained by the mechanism of thermal expansion of the complex coordinates at higher temperatures.

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† Electronic Supplementary Information (ESI) available. Table S1: Potentiometric titration conditions for the p*K*a determination of picolinate (denoted as HL). Table S2: Calorimetric titration conditions for the enthalpy determination of picolinate (denoted as HL) protonation. Table S3: Selected speciation data points of Fig. 4. Fig. S1: Fitting of potentiometric titration data for the p*K*a determination at 298 and 328 K. Fig. S2: Spectrum deconvolued results from the 298 K spectrophotometric titration. Fig. S3: Slope analysis for the stepwise formation of $NpO_2(L)_n^{1-n}$ (n=1,2) in the spectrophotometric titration at 298 K. Fig. S4: Calorimetric titration of picolinate protonation (titration NO. 2 in Table S2).

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