

# The complexation of neptunium(V) with fluoride at elevated temperatures: Speciation and thermodynamics

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The complexation of  $\text{NpO}_2^+$  with fluoride is studied in aqueous solution using Vis/NIR absorption spectroscopy. The total ligand concentration (NaF), ionic strength ( $\text{NaClO}_4$ ), and temperature ( $T = 20\text{--}85^\circ\text{C}$ ) is varied, yielding detailed information on the thermodynamics of the complexation reaction. Two distinct complex species ( $\text{NpO}_2\text{F}_n^{1-n}$ ,  $n = 1, 2$ ) are identified by peak deconvolution of the absorption spectra. At  $20^\circ\text{C}$  and  $I_m = 1.0$  the absorption band of  $\text{NpO}_2\text{F}$  is located at  $983.8 \pm 0.2$  nm. The absorption band of the  $\text{NpO}_2\text{F}_2^-$  complex is located at  $988.4 \pm 0.2$  nm. With increasing temperature and ionic strength the chemical equilibrium of the complexation reaction shifts towards the complexed Np(V) species. The conditional stability constants  $\log \beta'_n(T)$  are calculated according to the law of mass action and are extrapolated to  $I_m = 0$  for each temperature with the specific ion interaction theory (SIT). The determined  $\log \beta_n^0(T)$  values increase by 0.2–0.6 in the studied temperature range. Furthermore, the  $\log \beta_n^0(T)$  values correlate linearly with the reciprocal temperature and fitting the data according to the integrated Van't Hoff equation yields the standard reaction enthalpies ( $\Delta_r H_m^0$ ) and entropies ( $\Delta_r S_m^0$ ). The reactions are endothermic and are solely driven by the high gain of entropy. In addition, the binary SIT ion-ion interaction coefficient  $\epsilon_{j,k}$  of the respective complex species are determined.

## 1. Introduction

The disposal of highly active nuclear waste is still a pressing topic in countries using nuclear fission for electrical power generation. Besides uranium and fission products, plutonium and minor actinides (Np, Am, Cm) are present in the waste due to neutron capture reactions in the reactor. Due to their long half-lives, these radionuclides contribute mainly to the long-term radiotoxicity and long-term heat load of the nuclear waste. Thus, an effective isolation of the high-level nuclear waste from the biosphere is required over very long timescales. Worldwide it is considered that the waste will be stored in deep geological formations. For the safety case of a nuclear waste repository, different incident scenarios are considered. One of the most important scenario is the intrusion of water and subsequent dissolution of the radioactive waste. Reactions at liquid-solid interfaces (e.g. dissolution of the waste matrix, sorption processes, etc.) and complexation reactions in the aqueous phase can influence the geochemistry and migration behaviour of the actinides considerably. Thus, detailed knowledge of these processes, based on thermodynamic data such as standard-state stability constants ( $\log \beta_n^0$ ), standard reaction enthalpies ( $\Delta_r H^0$ ) and entropies ( $\Delta_r S^0$ ) are required.

The early actinides U – Am exist as An(III) to An(VI) within the thermodynamic stability field of water. Within the An(V) series the pentavalent Np(V) is thermodynamically most stable and highly soluble in aqueous solution. Thus, numerous studies on the complexation of Np(V) with inorganic ligands in natural ground waters (e.g.  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ , etc.) were performed (Guillaumont et al., 2003; Hummel et al., 2002; Lemire, 2001). However, in the literature most data are limited to ambient temperatures and/or fixed ionic strengths and thermodynamic functions at IUPAC reference state conditions are missing for a number of systems.

In some countries, salt rock formations are in discussion for a final nuclear waste repository. In this case, the geochemical behaviour of the actinides in diluted and concentrated brines is of particular interest to model their migration behaviour in the near- and far-field of the repository.

Fluoride is an integral part of salt rock formations, and natural brines exhibit fluoride concentrations up to  $10^{-2}$  mol  $\text{kg}^{-1}$   $\text{H}_2\text{O}$ . In the past considerable effort was made to study the complexation of different actinides with fluoride by absorption spectroscopy, solvent extraction and calorimetry. In the case of Np(V) controversial results on the speciation of fluoride complexes are reported in the literature (Xia

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et al., 2006; Tian et al., 2009; Rao et al., 2006; Al-Niaimi et al., 1970). Depending on the experimental method used for the determination of the solution speciation of the Np(V) fluoride complexes either different complex stoichiometries are obtained or significant deviations between the reported stability constants are observed (Lemire, 2001).

In the present work the complexation of Np(V) with fluoride as a function of temperature ( $T = 20\text{--}85\text{ }^{\circ}\text{C}$ ) and ionic strength ( $I_m = 0.5\text{--}3.0\text{ mol kg}^{-1}\text{ NaClO}_4$ ) is studied by near-infrared (NIR) absorption spectroscopy. Application of the specific ion interaction theory (SIT) and the integrated Van't Hoff equation yields the temperature dependent standard-state stability constants ( $\log \beta_n^0(T)$ ) and thermodynamic functions  $\Delta_r H^0$  and  $\Delta_r S^0$  of the different complexation reactions and the binary ion-ion interaction parameters  $\epsilon_T(i,k)$  of the different Np(V) species.

## 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") to avoid changes of the concentration due to changes of the solution density induced by increasing temperature or electrolyte concentration. The chemicals used for the preparation of the solutions were reagent grade or higher and purchased from Merck Millipore. The sodium fluoride salt was of Suprapur<sup>®</sup> grade. Ultrapure water (Milli-Q academic, Millipore) was used for sample preparation. An isotope pure  $^{237}\text{Np(V)}$  stock solution ( $5.9 \times 10^{-3}\text{ mol kg}^{-1}\text{ H}_2\text{O}$ ) was used to prepare the samples with an initial Np(V) concentration of  $7.4 \times 10^{-4}\text{ mol kg}^{-1}\text{ H}_2\text{O}$ . The oxidation state of Np in the stock solution was validated by absorption spectroscopy (Np(V):  $\lambda_{\text{max}} = 980\text{ nm}$ ,  $\epsilon_{\text{max}} = 395\text{ l mol}^{-1}\text{ cm}^{-1}$ ). Details on the preparation of the Np(V) stock solution is given elsewhere (Fellhauer et al., 2016). The total proton concentration in the samples was adjusted to  $[\text{H}]_{\text{total}}^+ = 5.0 \times 10^{-5}\text{ mol kg}^{-1}\text{ H}_2\text{O}$  by addition of small aliquots of a 0.02 and 0.2  $\text{mol kg}^{-1}\text{ HClO}_4$  diluted from a 70%  $\text{HClO}_4$ . The concentration of the used  $\text{HClO}_4$  was verified by titration with a 0.1 N NaOH (Merck Titripur) using a Metrohm 686 Titroprocessor equipped with a Metrohm 665 Dosimat. The fluoride concentration was increased by successive titration. The titration solutions were prepared by dissolving solid NaF in water with a proton concentration identical to that of the samples. Three different titration series at ionic strengths of  $I_m(\text{NaClO}_4) = 0.5, 1.0,$  and  $1.8\text{ mol kg}^{-1}\text{ H}_2\text{O}$  were performed with increasing  $[\text{F}^-]$  concentration at room temperature. The ionic strength of the samples and the titration solutions were adjusted by addition of aliquots of a saturated  $\text{NaClO}_4$  solution. Saturation of the  $\text{NaClO}_4$  solution was checked by ICP-OES. Additionally, the titration series at  $I_m(\text{NaClO}_4) = 1.0\text{ mol kg}^{-1}\text{ H}_2\text{O}$  with increasing  $[\text{F}^-]$  concentration was performed at various temperatures ( $T = 20\text{--}85\text{ }^{\circ}\text{C}$ ). Furthermore, two series of samples were prepared at fixed ligand concentrations ( $[\text{F}^-]_{\text{tot}} = 9.0 \times 10^{-2}, 1.4 \times 10^{-1}\text{ mol kg}^{-1}\text{ H}_2\text{O}$ ) and increasing concentrations of  $\text{NaClO}_4$  at variable temperatures. The concentration of  $\text{NaClO}_4$  was adjusted by addition of aliquots of an aqueous  $14.3\text{ mol kg}^{-1}\text{ H}_2\text{O}\text{ NaClO}_4$  solution prepared from a saturated  $\text{NaClO}_4$  solution. The absorption spectra were recorded at  $T = 20\text{--}85\text{ }^{\circ}\text{C}$ .

### 2.2. NIR absorption spectroscopy

Spectrophotometric measurements were conducted in the wavelength range of  $\lambda = 950\text{--}1050\text{ nm}$  using a Varian Cary-5G UV/Vis/NIR spectrophotometer. The temperature of the sample holder was set to  $T = 20, 30, 40, 50, 60, 70, 80,$  and  $85\text{ }^{\circ}\text{C}$  controlled by a Lauda Eco E100 thermostatic system. The cuvettes (quartz glass with air tight screw caps, 1 cm path length, Hellma Analytics) were pre-equilibrated at the respective temperatures in a custom-made sample holder. Each sample was tempered for 15 minutes to ensure chemical equilibrium before measurement. Spectra were recorded with 0.1 nm data intervals,

a scan rate of  $60\text{ nm min}^{-1}$  (average accumulation time: 0.1 s) and a slit width of 0.7 nm in double beam mode. The spectra of the single complex species and the stability constants of the Np(V)-F<sup>-</sup> complex were obtained by peak deconvolution and slope analyses of the molar fractions. Further information on this procedure is given in the literature (Vasiliev et al., 2015; Skerencak et al., 2009, 2010; Skerencak-Frech et al., 2014).

### 2.3. Solvent extraction

Liquid-liquid extraction was used to determine the oxidation state of Np before and after heating the samples up to  $85\text{ }^{\circ}\text{C}$ . 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one (PMBP) in xylene and di-(2-ethylhexyl) phosphoric acid (HDEHP) in toluene were used as diluents to separate Np (IV) and Np(IV, VI). Details on the extraction methods are given elsewhere (Schramke et al., 1989; Nitsche et al., 1987; Moore and Hudgens, 1957; Tasi et al., 2018).

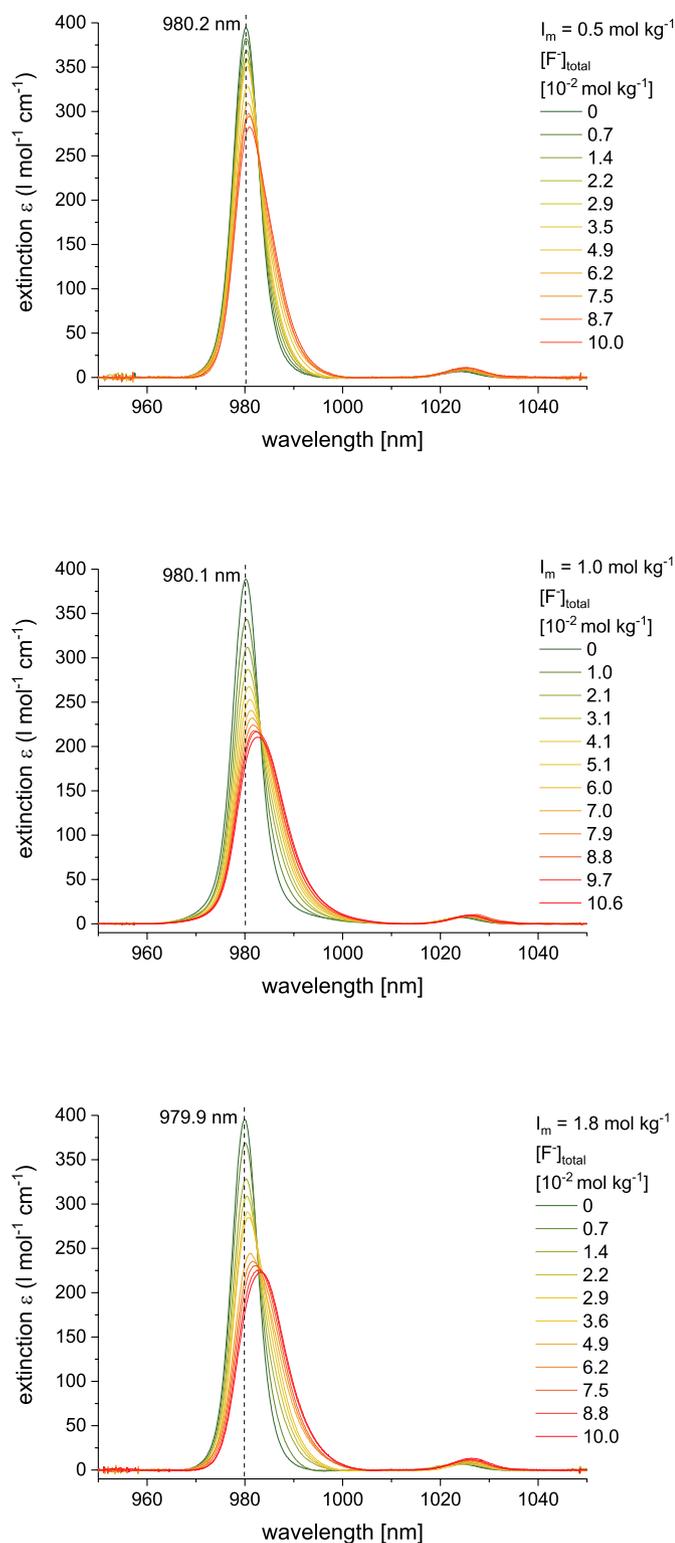
After each titration step and temperature cycle 20  $\mu\text{L}$  of the sample were diluted to 400  $\mu\text{L}$  in total and acidified to  $\text{pH} = 0$  with 400  $\mu\text{L}$   $2.0\text{ mol L}^{-1}\text{ HCl}$ . 50  $\mu\text{L}$  of this solution were added to 10 ml of LSC cocktail (Ultima Gold XR, Perkin Elmer) to determine the total Np concentrations. Subsequently, 750  $\mu\text{L}$  of 0.1 M HDEHP in toluene or 0.1 M PMBP in xylene were added to the remaining dilution. The extraction samples were shaken for 5 min. After the separation of the aqueous and organic phases, 20  $\mu\text{L}$  aliquots of the aqueous phases and 300  $\mu\text{L}$  aliquots of the organic phases were added to 10 mL of LSC cocktail. The concentration of the alpha emitting  $^{237}\text{Np}$  isotope was determined by LSC on a Quantulus 1220 LKB WallacOy (Perkin Elmer). The contribution of the daughter nuclide  $^{233}\text{Pa}$  in the LSC measurements is eliminated by  $\alpha/\beta$ -discrimination. This is automatically performed by the used Quantulus 1220 LKB WallacOy (Perkin Elmer).

## 3. Results and discussion

### 3.1. Absorption spectra

The absorption spectra of Np(V) at various ionic strengths as a function of the total  $[\text{F}^-]$  at  $T = 20\text{ }^{\circ}\text{C}$  are displayed in Fig. 1. At the lowest ionic strength of  $I_m(\text{NaClO}_4) = 0.5\text{ mol kg}^{-1}\text{ H}_2\text{O}$  the  $\text{NpO}_2(\text{H}_2\text{O})_5^+$  ion shows an absorption band at 980.2 nm. With increasing  $[\text{F}^-]$  the absorption band is bathochromically shifted accompanied with an increase of the Full Width at Half Maximum (FWHM) from 6.3 to 10.1 nm. The integrated molar attenuation coefficients  $\int \epsilon$  remains constant with increasing  $[\text{F}^-]$ . Furthermore, an isosbestic point at 982.7 nm is observed indicating the formation of a 1:1-Np(V)-F<sup>-</sup> complex species. At increased ionic strengths the absorption band of the Np(V) aquo ion shifts hypsochromically to 980.1 nm ( $I_m(\text{NaClO}_4) = 1.0\text{ mol kg}^{-1}\text{ H}_2\text{O}$ ) and 979.9 nm ( $I_m(\text{NaClO}_4) = 1.8\text{ mol kg}^{-1}\text{ H}_2\text{O}$ ). This corresponds to a linear hypsochromic shift of about  $0.2 \pm 0.04\text{ nm per } \Delta I_m = 1.0\text{ mol kg}^{-1}\text{ H}_2\text{O}$ . Similar hypsochromic shifts for the solvated Np(V) ion with increasing  $I_m$  are reported in the literature (see Table 1). (Maiwald et al., 2018a, 2018b) The molar attenuation coefficient  $\epsilon_{\text{max}}$  and the FWHM of the Np(V) aquo ion is not influenced by increasing  $I_m$ . At higher  $I_m$  the bathochromic shift of the absorption band with increasing  $[\text{F}^-]$  is more pronounced and the FWHM increases from 6.4 to 11.0 nm ( $I_m(\text{NaClO}_4) = 1.0\text{ mol kg}^{-1}\text{ H}_2\text{O}$ ) and 6.3–11.3 nm ( $I_m(\text{NaClO}_4) = 1.8\text{ mol kg}^{-1}\text{ H}_2\text{O}$ ). The isosbestic point shifts to 982.6 nm ( $I_m(\text{NaClO}_4) = 1.0\text{ mol kg}^{-1}\text{ H}_2\text{O}$ ) and 982.4 nm ( $I_m(\text{NaClO}_4) = 1.8\text{ mol kg}^{-1}\text{ H}_2\text{O}$ ). The hypsochromic shift of the isosbestic point equals the shift of the absorption band of the solvated Np(V) ion with increasing ionic strength. Furthermore, at increased ionic strength a second isosbestic point occurs at 983.9 nm ( $I_m(\text{NaClO}_4) = 1.0\text{ mol kg}^{-1}\text{ H}_2\text{O}$ ) and 983.7 nm ( $I_m(\text{NaClO}_4) = 1.8\text{ mol kg}^{-1}\text{ H}_2\text{O}$ ) which is also shifted to lower wavelengths with increasing ionic strength. The second isosbestic point clearly indicates that a second Np(V)-F<sup>-</sup> complex forms which is assumed to be the  $\text{NpO}_2\text{F}_2^-$  complex.

The observed hypsochromic shifts of the Np(V) absorbance with



**Fig. 1.** Absorption spectra of Np(V) as a function of the total  $F^-$  concentration at 20 °C and  $I_m = 0.5$  (top), 1.0 (middle), 1.8 (bottom) mol  $kg^{-1}$  (NaF + NaClO<sub>4</sub>).

increasing ionic strength are mentioned before in the literature. There, similar hypsochromic shifts in the absorption spectra of the solvated Np(V) ion and the single component spectra of the complexed Np(V) ion were observed with increasing ionic strength (Maiwald et al., 2018a, 2018b; Neck et al., 1995). This effect was attributed to changes in the outer hydration sphere of the Np(V) ion and changes in the physical

properties of water like the dielectric constant, refractive index and polarity due to increasing electrolyte concentrations (Maiwald et al., 2018b; Neck et al., 1995). Similar changes of the chemical and physical properties of the solvent are also induced by varying the temperature (see section 3.3). This results in a comparable hypsochromic shift of the Np(V) absorbance. Due to this temperature- and ionic strength dependence of the absorption band of the Np(V) ion, each series of spectra has to be treated separately and single component spectra have to be determined for all studied experimental conditions.

### 3.2. Peak deconvolution and speciation

The presence of the two isosbestic points indicates that two Np(V)- $F^-$  complexes with the stoichiometry of  $NpO_2F$  and  $NpO_2F_2^-$  are formed. The stoichiometry of the complexes is verified by slope analyses (see below). The single component spectra of these species are derived via subtractive peak deconvolution using the measured absorption spectra of the Np(V) aquo ion. The absorption spectra of the solvated Np(V) ion and the complexed species at  $I_m(NaClO_4) = 0.5$  and 1.8 mol  $kg^{-1}$  H<sub>2</sub>O are displayed in Fig. 2. The spectra of the  $NpO_2F_n^{1-n}$  ( $n = 1, 2$ ) complexes show comparable hypsochromic shifts with increasing ionic strength as observed for the solvated Np(V) ion. Furthermore, the complexation of  $NpO_2^+$  by one  $F^-$  ion results in a bathochromic shift of the absorption band of  $3.8 \pm 0.1$  nm and the complexation of two  $F^-$  ions results in a bathochromic shift of  $8.1 \pm 0.3$  nm compared to the Np(V) aquo ion. These shifts are found to be identical for all studied ionic strengths. Thus, the spectra of the  $NpO_2F_n^{1-n}$  ( $n = 0, 1, 2$ ) are all affected in a similar way by changes in the solvent polarity or hydration of the Np(V) species due to increasing background electrolyte concentrations. In Table 1 the spectral features of the single component spectra are summarized for  $I_m(NaClO_4) = 0.5, 1.0$  and 1.8 mol  $kg^{-1}$  H<sub>2</sub>O. Comparison of the data shows an increase of the FWHM with the number of coordinating  $F^-$  whereas the molar absorptivity decreases. Nonetheless, the peak area of the absorption spectra remains constant for all complexes showing that the integrated extinction coefficient is identical for all complex species. Thus, the evaluation of the absorption spectra is performed using spectra that are normalized to equal peak area. As shown in Table 1, the absorption spectra of the  $NpO_2F_n^{1-n}$  ( $n = 1, 2$ ) determined in this work are in excellent agreement with literature spectra (Tian et al., 2009). Only, a slight difference is observed regarding the molar attenuation coefficients obtained by Tian et al.

To derive the molal fractions of the different chemical species the single component spectra are used to deconvolute the absorption spectra by principle component analyses. Details of this method are given elsewhere (Skerencak et al., 2009, 2013; Skerencak-Frech et al., 2014). The equilibrium concentration of  $F^-$  in solution for each titration series,  $[F^-]_{eq}$ , is calculated according to equation (1), which is derived from the mass balances of total  $F^-$  (eqn. (2)) and total  $H^+$  (eqn. (3)). The complexation of Np(V) with fluoride has no significant effect on the calculation of  $[F^-]_{eq}$ . The total amount of fluoride in the samples is much higher compared to the Np(V) concentration ( $[NpO_2^+]_{total} \ll [F^-]_{total}$ ). Thus, the Np(V) fluoride species are omitted in the mass balance equation for the total fluoride concentration (eqn. (2)).

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

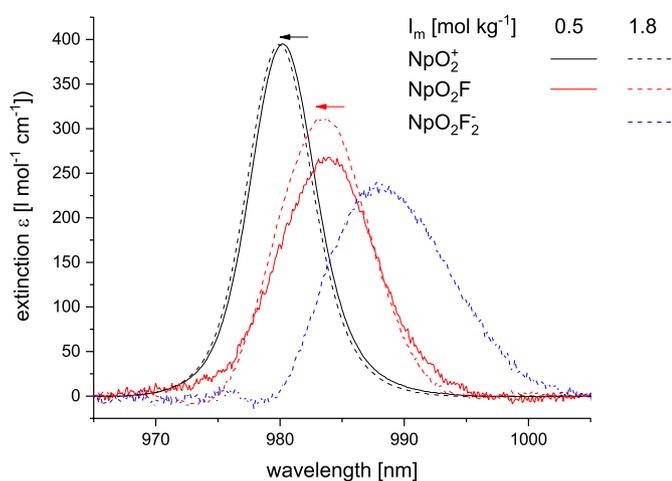
$$[F^-]_{total} = [F^-]_{eq} + [HF]_{eq} \quad (2)$$

$$[H^+]_{total} = [H^+]_{eq} + [HF]_{eq} \quad (3)$$

The required  $\log K'_{HF}(T)$  values are calculated at each studied experimental condition according to literature procedure (Skerencak et al., 2010). The temperature dependence of  $\log K'_{HF}(T)$  is described with the

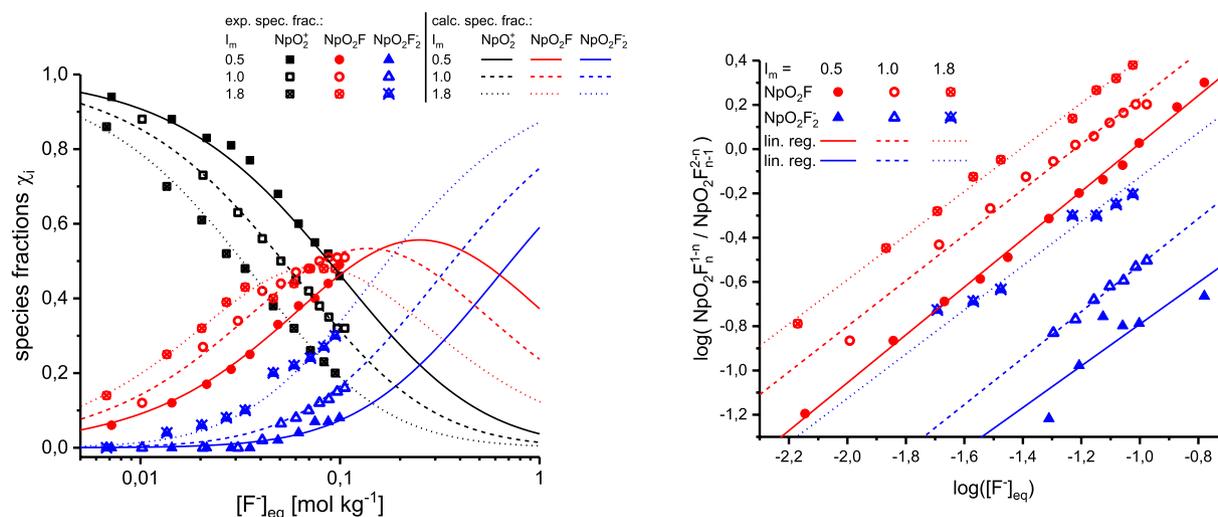
**Table 1**Spectral characteristics of the absorption bands of the  $\text{NpO}_2(\text{F})_n^{1-n}$  ( $n = 0, 1, 2$ ) species compared to literature data in  $\text{NaClO}_4$  media (Tian et al., 2009).

Complex species	T [°C]	$I_m$	Center [nm]	FWHM [nm]	$\epsilon_{\lambda(\text{max})}$ [ $\text{l mol}^{-1} \text{cm}^{-1}$ ]	Ref.
$\text{NpO}_2^+$	20	0	982.3	6.7	395	Neck et al. (1995)
$\text{NpO}_2^+$		0.5	$980.2 \pm 0.1$	$7.3 \pm 0.4$	$387 \pm 8$	p.w.
$\text{NpO}_2\text{F}$		1.0	$984.0 \pm 0.2$	$9.1 \pm 0.5$	$263 \pm 5$	p.w.
$\text{NpO}_2^+$		1.8	$980.1 \pm 0.1$	$7.4 \pm 0.2$	$392 \pm 8$	p.w.
$\text{NpO}_2\text{F}$			$980.0^a$		$395^a$	Tian et al. (2009)
			$983.8 \pm 0.2$	$9.3 \pm 0.6$	$269 \pm 6$	p.w.
			$984.1^a$		$285^a$	Tian et al. (2009)
$\text{NpO}_2\text{F}_2^-$			$988.4 \pm 0.2$	$13.3 \pm 0.8$	$212 \pm 8$	p.w.
			$988.9^a$		$210^a$	Tian et al. (2009)
$\text{NpO}_2^+$	85	1.8	$979.9 \pm 0.1$	$7.3 \pm 0.4$	$392 \pm 8$	p.w.
$\text{NpO}_2\text{F}$		4.0	$983.6 \pm 0.2$	$8.6 \pm 0.6$	$310 \pm 12$	p.w.
$\text{NpO}_2\text{F}_2^-$		2	$988.2 \pm 0.2$	$11.2 \pm 0.7$	$238 \pm 10$	p.w.
$\text{NpO}_2^+$		5	980		395	Hagan and Cleveland (1966)
$\text{NpO}_2^+$		4.0	979.5	7.3	$392^a$	Maiwald et al. (2018a)
$\text{NpO}_2^+$		5	981.1	6.7	395	Neck et al. (1995)
$\text{NpO}_2^+$		1.0	$978.6 \pm 0.1$	$7.0 \pm 0.4$	$407 \pm 8$	p.w.
$\text{NpO}_2\text{F}$		1.0	$982.2 \pm 0.2$	$10.2 \pm 0.6$	$283.1 \pm 2$	p.w.
$\text{NpO}_2\text{F}_2^-$		4.0	$986.8 \pm 0.2$	$10.6 \pm 0.6$	$326 \pm 21$	p.w.
$\text{NpO}_2^+$		4.0	977.8	7.3	$359^a$	[17]

<sup>a</sup> Calculated from literature data.**Fig. 2.** Absorption spectra of the solvated Np(V) ion and the  $\text{NpO}_2\text{F}_n^{1-n}$  complexes ( $n = 1, 2$ ) at  $T = 20^\circ\text{C}$  and  $I_m(\text{NaClO}_4) = 0.5$  and  $1.8 \text{ mol kg}^{-1} \text{H}_2\text{O}$ .

integrated Van't Hoff equation (Puigdomènech et al., 1999). The  $K_{\text{HF}}^0(T)$  values from 25 to 200 °C are available in the literature (Ellis, 1963). The ionic strengths corrections are then performed according to the SIT using the  $\epsilon_{j,K}$  values given in the NEA-TDB ( $\epsilon(\text{Na}^+, \text{F}^-) = 0.02 \pm 0.02$ ,  $\epsilon(\text{H}^+, \text{ClO}_4^-) = 0.14 \pm 0.02$ ) (Guillaumont et al., 2003). The speciation of the Np(V)-F<sup>-</sup> system (symbols) and the calculated speciation (lines) using the derived conditional stability constants  $\log \beta'_n(T)$  (see eqns. (4)–(6)) at  $I_m(\text{NaClO}_4) = 0.5, 1.0$ , and  $1.8 \text{ mol kg}^{-1} \text{H}_2\text{O}$  are displayed in Fig. 3 (left). For  $[\text{F}^-]_{\text{eq}} \leq 0.1 \text{ mol kg}^{-1} \text{H}_2\text{O}$  the speciation at  $I_m = 0.5 \text{ mol kg}^{-1} \text{H}_2\text{O}$  is mainly dominated by the Np(V) aquo ion, and the  $\text{NpO}_2\text{F}$  complex is formed up to 46% molal fractions.  $\text{NpO}_2\text{F}_2^-$  is present only as a minor species with fractions below 10%. With increasing ionic strength, the speciation shows higher fractions of the complexed species at similar  $[\text{F}^-]_{\text{eq}}$  indicating an increase of the stability constants with increasing  $I_m$ .

The single component spectra, the stoichiometry of the formed complexes and the experimentally determined speciation are verified by slope analyses according to the law of mass action (see equation (4)–(6)).

**Fig. 3.** (left) species distribution of Np(V) as a function of the equilibrium fluoride concentration at  $T = 20^\circ\text{C}$  and  $I_m(\text{NaClO}_4) = 0.5, 1.0$ , and  $1.8 \text{ mol kg}^{-1} \text{H}_2\text{O}$ ; (right) plots of  $\log([\text{NpO}_2\text{F}_n]^{1-n} / [\text{NpO}_2\text{F}_{n-1}]^{2-n})$  vs.  $\log([\text{F}^-]_{\text{eq}})$  and linear regression analyses.  $I_m(\text{NaClO}_4) = 0.5; 1.0$  and  $1.8 \text{ mol kg}^{-1} \text{H}_2\text{O}$ ;  $[\text{NpO}_2^+]_{\text{total}} = 7.4 \times 10^{-4} \text{ mol kg}^{-1} \text{H}_2\text{O}$ ;  $[\text{F}^-]_{\text{eq}} = 0\text{--}0.1 \text{ mol kg}^{-1} \text{H}_2\text{O}$ .

$$K'_n = \frac{[\text{NpO}_2\text{F}_n]^{1-n}}{[\text{NpO}_2\text{F}_{n-1}]^{1-(n-1)} \cdot ([\text{F}^-]_{\text{eq}})} \quad (4)$$

$$\log \frac{[\text{NpO}_2\text{F}_n]^{1-n}}{[\text{NpO}_2\text{F}_{n-1}]^{1-(n-1)}} = \log K'_n + 1 \cdot \log [\text{F}^-]_{\text{eq}} \quad (5)$$

$$\beta'_n = \prod_1^n K'_n = \frac{[\text{NpO}_2\text{F}_n]^{1-n}}{[\text{NpO}_2^{2+}] \cdot ([\text{F}^-]_{\text{eq}})^n} \quad (6)$$

Double logarithmic plotting of the determined species fractions versus  $\log[\text{F}^-]_{\text{eq}}$  according to eqn. (5), and linear fitting of the data for  $I_m$  ( $\text{NaClO}_4$ ) = 0.5, 1.0, and 1.8  $\text{mol kg}^{-1}$   $\text{H}_2\text{O}$  are displayed in Fig. 3 (right). The obtained slopes are  $n = (0.9\text{--}1.1) \pm 0.1$  confirming the successive formation of complexes with the stoichiometry of  $\text{NpO}_2\text{F}_n^{1-n}$  ( $n = 1, 2$ ). The formation of the 1:1 - and 1:2 -  $\text{Np(V)-F}^-$  complex species is in excellent agreement with spectroscopic results by Tian et al. confirming both species (Tian et al., 2009). However, the results obtained by the present work deviate from results of solvent extraction experiments and calorimetric titrations (Xia et al., 2006; Rao et al., 2006). There the formation of only  $\text{NpO}_2\text{F}$  up to  $[\text{F}^-]_{\text{total}} \leq 0.2 \text{ M}$  at  $I = 1 \text{ M NaClO}_4$  and  $T \leq 70^\circ\text{C}$  is postulated.

### 3.3. Complexation at elevated temperature

The temperature dependence of the complexation of  $\text{Np(V)}$  with  $\text{F}^-$  is determined at  $T = 20\text{--}85^\circ\text{C}$  and  $I_m = 0.5\text{--}3.0 \text{ mol kg}^{-1}$   $\text{H}_2\text{O}$ . In Fig. 4 the absorption spectra of  $\text{Np(V)}$  as a function of  $[\text{F}^-]_{\text{total}}$  are displayed at  $T = 20$  and  $85^\circ\text{C}$  and  $I_m = 1.0 \text{ mol kg}^{-1}$   $\text{H}_2\text{O}$ . At  $85^\circ\text{C}$  the solvated  $\text{Np(V)}$  ion shows an absorption band at  $978.4 \text{ nm}$  and thus is blue shifted by  $1.7 \text{ nm}$  compared to  $20^\circ\text{C}$ . The molar attenuation coefficient and the FWHM of the  $\text{Np(V)}$  aquo ion is only slightly affected by increasing temperature (see Table 1) and the changes are within the error range of the data. With increasing  $[\text{F}^-]_{\text{total}}$  the absorption band shifts to higher wavelengths and the FWHM is broadened by  $\Delta\lambda_{\text{FWHM}} = 5.2 \text{ nm}$  from  $6.4$  to  $11.6 \text{ nm}$  due to increasing complexation with  $\text{F}^-$ . The bathochromic shift and the broadening of the FWHM is more pronounced at elevated temperature than at  $20^\circ\text{C}$  indicating a fostered complexation of  $\text{Np(V)}$  with  $\text{F}^-$ . Furthermore, at  $85^\circ\text{C}$  the isosbestic points are observed at  $981.1 \text{ nm}$  and  $982.5 \text{ nm}$  and are hypsochromically shifted by approximately  $1.5 \text{ nm}$  compared to  $20^\circ\text{C}$ , reflecting the general hypsochromic shift of the  $\text{Np(V)}$  absorption with increasing temperature (see section 3.1). Comparable shifts were observed in the literature for the complexation of  $\text{Np(V)}$  with acetate, sulfate, benzoate and picolinate (Maiwald et al., 2018a, 2018b; Yang et al., 2015; Zhang et al., 2015).

The single component spectra of the different  $\text{Np(V)-F}^-$  species at elevated temperatures ( $T = 20, 50$  and  $85^\circ\text{C}$ ) are displayed in Fig. 5. The complexation of  $\text{NpO}_2^{2+}$  by  $\text{F}^-$  ions results in similar bathochromic

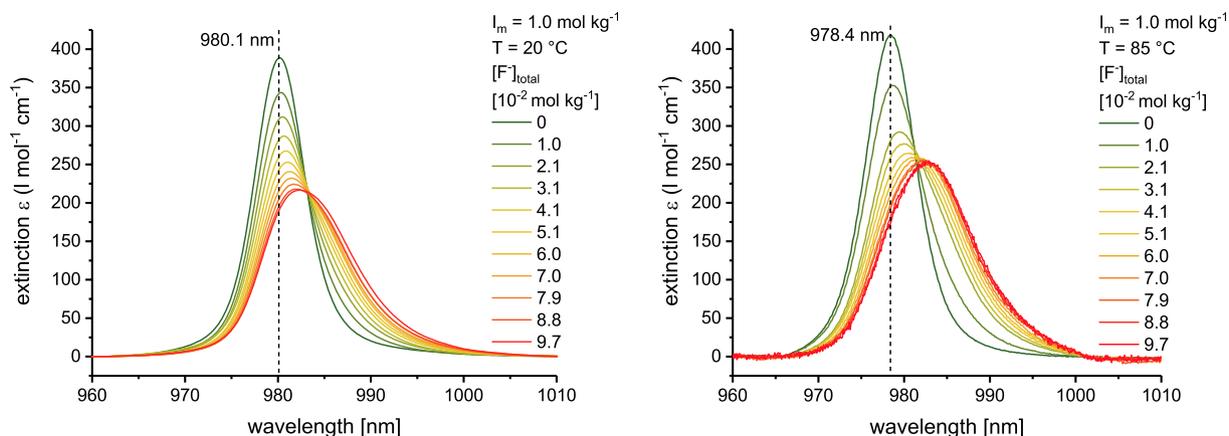


Fig. 4. Absorption spectra of  $\text{Np(V)}$  as a function of the total  $\text{F}^-$  concentration at  $20$  and  $85^\circ\text{C}$  ( $I_m = 1.0 \text{ mol kg}^{-1}$  ( $\text{NaF} + \text{NaClO}_4$ )).

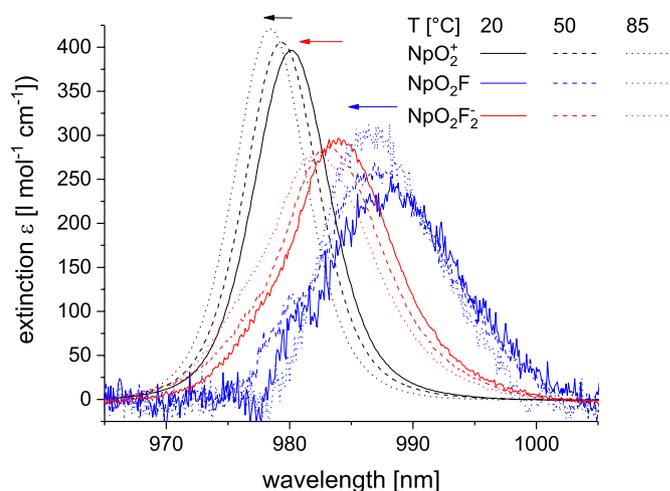


Fig. 5. Absorption spectra of the solvated  $\text{Np(V)}$  ion and the  $\text{NpO}_2\text{F}_n^{1-n}$  complex ( $n = 1, 2$ ) at  $T = 20, 50$  and  $85^\circ\text{C}$  and  $I_m(\text{NaClO}_4) = 1.0 \text{ mol kg}^{-1}$   $\text{H}_2\text{O}$ .

shifts of the absorption bands of the  $\text{NpO}_2\text{F}_n^{1-n}$  complexes ( $n = 1, 2$ ) compared to the  $\text{Np(V)}$  aquo ion as observed at  $20^\circ\text{C}$  (see previous section). Furthermore, the absorption bands of the respective complexes are blue shifted with increasing temperature by about  $1.5\text{--}1.7 \text{ nm}$  from  $20$  to  $85^\circ\text{C}$ . These shifts equal the shift of the solvated  $\text{Np(V)}$  ion with increasing temperature. In addition, slight changes in the molar attenuation coefficient of about  $\Delta\epsilon_i = \pm 0.062\epsilon_i$  and in FWHM off  $\pm 0.3 \text{ nm}$  are observed with increasing temperature. Nonetheless, the integrated extinction coefficient remains constant and thus, normalized spectra are used for the evaluation of the absorption spectra. The spectroscopic characteristics of the  $\text{Np(V)}$  species at elevated temperature are summarized in Table 1. All these results confirm that the  $T$  and  $I_m$  induced blue shifts are independent of the chemical speciation and result from changes in the absorption properties of the  $\text{Np(V)}$  ion affected by secondary effects like outer sphere complexation, changes of the complex geometry or changes of the dielectric constant of the medium (Maiwald et al., 2018a, 2018b; Neck et al., 1995; Yang et al., 2015; Zhang et al., 2015).

To determine thermodynamic functions it is necessary to confirm that irreversible reactions do not occur during the heating process affecting the equilibrium of the complexation reaction. In Fig. 6 the absorption spectra of  $\text{Np(V)}$  at two different  $[\text{F}^-]_{\text{total}}$  are displayed at  $20^\circ\text{C}$  before and after heating the sample to  $85^\circ\text{C}$ . The results show that with increasing fluoride concentration the absorbance decreases successively after heating the sample to  $85^\circ\text{C}$ . This indicates an irreversible reaction involving  $\text{Np(V)}$ , which is triggered by increasing temperature and fostered at higher fluoride concentrations. Nonetheless, comparison

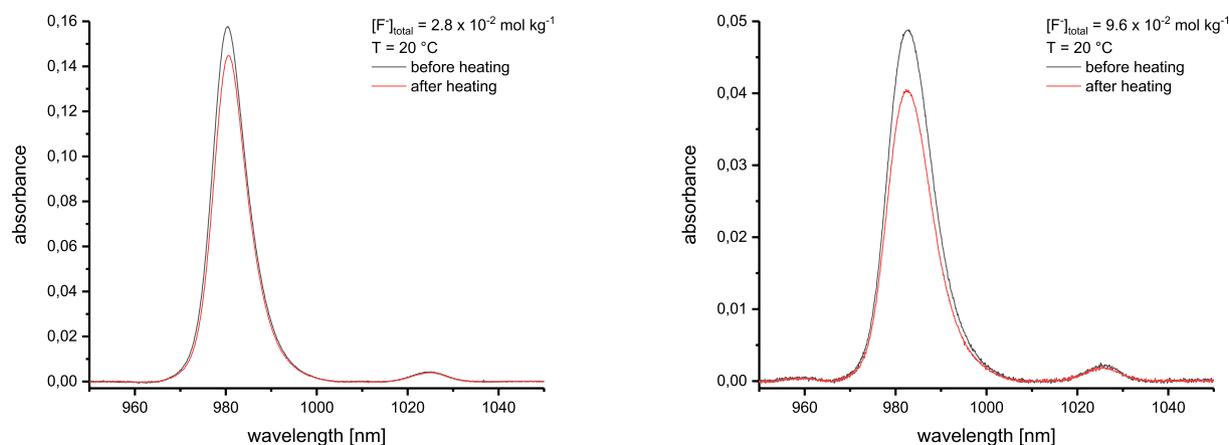


Fig. 6. Absorption spectra of Np(V) at  $[F^-]_{\text{total}} = 2.8 \times 10^{-2}$ ,  $9.6 \times 10^{-2} \text{ mol kg}^{-1}$  at 20 °C before and after the sample was heated to 85 °C;  $[\text{NpO}_2^+]_{\text{total}} = 7.4 \times 10^{-4} \text{ mol kg}^{-1} \text{ H}_2\text{O}$ ;  $I_m = 1.0 \text{ mol kg}^{-1} \text{ H}_2\text{O}$ .

of the absorption spectra reveals congruent band shapes and identical absorption maxima. Consequently, the speciation in each sample remains unaffected. The loss in absorbance is a result of minor changes in the total Np(V) concentrations and is below 7% and thus is negligible.

Possible explanations for the decrease in the absorbance are the formation of precipitates or redox processes. A closer look at the absorption spectra in the data interval from 700 to 1250 nm reveals that two additional absorption bands arise at approximately 723 nm and 960 nm (see Figure S1 in the ESI). These two bands are attributed to Np(IV). The formation of Np(VI), showing an absorption band at 1223 nm, is not observed. The reduction of Np(V) to Np(IV) is also verified by solvent extractions using HDEHP in toluene and PMPB in hexane as diluents. Here, batch experiments are performed over an extended time period at various  $[F^-]_{\text{total}}$  and temperatures to study the reduction of Np(V) to Np(IV) in more detail. The results show that no reduction of Np(V) occurs within 60 h at 25 °C and  $[F^-]_{\text{total}} = 0.05\text{--}1.0 \text{ mol kg}^{-1}$  and  $I_m(\text{NaF} + \text{NaClO}_4) = 1.0 \text{ mol kg}^{-1} \text{ H}_2\text{O}$ . However, an increase of the temperature results in a successive increase of  $[\text{Np(IV)}]$ . After 4 h at 80 °C up to 25.0% of the initial Np(V) concentration are reduced to Np(IV) and after 10 h the maximum reduction of 33.0% Np(V) is achieved. A detailed summary of the results is given in Table 2. The origin of the reduction process is still an unsolved problem and is not yet fully understood. A reduction induced by impurities in the used chemicals or the Np(V) samples is unlikely as different batches of chemicals were used and no Np(IV) is formed in the absence of NaF.

### 3.4. Thermodynamic data

The absorption spectra of Np(V) as a function of temperature and  $[F^-]_{\text{total}}$  are used to determine the thermodynamic functions ( $\Delta_r H_{n,m}^0$  and  $\Delta_r S_{n,m}^0$ ) of the complexation reactions taking into account the concentration of Np(V) and Np(IV) in the samples determined by solvent extraction. In Fig. 7 (left) the experimental data (symbols) and the calculated speciations (lines) using the derived  $\log \beta'_n(T)$  values (see eqns. (4)–(6)) at  $T = 20, 50,$  and  $85 \text{ °C}$  and  $I_m(\text{NaClO}_4) = 1.0 \text{ mol kg}^{-1}$

Table 2

Quantification of  $[\text{NpO}_2^+]$  at various  $[F^-]_{\text{total}}$  and different time intervals at 25 and 80 °C.

$[F^-]_{\text{total}}$ [mol kg <sup>-1</sup> ]	$[\text{NpO}_2^+]$ (60 h, 25 °C)	$[\text{NpO}_2^+]$ (4h, 80 °C)	$[\text{NpO}_2^+]$ (10h, 80 °C)
0.0	$-0 \pm 0.2\%$	$-0 \pm 0.2\%$	$-0 \pm 0.3\%$
0.05	$-0 \pm 0.3\%$	$-4.7 \pm 2.3\%$	$-10.1 \pm 1.8\%$
0.1	$-0 \pm 0.3\%$	$-7.0 \pm 1.6\%$	$-12.3 \pm 1.5\%$
0.3	$-0 \pm 0.2\%$	$-10.4 \pm 1.2\%$	$-15.0 \pm 1.2\%$
1.0	$-0 \pm 0.2\%$	$-25.0 \pm 0.8\%$	$-33.0 \pm 0.7\%$

$\text{H}_2\text{O}$  are displayed. With increasing temperature the speciation shifts towards the higher Np(V)-F complexes indicating an endothermic complexation reaction. The slope analyses confirm the formation of the  $\text{NpO}_2\text{F}_n^{1-n}$  complexes ( $n = 1, 2$ ) at elevated temperature as already observed at 20 °C (Fig. 7 (right)).

The conditional  $\log \beta'_n(T)$  values for the formation of the  $\text{NpO}_2\text{F}_n^{1-n}$  ( $n = 1, 2$ ) complexes at various ionic strengths and temperatures are calculated according to the law of mass action and are extrapolated to  $I_m = 0$  with the specific ion interaction theory (SIT) as recommended by the NEA-TDB (see eqn (7)). (Guillaumont et al., 2003)

$$\log K' - \Delta z^2 D = \log K^0 + \Delta \epsilon I_m \quad (7)$$

$D$  is the temperature dependent Debye-Hückel term and  $\Delta \epsilon$  is the stoichiometric sum of the binary ion-ion interaction coefficients  $\epsilon_{j,k}$ . Using these values the thermodynamic functions of the complexation reactions are determined at IUPAC reference state conditions ( $T = 25 \text{ °C}$ ,  $p = 1 \text{ atm}$ ,  $I = 0$ ). (Guillaumont et al., 2003) These data can be implemented into existing databases and used for modelling of the geochemical behaviour of actinides. The here determined  $\log \beta'_n(T)$  values as a function of the reciprocal temperature  $T^{-1}$  are displayed in Fig. 8 and are compared with literature data. The calculated values at ambient temperature are  $\log \beta_1^0(20 \text{ °C}) = 1.55 \pm 0.10$  ( $\text{NpO}_2\text{F}$ ) and  $\log \beta_2^0(20 \text{ °C}) = 1.77 \pm 0.31$  ( $\text{NpO}_2\text{F}_2^-$ ). With increasing temperature the stability constant of  $\text{NpO}_2\text{F}$  increases by approximately 0.2 logarithmic units to  $\log \beta_1^0(85 \text{ °C}) = 1.78 \pm 0.25$  and the stability constant  $\text{NpO}_2\text{F}_2^-$  increases by 0.6 to  $\log \beta_2^0(85 \text{ °C}) = 2.36 \pm 0.34$ .

So far, the ionic strength dependence of the complexation reactions was never studied and thermodynamic stability constants derived from experimental data by SIT or Pitzer modelling are not reported in the literature. However, Tian et al. determined  $\log \beta'_n(T)$  and extrapolated these values to  $\log \beta_n^0(T)$  assuming that  $\epsilon(\text{NpO}_2\text{F}_2^-, \text{Na}^+) = \epsilon(\text{NpO}_2(\text{OH})_2^-, \text{Na}^+)$  as  $\epsilon_{j,k}$  values for the complexation of Np(V) with  $\text{F}^-$  are so far not available in the literature (Tian et al., 2009). In the present work  $\epsilon(\text{NpO}_2\text{F}, \text{Na}^+/\text{Cl}^-)$  and  $\epsilon(\text{NpO}_2\text{F}_2^-, \text{Na}^+)$  were determined (see below) and were used for extrapolation of the stability constant reducing the uncertainties of the  $\log \beta_n^0$  values. Nevertheless, the  $\log \beta_n^0$  data acquired by Tian et al. show a comparable increase with increasing temperature from  $\log \beta_1^0(20 \text{ °C}) = 1.38$  ( $\text{NpO}_2\text{F}$ ) by 0.5 to  $\log \beta_1^0(85 \text{ °C}) = 1.68$  and  $\log \beta_2^0(20 \text{ °C}) = 1.76$  ( $\text{NpO}_2\text{F}_2^-$ ) by 0.8 to  $\log \beta_2^0(85 \text{ °C}) = 2.54$ . (Tian et al., 2009) (see Fig. 8). The stability constant of  $\text{NpO}_2\text{F}$  reported in the NEA-TDB deviates from the present data and is lower by 0.3 logarithmic units (Lemire, 2001). This deviation occurs due to the data used in the NEA-TDB to calculate the  $\log \beta_1^0(25 \text{ °C})$  value. In the NEA-TDB review conditional stability constants obtained by solvent extraction studies, spectrophotometry and potentiometric techniques at different experimental conditions are

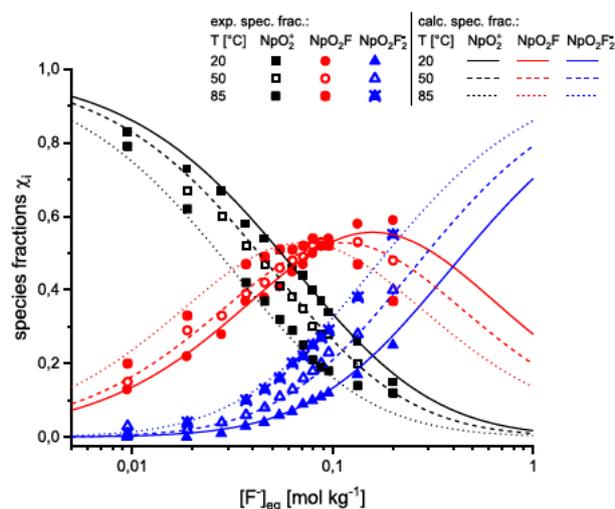


Fig. 7. (left) Species distribution of Np(V) as a function of the equilibrium fluoride concentration and (right) plots of  $\log([NpO_2L_n]^{1-n}/[NpO_2F_{n-1}]^{2-n})$  vs.  $\log([F^-]_{eq})$  and linear regression analyses at  $T = 20, 50,$  and  $85\text{ }^\circ\text{C}$  ( $I_m(\text{NaClO}_4) = 1.0\text{ mol kg}^{-1}\text{ H}_2\text{O}$ );  $[NpO_2^+]_{total} = 7.4 \times 10^{-4}\text{ mol kg}^{-1}\text{ H}_2\text{O}$ ;  $[F^-]_{eq} = 0-0.2\text{ mol kg}^{-1}\text{ H}_2\text{O}$ .

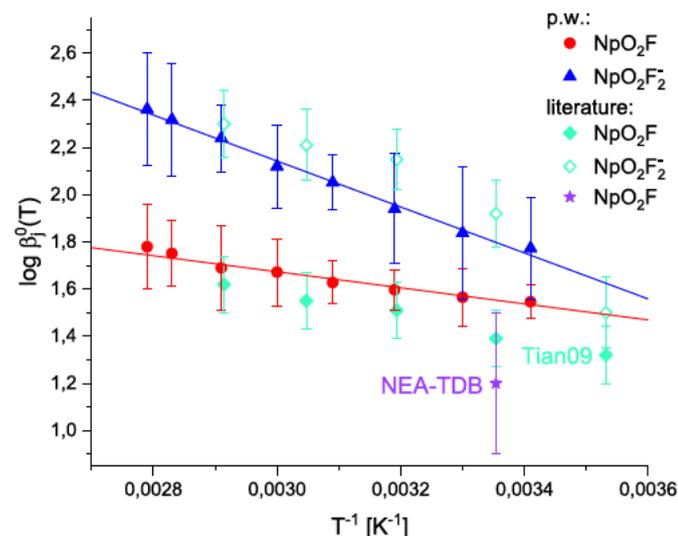
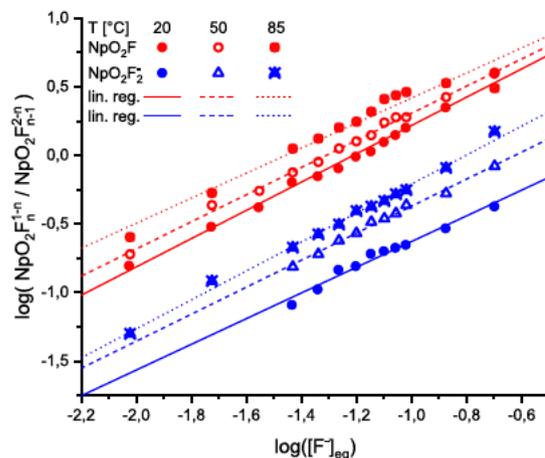


Fig. 8. Plot of  $\log \beta_n^0(T)$  ( $NpO_2F_n^{1-n}$ ) ( $n = 1, 2$ ) versus  $T^{-1}$  and fitting according to the integrated Van't Hoff equation (eqn. (6)) and comparison with data provided by Tian et al. and the NEA-TDB (Lemire, 2001; Tian et al., 2009).

compared (Lemire, 2001). The  $\log \beta_1^0(25\text{ }^\circ\text{C})$  value is then calculated by single point extrapolation using the SIT with a  $\Delta \epsilon_{01} = 0 - \epsilon(\text{Na}^+, \text{F}^-) - \epsilon(\text{NpO}_2^+, \text{ClO}_4^-) = -0.27 \pm 0.10$ . This results in a wide variation of the  $\log \beta_1^0(25\text{ }^\circ\text{C})$  values between  $0.82 \pm 0.24$  and  $1.70 \pm 0.50$  resulting in an averaged value of  $\log \beta_1^0(25\text{ }^\circ\text{C}) = 1.2 \pm 0.3$ . A  $\log \beta_2^0(25\text{ }^\circ\text{C})$  value for the formation of  $NpO_2F_2^-$  is not given in the NEA-TDB.

The standard reaction enthalpies  $\Delta_r H_{nm}^0$  and entropies  $\Delta_r S_{nm}^0$  are determined by plotting of  $\log \beta_n^0(T)$  versus the reciprocal temperature

Table 3

Thermodynamic stability constants  $\log \beta_n^0(T = 25\text{ }^\circ\text{C})$  and thermodynamic functions ( $\Delta_r H_{nm}^0, \Delta_r S_{nm}^0$ ) for the complexation of Np(V) with  $F^-$ , sp = spectrophotometry.

	Method	$\log \beta_1^0(T = 25\text{ }^\circ\text{C})$	$\Delta_r H_{0n,m}^0$ [kJ mol $^{-1}$ ]	$\Delta_r S_{0n,m}^0$ [J mol $^{-1}$ K $^{-1}$ ]	Reference
NpO $_2$ F	sp	$1.56 \pm 0.20$	$6.4 \pm 1.5$	$51 \pm 5$	p.w.
	sp	$1.39 \pm 0.12$			Tian et al. (2009)
	NEA-TDB	$1.2 \pm 0.3$			NEA-TDB Lemire (2001)
NpO $_2$ F $_2^-$	sp	$1.80 \pm 0.36$	$18.7 \pm 3.9$	$97 \pm 12$	p.w.
	sp	$1.92 \pm 0.12$			Tian et al. (2009)

\*calculated from literature data.

$T^{-1}$  as displayed in Fig. 8. The data correlate linearly with  $T^{-1}$  and the temperature dependence is well described by the integrated Van't Hoff equation (eqn. (8)).

$$\log \beta_n^0(T) = \log \beta_n^0(T_0) + \frac{\Delta_r H_m^0(T_0)}{R \ln(10)} \left( \frac{1}{T_0} - \frac{1}{T} \right) \quad (8)$$

With  $R$  as universal gas constant,  $T_0 = 298.15\text{ K}$ , and  $T$  being the absolute temperature. The equation is valid in the studied temperature range of  $20-85\text{ }^\circ\text{C}$ , assuming  $\Delta_r C_{m,p}^0 = 0$  and  $\Delta_r H_m^0 = \text{const}$ . The  $\Delta_r H_{0n,m}^0$  and  $\Delta_r S_{0n,m}^0$  values determined in the present work are compared with literature data in Table 3.

The interpolated  $\log \beta_{25\text{ }^\circ\text{C}}^0$  ( $NpO_2F$ ) =  $1.56 \pm 0.20$  is slightly higher whereas  $\log \beta_{25\text{ }^\circ\text{C}}^0$  ( $NpO_2F_2^-$ ) =  $1.80 \pm 0.36$  is slightly lower than the values at  $25\text{ }^\circ\text{C}$  reported in literature but still agree within the error range (Lemire, 2001; Tian et al., 2009). In the literature no  $\Delta_r H_{0n,m}^0$  and  $\Delta_r S_{0n,m}^0$  values are reported.

Due to missing thermodynamic data at IUPAC reference state conditions the temperature dependence of the Np(V) complexation with fluoride is additionally compared with literature data at  $I_m(\text{NaClO}_4) = 1\text{ mol kg}^{-1}\text{ H}_2\text{O}$ . The respective conditional stability constants  $\log \beta'_n(T = 25\text{ }^\circ\text{C})$  and  $\Delta_r H'_m$  and  $\Delta_r S'_m$  are summarized in Table 4.

Rao, Xia, and Tian et al. studied the complexation of Np(V) with  $F^-$  using spectrophotometry, solvent extractions and calorimetric titrations. (Xia et al., 2006; Tian et al., 2009; Rao et al., 2006) The conditional stability constants of the complexes determined by spectrophotometry are  $\log \beta'_1 = 1.25 \pm 0.05$  and  $\log \beta'_2 = 1.77 \pm 0.09$  at  $I_m(\text{NaClO}_4) = 1\text{ mol kg}^{-1}\text{ H}_2\text{O}$  and are in excellent agreement with the present work. The  $\Delta_r H'_m$  and  $\Delta_r S'_m$  values are determined by calorimetric titrations. These values are also in very good agreement with the present data. Deviations are observed for the results described in Xia et al. (2006) based on solvent extractions or in Rao et al. (2006) based

**Table 4**

Conditional stability constants  $\log \beta'_n(T = 25^\circ\text{C})$  and thermodynamic functions ( $\Delta_r H_m^\circ$ ,  $\Delta_r S_m^\circ$ ) for the formation of  $\text{NpO}_2\text{F}_n^{1-n}$  ( $n = 1, 2$ ) at  $I_m = 1.0 \text{ mol kg}^{-1} \text{ NaClO}_4$  and comparison with literature data. sp = spectrophotometry, sx = solvent extraction, cal = calorimetric titration.

	method	$\log \beta'_{25^\circ\text{C}}(I_m = 1.0 \text{ mol kg}^{-1})$	$\Delta_r H_m^\circ$ [kJ mol $^{-1}$ ]	$\Delta_r S_m^\circ$ [J mol $^{-1}$ K $^{-1}$ ]	Reference
NpO <sub>2</sub> F	sp	1.26 ± 0.15	7.3 ± 3.6	48 ± 11	p.w.
	sp, cal	1.25 ± 0.05	8.1 ± 1.0	51 ± 5	Tian et al. (2009)
	sx	1.42 ± 0.10	20.8	96.9	Xia et al. (2006)
	cal	1.47 ± 0.10	18.0 ± 0.3	64 ± 12	Rao et al. (2006)
NpO <sub>2</sub> F <sub>2</sub> <sup>-</sup>	sp	1.79 ± 0.20	17.2 ± 6.0	90 ± 18	p.w.
	sp, cal	1.77 ± 0.09	14.2 ± 3.1	82 ± 12	Tian et al. (2009)

\*calculated from literature data.

on calorimetric titrations. These studies provide higher conditional stability constants by about 0.2 logarithmic units and the complexation reactions are more endothermic. These deviations might be explained by the formation of  $\text{NpO}_2\text{F}_2^-$  as this species was not taken into account in the latter studies. Thus, the conditional stability constants  $\log \beta'$  might be overestimated, which also affect the thermodynamic functions  $\Delta_r H_m^\circ$  and  $\Delta_r S_m^\circ$ .

### 3.5. Ion interaction coefficients

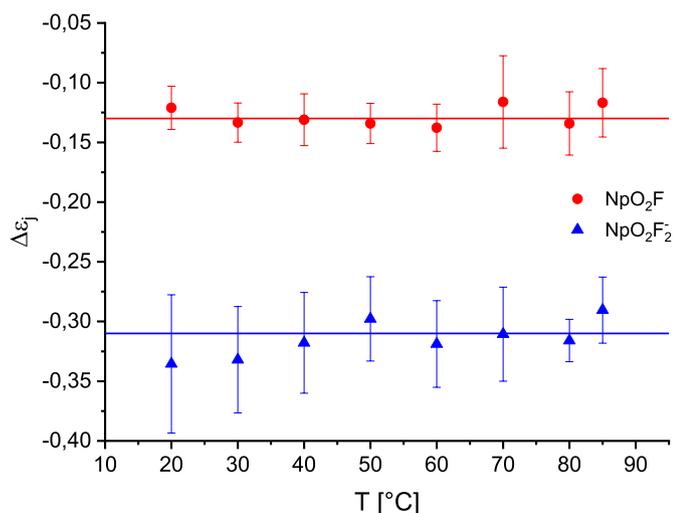
The application of the SIT to extrapolate the conditional stability constants to  $I_m = 0$  yields the SIT specific ion-ion interaction coefficients  $\Delta \epsilon_{0n}$  for the complexation reactions (Guillaumont et al., 2003). The  $\Delta \epsilon_{01}$  and  $\Delta \epsilon_{02}$  values for the formation of  $\text{NpO}_2\text{F}_n^{1-n}$  ( $n = 1, 2$ ) are displayed in Fig. 9 as a function of the temperature. With increasing temperature no systematic trend of the  $\Delta \epsilon_{0n}$  values is observable. Thus, averaged, temperature-independent  $\Delta \epsilon_{0n}$  values are calculated. The averaged values are  $\Delta \epsilon_{01} = -0.13 \pm 0.03$  and  $\Delta \epsilon_{02} = -0.31 \pm 0.04$  (solid lines). The binary ion-ion interaction coefficients of  $\text{NpO}_2\text{F}$  with  $\text{Na}^+/\text{ClO}_4^-$  and  $\text{NpO}_2\text{F}_2^-$  with  $\text{Na}^+$  are calculated with the SIT according to eqn. (9). The following interaction coefficients are used as given in the NEA-TDB (Guillaumont et al., 2003; Lemire, 2001):  $\epsilon(\text{Na}^+, \text{F}^-) = 0.02 \pm 0.02$  and  $\epsilon(\text{NpO}_2^+, \text{ClO}_4^-) = 0.25 \pm 0.05$ .

$$\Delta \epsilon = \sum \epsilon_{\text{products}} - \sum \epsilon_{\text{educts}} \quad (9)$$

The binary ion-ion interaction coefficients for the Np(V)-fluoride complexes determined in the present work are:

$$\epsilon(\text{NpO}_2\text{F}, \text{Na}^+/\text{ClO}_4^-) = \Delta \epsilon_{01} + \epsilon(\text{Na}^+, \text{F}^-) + \epsilon(\text{NpO}_2^+, \text{ClO}_4^-) = 0.14 \pm 0.07$$

and



**Fig. 9.**  $\Delta \epsilon_{0n}$  values for the formation of  $\text{NpO}_2\text{F}$  and  $\text{NpO}_2\text{F}_2^-$  as a function of the temperature.

$$\epsilon(\text{NpO}_2\text{F}_2^-, \text{Na}^+) = \Delta \epsilon_{02} + 2 \epsilon(\text{Na}^+, \text{F}^-) + \epsilon(\text{NpO}_2^+, \text{ClO}_4^-) = -0.02 \pm 0.10.$$

In case of an uncharged species  $\epsilon_{i,k}$  is assumed to be zero according to the SIT. This is in discrepancy to  $\epsilon(\text{NpO}_2\text{F}, \text{Na}^+/\text{ClO}_4^-)$  determined in this work. This deviation from zero was also observed for the uncharged  $\text{NpO}_2(\text{Ac})$  species described in the literature (Maiwald et al., 2018a). There, the complexation of Np(V) with acetate was studied as a function of ionic strength in NaCl and  $\text{NaClO}_4$  media. In case of NaCl as electrolyte the determined  $\epsilon(\text{NpO}_2(\text{Ac}), \text{Na}^+/\text{Cl}^-) = 0.02 \pm 0.06$  is equal to zero being in agreement with the requirements of the SIT for an uncharged species. The determined  $\epsilon(\text{NpO}_2(\text{Ac}), \text{Na}^+/\text{ClO}_4^-)$  value is  $0.15 \pm 0.06$  and equals the value in the present work for  $\epsilon(\text{NpO}_2\text{F}, \text{Na}^+/\text{ClO}_4^-)$ . This discrepancy of  $\epsilon_{i,k}$  for uncharged Np(V) complexes determined in  $\text{NaClO}_4$  media might result from an inaccurate  $\epsilon(\text{NpO}_2^+, \text{ClO}_4^-)$  reported in the NEA-TDB (Guillaumont et al., 2003). Nonetheless, the obtained  $\log \beta'_n(T)$  values correlate linearly with the reciprocal temperature confirming that the ionic strength dependence of  $\log \beta'_n(T)$  is accurately described using the determined  $\Delta \epsilon_{0n}$  values of the respective complexation reactions. However, it should be noted that the determined  $\epsilon_{i,k}$  values are only valid in  $\text{NaClO}_4$  media and if the  $\epsilon(\text{NpO}_2^+, \text{ClO}_4^-)$  value reported in the NEA-TDB is used for SIT modelling. The comparison with literature data is not possible as specific binary ion-ion interaction coefficients for the Np(V)-F system are not available.

## 4. Summary and conclusion

The present work focuses on the complexation of Np(V) with fluoride as a function of the  $[\text{F}^-]$  concentration, ionic strength  $I_m$ , and temperature ( $T = 20\text{--}85^\circ\text{C}$ ) studied by absorption spectroscopy. Deconvolution of the spectra and slope analyses of the species distributions show the formation of two distinct complex species, which are identified as  $\text{NpO}_2\text{F}$  and  $\text{NpO}_2\text{F}_2^-$ . Higher complexes are not formed at the experimental conditions ( $[\text{F}^-]_{\text{total}} = 0\text{--}0.1 \text{ mol kg}^{-1}$  and  $T_{\text{max}} \leq 85^\circ\text{C}$ ). With increasing temperature the complexation becomes more pronounced and the equilibrium between the  $\text{NpO}_2^+$  aquo ion and  $\text{NpO}_2\text{F}_n^{1-n}$  ( $n = 1, 2$ ) is shifted towards the latter species. The thermodynamic stability constants increase by approximately 0.2 logarithmic units for  $\log \beta_1^0(T)$  and 0.6 for  $\log \beta_2^0(T)$ . The  $\log \beta_n^0(T)$  values correlate linearly with the reciprocal temperature. Thus, application of the integrated Van't Hoff equation yields the standard reaction enthalpy and entropy of the complexation reactions ( $\Delta_r H_{0n,m}^\circ$ ,  $\Delta_r S_{0n,m}^\circ$ ). Both complexation reactions have positive  $\Delta_r H_{0n,m}^\circ$  and  $\Delta_r S_{0n,m}^\circ$  values confirming that the complexation reactions are endothermic and solely driven by a high gain of entropy. Furthermore, the SIT ion-ion interaction coefficients  $\Delta \epsilon_{01}$  and  $\Delta \epsilon_{02}$  are determined as a function of temperature. The  $\Delta \epsilon_{0n}$  values show no temperature dependence and thus temperature-independent values for  $\epsilon(\text{NpO}_2\text{F}, \text{Na}^+/\text{ClO}_4^-)$  and  $\epsilon(\text{NpO}_2\text{F}_2^-, \text{Na}^+)$  are calculated.

This work provides a detailed spectroscopic and thermodynamic insight into the complexation of  $\text{NpO}_2^+$  with  $\text{F}^-$  in aqueous  $\text{NaClO}_4$ . The thermodynamic functions ( $\Delta_r H_{0n,m}^\circ$ ,  $\Delta_r S_{0n,m}^\circ$ ,  $\log \beta_1^0(T)$ ) of this work

will be implemented in thermodynamic data bases. These data bases than will be used for modelling of (geo)chemical processes of actinides with regard to the safety case of a high-level nuclear waste repository in deep geological formations. Furthermore, the work shows that increased temperatures can favour chemical processes that may be irrelevant at 25 °C, highlighting the need of an in-depth understanding of the aqueous geochemistry of actinides at ambient as well as at increased temperatures.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.apgeochem.2019.03.004>.

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