

Spectroscopic characterisation and thermodynamics of the complexation of Np(V) with sulfate up to 200 °C

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ABSTRACT

In the present work the complexation of Np(V) with sulfate in aqueous solution is studied in a temperature range up to 200 °C by absorption spectroscopy. For this purpose, a new spectroscopic setup is implemented and tested for its suitability for Vis/NIR absorption spectroscopy at elevated temperatures. The complexation of Np(V) with sulfate is studied as a function of the total ligand concentration at various temperatures ($T = 25\text{--}200\text{ °C}$) and ionic strengths ($I_m(\text{NaClO}_4) = 1.0\text{--}4.0\text{ mol kg}^{-1}\text{ NaClO}_4$). The exclusive formation of $\text{NpO}_2(\text{SO}_4)^-$ up to 200 °C is confirmed by peak deconvolution and slope analyses. The thermodynamic stability constants $\log \beta_1^0(T)$ are obtained from linear regressions according to the specific ion interaction theory (SIT). A systematic increase of the $\log \beta_1^0(T)$ is observed with increasing temperature, resulting in a linear correlation of $\log \beta_1^0(T)$ with T^{-1} . The magnitude of the increase is 1.9 logarithmic units at 200 °C in comparison to $\log \beta_1^0(25\text{ °C}) = 1.05 \pm 0.16$. Thus, the standard reaction enthalpy and entropy ($\Delta_r H_m^0$, $\Delta_r S_m^0$) are determined with the integrated Van't Hoff equation revealing $\Delta_r H_m^0 = 31.0 \pm 1.0\text{ kJ mol}^{-1}$ and $\Delta_r S_m^0 = 123 \pm 9\text{ J mol}^{-1}\text{ K}^{-1}$. In addition, the stoichiometric sum of the specific binary ion ion interaction coefficient ($\Delta \epsilon_{01}(T)$) is determined up to 200 °C showing an insignificant temperature dependence. Thus, a temperature independent $\epsilon(\text{Na}^+, \text{NpO}_2(\text{SO}_4)^-) = 0.07 \pm 0.11$ is calculated for the temperature range up to 200 °C. Comparison of the present results with literature data confirms the excellent applicability of the new high temperature absorption spectroscopic setup for complexation studies up to 200 °C.

1. Introduction

Nuclear fission is commercially used for the generation of electrical power and leads to an accumulation of radioactive waste. Due to neutron capture reactions transuranium elements with very long half lives are present in the spent nuclear fuels, which determine its long term radiotoxicity. The generally pursued disposal strategy is the final emplacement of the waste in deep geological formations like salt, clay, or crystalline rocks. For the safety case of a nuclear waste repository different incident scenarios must be considered such as the intrusion of water and subsequent dissolution of the waste form and mobilisation of radionuclides by complexation reactions with different ligands in the aqueous phase. In particular, in salt rock formations the intrusion of water leads to the formation of highly concentrated brines which provide a variety of inorganic complexing agents like SO_4^{2-} , Cl^- , F^- , OH^- , CO_3^{2-} [1–5].

Furthermore, depending on the type of repository and waste form, temperatures up to 200 °C are expected in the first time period of the

postclosure of a nuclear waste repository. Thus, detailed knowledge on the temperature dependence of the relevant processes affecting the dissolution and mobilisation of the actinides is of high importance for a better understanding of the chemical behaviour of the actinides at near field conditions. Therefore, thermodynamic data like standard state stability constants ($\log \beta_n^0$) as a function of temperature, standard reaction enthalpies ($\Delta_r H^0$) and entropies ($\Delta_r S^0$) of these reactions have to be determined.

In the present work the complexation of Np(V) with sulfate is studied in the temperature range of 20–200 °C. Within the An(V) series the pentavalent Np(V) ion is the thermodynamically most stable species in aqueous solution and is used as an analogue for the An(V) due to its excellent spectroscopic properties in the near infrared region (NIR).

Existing literature data on the Np(V) complexation with SO_4^{2-} are mainly limited to fixed ionic strengths or ambient temperatures [6–10]. A critical review of the available literature data is given in the NEA TDB recommending $\log \beta_1^0(25\text{ °C}) = 0.44 \pm 0.27$ for $\text{NpO}_2(\text{SO}_4)^-$ [1,3]. This value is based on two solvent extraction studies [11,12]. Recent studies on the Np(V) sulfate complexation by absorption spectroscopy and microcalorimetry are not considered in the NEA TDB review [6,10,13,14]. These studies provide $\log \beta_1^0(25\text{ °C})$ of 0.92 ± 0.13 to

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1.03 ± 0.25 , which are distinctively higher compared to the value reported in the NEA TDB. In general, a wide scattering of the reported stability constants up to 0.7 logarithmic units is found in the literature [7,11,12].

Regarding the temperature dependency of the Np(V) sulfate complexation only limited data are available. In a spectroscopic study by Rao et al. the formation of $\text{NpO}_2(\text{SO}_4)^-$ is studied between 10 and 70 °C. There an increase of $\log \beta_1^0(25\text{ °C}) = 1.03 \pm 0.25$ by 0.2 logarithmic units is observed [6]. In a calorimetric study by Rao et al. $\log \beta_1^0(25\text{ °C}) = 0.97$ is reported which increases by 0.5 from 25 up to 70 °C. In good agreement to this result, our recent spectroscopic study provided $\log \beta_1^0(25\text{ °C}) = 0.92 \pm 0.13$ for $\text{NpO}_2(\text{SO}_4)^-$ increasing by 0.9 logarithmic units in the temperature range of 25–85 °C [13].

In the present work a new experimental setup is implemented for absorption spectroscopic measurements of Np(V) in aqueous solution up to 200 °C providing access to thermodynamic data for the Np(V) complexation in a temperature interval of 25–200 °C. Thermodynamic data for $T = 100\text{ °C}$ is of particular interest as distinct changes of the physical properties of the water and its bulk structure occur at these temperatures, resulting in significant changes of the complexation properties of actinide ions in aqueous solution [15].

Up to now, thermodynamic data for $T = 100\text{ °C}$ have been determined only for trivalent actinides indicating an increase of the stability constants of $[\text{Cm(III)}(\text{SO}_4)_n]^{3-2n}$ $n = 1, 2, 3$ by 2.4 to 4.1 logarithmic units in the temperature range of 25–200 °C [16–19]. Comparable data for An(V) is not available.

2. Experimental section

2.1. Sample preparation

All concentrations are given on the molal concentration scale ($\text{mol kg}^{-1}\text{ H}_2\text{O}$; “m”) which avoids changes of the concentration due to changes of the solution density resulting from variation of the temperature or salt concentration. The chemicals used were reagent grade or higher and purchased from Merck Millipore. Ultrapure water (Milli Q academic, Millipore) was used for dissolution of the salts and sample preparation. In all samples an initial Np(V) concentration of $3.5 \times 10^{-4}\text{ mol kg}^{-1}$ was adjusted by dilution of a $^{237}\text{Np(V)}$ stock solution ($5.9 \times 10^{-3}\text{ mol kg}^{-1}\text{ NpO}_2^+$ in $1.0 \times 10^{-1}\text{ mol kg}^{-1}\text{ HClO}_4$). The oxidation state of Np in the stock solution was validated by absorption spectroscopy and solvent extraction using HDEHP and PMBP [20]. Details on the preparation of the Np(V) stock solution are given in the literature [21]. The total proton concentration of $[\text{H}^+]_{\text{total}} = 9.4 \times 10^{-4}\text{ mol kg}^{-1}$

in all samples was adjusted by addition of a $0.1\text{ mol kg}^{-1}\text{ HClO}_4$ solution. The sulfate concentration was increased by successive titration using an $0.55\text{ mol kg}^{-1}\text{ Na}_2\text{SO}_4$ solution with $[\text{H}^+]_{\text{total}} = 1.7 \times 10^{-3}\text{ mol kg}^{-1}$ or by addition of solid Na_2SO_4 to the sample solutions. In total four different titration series at fixed ionic strengths of $I_m(\text{NaClO}_4) = 1.0, 2.5, 3.0,$ and $4.0\text{ mol kg}^{-1}\text{ NaClO}_4$ were performed. The ionic strengths of the samples were adjusted by dissolution of solid $\text{NaClO}_4 \cdot \text{H}_2\text{O}$.

2.2. NIR absorption spectroscopy

Spectrophotometric measurements were conducted on a Varian Cary 6000i UV/Vis/NIR spectrophotometer. All spectra were recorded in the wavelength range of $\lambda = 960\text{--}1020\text{ nm}$ with a 0.05 nm data interval, a scan rate of 30 nm min^{-1} and a slit width of 0.7 nm in double beam mode. Five scans were accumulated to obtain a better signal to noise ratio. The absorption spectroscopic measurements were performed in a custom built high temperature and high pressure cell made from TiPd alloy coupled to the spectrometer via fiber optics. The technical specifications of this cell are described in the following section and in the literature [17]. The temperatures studied were $T = 25, 50, 75, 100, 120, 140, 160, 180$ and 200 °C . The samples were tempered for 30 min at each temperature to ensure chemical equilibrium before measurement.

2.3. Spectroscopic setup

Fig. 1 shows a scheme of the experimental setup of the high temperature and high pressure cell initially developed for time resolved laser fluorescence spectroscopic measurements [17]. The cell body is made of TiPd alloy with 0.2 w% Pd, a material with low thermal expansion and high resistance against corrosion. The cell is heated by two heating sleeves and the temperature is controlled by J thermal elements made of Fe–CuNi alloy. For infilling of sample solution PEEK (polyetheretherketone) fittings and valves are mounted to the TiPd body. The sample volume required for spectrophotometric measurements is about 2 ml. The setup is certified for temperatures up to $T_{\text{max}} = 220\text{ °C}$ and a maximum pressure of $p_{\text{max}} = 60\text{ bar}$. To avoid overheating or overpressure the setup is equipped with an emergency stop switch at $T_{\text{stop}} = 220\text{ °C}$ and a pressure relief valve ($p_{\text{relief}} = 35\text{ bar}$). For measurements at temperatures above 100 °C an initial pressure of 25 bar is applied using an external pressure pump to avoid evaporation of the aqueous samples. Thus, the sample solutions are kept at conditions below the vapour pressure of water at 200 °C ($p_{\text{vapor}}(200\text{ °C}) = 15.53\text{ bar}$).

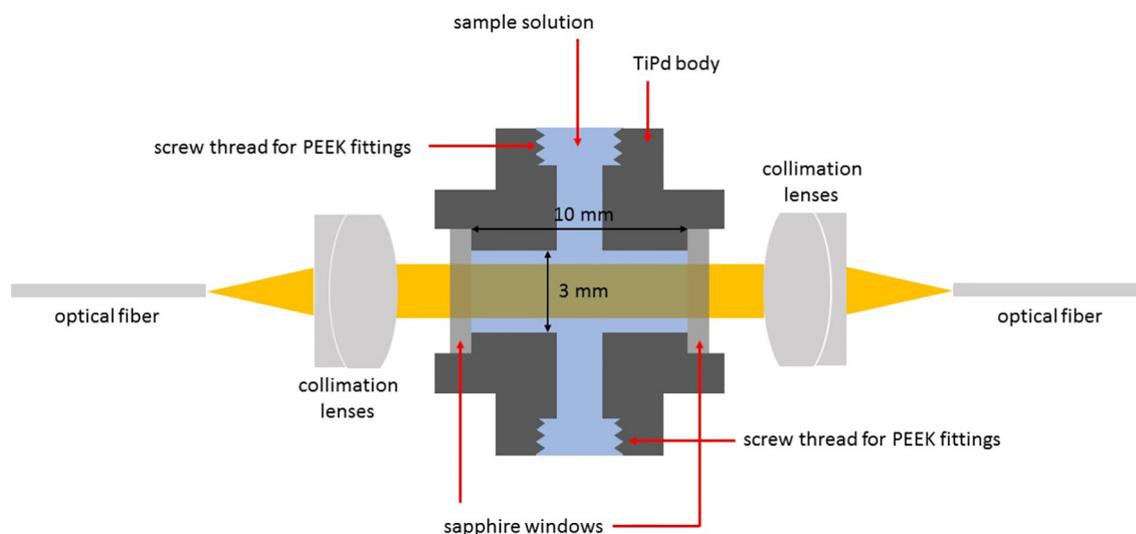


Fig. 1. Scheme of the experimental setup of the high-temperature and high-pressure cell with optical components.

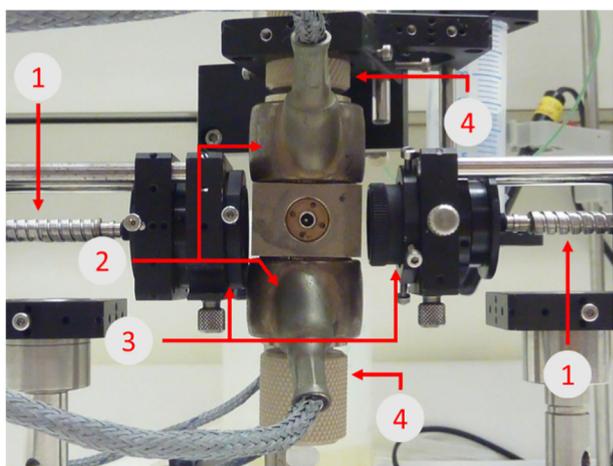


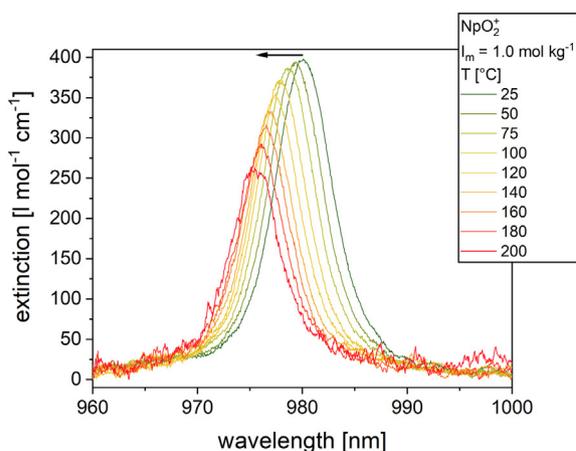
Fig. 2. Picture of the high-temperature and high-pressure cell with optical fibers, collimation lenses and PEEK fittings. (1) optical fiber, (2) heating sleeves with J-thermocouples, (3) collimation lenses, (4) PEEK fittings with valves.

Based on the prototype of the high temperature and high pressure cell, originally developed for time resolved laser fluorescence spectroscopy, some modifications were made for its applicability for absorption spectroscopy [17]. For measurements in the Vis/NIR region the cell is equipped with four sapphire windows. Two quartz glass fibers with a diameter of 600 μm optimized for Vis/IR and temperatures up to 200 $^{\circ}\text{C}$ were connected to the spectrophotometer and the experimental setup for optical coupling (Lobtek GmbH&Co.KG, type: LLA 600/660IRST/2000 FSMA VA). At the connection to the high temperature cell collimation lenses were used to correct the aperture (0.2) of the optical fibers to obtain a parallel beam with a diameter of 3 mm used for excitation of the samples. At the connection to the spectrophotometer a coupling unit with parabolic mirrors is used provided by Agilent Technologies. A picture of the experimental setup is shown in Fig. 2.

3. Results and discussion

3.1. Absorption spectra

Prior to the complexation studies with sulfate, the absorption spectra of the Np(V) aquo ion are recorded in the temperature range of 25–200 $^{\circ}\text{C}$ using the new experimental setup to determine the spectroscopic characteristics of the Np(V) ion up to 200 $^{\circ}\text{C}$. In Fig. 3 (left) the spectra are displayed as a function of the temperature at $I_m =$



1.0 mol kg^{-1} NaClO_4 . With increasing temperature a successive hypsochromic shift of the absorption band from 980.1 ± 0.2 nm to 975.2 ± 0.6 is observed accompanied by a decrease of the molar attenuation coefficient from $\epsilon_{25\text{ }^{\circ}\text{C}} = 398 \pm 12$ l mol^{-1} cm^{-1} to $\epsilon_{200\text{ }^{\circ}\text{C}} = 264 \pm 60$ l mol^{-1} cm^{-1} . In Fig. 3 (right) the position of the absorption band is correlated to the temperature and compared to literature values obtained in quartz glass cuvettes [13]. With increasing temperature a linear hypsochromic shift of -0.027 ± 0.003 nm K^{-1} is observed which is in excellent agreement with our previous results obtained in quartz glass cuvettes where a shift of -0.026 ± 0.006 nm K^{-1} was observed up to 85 $^{\circ}\text{C}$ [13,22,23].

In Fig. 4 (left) the effect of the ionic strength $I_m = [\text{NaClO}_4]$ on the absorption band of the Np(V) aquo ion is displayed for 25 $^{\circ}\text{C}$. With increasing ionic strength the absorption band shifts hypsochromically while the molar attenuation coefficient remains constant. In Fig. 4 (right) the hypsochromic shift of the absorption band of the Np(V) aquo ion is correlated to I_m at 25 and 200 $^{\circ}\text{C}$. At both temperatures comparable hypsochromic shifts of -0.21 ± 0.02 nm kg mol^{-1} NaClO_4 at 20 $^{\circ}\text{C}$ and -0.19 ± 0.03 nm kg mol^{-1} NaClO_4 at 200 $^{\circ}\text{C}$ are observed. Our results show that regardless of the temperature the hypsochromic shift induced by increasing ionic strengths is constant. In the literature an ionic strength dependence of -0.2 nm kg mol^{-1} NaClO_4 is reported which is in excellent agreement with the present results [13,24].

In the present work the effect of increasing temperature and increasing ionic strength in the temperature range up to 200 $^{\circ}\text{C}$ is studied for the first time. It is known that increasing temperatures and increasing ionic strengths affect the position of the absorption band of the Np(V) ion resulting both in a hypsochromic shift of the spectrum whereas the FWHM (Full Width at Half Maximum) and molar attenuation coefficient remain largely unaffected [13,22–30]. According to the literature, these effects are attributed to changes in the outer hydration sphere of the Np(V) ion, temperature induced changes of the metal ligand bonds or changes of the solvent's polarizability. A precise determination of the hypsochromic shift parameters of the absorption spectra of each complex species up to 200 $^{\circ}\text{C}$ is of particular importance for the correct evaluation of the spectra and the precise determination of the species distributions and thermodynamic functions ($\log \beta_i^0(T)$, $\Delta_r H_m^0$, $\Delta_r S_m^0$).

In Fig. 5 the absorption spectra of Np(V) at increasing total sulfate concentration $[\text{SO}_4^{2-}]_{\text{total}}$ are displayed at 25, 75, 140 and 200 $^{\circ}\text{C}$. With increasing $[\text{SO}_4^{2-}]_{\text{total}}$ a bathochromic shift of the spectra occurs which is fostered at increasing temperature. Furthermore, only one isosbestic point is observed at all experimental conditions indicating that only one Np(V) SO_4^{2-} species is formed up to 200 $^{\circ}\text{C}$ and $I_m \leq 4.0$ mol kg^{-1} NaClO_4 . With increasing temperature the isosbestic point is

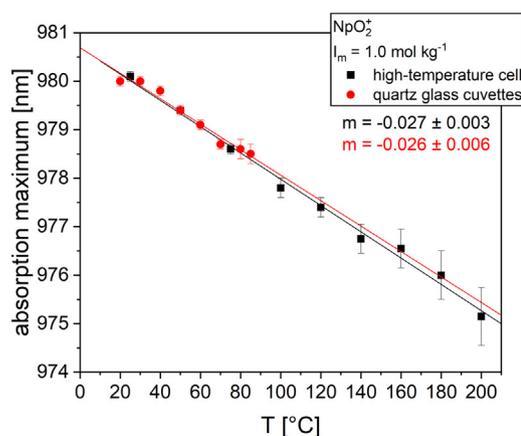


Fig. 3. Absorption spectra of the Np(V) aquo ion as a function of the temperature ($I_m = 1.0$ mol kg^{-1}) (left) and hypsochromic shifts of the absorption band with increasing temperature obtained by measurements in the high-temperature cell and in quartz glass cuvettes (right) [13].

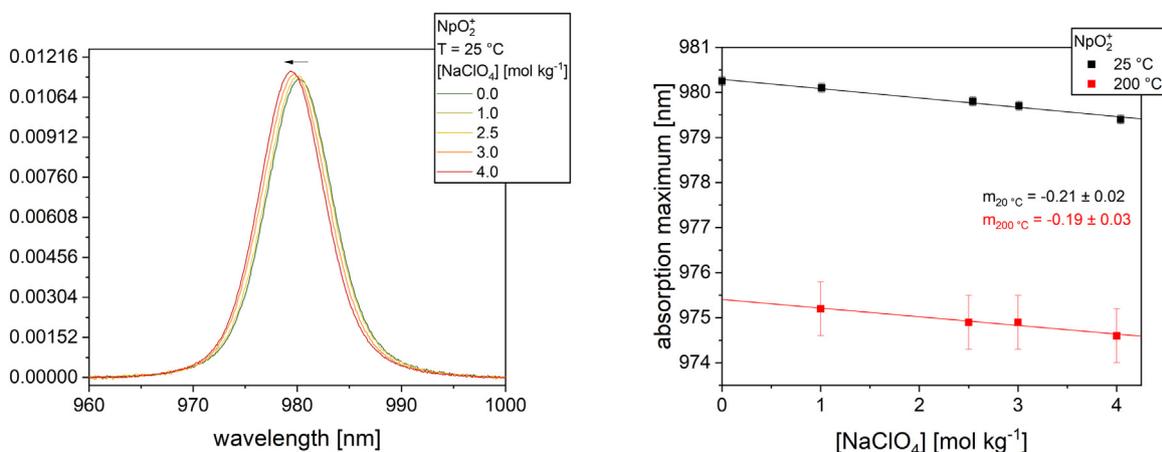


Fig. 4. Absorption spectra of the Np(V) aquo ion as a function of the ionic strength ($T = 25\text{ }^{\circ}\text{C}$) (left) and the hypsochromic shift of the absorption band with increasing ionic strength at 25 and 200 $^{\circ}\text{C}$ (right).

hypsochromically shifted by $0.023 \pm 0.002\text{ nm K}^{-1}$ which is in excellent agreement with the temperature dependence of the spectrum of the Np(V) aquo ion.

3.2. Peak deconvolution and speciation

The single component spectrum of the formed Np(V) SO_4^{2-} complex is obtained by subtractive peak deconvolution of the experimental spectra using the spectrum of the Np(V) aquo ion at the same experimental conditions. Due to the contrary effects of the temperature and ionic

strength induced blue shift and the bathochromic shift caused by the complexation of Np(V) with sulfate each series of spectra has to be treated separately, and single component spectra have to be determined for all experimental temperature and ionic strength conditions.

The spectra of the Np(V) SO_4^{2-} complex and of the Np(V) aquo ion at 25, 100 and 160 $^{\circ}\text{C}$ and $I_m = 1.0\text{ mol kg}^{-1}\text{ NaClO}_4$ are displayed in Fig. 6. The spectrum of the Np(V) SO_4^{2-} complex is bathochromically shifted by $4.1 \pm 0.4\text{ nm}$ relative to the Np(V) aquo ion. This shift is independent of the experimental conditions. Furthermore, the integrated attenuation coefficients of the single component spectra remain constant with

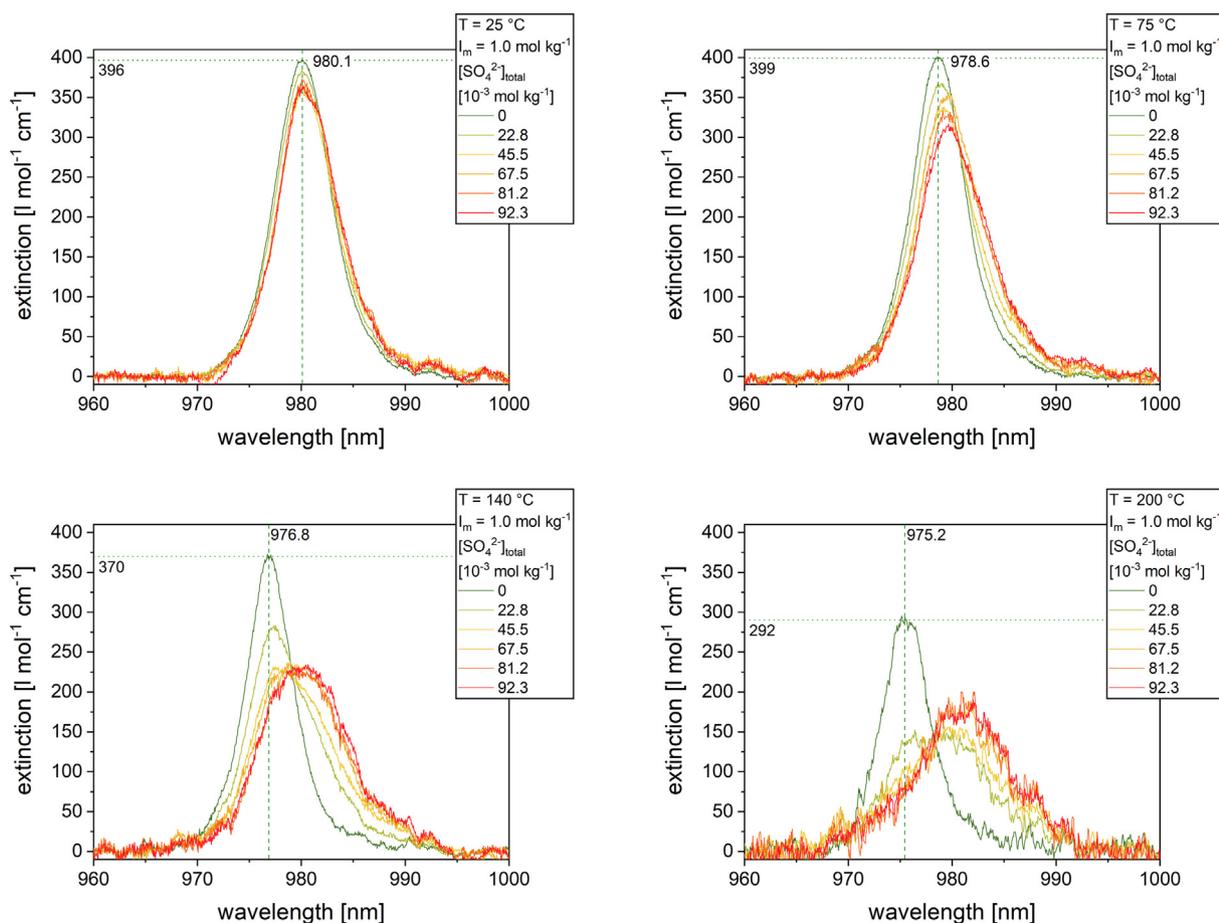


Fig. 5. Absorption spectra of Np(V) as a function of $[\text{SO}_4^{2-}]_{\text{total}}$ at 25, 75, 140 and 200 $^{\circ}\text{C}$ and $I_m = 1.0\text{ mol kg}^{-1}$.

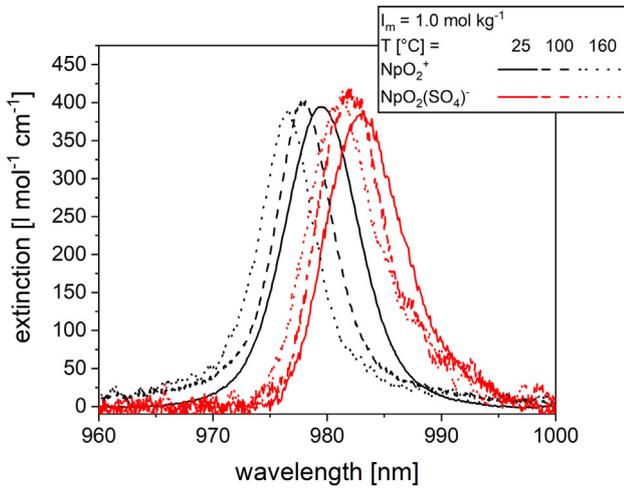


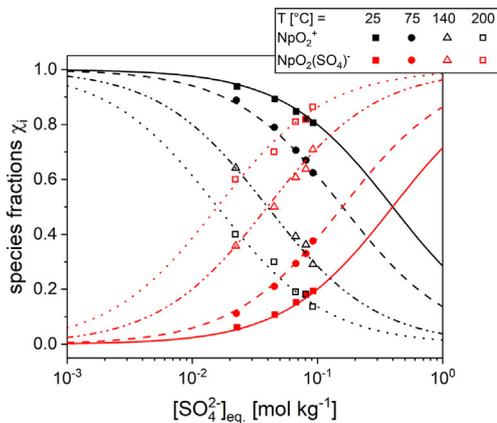
Fig. 6. Single component spectra of the Np(V) aquo ion and the $\text{NpO}_2(\text{SO}_4)^-$ complex at 25 °C, 100 °C and 160 °C and $I_m = 1.0 \text{ mol kg}^{-1}$.

increasing temperature or ionic strength. The observed changes in ϵ_{max} are within the error range of the deconvolution.

The entire data set of the experimental absorption spectra is evaluated by principle component analyses using the temperature dependent single component spectra. Details on this procedure are given in the literature [16].

The experimental distribution (dots) of the formed Np(V) species and the calculated speciation (lines) using the derived $\log \beta'_1(T)$ values (see table S1 in the SI) as a function of the equilibrium sulfate concentration $[\text{SO}_4^{2-}]_{\text{eq}}$ are displayed in Fig. 7 (left) for 25, 75, 140 and 200 °C. With increasing $[\text{SO}_4^{2-}]_{\text{eq}}$ the complexation reaction shifts toward the Np(V) sulfate complex and the formation is fostered at elevated temperatures. This indicates an endothermic complexation reaction.

The equilibrium sulfate concentration $[\text{SO}_4^{2-}]_{\text{eq}}$ in solution is calculated as a function of the temperature and ionic strength according to literature procedure using the Henderson Hasselbalch equation (Eq. (6)) [16]. In this context, the mass balances of the total SO_4^{2-} (Eq. (2)) and total H^+ (Eq. (3)) are required. The $\log K'_{\text{HSO}_4}(T)$ are taken from the literature [31–34]. The temperature dependence of $\log K'_{\text{HSO}_4}(T)$ is calculated using the integrated Van't Hoff equation (Eq. (6)) and the ionic strength effects are accounted for by the SIT revealing the conditional $\log K'_{\text{HSO}_4}(T)$ values [1].



$$[\text{SO}_4^{2-}]_{\text{eq}} = \frac{[\text{H}^+]_{\text{total}} + [\text{SO}_4^{2-}]_{\text{total}} K'_{\text{HSO}_4}(T) + \sqrt{([\text{H}^+]_{\text{total}} + [\text{SO}_4^{2-}]_{\text{total}} K'_{\text{HSO}_4}(T))^2 + 4K'_{\text{HSO}_4}(T) \cdot [\text{SO}_4^{2-}]_{\text{total}}}}{2} \quad (1)$$

$$[\text{SO}_4^{2-}]_{\text{total}} = [\text{SO}_4^{2-}]_{\text{eq}} + [\text{HSO}_4^-]_{\text{eq}} \quad (2)$$

$$[\text{H}^+]_{\text{total}} = [\text{H}^+]_{\text{eq}} + [\text{HSO}_4^-]_{\text{eq}} \quad (3)$$

The single component spectra and the stoichiometry of the formed complex are verified by slope analyses at each temperature and ionic strength condition according to Eqs. (4) and (5).

$$\beta'_n = \frac{[\text{NpO}_2(\text{SO}_4)_n]^{1-2n}}{[\text{NpO}_2^{2+}] \cdot ([\text{SO}_4^{2-}]_{\text{eq}})^n} \quad (4)$$

$$\log \frac{[\text{NpO}_2(\text{SO}_4)_n]^{1-2n}}{[\text{NpO}_2^{2+}]} = \log \beta'_n + n \log [\text{SO}_4^{2-}]_{\text{eq}} \quad (5)$$

The slope of the linear regression analyses of the molar ratios of the formed complexes $\log \frac{[\text{NpO}_2(\text{SO}_4)_n]^{1-2n}}{[\text{NpO}_2^{2+}]}$ versus $\log [\text{SO}_4^{2-}]_{\text{eq}}$ reveals the information on the number of coordinating SO_4^{2-} ions. Fig. 7 (right) shows the slope analyses for 25, 75, 140 and 200 °C. At all temperature and ionic strength conditions a linear correlation is observed and linear regression analyses reveal slopes between 0.8 ± 0.3 and 1.1 ± 0.2 (compare table S2 in the SI). Thus, the exclusive formation of $\text{NpO}_2(\text{SO}_4)^-$ is confirmed up to 200 °C and $I_m \leq 4.0 \text{ mol kg}^{-1} \text{ NaClO}_4$. The obtained slopes do not suggest the formation of higher complex species. In agreement to the present result, the exclusive formation of $\text{NpO}_2(\text{SO}_4)^-$ was also reported in numerous literature studies using absorption spectroscopy, EXAFS and solvent extraction [1,6,7,9,11,23,35,36]. However, these studies were limited to temperatures below $T \leq 85 \text{ °C}$ and data at $T = 100 \text{ °C}$ were missing.

3.3. Thermodynamic data

The $\log \beta'_1(T)$ values for the formation of $\text{NpO}_2(\text{SO}_4)^-$ at various ionic strengths and temperatures are calculated according to the law of mass action (Eq. (4)). Then, the conditional stability constants are extrapolated to $I_m = 0$ with the specific ion interaction theory (SIT) by plotting $\log \beta'_1(T) - \Delta z^2 D(T)$ versus I_m as recommended by the NEA TDB [1,3]. In Fig. 8 the SIT plots at different temperatures are displayed.

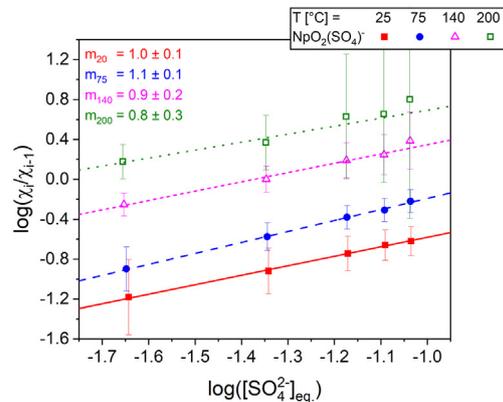


Fig. 7. (left) Experimental species distribution (dots) and calculated speciation (lines) using the derived conditional stability constants $\log \beta'_1(T)$ of Np(V)-sulfate complexes as a function of $[\text{SO}_4^{2-}]_{\text{eq}}$; (right) corresponding slope analyses. $I_m = 1.0 \text{ mol kg}^{-1} \text{ NaClO}_4$; $T = 25, 75, 140, 200 \text{ °C}$.

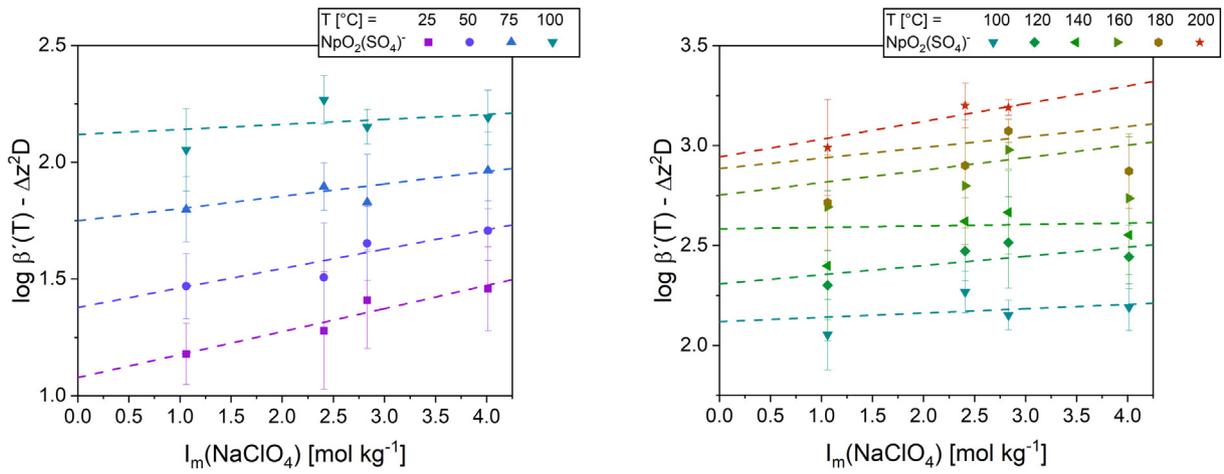


Fig. 8. Extrapolation of $\log \beta'_1(T) - \Delta z^2 D$ to $I_m = 0$ according to the SIT at various temperatures in NaClO_4 medium. (left) $T = 25\text{--}100\text{ }^\circ\text{C}$; (right) $T = 100\text{--}200\text{ }^\circ\text{C}$.

For all temperatures a linear correlation of $\log \beta'_1(T) - \Delta z^2 D(T)$ versus I_m is observed and the $\log \beta_1^0(T)$ values are obtained from linear extrapolations to $I_m = 0$.

With increasing temperature $\log \beta_1^0(25\text{ }^\circ\text{C}) = 1.05 \pm 0.16$ increases to $\log \beta_1^0(200\text{ }^\circ\text{C}) = 2.94 \pm 0.46$ displaying a linear correlation of $\log \beta_1^0(T)$ to the reciprocal temperature T^{-1} (see Fig. 9). The standard reaction enthalpy $\Delta_r H_{1,m}^0$ and entropy $\Delta_r S_{1,m}^0$ for the formation of $\text{NpO}_2(\text{SO}_4)^-$ are calculated with the integrated Van't Hoff equation by linear regression analyses according to Eq. (6) [37].

$$\log \beta_n^0(T) = \log \beta_n^0(T_0) + \frac{\Delta_r H_{n,m}^0(T_0)}{R \ln(10)} \left(\frac{1}{T_0} - \frac{1}{T} \right) \quad (6)$$

R is the universal gas constant, $T_0 = 298.15\text{ K}$ is the temperature of the IUPAC reference state, and T the absolute temperature. In general, the integrated Van't Hoff equation can be applied only in a small temperature range of ΔT b 100 K, where the temperature dependence of $\Delta_r H_{n,m}^0$ is negligible. The temperature dependence of $\Delta_r H_{n,m}^0$ is expressed as a function of the molal reactions heat capacity $\Delta_r C_{p,m}^0$ according to Eq. (7) [37].

$$\Delta_r H_{n,m}^0(T) = \Delta_r H_{n,m}^0(T_0) + \int_{T_0}^T \Delta_r C_{p,m}^0 dT \quad (7)$$

A significant temperature dependence of $\Delta_r H_{n,m}^0$ results in a nonlinear correlation of $\log \beta_1^0(T)$ versus T^{-1} . In case of our data a linear

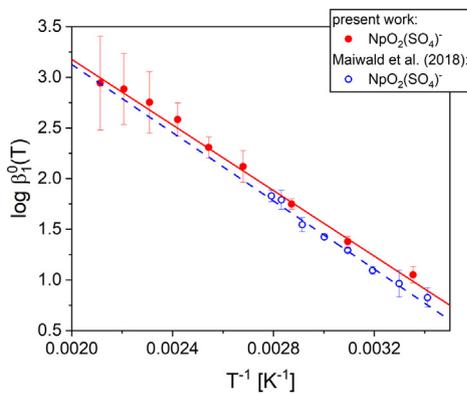


Fig. 9. Plot of $\log \beta_1^0(T)$ versus T^{-1} and fitting according to the integrated van't Hoff equation (Eq. (6)) and comparison with previous results obtained in quartz glass cuvettes [13].

correlation is observed up to $200\text{ }^\circ\text{C}$. Thus, $\Delta_r C_{p,m}^0$ is close to zero and $\Delta_r H_{n,m}^0$ is mainly independent of the temperature in the temperature range studied.

The standard reaction enthalpy is $\Delta_r H_{n,m}^0 = 31.0 \pm 1.0\text{ kJ mol}^{-1}$ and confirms the endothermic complexation reaction observed in the species distributions at increasing temperature. The standard reaction entropy is $\Delta_r S_{n,m}^0 = 123 \pm 9\text{ J mol}^{-1}\text{ K}^{-1}$, proving that the complexation reaction is driven by the high gain of entropy. The $\Delta_r H_{n,m}^0$ and $\Delta_r S_{n,m}^0$ values are summarized in Table 1.

In Fig. 9 the $\log \beta_1^0(T)$ values up to $200\text{ }^\circ\text{C}$ are additionally compared to our previous data obtained in quartz glass cuvettes in the temperature range up to $85\text{ }^\circ\text{C}$ [13]. Between 20 and $85\text{ }^\circ\text{C}$ the results of both studies are in excellent accordance, revealing exactly the same temperature dependence of the complexation reaction.

The results of the present work at $25\text{ }^\circ\text{C}$ are also in excellent agreement with the literature values reported by Rao et al. using spectrophotometry and solvent extraction (see Table 1) [6,14]. In comparison, the extrapolated values given in the NEA TDB are significantly lower [1]. Due to this discrepancy, the data reported in the NEA TDB have to be re-evaluated. More thermodynamic data at IUPAC reference state conditions are not available, in particular not for $T_N 100\text{ }^\circ\text{C}$.

In addition to the thermodynamic data, the sum of the specific binary ion-ion interaction coefficients ($\Delta \varepsilon_{01}(T)$) are obtained from linear fitting of $\log \beta'_1(T) - \Delta z^2 D(T)$ versus I_m according to the SIT in the temperature range between 25 and $200\text{ }^\circ\text{C}$. The $\Delta \varepsilon_{01}(T)$ values are displayed in Fig. 10 as a function of the temperature and are compared to our previous values up to $85\text{ }^\circ\text{C}$ [13]. With increasing temperature up to $100\text{ }^\circ\text{C}$ a slight increase of $\Delta \varepsilon_{01}(T)$ is observed in accordance to the literature data. For $T_N 100\text{ }^\circ\text{C}$ a further increase of the temperature does not result in an additional increase of $\Delta \varepsilon_{01}(T)$ and the values scatter around an arithmetic mean value. Regarding the error range of the data, the increase of $\Delta \varepsilon_{01}(T)$ between 25 and $200\text{ }^\circ\text{C}$ should not be overinterpreted. Therefore, an average temperature-independent value $\Delta \varepsilon_{01} = -0.06 \pm 0.08$ is used for calculating the binary ion-ion interaction coefficient $\varepsilon(\text{Na}^+$,

Table 1

Thermodynamic data for the formation of $[\text{NpO}_2(\text{SO}_4)]^-$ ($\log \beta_1^0(25\text{ }^\circ\text{C})$, $\Delta_r H_{1,m}^0$, $\Delta_r S_{1,m}^0$) and comparison with literature data.

Method/data base	$\log \beta_1^0(25\text{ }^\circ\text{C})$	$\Delta_r H_{1,m}^0$ [kJ mol ⁻¹]	$\Delta_r S_{1,m}^0$ [J mol ⁻¹ K ⁻¹]	Reference
sp	1.05 ± 0.16	31.0 ± 1.0	123 ± 9	p.w.
sp	0.92 ± 0.13	30.3 ± 2.8	119 ± 9	[13]
NEA-TDB	0.44 ± 0.27	23.2 ± 7.2	86.2 ± 24.6	[1]
sp	1.03 ± 0.25			[6]
sx	0.97			[14]

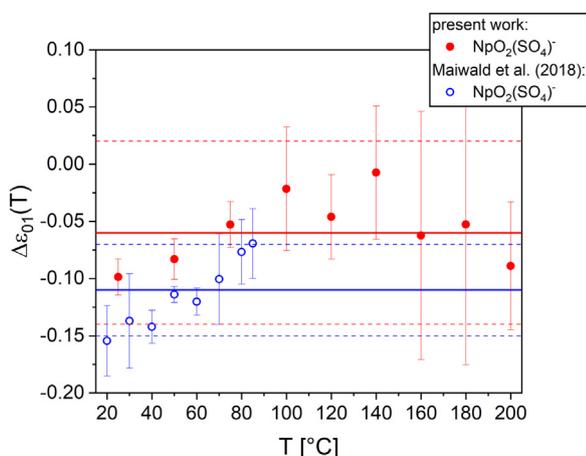


Fig. 10. $\Delta\varepsilon$ values for the formation of $[\text{NpO}_2(\text{SO}_4)]^-$ as a function of temperature and comparison with previous results obtained in quartz glass cuvettes [13].

$\text{NpO}_2(\text{SO}_4)^-$, with $\varepsilon(\text{Na}^+, \text{SO}_4^{2-}) = -0.12 \pm 0.06$ and $\varepsilon(\text{NpO}_2^+, \text{ClO}_4^-) = 0.25 \pm 0.05$ given in the NEA TDB: [1,3].

$$\varepsilon(\text{Na}^+; \text{NpO}_2(\text{SO}_4)^-) = \Delta\varepsilon_{01} + \varepsilon(\text{Na}^+; \text{SO}_4^{2-}) + \varepsilon(\text{NpO}_2^+; \text{ClO}_4^-)$$

$$0.07 \pm 0.11$$

This result is in excellent agreement with our recently published value: $\varepsilon(\text{Na}^+, \text{NpO}_2(\text{SO}_4)^-)_{25^\circ\text{C}} = 0.02 \pm 0.19$ [13].

4. Summary and conclusion

For the first time the complexation of the Np(V) ion with sulfate is studied up to 200 °C by absorption spectroscopy. In order to determine thermodynamic functions ($\log \beta_1^0(T)$, $\Delta_r H_m^0$, $\Delta_r S_m^0$) of the Np(V) complexation at $T \leq 100$ °C a new experimental setup is implemented for absorption spectroscopic measurements in this temperature range. The results show the exclusive formation of one complex species up to 200 °C, which is identified as $\text{NpO}_2(\text{SO}_4)^-$. With increasing temperature the formation of $\text{NpO}_2(\text{SO}_4)^-$ is fostered and the thermodynamic stability constant increases from $\log \beta_1^0(25^\circ\text{C}) = 1.05 \pm 0.16$ to $\log \beta_1^0(200^\circ\text{C}) = 2.94 \pm 0.46$. Furthermore, the determined $\log \beta_1^0(T)$ values correlate linearly with the reciprocal temperature and the integrated Van't Hoff equation is applied to calculate the standard reaction enthalpy and entropy ($\Delta_r H_m^0$, $\Delta_r S_m^0$) of the complexation reaction. The reaction is endothermic ($\Delta_r H_m^0 = 31.0 \pm 1.0 \text{ kJ mol}^{-1}$) and driven by the entropy gain ($\Delta_r S_m^0 = 123 \pm 9 \text{ J mol}^{-1} \text{ K}^{-1}$). In addition, the applicability of the integrated Van't Hoff equation reveals that the heat capacity of the reaction $\Delta_r C_{p,m}^0$ is close to zero. The $\Delta\varepsilon_{01}(T)$ values for the reaction $\text{NpO}_2^+ + \text{SO}_4^{2-} \rightleftharpoons \text{NpO}_2(\text{SO}_4)^-$ are determined by linear SIT plots as a function of the temperature showing no significant temperature dependence of $\Delta\varepsilon_{01}(T)$. Thus, a temperature independent $\varepsilon(\text{Na}^+, \text{NpO}_2(\text{SO}_4)^-) = 0.07 \pm 0.11$ is calculated for the temperature range up to 200 °C. The above listed thermodynamic functions ($\log \beta_1^0(T)$, $\Delta_r H_m^0$, $\Delta_r S_m^0$, $\Delta\varepsilon_{01}(T)$) are the first data available for the Np(V) complexation in the temperature range up to 200 °C.

The results of the present work are in excellent agreement with literature data for $T \leq 85$ °C [6,13,14]. Thus, the new spectroscopic setup allows highly sensitive and reproducible absorption spectroscopic studies on the complexation of Np(V) in aqueous solution and the determination of reliable thermodynamic functions up to 200 °C. This opens up new access to studies of the (geo)chemical behaviour of actinides at high temperature conditions which might occur in the direct vicinity of a nuclear waste repository emplaced in salt rock formations in the first period of the postclosure. At these temperature conditions the

chemical behaviour of the actinides changes considerably and reactions might gain in importance, which are negligible at ambient temperatures [18].

In case of the trivalent actinides the stability constants of complexation reactions with weakly coordinating ligands such as nitrate, chloride and sulfate increase by several orders of magnitude in the temperature range of 20–200 °C [16–19]. In the present work a similar increase of the complexation strength of Np(V) toward sulfate by two orders of magnitude is confirmed. Therefore, the data of the present work provide important information on the chemical behaviour of pentavalent actinide ions in aqueous solution at high temperature conditions ($T \leq 100$ °C) and are a valuable contribution to the thermodynamic databases of actinide elements to be used for the development of thermodynamic based models within the safety case of a nuclear waste repository.

CRedIt authorship contribution statement

Martin M. Maiwald: Methodology, Validation, Formal analysis, Investigation, Writing original draft, Visualization. **Andrej Skerencak-Frech:** Writing review & editing, Supervision. **Petra J. Panak:** Funding acquisition; Project administration; Supervision; Writing review & editing

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.saa.2020.118579>.

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