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Cation-Cation Interactions between NpO_2^+ and UO_2^{2+} at Different Temperatures and Ionic Strengths

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Cation-cation interactions between NpO_2^+ and UO_2^{2+} were studied at different temperatures (283.15 K to 358.15 K) and different ionic strengths (3 – 4.5 mol·dm⁻³) by spectrophotometry and microcalorimetry. The cation-cation complex between NpO_2^+ and UO_2^{2+} was weak and became stronger as the temperature was increased from 283.15 K to 358.15 K. The molar enthalpy of complexation was directly determined for the first time by microcalorimetry to be (4.2 ± 1.6) kJ·mol⁻¹ at 298.15K, in good agreement with the trend in the stability constant at different temperatures. The small and positive enthalpy and entropy of complexation support the argument that the cation-cation complex between NpO_2^+ and UO_2^{2+} is of inner-sphere type. At each temperature, the stability constants of the cation-cation complex were found to increase as the ionic strength was increased. The specific ion interaction approach (SIT) was used to obtain the stability constants at infinite dilution and variable temperatures.

Introduction

Since the discovery of the cation-cation complex between NpO_2^+ and UO_2^{2+} in the early 1960's¹, cation-cation interactions have been a subject of intensive studies. Following the pioneering work by Sullivan et al., cation-cation interactions between NpO_2^+ and a number of cations in solutions and solids have been identified. In aqueous solutions, stability constants and spectroscopic properties of the cation-cation complexes between NpO_2^+ and UO_2^{2+} , NpO_2^{2+} , NpO_2^+ , Th^{4+} , Al^{3+} , Fe^{3+} , Cr^{3+} and Rh^{3+} were reported.¹⁻¹⁴ In solids, interactions of NpO_2^+ with a number of cations through its “axial” oxygens were identified in crystal structures.¹⁵⁻¹⁹

The interest in the cation-cation interactions involving NpO_2^+ has been stimulated in recent years, due to the importance of such interactions at both the fundamental and applied levels, as well as the scarcity of the data concerning the thermodynamics and structure of the cation-cation complexes that results in many questions remaining to be answered. At the fundamental level, the stability constants of the NpO_2^+ cation-cation complexes are scarce and scattered (Table 1). The enthalpy of complexation for the NpO_2^+ cation-cation complexes has never been directly measured. The only value of enthalpy of complexation for the $\text{NpO}_2^+\cdot\text{UO}_2^{2+}$ complex, obtained by fitting the stability constants in a narrow temperature range, seems to be problematic because it implies that the NpO_2^+ cation-cation complex is of outer-sphere nature and contradicts to the observed slow kinetics of the formation of such complexes. Despite that a number of experimental^{6,7,13,14} and computational²⁰ attempts were made, the coordination mode(s) and the nature of the cation-cation interactions in solutions remain unclear.

It has also been found that cation-cation interactions affect the behavior of NpO_2^+ in redox reactions and separation processes.^{21,22} Such effects could have significant implications at the applied level, because neptunium is an important and yet problematic element in the reprocessing of the used nuclear fuel. For example, pentavalent neptunium, Np(V) , is known to be non-

extractable in the separation processes using tributyl phosphate as the extractant so that clean separation of Np(V) from uranium and plutonium is expected. However, a portion of neptunium is always found to be associated with the uranium or plutonium streams in the process. It is an interesting and important question whether the formation of Np(V) cation-cation complexes and its effect on the redox properties of Np(V) could be responsible for such unexpected behavior of neptunium in the separation process. Systematic studies of the Np(V) cation-cation complexes should help to understand and solve the problems with neptunium in the used nuclear fuel reprocessing.

Previous studies have indicated that cation-cation interactions between NpO_2^+ and other cations cause significant changes in its optical absorption and Raman spectra. In addition, the formation of the NpO_2^+ complexes with non-labile cations such as Cr^{3+} and Rh^{3+} were found to be slow, suggesting NpO_2^+ enters and replaces water molecules in the primary hydration sphere of Cr^{3+} or Rh^{3+} , forming the “inner-sphere” complex. Based on these observations, we hypothesize that the $\text{NpO}_2^+\cdot\text{UO}_2^{2+}$ complex is of the inner-sphere type, in which the NpO_2^+ moiety uses its axial oxygen to coordinate to UO_2^{2+} through the equatorial plane of the latter. However, the only enthalpy and entropy values in the literature, $\Delta H = -12$ kJ·mol⁻¹ and $\Delta S = -34$ J·mol⁻¹·K⁻¹ obtained from the temperature dependence in a narrow range at a single ionic strength, contradict this hypothesis. To test the validity of this hypothesis with more reliable data, the stability constants of the $\text{NpO}_2^+\cdot\text{UO}_2^{2+}$ complex at 10 - 85°C (doubling the temperature range of the previous study) and multiple ionic strengths were determined. More importantly, microcalorimetric titrations were conducted for the first time to determine the enthalpy of complexation for $\text{NpO}_2^+\cdot\text{UO}_2^{2+}$ and corroborate with the enthalpy value obtained from the temperature dependence. With the data at different ionic strengths and temperatures, the specific ion interaction approach (SIT) was used to obtain the stability constants of $\text{NpO}_2^+\cdot\text{UO}_2^{2+}$ at infinite dilution and different temperatures. Ionic interaction parameters associated with the formation of $\text{NpO}_2^+\cdot\text{UO}_2^{2+}$ at different temperatures were also obtained.

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 elsewhere²³.

Stock solutions of $1.5 \text{ mol} \cdot \text{dm}^{-3} \text{ UO}_2(\text{NO}_3)_2$ and $1.5 \text{ mol} \cdot \text{dm}^{-3} \text{ Mg}(\text{NO}_3)_2$ were prepared by dissolving $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2$ solids, respectively, in water with small additions of nitric acid. The concentration of uranium in the stock solution was determined by fluorimetry²⁴ using standard solutions of uranium(VI) in $1 \text{ mol} \cdot \text{dm}^{-3}$ phosphoric acid. The concentration of magnesium in the stock solution was determined by the weight of solid $\text{Mg}(\text{NO}_3)_2$ and the volume of the solution, without further standardization. The concentration of free nitric acid in both stock solutions was $0.01 \text{ mol} \cdot \text{dm}^{-3}$.

The ionic strength of the $\text{UO}_2(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ stock solutions was $4.5 \text{ mol} \cdot \text{dm}^{-3}$ at 298.15 K. Solutions of other ionic strengths were prepared by appropriate dilutions of the stock solutions. In this paper, all concentrations in the molarity unit are referred to 298.15 K.

All spectrophotometric and calorimetric titrations in this work were conducted with initial solutions of Np(V) in $\text{Mg}(\text{NO}_3)_2$ at a certain ionic strength, titrated with solutions of $\text{UO}_2(\text{NO}_3)_2$ of the same ionic strength. Therefore, the ionic strength was maintained constant in the titration, but the ionic media changed from 100% $\text{Mg}(\text{NO}_3)_2$ to a mixture of $\text{Mg}(\text{NO}_3)_2$ and $\text{UO}_2(\text{NO}_3)_2$. $\text{Mg}(\text{NO}_3)_2$ was selected as the ionic medium because previous studies^{1,3,12} as well as this work confirmed that there were no observable cation-cation interactions between Mg^{2+} and NpO_2^+ .

Spectrophotometry

Spectrophotometry titrations in the near-IR region were conducted at 283.15, 298.15, 313.15, 328.25, 343.15 and 358.15 K. At each temperature, the ionic strengths of the solutions ranged from 3.0 to $4.5 \text{ mol} \cdot \text{dm}^{-3}$. In the titrations, the initial solution in the sample cell contained Np(V) ($2.4 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) and $\text{Mg}(\text{NO}_3)_2$. This solution was titrated with a solution of $\text{UO}_2(\text{NO}_3)_2$ at the same ionic strength. The absorption spectra in the wavelength region of 950 to 1050 nm were collected on a Varian Cary-6000i spectrophotometer, using 10 mm quartz cells. The temperature of the samples was maintained at a constant level ($\pm 0.1^\circ\text{C}$) 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 spectrophotometric titrations with different initial concentrations of Np(V) were performed. The stability constants of the $\text{NpO}_2^+ \cdot \text{UO}_2^{2+}$ complex (on the molarity scale) at different temperatures and ionic strengths were calculated by non-linear

least-square regression using the Hyperspec 2008 program.²⁵

Microcalorimetry

Calorimetric titrations were conducted at 298.15 K with an isothermal microcalorimeter (ITC 4200, Calorimetry Sciences Corp.). The full volume of the sample and reference cells is about 1.2 mL. For each titration, 0.900 mL solution of Np(V) in $\text{Mg}(\text{NO}_3)_2$ (for maintaining the ionic strength) was placed in the sample cell, and titrated with a solution of $\text{UO}_2(\text{NO}_3)_2$ at the same ionic strength. The titrant was delivered into the sample cell through a long and thin needle from a 250 μL syringe. The syringe was driven by a precision stepper motor that guaranteed accurate delivery of the titrant. The reference cell contained 0.9 mL $\text{Mg}(\text{NO}_3)_2$ of the same ionic strength without Np(V). The performance of the calorimeter has been tested by measuring the enthalpy of protonation of tris(hydroxymethyl)-aminomethane (THAM). The results was $(47.2 \pm 1.2) \text{ kJ} \cdot \text{mol}^{-1}$ at 298 K, compared very well with the values in the literature.²³

Multiple titrations were conducted. 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 the separate runs. The net reaction heat at the j -th point ($Q_{\text{r},j}$) was obtained from the difference: $Q_{\text{r},j} = Q_{\text{ex},j} - Q_{\text{dil},j}$. From these values, the enthalpy of complexation between NpO_2^+ and UO_2^{2+} was calculated with a non-linear least-square program MQ90, obtained by the courtesy of Prof. P. Zanonato of University of Padova, Italy.²⁶

Results

Stability constants of the $\text{NpO}_2^+ \cdot \text{UO}_2^{2+}$ complex at different temperatures and ionic strengths

The absorption spectra of representative spectrophotometric titrations at 298.15 K and 343.15 K are shown in Fig.1. As the concentration of U(VI) was increased, the intensity of the absorption peak of free Np(V) at 980.5 nm decreased and a new peak appeared at $\sim 992 \text{ nm}$ and its intensity increased. The band at 992 nm was assigned to the $\text{NpO}_2^+ \cdot \text{UO}_2^{2+}$ complex, in agreement with previous observations.^{1,4} The trends of the spectral changes in the titrations at other temperatures (283.15, 313.15, 328.15 and 358.15 K) were similar. There was only one isobestic point, indicating that there were two absorbing species in the solution during the titration. Factor analysis of the absorption spectra supported the above argument and, accordingly, the two absorbing species were assigned to the free NpO_2^+ and the $\text{NpO}_2^+ \cdot \text{UO}_2^{2+}$ complex. The complexation reaction could be described by equation (1).

Fig.1 Spectrophotometric titrations of Np(V)/U(VI) complexation in 1.5 mol·dm⁻³ (Mg/UO₂)(NO₃)₂. Upper figures: normalized absorption spectra at 298 K and 343 K. Initial solution: 2 ml, C_H = 0.0020 mol·dm⁻³, C_{Np} = 2.42 × 10⁻³ mol·dm⁻³, titrant: C_H = 0.0020 mol·dm⁻³, C_U = 1.5 mol·dm⁻³.

Lower figures: calculated molar absorptivities of NpO₂⁺ and (NpO₂·UO₂)³⁺ at 298 K and 343 K

The stability constants of (NpO₂·UO₂)³⁺ in molarity at different temperatures and ionic strengths were calculated with Hyperspec 2008, and summarized in Table 2. The complexation of U(VI) with nitrate was included in the calculation using the stability constants of UO₂(NO₃)⁺ at different temperatures in the literature.²⁷

Enthalpy of complexation for the NpO₂⁺·UO₂²⁺ complex determined by microcalorimetry

Fig.2 shows the thermogram of a representative calorimetric titration (upper figure) and the stepwise reaction heat, $Q_{r,j}$, of two titrations and the corresponding speciation of Np(V) in the titration (lower figure). Fitting the data of $Q_{r,j}$ in conjunction with the stability constant of (NpO₂·UO₂)³⁺ determined by spectrophotometry in this work, the enthalpy of complexation for (NpO₂·UO₂)³⁺ was determined to be (4.2 ± 1.6) kJ·mol⁻¹ at 298.15 K and the ionic strength of 4.5 mol·dm⁻³ (Table 2). This is the first enthalpy data for the cation-cation (NpO₂·UO₂)³⁺ complex that have been directly determined by microcalorimetry. In the calculation, the contribution of the complexation of U(VI) with nitrate to the observed reaction heat was taken into consideration by using the enthalpy of complexation of UO₂(NO₃)⁺ at 298.15 K from the literature ($\Delta H = 3.9 \pm 0.5$ kJ·mol⁻¹).²⁷

Discussion

Effect of temperature

To allow the comparison of stability constants at different temperatures and the extrapolation of stability constants to infinite dilution with the Specific Ion Interaction Approach (SIT), the constants in molarity should be converted to those in molality according to equation (2).^{28,29}

$$\log_{10}\beta_m = \log_{10}\beta_M + \sum_i \nu_i \log_{10}\theta \quad (2)$$

Fig.2 Microcalorimetric titrations of Np(V)/U(VI) complexation at 298.15 K. Upper: a representative thermogram. Lower: accumulated reaction heat (left y-axis) and Np(V) speciation (right y-axis) vs. the volume of titrant; (●, ●) observed heats, (—) fit, (---) 95% confidence band. Cup solution: 0.900 ml 4.0 mmol·dm⁻³ Np(V)/1.5 mol·dm⁻³ Mg(NO₃)₂/0.1 mol·dm⁻³ HNO₃; titrant: 1.5 mol·dm⁻³ UO₂(NO₃)₂/0.1 mol·dm⁻³ HNO₃.

where β_m and β_M are the stability constants in molality and molarity, respectively, and $\sum_i \nu_i$ is the sum of stoichiometric coefficients of the reaction. ν_i is positive for products and negative for reactants.²⁸ For reaction (1), $\sum_i \nu_i = -1$. θ is the ratio of the values of molality to molarity for the ionic medium. For the mixed solutions of UO₂(NO₃)₂ and Mg(NO₃)₂, the medium values of $\log_{10}\theta$ are 0.038 ($I_m = 4.91$ mol·kg⁻¹), 0.035 ($I_m = 4.42$ mol·kg⁻¹), 0.032 ($I_m = 3.98$ mol·kg⁻¹), 0.029 ($I_m = 3.58$ mol·kg⁻¹), 0.026 ($I_m = 3.22$ mol·kg⁻¹). Accordingly, the stability constants in molality are obtained and shown in Table 2.

Data in Table 2 indicate that, at a constant ionic strength, the stability of the (NpO₂·UO₂)³⁺ complex increases as the temperature is increased. A van't Hoff plot of $\log_{10}\beta_m$ vs. $1/T$ was shown in Fig.3. The data could be fitted with straight lines. From the slopes of the linear fits (weighted by the uncertainties), the "average" enthalpies of complexation for (NpO₂·UO₂)³⁺ in the temperature range (283.15 - 358.15 K) were calculated to be (4.85 ± 0.31), (4.86 ± 0.42), (4.34 ± 0.42), (5.03 ± 0.73) and (4.84 ± 0.75) kJ·mol⁻¹ at ionic strengths of 4.91, 4.42, 3.98, 3.58 and 3.22 mol·kg⁻¹, respectively. These data indicate that there is little effect of ionic strength (3 - 4.5 mol·dm⁻³) on the enthalpy of complexation for (NpO₂·UO₂)³⁺.

The enthalpy of complexation for (NpO₂·UO₂)³⁺ at 298.15 K directly determined by microcalorimetry (4.2 ± 1.6 kJ·mol⁻¹) is in excellent agreement with the value from the van't Hoff plot. These data unequivocally indicate that the formation of the (NpO₂·UO₂)³⁺ complex in the nitrate media is an endothermic reaction and the complexation is enhanced at higher temperatures.

Fig. 3 $\log_{10}\beta$ vs. $1/T$ for the complexation of Np(V) with U(VI) at different ionic strengths.

A few enthalpy values for the complexation of NpO_2^{+} with cations (UO_2^{2+} , NpO_2^{2+} , NpO_2^{+} , Cr^{3+} and Rh^{3+}) have been reported, ranging from $-15 \text{ kJ}\cdot\text{mol}^{-1}$ to $0 \text{ kJ}\cdot\text{mol}^{-1}$.^{3,4,9,12} All values were obtained by the van't Hoff extrapolation of the stability constants in a narrow temperature range (25 or 40 degrees). In an ionic medium of $6.0 \text{ mol}\cdot\text{dm}^{-3}$ NaClO_4 , the enthalpy and entropy of complexation for $(\text{NpO}_2\cdot\text{UO}_2)^{3+}$ were calculated to be $-(12 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$ and $-(34 \pm 6) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, respectively.⁴ The negative values of enthalpy and entropy contradicts the authors' claim that $(\text{NpO}_2\cdot\text{UO}_2)^{3+}$ is an inner-sphere cation-cation complex that was strongly implied by the slow kinetics of the formation of $(\text{NpO}_2\cdot\text{Cr})^{4+}$ and $(\text{NpO}_2\cdot\text{Rh})^{4+}$ complexes.^{9,12} Further discussions on this discrepancy were provided in the following section.

Coordination mode: inner-sphere or outer-sphere complex

Whether the $(\text{NpO}_2\cdot\text{UO}_2)^{3+}$ cation-cation complex is "outer sphere" or "inner sphere" is a question that is still open for debate. The slow kinetics of the formation of cation-cation complexes between Np(V) and nonlabile cations^{9,12} such as Cr^{3+} and Rh^{3+} suggested that NpO_2^{+} enters the primary hydration sphere of aquo Cr^{3+} and Rh^{3+} ions, thus forming inner-sphere complexes.^{9,12} Besides, the strong perturbations of the UV-Vis-NIR absorption, Raman, IR and NMR spectra caused by the cation-cation interactions, observed in previous studies^{1,3,5,7,9} as well as this work, support the hypothesis of inner-sphere complexation.

However, thermodynamic parameters (ΔH and ΔS) for $(\text{NpO}_2\cdot\text{UO}_2)^{3+}$ that have been reported until now⁴ contradict this hypothesis. Usually, inner-sphere complexation is associated with endothermic enthalpy and positive entropy,^{30,31} because a significant amount of energy is spent on the de-solvation of the metal ion and the ligand, and the degree of disorder is increased due to the release of solvent molecules from the highly ordered solvation shell(s) into the bulk. On the other hand, outer-sphere complexation is often associated with exothermic enthalpy and negative entropy, because the primary solvation sphere is minimally perturbed, little energy is spent on desolvation, and little disordering occurs. In contrast to the previous results of negative enthalpy ($-12 \text{ kJ}\cdot\text{mol}^{-1}$) and negative entropy ($-34 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), the results from this work ($\Delta H = +4.2 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta S = +19 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ at 298.15 K), support the hypothesis of inner-sphere $(\text{NpO}_2\cdot\text{UO}_2)^{3+}$ complexation that can be depicted by Scheme 1. It should be noted that the results from this work were obtained from the temperature dependency of the stability

constants in a much wider temperature range ($10 - 85^\circ\text{C}$) and, for the first time, directly measured by microcalorimetry.

Scheme 1

The enthalpy and entropy values for $(\text{NpO}_2\cdot\text{UO}_2)^{3+}$ from this work are comparable to those for $\text{UO}_2\text{NO}_3^{+}$ ($\Delta H = +3.9 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta S = +25 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ at 298.15 K), also a weak inner-sphere complex previously reported.²⁷

Effect of ionic strengths: Calculation of stability constants at variable temperatures to infinite dilution using the Specific Ion Interaction Theory (SIT)

The SIT (Specific Ion Interaction Theory) approach, which originated from the Brønsted-Guggenheim-Scatchard model,³²⁻³⁴ is usually used to calculate the equilibrium constant at zero ionic strength from the data at different ionic strengths up to $4 - 5 \text{ mol}\cdot\text{kg}^{-1}$. For reaction (1), the equilibrium constant at infinite dilution ($\log_{10}\beta^\circ$) is related to $\log_{10}\beta_m$ at the ionic strength of I_m by equation (3):

$$\log_{10}\beta_m - \Delta Z^2 \times D = \log_{10}\beta^\circ - \Delta \epsilon I_m \quad (3)$$

where $\Delta Z^2 = \sum(Z_{\text{products}}^2) - \sum(Z_{\text{reactants}}^2)$, and equals 4 for reaction (1). D is the Debye-Hückel term and equals $A I_m^{1/2} / (1 + 1.5 I_m^{1/2})$, I_m is the ionic strength in molality, and ϵ is the ion interaction parameter ($\text{kg}\cdot\text{mol}^{-1}$). $\Delta \epsilon = \epsilon(\text{NpO}_2\cdot\text{UO}_2^{3+}, \text{NO}_3^-) - \epsilon(\text{NpO}_2^{+}, \text{NO}_3^-) - \epsilon(\text{UO}_2^{2+}, \text{NO}_3^-)$.

The SIT calculation is usually performed by a linear fit of the term of $(\log_{10}\beta_m - \Delta Z^2 \times D)$ as a function of I_m . The intercept and the slope of the fit represent $\log_{10}\beta^\circ$ and $\Delta \epsilon$, respectively. Data at different temperatures from this work are shown in Fig.4. From the intercepts of the linear fits, the values of $\log\beta^\circ$ for reaction (1) were calculated to be $-(1.24 \pm 0.04)$, $-(1.18 \pm 0.05)$, $-(1.18 \pm 0.05)$, $-(1.22 \pm 0.04)$, $-(1.15 \pm 0.06)$ and $-(1.24 \pm 0.07)$ at 283, 298, 313, 328, 343 and 358 K respectively.

Fig.4 SIT analysis. Data at other temperatures (298, 328 and 343 K) are not shown for clarity.

It is reasonable to assume that the extrapolated equilibrium constants at $I_m = 0$ are more precise if sufficient data at low ionic strengths (e.g., 0.01 to $0.1 \text{ mol}\cdot\text{kg}^{-1}$) are available.^{28,29} However, it

is impossible to obtain the equilibrium data for reaction (1) at such low ionic strengths because the weakness of the $(\text{NpO}_2 \cdot \text{UO}_2)^{3+}$ complex necessitates the use of highly concentrated U(VI) solutions and, due to the +2 charge of the uranyl cation, the ionic strength of the $\text{UO}_2(\text{NO}_3)_2$ solution is three times its molar concentration (e.g., the ionic strength of $1.5 \text{ mol} \cdot \text{dm}^{-3} \text{ UO}_2(\text{NO}_3)_2$ is $4.5 \text{ mol} \cdot \text{dm}^{-3}$ at 298 K). In this work, the ionic strengths of solutions range from 3 to $4.5 \text{ mol} \cdot \text{dm}^{-3}$ at 298 K. Understandably, lack of the equilibrium constants of reaction (1) at low ionic strengths would result in higher uncertainties in the extrapolated value of $\log_{10} \beta^\circ$.

From the slopes of the linear fits in Fig.4, the values of $\Delta \varepsilon$ for reaction (1) were calculated to be $-(0.087 \pm 0.010)$, $-(0.077 \pm 0.011)$, $-(0.081 \pm 0.011)$, $-(0.091 \pm 0.010)$, $-(0.076 \pm 0.013)$ and $-(0.094 \pm 0.014) \text{ kg} \cdot \text{mol}^{-1}$ at 283, 298, 313, 328, 343 and 358 K, respectively. As these data indicate, the values of $\Delta \varepsilon$ remain essentially the same in the temperature range of 283 – 358 K. A previous study³⁵ also shows that there is little effect of temperature on $\Delta \varepsilon$ for the complexation of Cm(III) with nitrate at temperatures up to 373 K. These observations support the assumption that, in the absence of the ion interaction parameters at different temperatures, the values of $\Delta \varepsilon$ at 298 K can be used for other temperatures without introducing significant uncertainties.

Summary

Thermodynamic parameters (stability constants and enthalpy of complexation) for the cation-cation interaction between NpO_2^+ and UO_2^{2+} in the nitrate media have been determined at different temperatures and ionic strengths. Increases in the temperature and ionic strength strengthens the formation of the $\text{NpO}_2 \cdot \text{UO}_2^{3+}$ complex. Data from this work, the directly determined enthalpy data by microcalorimetry for the first time in particular, support the hypothesis that the cation-cation $\text{NpO}_2 \cdot \text{UO}_2^{3+}$ complex is of the inner-sphere type, where the NpO_2^+ moiety enters the primary equatorial coordination sphere of UO_2^{2+} and coordinates to UO_2^{2+} with one axial oxygen of NpO_2^+ .

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Notes and references

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Table 1 Previous data on the cation-cation interactions of NpO_2^{2+} in aqueous solutions. $\beta = [\text{NpO}_2 \cdot \text{M}^{(n+1)+}] / ([\text{NpO}_2^{2+}] \times [\text{M}^{n+}])$, where M^{n+} represents the other cation including UO_2^{2+} , NpO_2^{2+} , Th^{4+} , Cr^{3+} , and Rh^{3+} .

Complex	Medium	I (M)	Method	T (K)	β	ΔH (kJ·mol ⁻¹)	ΔS (J·K ⁻¹ ·mol ⁻¹)	ref
$\text{NpO}_2^{2+} \cdot \text{UO}_2^{2+}$	NaClO_4 $\text{Na/Mg}(\text{ClO}_4)_2$ NaClO_4	<1	LIPAS	?	~ 0.6			9
		3.0	sp	298	0.69 ± 0.01	-12 ± 1.7	-34 ± 6	1
		6.0	sp	298	2.25 ± 0.03			4
				308	2.05 ± 0.04			
				318	1.76 ± 0.03			
				328	1.39 ± 0.07			
				338	1.16 ± 0.04			
	NaClO_4	6.0	LIPAS	?	2.4 ± 0.2			5
	$\text{Ca}(\text{ClO}_4)_2$	6.26	Raman	?	2.5 ± 0.5			7
	$\text{Mg}(\text{ClO}_4)_2$	7.0	sp	298	3.7 ± 0.1			3
$\text{NpO}_2^{2+} \cdot \text{NpO}_2^{2+}$	$\text{Mg}(\text{ClO}_4)_2$	7.0	sp	298	3.0 ± 0.15	~ 0	~ 9	3
				313	2.5 ± 0.2			
				323	2.7 ± 0.1			
				298	1.5 ± 0.03			3
	$\text{Mg}(\text{NO}_3)_2$	7.0	sp	298	1.5 ± 0.03			3
$\text{NpO}_2^{2+} \cdot \text{NpO}_2^{2+}$	HClO_4 NaClO_4 HClO_4	1.0	HEXS	?	~ 0.74			8
		4.26	Raman, sp	?	0.82 ± 0.05			7
		6.0	sp	298	1.41 ± 0.14	~ 0	3 ± 2	4
$\text{NpO}_2^{2+} \cdot \text{Th}^{4+}$	NaClO_4	6.0	LIPAS	?	1.8 ± 0.9			5
$\text{NpO}_2^{2+} \cdot \text{Cr}^{3+}$	$\text{Na/Mg/Y}(\text{ClO}_4)_3$, HClO_4	8.0	sp	298	2.62 ± 0.48	-13.8 ± 2.5	-38 ± 8	9
				308	1.95 ± 0.33			
				323	1.6 ± 0.24			
$\text{NpO}_2^{2+} \cdot \text{Rh}^{3+}$	$\text{Mg}(\text{ClO}_4)_2$	8.0	sp	298	3.31 ± 0.06	-15.1 ± 3.8	-42 ± 12	12
				308	2.37 ± 0.28			
				323	2.16 ± 0.22			

^s Methods: LIPAS - laser-induced photoacoustic spectroscopy, sp- spectrophotometry, HEXS - high-energy X-ray scattering.

Table 2 Thermodynamic parameters for the complexation between NpO_2^{2+} and UO_2^{2+} at different temperatures and ionic strengths. $\beta = [\text{NpO}_2 \cdot \text{UO}_2^{3+}] / ([\text{NpO}_2^{2+}] \times [\text{UO}_2^{2+}])$.

I_m (mol·kg ⁻¹)	T (K)	$\log_{10}\beta_M$	$\log_{10}\beta_m$	ΔH (kJ·mol ⁻¹)	ΔS (J·K ⁻¹ ·mol ⁻¹)
4.91	283.15	0.23 ± 0.01	0.19 ± 0.01		
	298.15	0.28 ± 0.01	0.25 ± 0.01	4.85 ± 0.31^a	21 ± 1
				4.2 ± 1.6^b	19 ± 5
	313.15	0.33 ± 0.01	0.29 ± 0.01		
	328.15	0.38 ± 0.01	0.34 ± 0.01		
4.42	343.15	0.40 ± 0.01	0.36 ± 0.01		
	358.15	0.44 ± 0.01	0.40 ± 0.01		
	283.15	0.18 ± 0.01	0.15 ± 0.01		
	298.15	0.21 ± 0.01	0.18 ± 0.01	4.86 ± 0.42^a	20 ± 1
	313.15	0.27 ± 0.01	0.23 ± 0.01		
	328.15	0.29 ± 0.01	0.26 ± 0.01		
	343.15	0.33 ± 0.02	0.30 ± 0.02		
	358.15	0.38 ± 0.02	0.34 ± 0.02		
	283.15	0.13 ± 0.01	0.095 ± 0.01		
	298.15	0.17 ± 0.03	0.14 ± 0.03	4.34 ± 0.42^a	17 ± 2
3.98	313.15	0.21 ± 0.02	0.18 ± 0.02		
	328.15	0.24 ± 0.01	0.21 ± 0.01		
	343.15	0.27 ± 0.02	0.24 ± 0.02		
	358.15	0.29 ± 0.02	0.26 ± 0.02		
	283.15	0.09 ± 0.02	0.061 ± 0.02		
	298.15	0.13 ± 0.02	0.10 ± 0.02	5.03 ± 0.73^a	19 ± 2
	313.15	0.17 ± 0.02	0.14 ± 0.02		
	328.15	0.21 ± 0.02	0.19 ± 0.02		
	343.15	0.26 ± 0.02	0.23 ± 0.02		
	358.15	0.26 ± 0.04	0.23 ± 0.04		
3.22	283.15	0.054 ± 0.020	0.028 ± 0.020		
	298.15	0.11 ± 0.02	0.083 ± 0.020	4.84 ± 0.75^a	18 ± 3
	313.15	0.14 ± 0.02	0.12 ± 0.02		
	328.15	0.18 ± 0.02	0.15 ± 0.02		
	343.15	0.24 ± 0.03	0.21 ± 0.03		
	358.15	0.23 ± 0.03	0.20 ± 0.03		

^a Average enthalpy of complexation for 283 - 358 K obtained by van't Hoff equation.

¹⁰ ^b Enthalpy of complexation at 298 K determined by microcalorimetry.