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# Determination of complex formation constants of neptunium(V) with propionate and lactate in 0.5 – 2.6 m NaCl solutions at 22-60 °C using a solvent extraction technique †

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†Dedicated to the memory of Professor Günter Herrmann.

**Abstract:** Natural clay rocks like Opalinus (OPA) and Callovo-Oxfordian (COx) clay rock are considered as potential host rocks for deep geological disposal of nuclear waste. However, small organic molecules such as propionate and lactate exist in clay rock pore water and might enhance Np mobility through a complexation process. Therefore, reliable complex formation data are required in the frame of the Safety Case for a nuclear waste repository. A solvent extraction technique was applied for the determination of  $\text{NpO}_2^+$  complexation with propionate and lactate. Extraction was conducted from isoamyl alcohol solution containing  $10^{-3}$  M TTA and  $5 \cdot 10^{-4}$  M 1,10-phenanthroline. Experiments were performed in 0.5-2.6 m NaCl solutions at temperatures ranging from 22 to 60 °C. Formation of 1:1 Np(V) complexes for propionate and lactate was found under the studied conditions. The SIT approach was applied to calculate equilibrium constants  $\beta^\circ(T)$  at zero ionic strength from the experimental data.  $\log \beta^\circ(T)$  is found linearly correlated to  $1/T$  for propionate and lactate, evidencing that heat capacity change is near 0. Molal reaction enthalpy and entropy ( $\Delta_r H_m^\circ$  and  $\Delta_r S_m^\circ$ ) could therefore be derived from the integrated van't Hoff equation. Data for  $\log \beta^\circ(298.15\text{K})$  are in agreement with literature values for propionate and lactate. Np(V) speciation was calculated for concentrations of acetate, propionate and lactate measured in clay pore waters of COx. In addition, the two site protolysis non-electrostatic surface complexation and cation exchange (2SPNE SC/CE) model was applied to quantitatively describe the influence of Np(V) complexation on its uptake on Na-illite, a relevant clay mineral of OPA and COx.

**Keywords:** Np(V); Complexation; Complex formation constant; Lactate; Propionate; Solvent extraction

## Introduction

High level nuclear waste in deep nuclear repositories contains considerable amounts of the radionuclide  $^{237}\text{Np}$ . The combination of its relatively high occurrence, its long half-life ( $T_{1/2} = 2.14 \cdot 10^6$  years) and high radiotoxicity makes this radionuclide environmentally important. While Np can exist in several oxidation states (IV, V and VI) under geological repository conditions depending on the redox conditions, Np(IV) and Np(V) are the most stable oxidation states of neptunium under circumneutral pH conditions. Np(V) is formed under oxidizing conditions and is considered to be mobile in the environment due to its relatively high solubility and low sorption affinity towards surrounding rocks and soil components [1]. The neptunyl ion ( $\text{NpO}_2^+$ ) is a linear dioxo cation with an effective charge on the Np atom of about +2.2 [2]. It forms complexes with penta-, hexa- and trigonal bipyramidal structures and the axial positions occupied by neptunyl oxygens [3].

The commonly adopted approach for nuclear wastes disposal is the isolation in deep geological formations. Clay rock is considered as a potential host rock for such deep geological repositories [4-6]. The migration of high level waste components and neptunium in particular will depend on the sorption reactions of the surrounding geological matter and on complexation with various ligands present in the near-field or far-field environment. In addition to inorganic ligands commonly found in the environment (e.g.  $\text{CO}_3^{2-}$ ,  $\text{OH}^-$ ), organic complexing ligands like high-molecular weight clay organics (e.g. humic substances-like compounds) and low-molecular weight organics (lactate, propionate, acetate, etc.) have been found in clay pore waters such as the Opalinus clay (OPA, Switzerland) and the Callovo-Oxfordian argillite (COx, France). The pore water samples from COx contains  $1865 \mu\text{M}$  acetate,  $127 \mu\text{M}$  propionate and  $8 \mu\text{M}$  lactate [7], for OPA the similar proportions have been measured [8]. The complexation with these ligands may enhance the neptunium mobility, a property, which is important for safety aspects of a repository.

Due to the radioactive decay of radionuclides in the waste, the temperature in the near-field of the repository is likely to be increased up to about  $100 \text{ }^\circ\text{C}$  or higher depending on the repository design and the type of the host-rock [9] in the early post closure phase. The temperature will remain significantly higher than ambient temperature during thousands of years. In addition, porewaters in clay rocks exhibit high ionic strength (I) conditions, e.g. in Northern Germany ( $I > 3.5 \text{ M}$ ) or for OPA ( $I = 0.3\text{-}0.5 \text{ M}$ ) [7]. It was shown earlier [8, 10] that increase of temperature and ionic strength may have a significant influence on the complexation processes under the near-field conditions and thus change the retardation efficiency of clay rock formations.

In light of the foregoing, it is necessary to outline the lack of information about the thermodynamic data of neptunium complex formation with ligands present in clay rocks. A recent study [11] investigated Np(V)-propionate complexation by spectroscopy and delivered related thermodynamic parameters. In [11], a solvent extraction method has been applied to determine the thermodynamic parameters for the Np(V)-propionate complexes at various I and T. The complexation of  $\text{NpO}_2^+$  with lactate has been studied previously at room temperature using solvent extraction technique [13-15]. The present paper is aiming to complete these data with complexation data at high temperatures that correspond to the HLW repositories conditions. Information on the temperature effect of the Np(V) complexation with low-molecular weight organic substances might also be useful to estimate the behavior of macromolecular organics such as humic substances [16], that also were found at some potential repository sites [17].

In the present work, the complexation of Np(V) with propionate and lactate was studied by using a solvent extraction as a function of NaCl concentration, ligand concentration, and temperature. The specific ion interaction theory (SIT) was used for correlation of ionic strength effects and the

temperature dependent thermodynamic stability constants as well as the standard molar reaction enthalpy  $\Delta_r H_m^\circ$  and the standard molar reaction entropy  $\Delta_r S_m^\circ$  of the complexation reactions are determined. Surface complexation modelling was applied to appraise the influence of Np(V) complexation with low-molecular weight organics on clay minerals retention of Np(V). Such studies render possible to assess the behavior of  $\text{NpO}_2^+$  in the environment and compare its properties with similar data for other actinides.

## Experimental

### Materials and Methods

#### Chemicals and Np(V) stock solution

All chemicals were of p.a. quality or higher and were obtained from Merck (Darmstadt, Germany) or Riedel de Haen (Seelze, Germany). All experiments were conducted using de-ionized “MilliQ” water ( $\rho = 18.2 \text{ M}\Omega \text{ cm}^{-1}$ ). A well characterized  $^{237}\text{Np(V)}$  stock solution ( $50 \mu\text{M}$ ) in  $0.01 \text{ M HCl}$  was used for all complexation experiments. Np(V) purity was verified by UV-Vis/NIR spectroscopy [18].  $^{237}\text{Np}$  concentration was determined by liquid scintillation counting (LSC) with  $\alpha/\beta$ -discrimination of the  $^{233}\text{Pa}$  daughter nuclide, using the scintillation cocktail Ultima Gold XR (Packard Instruments Co., USA) and the liquid scintillation counter (LSC) Tri-Carb (Packard Instruments Co., USA). The  $\alpha/\beta$ -discrimination procedure is given in detail in Marsac et al. [19].

#### Complexation experiments

All concentrations given in  $\text{mol L}^{-1}$  (molarity, M) were corrected to  $\text{mol kg}^{-1} \text{ H}_2\text{O}$  (molality, m) for later calculations to avoid changes in the concentration because of variations in the solution density with temperature and ionic strength. Also the SIT (specific ion interaction theory) which was used for ionic strength correction to deduce complex stability constant at ionic strength zero, is based on the molal scale. The concentration of Np(V) was held at  $3 \times 10^{-6} \text{ M}$  in all extraction experiments. A first set of samples was prepared at different NaCl concentrations ( $I = 0.5\text{--}2.6 \text{ m}$ ) with total propionate concentration ( $[\text{prop}]_{\text{tot}}$ ) being varied from  $0.005$  to  $0.33 \text{ M}$  and lactate concentration ( $[\text{lac}]_{\text{tot}}$ ) from  $0.01$  to  $0.13 \text{ M}$  to determine the ionic strength dependence of Np(V)-propionate/lactate complexation at room temperature. Furthermore, additional series were prepared at a constant ionic strength of  $0.5 \text{ m}$  with varying the ligand concentration in the same ranges and different temperatures from  $22^\circ\text{C}$  up to  $60^\circ\text{C}$ . To maintain constant temperature, a water thermostat was used. Ligand (prop, lac) concentrations were set by adding aliquots of a  $1.0 \text{ M}$  solution of propionic acid or a  $0.5 \text{ M}$  solution of sodium lactate. The  $\text{pH}_c$  (molality of the proton;  $-\log [\text{H}^+]$ ) in each experimental batch was adjusted to a desired value of  $7.0 \pm 0.1$  at room temperature with  $0.01 \text{ M HCl}$  or  $0.01 \text{ M NaOH}$  and stabilized with  $5 \cdot 10^{-3} \text{ M}$  piperazine- $N,N'$ -bis(2-ethanesulfonic acid) (PIPES) as buffer. 2-thenoyltrifluoroacetone (TTA) and 1,10-phenanthroline (1,10-phen) were used without purification. A  $1 \cdot 10^{-3} \text{ M TTA} + 5 \cdot 10^{-4} \text{ M 1,10-phen}$  solution in isoamyl alcohol [20] was prepared and used as an organic phase for the extraction of  $\text{NpO}_2^+$ .

#### Solvent extraction

The solvent extraction experiments were conducted following the well-known procedure [21]. The organic solution containing  $1 \cdot 10^{-3} \text{ M}$  of TTA and  $5 \cdot 10^{-4} \text{ M}$  of 1,10-phen in isoamyl alcohol was pre-equilibrated with the aqueous stock solutions. For each extraction experiment  $2.0 \text{ ml}$  of aqueous solution containing the ligand, background electrolyte, PIPES buffer solution ( $5 \cdot 10^{-3} \text{ M}$ ) and  $^{237}\text{Np(V)}$  tracer at  $\text{pH}_c 7.0 \pm 0.1$  was mixed with an equal volume of organic solution. The tubes were inserted into the holes of the temperature-controlled shaker for 3 hours at desired temperature. According to the kinetic studies this time is enough to reach the extraction equilibrium [22]. Afterwards the tubes were centrifuged and  $0.5 \text{ ml}$  aliquots were taken from both phases for  $^{237}\text{Np}$  determination by LSC. No

quenching effects were observed either in aqueous or organic phases under the experimental conditions. In the remaining aqueous phase  $\text{pH}_{\text{exp}}$  was determined and  $\text{pH}_c$  was calculated as described below. The hydrolysis of  $\text{NpO}_2^+$  is not significant at  $\text{pH}_c < 9$  at the present temperature range 22-60 °C [23]. At room temperature Np(V) carbonate complexation is negligible for  $\text{pH}_c < 7.5$  [24]. To our knowledge, there is no study on Np(V) carbonate complexation at elevated temperature. By comparison, Am(III) and U(VI) complexation by carbonate marginally increases and decreases, respectively, with temperature ranging between 22 and 60 °C [25, 26]. In addition,  $\text{CO}_{2(\text{g})}$  solubility in water decreases with temperature. Since this work was carried out at  $\text{pH}_c = 7.0 \pm 0.1$ , the hydrolysis and carbonate complexation reactions are not taken into account. Note also that the effect of TTA complexation with Np(V) in the aqueous phase as well as Np(V)  $\text{Cl}^-$  complex formation were found to be negligible at the presently investigated conditions [20]. This was confirmed in our experiments where we clearly did not see a difference in the extraction of Np(V) with TTA between  $I = 0.5 \text{ m}$  and  $I = 2.5 \text{ m}$  NaCl in the absence of complexing ligands.

### pH measurements

In the present study, operational pH values ( $\text{pH}_{\text{exp}}$ ) were measured with an Orion 2 Star Benchtop pH meter using an Orion 8103SC combination pH electrode. Commercial pH Titrisol buffer concentrates (Merck p.a.) were used to calibrate the setup at room temperature. For pH measurements at  $I > 0.1 \text{ m}$  NaCl, the  $\text{pH}_{\text{exp}}$  was converted to the thermodynamically well-defined proton concentration  $\text{pH}_c$  ( $-\log [\text{H}^+]$ ) according to equation 1 and 2 [27]:

$$\text{pH}_c = \text{pH}_{\text{exp}} + A_{\text{NaCl}} \quad (1)$$

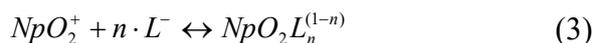
$$A_{\text{NaCl}} = 0.0013 * (m_{\text{NaCl}})^2 + 0.1715 * m_{\text{NaCl}} - 0.0988 \quad (2)$$

The empirical correction coefficient ( $A_{\text{NaCl}}$ ) depends on the background electrolyte composition and concentration. For that we have accurately measured the  $A_{\text{NaCl}}$  for the aqueous NaCl systems at room temperature.  $m_{\text{NaCl}}$  is the molality of the background electrolyte.  $\text{pH}_c$  was only determined at room temperature. The apparent proton dissociation constant of propionate/lactate ( $\text{p}K_a$ ) is below 5 within the range of  $[\text{NaCl}]$  and  $T$  investigated [11, 13]. For  $\text{pH}_c = 7$  (i.e.  $> \text{p}K_a + 2$ ), both ligands can be considered as fully unprotonated. PIPES was chosen as a buffer, because it shows maximum water solubility, minimum solubility in all other solvents (i.e. during the extraction experiment), minimal salt effects and minimal change in  $\text{p}K_a$  with temperature [28]. Hence,  $\text{pH}_c$  is not expected to be significantly affected when varying the temperature. For the calculations the total ligand concentration ( $[\text{Prop}]_{\text{tot}}$  or  $[\text{Lac}]_{\text{tot}}$ ) is considered to be equal to the free ligand concentration ( $[\text{Prop}]_{\text{eq}}$  or  $[\text{Lac}]_{\text{eq}}$ ).

## Results and Discussions

### Determination of the distribution ratio ( $D_0$ ) in absence of a ligand

The complexation reaction of Np(V) with a ligand  $L^-$  can be expressed as:

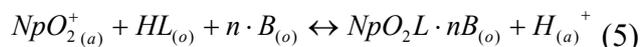


with the conditional stability constant ( $\beta_c$ , in  $(\text{kg} \cdot \text{mol}^{-1})^n$ ) defined as:

$$\beta_c = \frac{[\text{NpO}_2L_n^{(1-n)}]}{[\text{NpO}_2^+] \times [L^-]^n} \quad (4)$$

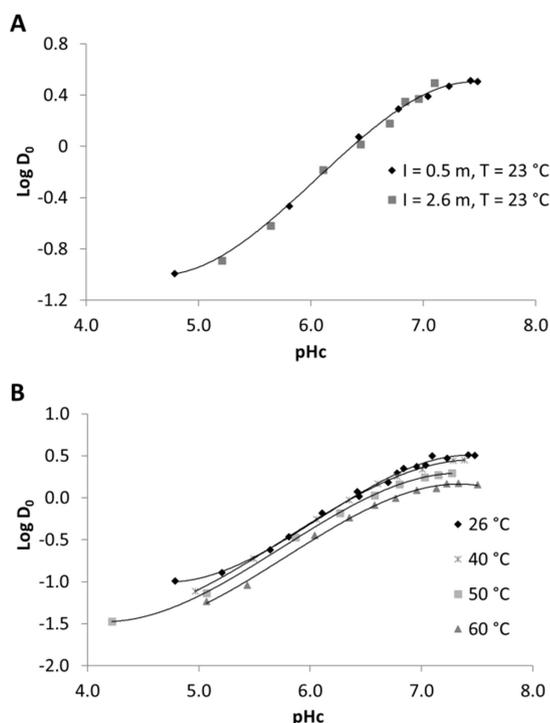
Neptunium (V) is a difficult ion to extract [29]. To enhance the extraction efficiency, the synergetic extraction by the mixture of 2-thenyltrifluoroacetone (TTA) and 1,10-phenanthroline (1,10-phen) was used [20].

The extraction reaction can be written as follows:



where (o) or (a) refers to the species in the organic or aqueous phase, respectively. B refers either to 1,10-phen or TTA. Extraction is characterized by a distribution ratio ( $D$ ) of Np(V) between the organic and aqueous phase:

$$D(pH, T, I) = \frac{\Sigma[M]_o}{\Sigma[M]_a} \quad (6)$$



**Fig. 1:** Distribution ratios of Np(V) upon extraction by  $1 \cdot 10^{-3}$  M TTA and  $5 \cdot 10^{-4}$  M 1,10-phen in the absence of complexing ligands: A: At 23 °C with two ionic strengths 0.5 m and 2.6 m NaCl; B: At varying temperature and at 0.5 m NaCl.

Where  $\Sigma[M]_o$  is the total concentration of metal ion in the organic phase and  $\Sigma[M]_a$  is the total concentration of metal ion in the aqueous phase.  $D$  depends on various factors like pH,  $T$ ,  $I$ , etc. Assuming the presence of various species in the aqueous phase and  $D_o$  as a distribution ratio in the absence of a ligand and L in the aqueous phase, equations (4) and (6) can be combined to:

$$D_o^k / D^k = 1 + \Sigma \beta_{c,n} \cdot [L_n]^n \quad (7)$$

where  $k$  is a serial number of a given experiment. In the particular case of a 1:1 Np-ligand complexation, as observed in the present study for both propionate and lactate (as shown later), equation (7) could be simplified to:

$$D_0^k / D^k = 1 + \beta_c [L^-] \quad (8)$$

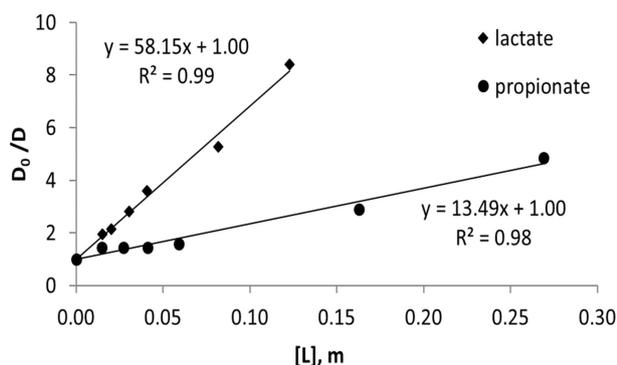
and the slope of  $D_0^k / D^k$  versus  $[L]$  corresponds to the conditional stability constant. To use the liquid-liquid extraction method according to equation (8) it is necessary to obtain  $D_0$  values for all the investigated conditions namely  $\text{pH}_c$ , ionic strength and temperature at fixed concentrations of extractants (TTA and 1,10-phen) and Np(V) ions.

**Table 1:** Experimentally obtained equations  $\log(D_0) = f(\text{pH}_c)$  for  $I = 0.5\text{-}2.6$  m.

$T$ (°C)	$\log(D_0) = f(\text{pH}_c)$
$26 \pm 1$	$-0.1535(\text{pH}_c)^3 + 2.7991(\text{pH}_c)^2 - 16.178 \text{pH}_c + 29.137$
$40 \pm 1$	$-0.0983(\text{pH}_c)^3 + 1.7022(\text{pH}_c)^2 - 8.9916 \text{pH}_c + 13.594$
$50 \pm 1$	$-0.1103(\text{pH}_c)^3 + 1.9015(\text{pH}_c)^2 - 10.094 \text{pH}_c + 15.548$
$60 \pm 1$	$-0.1162(\text{pH}_c)^3 + 2.0174(\text{pH}_c)^2 - 10.837 \text{pH}_c + 16.979$

Figure 1 shows the results of synergistic extraction of Np(V) as a function of  $\text{pH}_c$  in the absence of aqueous ligand at two ionic strengths (0.5 and 2.6 m). The slope of the linear part of this curve is equivalent to 0.74 that well fits to the literature data [20]. No significant influence of ionic strength on  $D_0$  values was observed. By contrast,  $D_0$  decreases with increasing temperature (Fig. 1-B). Third order polynomials were used to fit  $D_0$  versus  $\text{pH}_c$  at different temperature and the corresponding parameters are listed in Table 1. These equations were used to calculate the  $D_0$  value corresponding to the exact measured  $\text{pH}_c$  value of each extraction experiment in presence of aqueous ligand.

Figure 2 shows typical plots of the experimental values of  $D_0/D$  as a function of propionate or lactate concentrations.



**Fig. 2:** Representative plot of  $D_0/D$  versus free ligand concentration. Aqueous phase: 0.5 m NaCl. Organic phase: 0.001 M TTA + 0.0005 M 1,10-phen.

$D$  decreases with increasing concentration of both investigated ligands (s. Fig. 2,  $D_0$  is constant). The decrease in  $D$  is attributed to the increase in the concentration of Np(V)-L complexes in the aqueous

phase that are not extracted by TTA + 1,10-phen. The linear dependences of  $D_0/D$  from the concentration of the ligands indicate the formation of only 1:1 complexes for Np propionate and Np lactate complexes at the studied conditions. As stated before, the slope of  $D_0/D$  versus  $[L]$  (equation 8) corresponds to the conditional stability constants ( $\beta_c$ ). Table 2 summarizes the presently determined  $\beta_c$  values at 25 °C for Np(V) lactate and Np(V) propionate complexation from this work and from literature. For both ligands,  $\beta_c$  values slightly increase with increasing I and T.

**Table 2:** Conditional stability constants of neptunium (V) complex formation at 25±1 °C.

Complex <sup>1</sup>	[NaCl] (m)	pH	Method <sup>2</sup>	log $\beta_c$
<b>NpO<sub>2</sub>Acet</b>	0.30	6.0-7.2	e, [13]	1.05±0.04
	1.00	dto.	dto.	1.13±0.05
	2.00	dto.	dto.	1.25±0.05
	3.00	dto.	dto.	1.55±0.05
	4.00	dto.	dto.	1.70±0.20
	5.00	dto.	dto.	1.80±0.02
	1.05 *	7.0	e, cal, [32]	0.74±0.04
<b>NpO<sub>2</sub>Prop</b>	0.51	7.0±0.5	e, p.w.	0.99±0.03
	0.83	dto.	dto.	1.01±0.03
	1.67	dto.	dto.	1.14±0.03
	2.50	dto.	dto.	1.14±0.04
	0.51	7.0±0.5	sp, [11]	0.99±0.07
	0.51	dto.	dto.	1.04±0.12
	1.03 1	dto.	dto.	1.01±0.07
	2.10	dto.	dto.	1.15±0.19
	3.20	dto.	dto.	1.34±0.15
	4.38	dto.	dto.	1.51±0.16
<b>NpO<sub>2</sub>Lact</b>	0.51	7.0±0.5	e, p.w.	1.75±0.05
	0.83	dto.	dto.	1.75±0.03
	1.67	dto.	dto.	1.76±0.02
	2.50	dto.	dto.	1.84±0.02
	0.30	6.0-7.2	e, [13]	1.78±0.03
	1.00	dto.	dto.	1.43±0.04
	2.00	dto.	dto.	1.48±0.05
	3.00	dto.	dto.	1.76±0.02
	4.00	dto.	dto.	1.93±0.06
	5.00	dto.	dto.	1.95±0.04

<sup>1</sup>Complexation reaction:  $\text{NpO}_2^+ + \text{Ligand} = \text{NpO}_2\text{Ligand}$

<sup>2</sup>p.w. – present work, e – liquid-liquid extraction, sp – absorption spectroscopy, cal – calorimetry.; \* the medium is  $\text{NaClO}_4$

### Effect of ionic strength

Several equations can be used to extrapolate conditional stability constants to infinite dilution such as the specific ion interaction theory (SIT) and Pitzer approach [30]. SIT is applicable up to 3-4 m as recommended by NEA-TDB [31] and can be used in the present study. SIT is applied to estimate single-

ion activity coefficients ( $\gamma_i$ ) in solutions by taking into consideration the so called specific interaction coefficient ( $\varepsilon$ ) between various ions in solution.

This procedure allows evaluation of equilibrium constants ( $\beta^\circ$ ) at infinite dilution:

$$\beta^\circ = \beta_c \times \frac{\gamma(\text{NpO}_2\text{L})}{\gamma(\text{NpO}_2^+) \cdot \gamma(\text{L}^-)} \quad (9)$$

With SIT, activity coefficients can be expressed as:

$$\begin{aligned} \log \gamma_i &= -z^2 \frac{A(T)\sqrt{I}}{1+1.5\sqrt{I}} + \sum_k \varepsilon(i,k) \cdot m_k \\ &= -z^2 D + \sum_k \varepsilon(i,k) \cdot m_k \end{aligned} \quad (10)$$

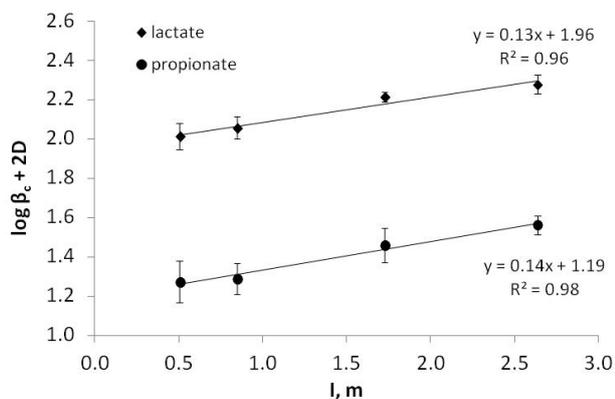
where  $m_k$  is the molality of the aqueous species  $k$ ;  $\varepsilon(i,k)$  is the specific ion interaction coefficient between species  $i$  and  $k$ ;  $D$  is the Debye-Hückel term;  $A(T)$  is the limiting Debye-Hückel equation slope, that depends on temperature:

$$A(T) = e^3 \sqrt{\frac{2\pi N \rho}{100(k\varepsilon_d T)^3}} \quad (11)$$

where  $N$  is the Avogadro number,  $e$  stands for absolute electronic charge,  $\varepsilon_d$  is the dielectric constant of water at the given temperature,  $\rho$  is the pure water density,  $k$  is the Boltzmann constant, and  $T$  is temperature (K). Combination of equations 9 and 10 gives:

$$\log \beta_c - \Delta z^2 \cdot D = \log \beta^\circ - \Delta\varepsilon \cdot I \quad (12)$$

where  $\Delta z^2 = \sum z^2(\text{products}) - \sum z^2(\text{reactants}) = -2$  for the reaction given in eq. (3), involving one propionate or lactate ion in the complex, and  $\Delta\varepsilon = \varepsilon(\text{Na}^+ + \text{Cl}^-; \text{NpO}_2\text{L}) - \varepsilon(\text{Na}^+; \text{L}^-) - \varepsilon(\text{Cl}^-; \text{NpO}_2^+)$ .



**Fig. 3:** SIT plot of the equilibrium reaction  $\text{NpO}_2^+ + \text{L}^- \rightleftharpoons \text{NpO}_2\text{L}$  in NaCl, yielding  $\log \beta^\circ = 1.19 \pm 0.03$  for propionate and  $\log \beta^\circ = 1.96 \pm 0.05$  for lactate.

Figure 3 presents the plot of  $\log \beta_c + 2D$  versus  $I$  (m). According to eq. 13, the intercept and the slope of the linear regression correspond to  $\log \beta^\circ$  and to  $-\Delta\varepsilon$ , respectively. From the data in Figure 3,  $\Delta\varepsilon$  is  $-0.14 \pm 0.02$  for propionate and  $-0.13 \pm 0.03$  for lactate and the  $\log \beta^\circ$  values are  $1.19 \pm 0.03$  and  $1.96 \pm 0.05$ , respectively. These values are shown in Table 4 and are compared with literature data.  $\log \beta^\circ$  and  $\Delta\varepsilon$  values are in excellent agreement with a previous spectroscopic study of Np(V) propionate complexation ( $\log \beta^\circ = 1.26 \pm 0.03$ ) [11]. Solvent extraction is a technique from which  $\log \beta$  is calculated by using the total complexed metal species, including outer and inner sphere complexes, whereas

spectroscopic technique takes into account only inner sphere species and might possibly result in understated  $\beta$  values [12]. The fact that both spectroscopic and solvent extraction methods provide similar thermodynamic parameters suggest that the  $\text{NpO}_2\text{Prop}$  complex is formed mainly via inner sphere complexation, as previously shown for Eu [12]. Literature data are also available for  $\text{Np(V)}$  complexation with acetate (Acet) [32]. The authors obtained  $\log \beta^\circ$  and  $\Delta\varepsilon$  values for the 1:1  $\text{NpO}_2\text{Acet}$  complex similar to the values for propionate derived in this work using NaCl as background electrolyte ( $\log \beta^\circ = 1.28 \pm 0.04$  and  $\Delta\varepsilon = -0.24 \pm 0.02$ ). Moore et al. [13] previously studied  $\text{Np(V)}$  complexation with acetate and lactate by liquid-liquid extraction (LLE) at 25°C and various ionic strengths ( $0 \leq I \leq 5$  m). Experimental  $\beta_c$  values are reported, but not the SIT parameters because the Pitzer model was used for ionic strength correction. For comparison purpose the original data from [13] were evaluated with eq. 12 to get  $\log \beta^\circ$  and  $\Delta\varepsilon$  values. The thus obtained values are in relatively good agreement with the present work (s. Table 4).

In the present study no hints of a chloride complexation of  $\text{NpO}_2^+$  could be found, because the chloride concentration was too small [33]. This confirms, that the chloride complexation of  $\text{Np(V)}$  is very weak and can be neglected to describe the studied system. In that case the interaction of  $\text{NpO}_2^+$  with the chloride ion can be regarded as an ion-ion interaction to be included in the specific interaction coefficients [33].

The stability constants  $\log \beta^\circ$  of  $\text{NpO}_2\text{Acet}$  and  $\text{NpO}_2\text{Prop}$  are similar with values between 1.19 and 1.29, suggesting that the extension of the carbon chain by one  $-\text{CH}_2$  group does not affect significantly the  $\log \beta^\circ$  value. It should be mentioned that for the  $\text{Np(V)}$  lactate complexation, the formation of a 1:2 complex was observed at larger lactate concentrations (0.1-1 M  $\text{NaClO}_4$ ) by Tochiyama et al. [14]. However, in the same publication Tochiyama et al. report a slightly smaller experimental  $\log \beta_{c1}$  value ( $1.40 \pm 0.02$ ) for the first lactate complex than the one obtained in the present paper ( $\log \beta_{c1} 1.75 \pm 0.03$ ).

## Effect of temperature

Effect of temperature on  $\text{Np(V)}$ -L complexation was investigated at  $T = 22, 40, 50,$  and  $60$  °C and  $[\text{NaCl}] = 0.51$  m (Table 3). Conditional  $\log \beta_c$  values were corrected to stability constant  $\log \beta^\circ(T)$  at infinite dilution for each temperature using SIT approach as described above. As suggested by previous work, variation of  $\varepsilon(i,k)$  with  $T$  ( $< \pm 0.05$   $\text{kg} \cdot \text{mol}^{-1}$ ) can be neglected [34,35]. With the hypothesis that the molal standard reaction enthalpy  $\Delta_r H_m^\circ$  and entropy  $\Delta_r S_m^\circ$  are not changing with temperature (i.e. that heat capacity is constant) under the experimental conditions, it is possible to determine these thermodynamic parameters from an Arrhenius plot on the basis of the van't Hoff equation:

$$\log \beta(T) = - \frac{\Delta_r H_m^\circ}{RT \ln 10} + \frac{\Delta_r S_m^\circ}{R \ln 10} \quad (13)$$

where  $R$  is the ideal gas constant. Figure 4 plots  $\log \beta(T)$  versus the reciprocal temperature (K)  $1/T$ . The linear dependences on temperature of  $\log \beta^\circ(T)$  validates our hypothesis. Calculated values of  $\Delta_r H_m^\circ$  and  $\Delta_r S_m^\circ$  are listed in the Table 4 with literature data for comparison. Presently determined parameters for propionate are consistent with a previous study on  $\text{Np(V)}$  propionate complexation by spectroscopy [11]. For  $[\text{NaClO}_4] = 1.05$  m, Rao et al. [32] determined  $\Delta_r H_m^\circ = 18.1 \pm 1.8$   $\text{kJ} \cdot \text{mol}^{-1}$  and  $\Delta_r S_m^\circ = 75 \pm 6$   $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ , which are comparable to our present results for the propionate system.

**Table 3:** Conditional stability constants of neptunium (V) complex formation at different temperatures.

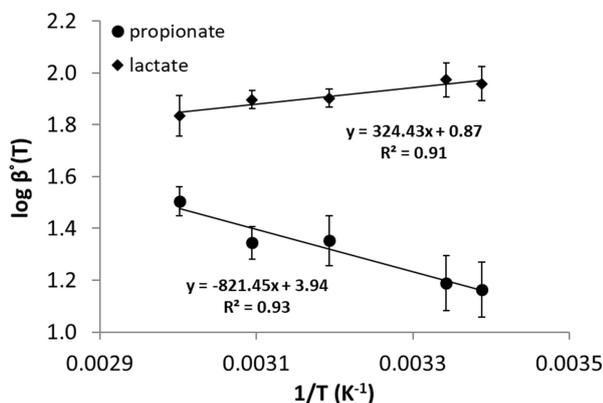
Complex <sup>1</sup>	T, °C	I (m)	log $\beta_c$	Method <sup>4</sup>
<b>NpO<sub>2</sub>Acet</b>	25	1.04 <sup>2</sup>	1.05±0.04*	sp,cal [32]
	40	dto.	1.11±0.03*	dto.
	55	dto.	1.19±0.03*	dto.
	70	dto.	1.34±0.05*	dto.
<b>NpO<sub>2</sub>Prop</b>	25	0.51 <sup>3</sup>	0.99±0.03	e, p.w.
	40	dto.	1.15±0.01	dto.
	50	dto.	1.29±0.10	dto.
	60	dto.	1.36±0.06	dto.
	20	dto.	1.07±0.10	sp [11]
	23	dto.	0.99±0.07	dto.
	23	dto.	1.04±0.06	dto.
	40	dto.	1.13±0.10	dto.
	60	dto.	1.19±0.10	dto.
	70	dto.	1.27±0.10	dto.
	85	dto.	1.36±0.13	dto.
<b>NpO<sub>2</sub>Lact</b>	25	0.51 <sup>3</sup>	1.75±0.05	e, p.w.
	40	dto.	1.77±0.03	dto.
	50	dto.	1.71±0.02	dto.
	60	dto.	1.69±0.02	dto.

\* In this work results of log  $\beta(T)$  were presented at zero ionic strength applying the SIT approach.

<sup>1</sup>Complexation reaction:  $\text{NpO}_2^+ + \text{Ligand}^- = \text{NpO}_2\text{Ligand}$ . <sup>2</sup>NaClO<sub>4</sub>; <sup>3</sup>NaCl.

<sup>4</sup>p.w. - present work; e - liquid-liquid extraction; sp - spectroscopy; cal - calorimetry.

Molar standard reaction enthalpy for NpO<sub>2</sub>Prop ( $\Delta_r H_m^\circ = 16.3 \pm 3.0 \text{ kJ} \cdot \text{mol}^{-1}$ ) is positive, which indicates that complexation of Np(V) with propionate is an endothermic reaction. In general, positive  $\Delta_r H_m^\circ$  and  $\Delta_r S_m^\circ$  are found for actinide complexes with monocarboxylic ligands, for example, Cm(III)Prop<sup>2+</sup> ( $\Delta_r H_m^\circ = 5.7 \pm 1.8 \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta_r S_m^\circ = 84 \pm 5 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  [34]; or UO<sub>2</sub>Acet<sup>+</sup> ( $\Delta_r H_m^\circ = 14.5 \pm 1.5 \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta_r S_m^\circ = 104 \pm 6 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  [36]). The energy effect of the complexation process is composed of (i) dehydration energy, which contributes to the positive enthalpy by removing of water molecules from the first hydration sphere of the cation and (ii) the energy of the metal-ligand interaction, which contributes to the negative enthalpy. The  $\Delta_r H_m^\circ > 0$  indicates that dehydration energy is required for complex formation and supports the model of inner sphere binding [37]. For both, NpO<sub>2</sub>Prop and NpO<sub>2</sub>Acet, the molar standard reaction entropy is positive indicating that the formation of these complexes is entropy driven. Relatively high values of  $\Delta_r S_m^\circ$  ( $75 \pm 6 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  [32] and  $77 \pm 9 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  for acetate and propionate, respectively) suggest a bidentate coordination mode of NpO<sub>2</sub>-OOC binding for acetate and propionate both with replacement of two water molecules from the inner sphere of Np(V), as previously confirmed by X-ray absorption spectroscopy [11].



**Fig. 4:** Np(V) complexation constants corrected to zero ionic strength ( $\log \beta^{\circ}$ ) versus the reciprocal of the temperature ( $K^{-1}$ ).

**Table 4:** Thermodynamic parameters of neptunium (V) complex formation.

Reaction (method)	$\log \beta^{\circ}$ (25°C)	$\Delta_r H_m^{\circ}$ ( $\text{kJ} \cdot \text{mol}^{-1}$ )	$\Delta_r S_m^{\circ}$ ( $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ )	$\Delta \epsilon$	Ref.
$\text{NpO}_2^{+} + \text{Acet}^{-} \leftrightarrow \text{NpO}_2\text{Acet}$ (spec, cal)	$1.28 \pm 0.04$	$18.1 \pm 1.8$ ( $I = 1.05\text{m}$ )	$75 \pm 6$ ( $I = 1.05\text{m}$ )	$-0.24 \pm 0.02$	[32]
$\text{NpO}_2^{+} + \text{Acet}^{-} \leftrightarrow \text{NpO}_2\text{Acet}$ (LLE)	$1.29 \pm 0.07^*$	-	-	$-0.23 \pm 0.03^*$	[13]
$\text{NpO}_2^{+} + \text{Prop}^{-} \leftrightarrow \text{NpO}_2\text{Prop}$ (LLE)	$1.19 \pm 0.03$	$16.3 \pm 3.0$	$77 \pm 9$	$-0.14 \pm 0.02$	p.w.
$\text{NpO}_2^{+} + \text{Prop}^{-} \leftrightarrow \text{NpO}_2\text{Prop}$ (spec)	$1.26 \pm 0.03$	$10.9 \pm 1.2$	$62 \pm 4$	$-0.17 \pm 0.03$	[11]
$\text{NpO}_2^{+} + \text{Lact}^{-} \leftrightarrow \text{NpO}_2\text{Lact}$ (LLE)	$1.85 \pm 0.29^*$	-	-	$-0.13 \pm 0.12^*$	[13]
$\text{NpO}_2^{+} + \text{Lact}^{-} \leftrightarrow \text{NpO}_2\text{Lact}$ (LLE)	$1.96 \pm 0.05$	$-5.4 \pm 1.4$	$19 \pm 4$	$-0.13 \pm 0.03$	p.w.
$\text{Nd}^{3+} + \text{Lact}^{-} \leftrightarrow \text{NdLact}^{2+}$ (spec, cal)		$-2.02 \pm 0.22$ ( $I = 1.05\text{m}$ )	$43 \pm 1$ ( $I = 1.05\text{m}$ )	-	[38]

\*the values were calculated using eq. 13 on the basis of published conditional stability constants.

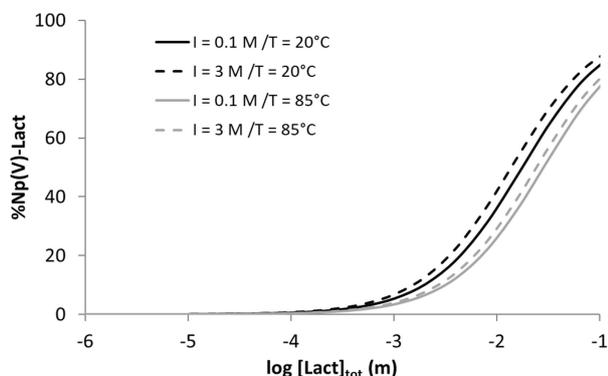
For lactate,  $\Delta_r H_m^{\circ}$  is negative ( $\Delta_r H_m^{\circ} = -5.4 \pm 1.4 \text{ kJ} \cdot \text{mol}^{-1}$ ). No stability constants at elevated temperature are available in the literature for Np(V) lactate complexation. However, a previous study of Nd(III) lactate complexation also showed a negative  $\Delta_r H_m^{\circ}$  [38]. The lactate contains a hydroxyl group beside the carboxyl group, which can participate in the formation of chelate structures. Lactate can either coordinate ‘end-on’ through the carboxylic group only or ‘side-on’ through both, the carboxylic and the hydroxyl group. It was shown earlier that lactate binds ‘side-on’ to Am(III) [39] as well as to Eu(III) [40]. A similar coordination can be expected for Np(V) lactate complexation. Indeed, similar observations to the present ones for Np(V) were made for lanthanide complexation by Choppin and Friedmann [41]. The enthalpies of lanthanide complexation were found to be exothermic for  $\alpha$ -hydroxycarboxylate ligands while they were endothermic for their simpler analogs like acetate and propionate. The entropy of complexation, though still positive, was likewise smaller for  $\alpha$ -hydroxycarboxylate ligands than for carboxylate ones.

### Np(V)- complexation with small organics at environmentally relevant concentrations

The Np(V) propionate complexation parameters determined in the present paper by solvent extraction technique are in a good agreement with the values obtained by UV-Vis/NIR spectroscopy earlier [11]. In the same publication the authors state that propionate has a minor impact on the Np(V) speciation at propionate concentrations found in natural clay. However, the relevance of lactate as a ligand that can increase Np mobility in natural clay formations should also be discussed.

Simulations were made with the geochemical speciation program PHREEQC [42] for  $\text{pH}_c = 7$ , with 0.1 and 3 m NaCl and at  $T = 20$  and  $85^{\circ}\text{C}$  using the presently obtained Np(V) lactate complexation

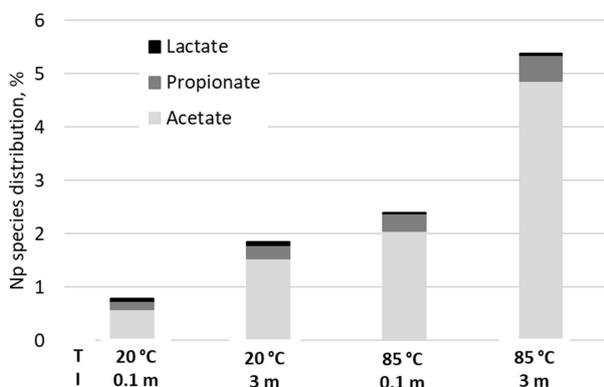
parameters. The percentage of Np(V) complexed to lactate versus  $\log [\text{Lact}]_{\text{tot}}$  is shown in Fig. 5 ( $[\text{Np(V)}]_{\text{tot}} = 10^{-10} \text{ m}$ ). Np(V) lactate complexation slightly increases with I between 0.1 and 3 m for a given T, and slightly decreases with T between 20 and 85°C for a given I because of the exothermic effect of complexation.



**Fig. 5:** Chemical equilibrium diagram for Np(V) complexed species present in solutions consisting lactate (0-0.1 m).

According to our calculations, at  $[\text{Lact}] = 10^{-3} \text{ m}$ , only about 5% of Np(V) is bound to the ligand. At  $\log [\text{Lact}]_{\text{tot}}$  higher than 0.1 M formation of a 1:2 Np(V) lactate complex becomes significant [14], but for small lactate concentrations even the  $\text{NpO}_2\text{Lac}$  complex plays a minor role for the Np(V) speciation. We never observed any hints of a 1:2 Np(V) lactate complex at our experimental conditions of  $[\text{Lact}]_{\text{tot}} < 0.1 \text{ M}$ . If we consider OPA and COx as representatives for clay formations designated to be a host rock for nuclear repository sites, the lactate concentrations in the pore water were found to be lower than  $10 \mu\text{M}$  [7,8]. This suggests that the influence of Np(V) lactate complexation is small under these conditions.

To get an overall picture of the influence of the low-molecular weight organic ligands acetate, propionate, and lactate on Np(V) speciation at COx conditions (1865  $\mu\text{M}$  acetate, 127  $\mu\text{M}$  propionate and 8  $\mu\text{M}$  lactate [7]), the speciation was calculated using previous (for acetate, [32]) and presently determined parameters (for lactate and propionate) at the same fixed I and T as studied in Figure 5 for various lactate concentrations. The results are plotted in Figure 6 for the three organic ligands. Although the total amount of Np(V) bound to these small organic molecules globally increases with temperature and salinity, it remains below 6% (in 3 m NaCl for  $T = 85^\circ\text{C}$ ). Therefore, these calculations suggest that small clay organic ligands have only little influence on Np(V) speciation in the aquatic solution at conditions relevant to clay pore waters of OPA and COx.



**Fig. 6:** Calculated Np(V) speciation in pore water of COx (1865  $\mu\text{M}$  acetate, 127  $\mu\text{M}$  propionate and 8  $\mu\text{M}$  lactate at  $\text{pH}_c = 7$  [7]) versus I and T.

## Surface complexation modeling

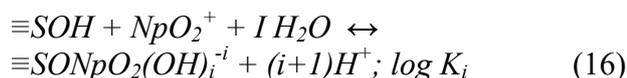
PHREEQC [42] was applied to evaluate the impact of small organics on Np(V) sorption to illite. Indeed, illite is the most important adsorbent for radionuclides in OPA and COx [43]. PHREEQC can perform aqueous speciation calculations under dilute to highly saline conditions with SIT, and has previously been applied in surface complexation modeling studies at various ionic strengths [44-46]. The 2-site protolysis non-electrostatic surface complexation and cation exchange model (2SPNE SC/CE model [47]) was used to simulate Np sorption to illite. The cation exchange capacity (CEC) of the illite was set to  $0.225 \text{ eq}\cdot\text{kg}^{-1}$ . In PHREEQC, the Gaines and Thomas convention [48] can be used, whereby cation exchange reactions, the thermodynamic exchange constant ( $K_{\text{exch}}$ ), and selectivity coefficient ( ${}_{Na}^{Np}K_c$ ) are expressed as follows:



$$K_{\text{exch}} = \frac{N_{\text{Np}}}{N_{\text{Na}}} \times \frac{f_{\text{Np}}}{f_{\text{Na}}} \frac{[\text{Na}^+]}{[\text{NpO}_2^+]} = {}_{Na}^{Np}K_c \times \frac{f_{\text{Np}}}{f_{\text{Na}}} \quad (15)$$

Here,  $N_i$  are equivalent fractions,  $f_i$  are surface activity coefficients and brackets denote activities in solution. 2SPNE SC/CE model accounts for the presence of abundant weak and few strong sites for the surface complexation of cations at illite edges.

Only the strong sites of the 2SPNE SC/CE model were considered in the adsorption calculations with a site density of  $2 \times 10^{-3} \text{ mol}\cdot\text{kg}^{-1}$  of illite, since the weak sites are irrelevant at trace levels of Np [19, 46]. Strong sites undergo protonation ( $\log K_{a,1} = 4$ ) and deprotonation reactions ( $\log K_{a,2} = -6.2$ ). Np(V) binding to these sites is written as follows:



with  $i = 0$  or  $1$ . Bradbury and Baeyens [47] determined a  $\text{NpO}_2^+ - \text{Na}^+$  selectivity coefficient ( $K_c = 1$ ) for illite as well as Np(V) surface complexation constants for illite within the 2SPNE SC/CE model ( $\log K_0 = -2$ ;  $\log K_1 = -10.3$ ).

Simulations were made at  $\text{pH}_c = 7$  in  $0.1$  and  $3 \text{ m}$  NaCl, at  $25$  and  $85^\circ\text{C}$ . Adsorption of small organics and ternary illite-Np-organic complexes were neglected. Surface complexation modeling was used to compute Np solid-liquid distribution ratios ( $R_d$ , in  $\text{L}/\text{kg}$ ):

$$R_d = ([\text{Np}]_{\text{tot}} / [\text{Np}]_{\text{aq}} - 1) \times V / m \quad (17)$$

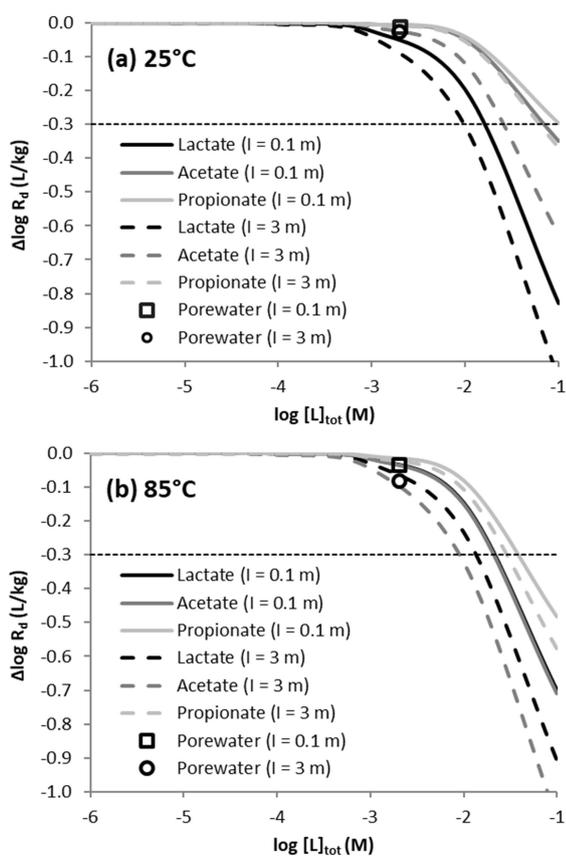
where  $[\text{Np}]_{\text{aq}}$  and  $[\text{Np}]_{\text{tot}}$  ( $\text{mol}\cdot\text{L}^{-1}$ ) are the dissolved (final) equilibrium and total (initial) concentrations of Np in solution, respectively. The term  $V/m$  corresponds to the aqueous solution volume to illite mass ratio ( $\text{L}\cdot\text{kg}^{-1}$ ). Note that calculations based on  $R_d$  values are independent of  $V/m$  values used for the calculations. Because temperature dependent Np(V) adsorption to illite is unknown, the temperature effect on sorption is neglected in the modeling and only temperature dependence of the aqueous

speciation is considered. The results of the modeling are presented in Figure 7 as the variation of  $\log R_d$  ( $\Delta \log R_d$ ) versus ligand concentration:

$$\Delta \log R_d = \log R_d([L]) - \log R_d([L] = 0M) \quad (18)$$

This allows visualizing only effects of small organic molecules on Np(V) adsorption. An uncertainty of  $\pm 0.3$  is commonly associated with  $\log R_d$  determination for radionuclide sorption to clay minerals [49], hence no significant effects of ligands on Np(V) adsorption on illite can be expected for  $\Delta \log R_d \leq 0.3$ . Decreasing of  $\log R_d$  at relevant concentrations of small clay organic ligands found in COx pore water (1865  $\mu\text{M}$  acetate, 127  $\mu\text{M}$  propionate and 8  $\mu\text{M}$  lactate [7]) were also calculated for high temperature and ionic strength (in 3 m NaCl for  $T = 85^\circ\text{C}$ ) and plotted in Figure 7.

According to modeling results, the expected influence of Np(V) complexation with small organic molecules even at higher temperature and ionic strength is several times smaller than the uncertainty on  $\log R_d$  determination for radionuclide sorption to clay minerals [47]. This suggests no significant influence of small organic molecules on Np(V) retention on clay minerals at OPA and COx conditions, even at elevated temperatures. Note that ternary clay-Np-organic complexes formation, omitted in these calculations because unknown, should further decrease the negative effect of small organic ligands on Np adsorption. Hence, these calculations correspond to an upper limit scenario related to the Np(V) complexation with small organic ligands. This is corroborated by Fröhlich et al. [50], which show that the sorption of Np(V) on OPA (OPA contains illite as the main clay mineral phase) increases with increasing temperature. From this work we can conclude, that Np(V)-clay adsorption increases more strongly with increasing temperature than Np(V) complexation with small organics.



**Fig. 7:** Variations of Np(V) sorption ( $\Delta \log R_d$ ) on Na-illite at different concentrations of small organics, T and I in comparison with variation of sorption at pore water conditions of COx (1865  $\mu\text{M}$  acetate, 127  $\mu\text{M}$  propionate and 8  $\mu\text{M}$  lactate at pH = 7 [7]).

## Conclusions

In the present study, liquid-liquid extraction was successfully applied and distribution ratios for Np(V) propionate and Np(V) lactate solutions were calculated.

The present study clearly identifies the 1:1  $\text{NpO}_2^+$  propionate and lactate complexes as the dominant species under the investigated conditions with  $\log \beta^\circ (25^\circ\text{C}) = 1.19 \pm 0.03$  for propionate and  $\log \beta^\circ (25^\circ\text{C}) = 1.96 \pm 0.05$  for lactate. Both stability constants increase with increasing ionic strength ( $0.5 < \text{NaCl} < 2.6 \text{ m}$ ) and with increasing temperature ( $22 < T < 60^\circ\text{C}$ ). The complex formation reaction is endothermic for propionate complexation and entropy driven, as evidenced by  $\Delta_r H_m^\circ = 16.3 \pm 3.0 \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_r S_m^\circ = 77 \pm 9 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . The magnitude of  $\Delta_r S_m^\circ$  is consistent with an inner sphere bidentate coordination mode of the carboxylate, as previously observed by spectroscopy [11]. The results are in a good agreement with literature [11, 13]. However, formation reaction is exothermic for lactate complexation. It is both enthalpy and entropy driven, as evidenced by  $\Delta_r H_m^\circ = -5.4 \pm 1.4 \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_r S_m^\circ = 19 \pm 4 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ , which supports the formation of a chelate structure involving the carboxylate and the hydroxyl group of the lactate ligand. These derived thermodynamic data ( $\Delta_r H_m^\circ$ ,  $\Delta_r S_m^\circ$ ,  $\log \beta^\circ(T)$ ) for Np(V)-propionate and lactate complexation complements the thermodynamic databases for modeling of environmentally significant processes which is relevant for safety assessment of nuclear waste disposal scenarios. Using the present data it is possible to assess the impact of complexation processes on the geochemical behavior of Np(V). According to the obtained results small clay organic molecules (acetate, lactate, propionate) have only little influence on Np(V) retention under the conditions that were found for OPA and COx pore waters.

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