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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 298.15 K, 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’s, 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$_2^+$, Th$^{4+}$, Al$^{3+}$, Fe$^{3+}$, Cr$^{3+}$ and Rh$^{3+}$ were reported. In solids, interactions of NpO$_2^+$ with a number of cations through its “axial” oxygens were identified in crystal structures.

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 NpO$_2^+$-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 and computational 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. 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 NpO$_2^+$-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 NpO$_2^+$-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 NpO$_2^+$-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 NpO$_2^+$-UO$_2^{2+}$ at infinite dilution and different temperatures. Ionic interaction parameters associated with the formation of NpO$_2^+$-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 elsewhere.

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

The ionic strength of the \( \text{UO}_2(\text{NO}_3)_2 \) and \( \text{Mg(NO}_3)_2 \) stock solutions was 4.5 mol 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 \( \text{Mg(NO}_3)_2 \) 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% \( \text{Mg(NO}_3)_2 \) to a mixture of \( \text{Mg(NO}_3)_2 \) and \( \text{UO}_2(\text{NO}_3)_2 \). \( \text{Mg(NO}_3)_2 \) was selected as the ionic medium because previous studies as well as this work confirmed that there were no observable cation-association interactions between \( \text{Mg}^{2+} \) and \( \text{NpO}_2^{+} \).

Spectrophotometry

Spectrophotometric 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 mol dm⁻³. In the titrations, the initial solution in the sample cell contained Np(V) \((2.4 \times 10^{-5} \text{ mol dm}^{-3})\) and \( \text{Mg(NO}_3)_2 \). 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-600i spectrophotometer, using 10 mm quartz cells. The temperature of the samples was maintained at a constant level (± 0.1°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-squares regression using the Hyperspec 2008 program.

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 \( \text{Mg(NO}_3)_2 \) (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 Mg(NO₃)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 \((47.2 ± 1.2) \text{ kJ mol}^{-1}\) at 298 K, compared very well with the values in the literature.

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 \( \text{NpO}_2^{+} \) and \( \text{UO}_2^{2+} \) was calculated with a non-linear least-square program MO90, obtained by the courtesy of Prof. P. Zanonato of University of Padova, Italy.

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 ~ 992 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. 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 \( \text{NpO}_2^{+} \) and the \( \text{NpO}_2^{+} \cdot \text{UO}_2^{2+} \) complex. The complexation reaction could be described by equation (1).

\[
\text{NpO}_2^{+} + \text{UO}_2^{2+} \rightleftharpoons (\text{NpO}_2 \cdot \text{UO}_2)^{3+}
\]
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⁻⋅UO₂⁺ complex determined by microcalorimetry

Fig.2 shows the thermogram of a representative calorimetric titration (upper figure) and the stepwise reaction heat, Qᵣ,j, of two titrations and the corresponding speciation of Np(V) in the titration (lower figure). Fitting the data of Qᵣ,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. This is the first enthapy 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 (ΔH = 3.9 ± 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

\[ \log_{10} \beta_m = \log_{10} \beta_M + \sum \nu_i \log_{10} \vartheta \]  

(2)
A few enthalpy values for the complexation of \( \text{NpO}_2^+ \) with cations (\( \text{UO}_2^{2+}, \text{NpO}_2^{2+}, \text{NpO}_4^{3+}, \text{Cr}^{3+} \) and \( \text{Rh}^{3+} \)) have been reported, ranging from \(-15 \text{ kJ mol}^{-1}\) to \(0 \text{ kJ mol}^{-1}\). 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 mol\( \cdot \text{dm}^{-3} \) \( \text{NaClO}_4 \), the enthalpy and entropy of complexation for \( \text{NpO}_2^+\text{UO}_2^{3+} \) were calculated to be \((-12 \pm 1.7) \text{ kJ mol}^{-1}\) and \(-(34 \pm 6) \text{ J mol}^{-1} \text{K}^{-1}\), respectively. The negative values of enthalpy and entropy contradict the authors’ claim that \( \text{NpO}_2^+\text{UO}_2^{3+} \) is an inner-sphere cation-cation complex that was strongly implied by the slow kinetics of the formation of \( \text{NpO}_2\text{Cr}^{3+} \) and \( \text{NpO}_2\text{Rh}^{3+} \) complexes. Further discussions on this discrepancy were provided in the following section.

Coordination mode: inner-sphere or outer-sphere complex

Whether the \( \text{NpO}_2^+\text{UO}_2^{3+} \) 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 \( \text{Np(V)} \) and nonlabile cations such as \( \text{Cr}^{3+} \) and \( \text{Rh}^{3+} \) suggested that \( \text{NpO}_2^+ \) enters the primary hydration sphere of aquo \( \text{Cr}^{3+} \) and \( \text{Rh}^{3+} \) ions, thus forming inner-sphere complexes. 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, as well as this work, support the hypothesis of inner-sphere complexation.

However, thermodynamic parameters (\(\Delta H\) and \(\Delta S\)) for \( \text{NpO}_2^+\text{UO}_2^{3+} \) that have been reported until now contradict this hypothesis. Usually, inner-sphere complexation is associated with endothermic enthalpy and positive entropy, 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 \((-12 \text{ kJ mol}^{-1})\) and negative entropy \((-34 \text{ J mol}^{-1} \text{K}^{-1})\), the results from this work \(\Delta H = +4.2 \text{ kJ mol}^{-1}\) and \(\Delta S = +19 \text{ J mol}^{-1} \text{K}^{-1}\) at 298.15 K), support the hypothesis of inner-sphere \( \text{NpO}_2^+\text{UO}_2^{3+} \) 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°C) and, for the first time, directly measured by microcalorimetry.

The enthalpy and entropy values for \( \text{NpO}_2^+\text{UO}_2^{3+} \) from this work are comparable to those for \( \text{UO}_2\text{NO}_3^{2+} \) (\(\Delta H = +3.9 \text{ kJ mol}^{-1}\) and \(\Delta S = +25 \text{ J mol}^{-1} \text{K}^{-1}\) at 298.15 K), also a weak inner-sphere complex previously reported.

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 Bromsgood-Guggenheim-Scatchard model, is usually used to calculate the equilibrium constant at zero ionic strength from the data at different ionic strengths up to 4 – 5 mol\( \cdot \text{kg}^{-1}\). For reaction (1), the equilibrium constant at infinite dilution \(\log_{10} \beta_m\) is related to \(\log_{10} \beta_m\) at the ionic strength of \(I_m\) by equation (3):

\[
\log_{10} \beta_m = \Delta Z^2 \times D = \log_{10} \beta^0 - \Delta \varepsilon I_m
\]

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

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 \(\log_{10} \beta^0\) and \(\Delta \varepsilon\), respectively. Data at different temperatures from this work are shown in Fig.4. From the intercepts of the linear fits, the values of \(\log_{10} \beta^0\) 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.

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 mol\( \cdot \text{kg}^{-1}\)) are available. However, it
is impossible to obtain the equilibrium data for reaction (1) at such low ionic strengths because the weakness of the (NpO₂⁻-UO₂³⁺) 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 UO₂(NO₃)₂ solution is three times its molar concentration (e.g., the ionic strength of 1.5 mol·dm⁻³ UO₂(NO₃)₂ is 4.5 mol·dm⁻³ at 298 K). In this work, the ionic strengths of solutions range from 3 to 4.5 mol·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 β₂⁰⁰.

From the slopes of the linear fits in Fig.4, the values of Δε for reaction (1) were calculated to be -(0.087 ± 0.010), -(0.077 ± 0.011), -(0.081 ± 0.011), -(0.091 ± 0.010), -(0.076 ± 0.013) and -(0.094 ± 0.014) kg·mol⁻¹ at 283, 298, 313, 328, 343 and 358 K, respectively. As these data indicate, the values of Δε remain essentially the same in the temperature range of 283 – 358 K. A previous study also shows that there is little effect of temperature on Δε 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 Δε 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 NpO₂⁺ and UO₂²⁺ 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 NpO₂⁻-UO₂³⁺ complex. Data from this work, the directly determined enthalpy and UO₂ solution is three times its molar concentration. Data from this work, the directly determined enthalpy and UO₂ solution is three times its molar concentration, support complexation (for the cation-cation interaction between NpO₂⁻ and UO₂³⁺) for the cation-cation interaction between NpO₂⁻ and UO₂³⁺. Data from this work, the directly determined enthalpy and UO₂ solution is three times its molar concentration, support complexation (for the cation-cation interaction between NpO₂⁻ and UO₂³⁺) for the cation-cation interaction between NpO₂⁻ and UO₂³⁺.

Acknowledgements

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Notes and references

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5 Department of Radiochemistry, China Institute of Atomic Energy, Beijing, China; E-mail: xianliang527@sohu.com

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

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<td>4.26</td>
<td>Raman</td>
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<td>~ 0</td>
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<td>NaClO$_4$</td>
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<td>1.8 ± 0.9</td>
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<td>1.6 ± 0.24</td>
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<tr>
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<td>Mg(ClO$_4$)$_2$</td>
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<td>sp</td>
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<td>2.16 ± 0.22</td>
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Methods: LIPAS - laser-induced photoacoustic spectroscopy, sp- spectrophotometry, HEXS - high-energy X-ray scattering.

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

<table>
<thead>
<tr>
<th>$I_m$ (mol·kg$^{-1}$)</th>
<th>$T$ (K)</th>
<th>$\log_{10}\beta_{4.91}$</th>
<th>$\log_{10}\beta_{4.42}$</th>
<th>$\log_{10}\beta_{3.98}$</th>
<th>$\log_{10}\beta_{3.58}$</th>
<th>$\log_{10}\beta_{3.22}$</th>
<th>$\Delta H$ (kJ·mol$^{-1}$)</th>
<th>$\Delta S$ (J·K$^{-1}$·mol$^{-1}$)</th>
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<td>4.91</td>
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<td>0.23 ± 0.01</td>
<td>0.19 ± 0.01</td>
<td>0.13 ± 0.01</td>
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<td>0.05 ± 0.02</td>
<td>4.85 ± 0.31$^a$</td>
<td>21 ± 1</td>
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<td>0.28 ± 0.01</td>
<td>0.25 ± 0.01</td>
<td>0.17 ± 0.03</td>
<td>0.14 ± 0.03</td>
<td>0.10 ± 0.02</td>
<td>4.2 ± 1.6$^a$</td>
<td>19 ± 5</td>
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<td>313.15</td>
<td>0.33 ± 0.01</td>
<td>0.29 ± 0.01</td>
<td>0.21 ± 0.02</td>
<td>0.18 ± 0.02</td>
<td>0.14 ± 0.02</td>
<td>4.6 ± 0.42$^a$</td>
<td>20 ± 1</td>
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<td>4.86 ± 0.42$^a$</td>
<td>20 ± 1</td>
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<td>0.083 ± 0.02</td>
<td>4.84 ± 0.75$^a$</td>
<td>18 ± 3</td>
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<td>4.84 ± 0.75$^a$</td>
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<td>0.21 ± 0.03</td>
<td>4.84 ± 0.75$^a$</td>
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<td>358.15</td>
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<td>0.20 ± 0.03</td>
<td>4.84 ± 0.75$^a$</td>
<td>18 ± 3</td>
</tr>
</tbody>
</table>

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

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