

A spectroscopic study of the hydrolysis, colloid formation and solubility of Np(IV)

By V. Neck^{1,*}, J.I. Kim¹, B.S. Seidel¹, C.M. Marquardt¹, K. Dardenne¹, M.P. Jensen² and W. Hauser¹

¹ Forschungszentrum Karlsruhe, Institut für Nukleare Entsorgung, Postfach 3640, D-76021 Karlsruhe, Germany

² Argonne National Laboratory Chemistry Division, 9700 South Cass Avenue, Argonne, Illinois 60439-4831, USA

Neptunium(IV) / Hydrolysis / Colloid formation / Solubility product / Spectroscopy / LPAS / LIBD

Summary. The hydrolysis, colloid formation and solubility of Np(IV) are investigated in aqueous HClO₄-NaClO₄ solutions (log [H⁺] = 0 to -2.5) by absorption spectroscopy in the wavelength range of 680–1000 nm. Applying Laser induced photoacoustic spectroscopy (LPAS) in the range of 680–760 nm, the study is extended to low Np(IV) concentrations of 10⁻⁶ mol/l in DClO₄-NaClO₄-D₂O solutions up to log [D⁺] = -3.3. Laser induced breakdown detection (LIBD) demonstrates the formation of Np(IV) colloids when the Np(IV) concentration exceeds the solubility of Np(OH)₄(am) at given pH. The simultaneous decrease of the Np(IV) absorption bands at 723 and 960 nm cannot be ascribed to the formation of the mononuclear complex Np(OH)₂²⁺ as assumed in the literature. It is found to be caused by polynucleation. In undersaturated Np(IV) solutions below 10⁻⁴ mol/l, the position and intensity of the absorption maximum at 723 nm are practically insensitive to the pH change. In oversaturated solutions the absorption band decreases significantly. The spectroscopically determined pH-dependent equilibrium concentration of mononuclear Np(IV) species above freshly formed solid or colloidal Np(IV) particles indicates that Np(OH)₂²⁺ is the predominant species in the pH range of 1.5–3. This finding is in agreement with the Np(IV) hydrolysis constants reported in the literature from a solvent extraction study with ²³⁹Np(IV) trace concentrations. The solubility product of freshly formed Np(OH)₄(am) particles is determined to be log K'_{sp} = -54.4 ± 0.4 in 0.1 M HClO₄-NaClO₄ and log K^o_{sp} = -56.5 ± 0.4 (converted to I = 0 by applying the SIT).

1. Introduction

The strong tendency toward hydrolysis and colloid formation in aqueous solution even at low pH and the low solubility of Np(IV) hydroxide or hydrous oxide complicate the evaluation of thermodynamic data for Np(IV). The reported hydrolysis constants are based either on absorption spectroscopy [1–3] or on solvent extraction [4]. In the spectroscopic studies [1–3], a decrease of the characteristic Np(IV) absorption bands was observed when pH was increased from 0 to 2. This effect was ascribed to the

initial mononuclear hydrolysis reaction (Np⁴⁺ + H₂O ⇌ NpOH³⁺ + H⁺). However, the concentrations used in these studies ([Np(IV)] = 1.4 × 10⁻³–7.5 × 10⁻³ mol/l) considerably exceed the solubility of Np(IV) hydroxide or hydrous oxide [6]. As demonstrated in recent papers on the solubility, hydrolysis and colloid formation of Pu(IV) [7] and Th(IV) [8], the formation of colloids is the predominant reaction when the concentration exceeds the solubility of the corresponding hydroxide or hydrous oxide.

In the present study, the hydrolysis and colloid formation of Np(IV) is investigated in the pH range of 0–3. Compared to the previous literature studies [1–3, 15–18], advanced spectroscopy allows investigation at lower Np(IV) concentrations. Laser-induced photoacoustic spectroscopy (LPAS), based on the absorption of light which generates acoustic signals by the nonlinear relaxation of the excited molecules, is known to be very sensitive and has been successfully applied for the speciation of actinides in the sub μmol concentration range [19]. However, as the solvent H₂O possesses a high absorbance in the spectral range of interest [20], the investigation at Np(IV) concentrations below 10⁻⁵ mol/l requires the use of the less absorbing solvent D₂O. The formation of Np(IV) colloids in solutions exceeding the solubility limit of Np(OH)₄(am) at given pH is investigated by laser induced breakdown detection (LIBD). The principle of this method, which is based on the plasma generation on colloids in the focal volume of a pulsed laser beam, is described in detail elsewhere [21–25]. Since the critical irradiance to produce plasma is lower on solids than on liquids, the plasma can be generated selectively on dispersed particles by adjusting the laser pulse irradiance below the breakdown threshold of water. The applicability of LIBD to actinide colloids has been verified by direct measurement of Pu(IV) colloids [7] and Th(IV) colloids with a diameter ≤ 20 nm [8, 25].

1.1 Thermodynamic data for Np(IV)

The hitherto available data on the solubility and hydrolysis of tetravalent actinides have been critically discussed in our recent review [6]. The Np(IV) hydrolysis constants determined by spectroscopy (log K'₁ = -2.30 in 2.0 M HClO₄-NaClO₄ [1], -1.90 [2] and -2.25 [3] in 1.0 M HClO₄-NaClO₄) are more than one order of magnitude lower than the value determined by solvent extraction (log K'₁ = -0.5 and log K'₂ = -1.5 in 1.0 M

* Author for correspondence (E-mail: neck@ine.fzk.de).

HClO₄-LiClO₄ [4]). As all the spectroscopic studies include data in more or less oversaturated solutions, the solvent extraction experiment of Duplessis and Guillaumont [4] performed with Np-239 in trace concentrations is the only study where the interference of colloid formation can be excluded. In addition, a similar solvent extraction study with Pu-238 trace concentrations [5] led to comparable values for the hydrolysis constants of Pu(IV). As the latter study was performed up to pH 8, a complete set of mononuclear hydrolysis constants $\log K'_1$ to $\log K'_4$ could be evaluated, which describe well the available solubility data for Pu(OH)₄(am) over the whole range of pH = 0–13 [6, 7]. The hydrolysis constants determined in the solvent extraction studies of Guillaumont *et al.* [4, 5] are therefore considered to be the most reliable values among the published data for Np(IV) and Pu(IV). Based on the hydrolysis constants $\log K'_1$ and $\log K'_2$ of Np(IV) [4], the solubility product of NpO₂·xH₂O(am) ($\log K^\circ_{sp} = -56.7 \pm 0.5$ [6]) is calculated from a few solubility data determined by Rai *et al.* [9] in diluted acidic solutions. The formation constants of Np(OH)³⁺ and Np(OH)₄(aq) are based on semi-empirical estimation methods and the available solubility data in neutral to alkaline solutions [10–12]. There are no data available for polynuclear hydroxide complexes of Np(IV). The thermodynamic data selected in [6] are summarized in Table 1. The solubility product of amorphous Np(IV) hydroxide or hydrous oxide (K'_{sp} in a given medium and K°_{sp} at $I = 0$), formation constants of mononuclear complexes Np(OH)_n⁴⁻ⁿ (β_n) and corresponding hydrolysis constants (K_n) are defined by

$$\begin{aligned} K'_{sp} &= [\text{Np}^{4+}][\text{OH}^-]^4 \\ &= K^\circ_{sp}/\gamma_{\text{Np}}(\gamma_{\text{OH}})^4 \end{aligned} \quad (1)$$

$$\begin{aligned} \beta'_n &= [\text{Np}(\text{OH})_n^{4-n}]/[\text{Np}^{4+}][\text{OH}^-]^n \\ &= \beta^\circ_n \gamma_{\text{Np}}(\gamma_{\text{OH}})^n/\gamma_{\text{Np}(\text{OH})_n} \end{aligned} \quad (2)$$

$$\begin{aligned} K'_n &= [\text{Np}(\text{OH})_n^{4-n}][\text{H}^+]^n/[\text{Np}^{4+}] \\ &= K^\circ_n \gamma_{\text{Np}}(a_w)^n/\gamma_{\text{Np}(\text{OH})_n}(\gamma_{\text{H}})^n \end{aligned} \quad (3)$$

[*i*] is the concentration of species *i*, γ_i its activity coefficient and a_w the activity of water. Activity coefficients are calculated by using the specific ion interaction theory (SIT) [13, 14]:

$$\log \gamma_i = -z_i^2 D + \sum \varepsilon_{ij} m_j, \quad (4)$$

where z_i is the charge of ion *i*, m_j (mol/kg H₂O) the molal concentration of ion *j*, and D the Debye-Hückel term, at 25 °C: $D = 0.509\sqrt{I}/(1 + \text{B}\hat{a}\sqrt{I})$, with $\text{B}\hat{a} = 1.5$. I is the molal ionic strength and ε_{ij} the ion-ion interaction parameter for a pair of oppositely charged ions.

Fig. 1 shows the experimental solubility data reported in the literature [9–12] for Np(IV) hydroxide or hydrous oxide and the solubility calculated as a function of the H⁺ concentration (solid line) with the thermodynamic data given in Table 1. As the selected Np(IV) hydrolysis constants and solubility product are based only on a few experimental data, the present work is performed in order to ascertain these data by additional new experiments.

Table 1. Thermodynamic constants at $I = 0$ and ion interaction (SIT) coefficients for Np(IV) species at 25 °C (from Neck and Kim [6]).

Solubility product of Np(OH) ₄ (am) or NpO ₂ ·xH ₂ O(am):		
$\log K^\circ_{sp} = -56.7 \pm 0.5$		
Formation constants $\log \beta_n^\circ$ of mononuclear hydroxide complexes Np(OH) _n ⁴⁻ⁿ		
$\log \beta_1^\circ = 14.5 \pm 0.2$	$(\log K^\circ_1 = 0.5 \pm 0.2)$	
$\log \beta_2^\circ = 28.3 \pm 0.3$	$(\log K^\circ_2 = 0.3 \pm 0.3)$	
$\log \beta_3^\circ = 39.2 \pm 1.0$	$(\log K^\circ_3 = -2.8 \pm 1.0)$	
$\log \beta_4^\circ = 47.7 \pm 1.1$	$(\log K^\circ_4 = -8.3 \pm 1.1)$	
Ion interaction (SIT) coefficients:		
<i>i</i>	<i>j</i>	ε_{ij}
H ⁺	ClO ₄ ⁻	0.14 ± 0.02^b
OH ⁻	Na ⁺	0.04 ± 0.01^b
Np ⁴⁺	ClO ₄ ⁻	0.82 ± 0.05^b
Np(OH) ³⁺	ClO ₄ ⁻	0.5 ± 0.1^c
Np(OH) ₂ ²⁺	ClO ₄ ⁻	0.3 ± 0.1^c
Np(OH) ₃ ⁺	ClO ₄ ⁻	0.15 ± 0.1^c
Np(OH) ₄ ⁰	Na ⁺ , ClO ₄ ⁻	0^b

- a: $\log \beta_1^\circ$ and $\log \beta_2^\circ$ are based on experimental data from [4], $\log \beta_3^\circ$ and $\log \beta_4^\circ$ are estimates. The $\log K^\circ_n$ values (in brackets) refer to the reactions $\text{Np}^{4+} + n\text{H}_2\text{O} \rightleftharpoons \text{Np}(\text{OH})_n^{4-n} + n\text{H}^+$;
 b: From the NEA-TDB [14];
 c: Estimated in [6] according to the analogies and systematics pointed out in the NEA-TDB [14].

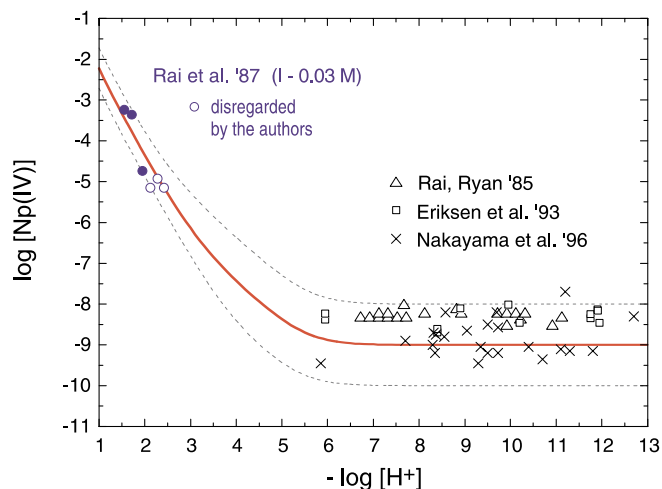


Fig. 1. Solubility of Np(IV) hydroxide at 25 °C. The experimental data in diluted acidic solution are taken from Rai *et al.* [9], those in neutral and alkaline solutions of $I < 1$ M from Refs. [10–12]. The solid line is calculated for $I = 0.03$ M with the thermodynamic data given in Table 1. The dashed lines show the associated uncertainty limits.

2. Experimental

2.1 Chemicals

A solution of isotope ²³⁷Np is prepared by dissolving NpO₂ in 8 M HNO₃ and purified by anion exchange. The effluent is evaporated to dryness with addition of HClO₄ and redissolved in 1.0 or 0.1 M HClO₄, yielding in a ca. 0.05 M Np(V) solution, which is electrochemically reduced to Np(III). The Np(III) solution is converted to Np(IV), either electrochemically or by autoxidation within about three days. The complete reduction and oxidation process is verified by spectroscopy. Corresponding solutions are

prepared with D₂O and DCIO₄ (68 mass %) from Sigma-Aldrich (99.9% deuterium). The Np(IV) solutions are stored in an argon box to avoid oxidation to Np(V). The concentration of ²³⁷Np is determined by liquid scintillation α -spectrometry (Tri-Carb 2500 TR/AB), discriminating the β -activity of its daughter nuclide ²³³Pa. Samples at desired H⁺ or D⁺ concentration are prepared batchwise by dilution of the stock solution with deaerated HClO₄ or DCIO₄ (in D₂O) containing dried anhydrous NaClO₄ (Alfa) to keep ionic strength constant at $I = 0.1$ mol/l. The H⁺ concentration of solutions in H₂O is measured with a combined ROSS electrode (Orion) calibrated against pH buffers (Merck) and 0.1 M HClO₄-NaClO₄ standards with log [H⁺] in the range of -1.00 to -3.00 .

2.2 Spectroscopic studies

Absorption spectra are recorded in the wavelength range of 680 to 1000 nm to study the most intense Np(IV) absorption bands with maxima at 723 and 960 nm. Most of the spectra were recorded at FZK-INE with a CARY 5E spectrometer (Varian) using 1 cm quartz cuvettes. One series of spectra was measured at Argonne National Laboratory Chemistry Division with a CARY 14 spectrometer. The experimental setup of LPAS, developed for the present investigations, is based on a pulsed (20 Hz), frequency doubled Nd-YAG laser (532 nm, Continuum, NY 82-20) used as pump source for a tunable dye laser (Continuum, Nd-60), which is suitable for the spectral range of 680–760 nm (laser dye Exciton LDS 720). The position of the 1 cm quartz dye laser cell is adjusted in the plane perpendicular to the laser axis. The acoustic signal, proportional to the absorption of the sample, is detected by a pressure sensor containing a piezoelectric transducer horizontally pressed to the cuvette wall. The sensor converts the pressure wave into a voltage signal, which is preamplified with a 40 dB low-noise amplifier and, after high pass filtering to suppress low frequency interferences, transmitted to a digital signal analyzer. The amplitude of the third maximum of the pressure wave is used as the LPAS signal. As the energy of the dye laser system varies during the wavelength scan according to the efficiency of the laser dye, the pulse energy of up to 512 laser shots at each wavelength is averaged and used for normalization of the LPAS signal. The UV/VIS and LPAS spectra of the solutions at $I = 0.1$ mol/l are recorded after equilibration for one day, partly after filtration with Amicon 10 kD filters to remove solid or colloidal particles.

2.3 Colloid detection by LIBD

In a separate experiment, the generation of Np(IV) colloids is investigated as a function of the H⁺ concentration at $I = 0.1$ M (HClO₄-NaClO₄) by means of laser-induced breakdown detection (LIBD). An analogous experiment is performed for comparison in 0.1 M DCIO₄-NaClO₄. The batch solutions are prepared as described above, but the initial solutions are filtered several times (Amicon 10 kD filters, pore size about 1 nm) to minimize the presence of other colloids. The experimental setup of the LIBD apparatus and its calibration with reference colloids have been described previously [23–25]. The breakdown probability, i.e. the number

of breakdown events per laser pulse for an adjusted energy threshold, is correlated with the mass concentration of colloids of given particle size and material.

All experiments are performed at room temperature (23 ± 2 °C).

3. Results and discussion

3.1 UV/VIS absorption spectroscopy and LIBD in HClO₄-NaClO₄ solution

The absorption spectra of Np(IV) in acidic solutions were investigated decades ago [15–18] usually at high Np(IV) concentrations ranging from 10^{-3} to 10^{-2} mol/l. The most intense absorption bands with maxima at 723 and 960 nm are well known, but the reported molar absorption coefficients vary considerably: $\epsilon_{723} = 126$ L mol⁻¹ cm⁻¹ in 1 M HCl [15], 144 ± 1 in 1 M HClO₄ [16], 121 in 1 M HClO₄ [17], 127 in 2 M HClO₄ [18], and $\epsilon_{960} = 160$ L mol⁻¹ cm⁻¹ in 1 M HCl [15], 146–197 (depending on the Np concentration) in 1 M HClO₄ [16], 141 in 1 M HClO₄ [17], and 162 in 2 M HClO₄ [18]. It is further reported that the molar absorption in 10^{-3} to 10^{-2} M Np(IV) solutions decreases continuously if the pH is increased from 0 to 2 [1, 2, 16].

The present results obtained for a series of absorption spectra at a constant Np(IV) concentration of 1.04×10^{-3} mol/l in 1.0 M HClO₄ and varying pH in 0.1 M HClO₄-NaClO₄ remain consistent. The molar absorption coefficients in 1.0 M HClO₄ ($\epsilon_{723} = 143$ L mol⁻¹ cm⁻¹ and $\epsilon_{960} = 206 \pm 10$ L mol⁻¹ cm⁻¹) are comparable with those of Sjoblom and Hindman [16]. Fig. 2 shows the absorption spectra in 0.1 M HClO₄-NaClO₄ solutions with log [H⁺] in the range -1.0 to -2.0 . In accordance with the observations in a literature study [1] at comparable Np(IV) concentrations (1.4×10^{-3} and 2.7×10^{-3} mol/l in 2 M HClO₄-NaClO₄), the position of the absorption maxima at 960 nm and the multiplett at 713, 723.4 and 741 nm are not shifted but the absorbances decrease with increasing pH. Simultaneously a diffused broad band arises in the range

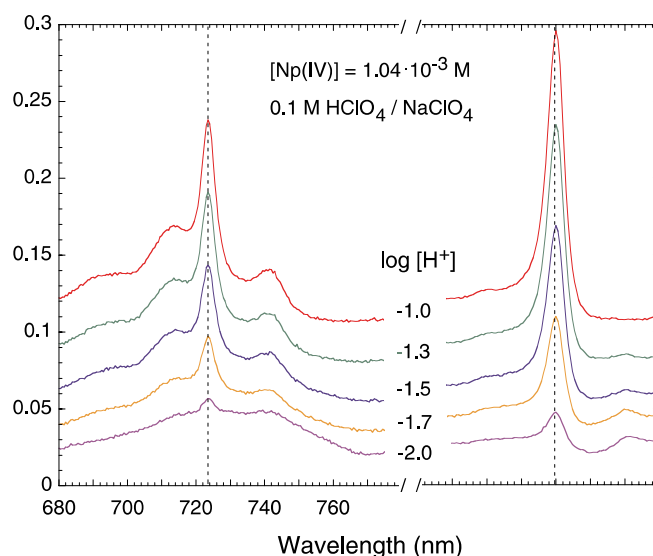


Fig. 2. Absorption spectra of 1.04×10^{-3} M Np(IV) solutions at different H⁺ concentrations in 0.1 M HClO₄-NaClO₄. For easier survey the spectra are shifted upwards.

700–750 nm and overlaps with the characteristic Np(IV) multiplet in this wavelength region. The contribution of the broad band is illustrated in Fig. 3 by comparing the spectra at $\log [H^+] = -1.0, -1.7$ and -2.0 . The original spectra cross each other (Fig. 3a), whereas after subtraction of the contributions of the broad band (Fig. 3b), the absorbance of the characteristic Np(IV) multiplet is decreased by a constant factor (Fig. 3c). In absorption spectra recorded after 10 kD filtration the broad band is absent, indicating that it is caused by colloidal Np(IV) particles. Fig. 4 shows UV/VIS spectra obtained from filtered solutions with an

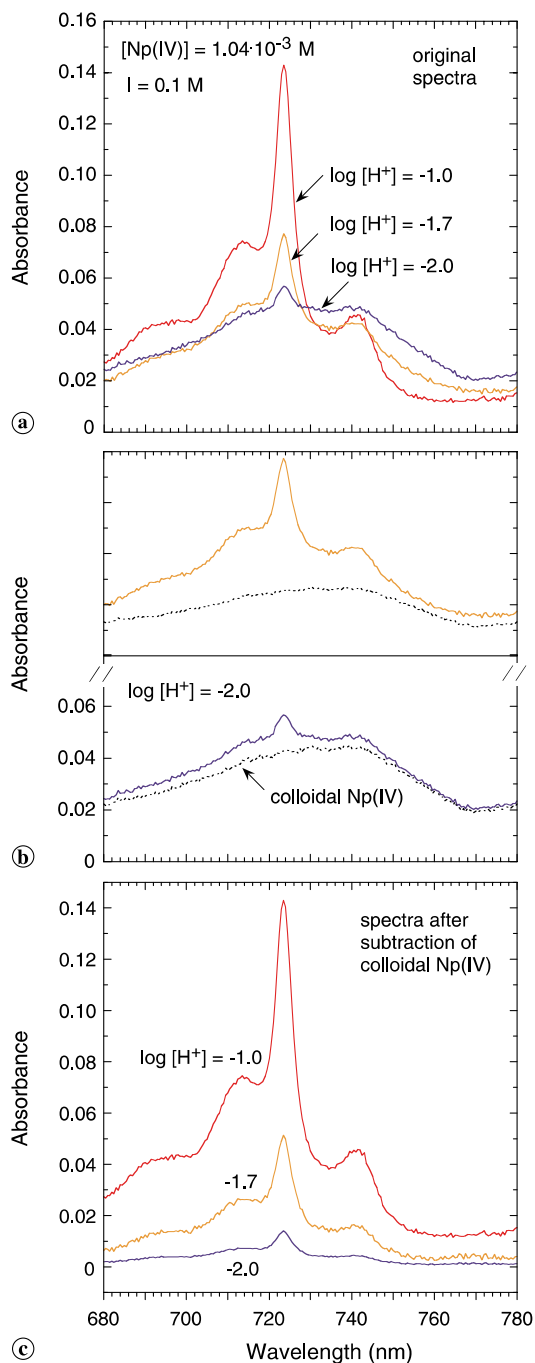


Fig. 3. Absorption spectra of 1.04×10^{-3} M Np(IV) solutions at $\log [H^+] = -1.0, -1.7$ and -2.0 in 0.1 M $HClO_4$ - $NaClO_4$; (a) original spectra in the wavelength range of 680–780 nm, (b) deconvolution of the spectra at $\log [H^+] = -1.7$ and -2.0 , (c) after subtraction of the colloidal contributions from the characteristic Np(IV) multiplet.

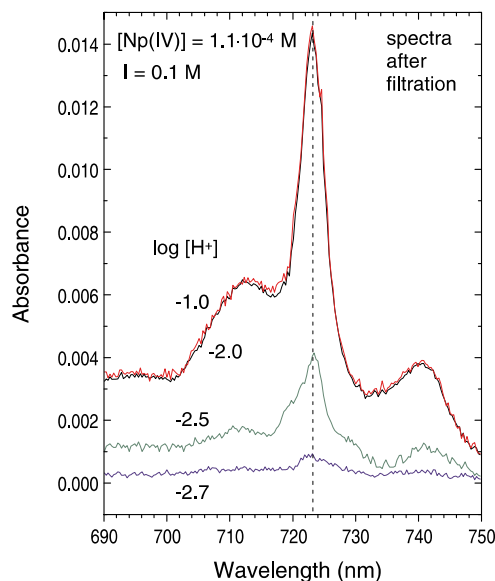


Fig. 4. Absorption spectra recorded after filtration of 1.12×10^{-4} M Np(IV) solutions at different H^+ concentrations in 0.1 M $HClO_4$ - $NaClO_4$.

initial Np(IV) concentration of 1.12×10^{-4} mol/l. At this lower Np(IV) concentration, the absorbance remains constant up to pH 2, whereas at $[Np(IV)] = 1.04 \times 10^{-3}$ mol/l the absorbance at pH 2 decreases to 10% of the value at pH 1 (c.f. Table 2). At $pH > 2.5$, the absorbance decreases as well in the case of the 1.12×10^{-4} M Np(IV) solutions.

In Fig. 5a the decrease of the molar absorption at 723 nm is shown as a function of the H^+ and Np(IV) concentrations. (The ratio A/A° describes the decrease of absorbance A at given H^+ and initial Np concentration relative to A° for the same Np(IV) concentration in 0.1 M $HClO_4$.) For comparison, the dashed line illustrates the solubility of $Np(OH)_4(am)$ at $I = 0.1$ mol/l, calculated according to the thermodynamic constants given in Table 1. The following observations and conclusions are made:

- 1) If the Np(IV) concentration exceeds the calculated solubility at increased pH, the Np(IV) absorption band at 723 nm decreases dramatically. This effect is ascribed to the formation of solid particles of Np(IV) hydroxide or hydrous oxide. At the low Np concentrations, there is no visible precipitation. The solid particles remain in solution as colloidal suspension. This explains the broad absorption band arising at 700–750 nm. In order to prove this conclusion, laser-induced breakdown detection (LIBD) is applied to monitor the formation of Np(IV) colloids. Increasing pH at a given metal ion concentration, the initial formation of colloids indicates that the solubility of the corresponding oxide or hydroxide is exceeded [7, 8]. As LIBD cannot distinguish between Np colloids and other colloids usually present in solution, the batch solutions for the LIBD experiment are prepared from stock solutions filtered several times until the colloid background level has been depressed to a breakdown probability below 10%. Fig. 5b shows the breakdown probability measured in 3.1×10^{-5} M Np(IV) solutions of different pH. At $\log [H^+] \geq -2$ the breakdown probability remains at the background level. No Np(IV)

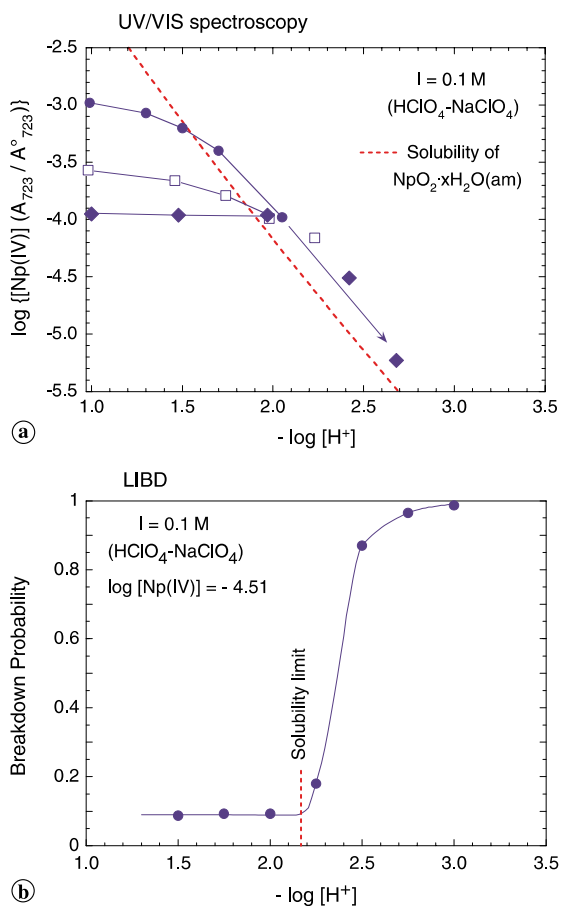


Fig. 5. (a) Decrease of the absorbance of the Np(IV) band at 723 nm (measured after 1 day) as a function of the H^+ concentration. The different symbols refer to three series at initial Np(IV) concentrations of 1.04×10^{-3} , 2.70×10^{-4} , and 1.12×10^{-4} mol/l in 0.1 M $\text{HClO}_4\text{-NaClO}_4$. (b) Colloid detection by LIBD: breakdown probability measured in 3.1×10^{-5} M Np(IV) solutions as a function of the H^+ concentration in 0.1 M $\text{HClO}_4\text{-NaClO}_4$.

colloids are formed. In excellent agreement with the expectation according to the calculated solubility limit, the breakdown probability is significantly increased by the formation of Np(IV) colloids in the range $-2 > \log [\text{H}^+] > -2.5$, and reaches values close to 100% at $\log [\text{H}^+] < -2.5$. The mean diameter of these Np(IV) colloids has been determined to be about 50–60 nm.

- 2) At the Np(IV) concentration of 1.12×10^{-4} mol/l, the molar absorbance at 723 nm remains approximately constant up to $\log [\text{H}^+] = -2.0$, and in the LPAS spectra of Np(IV) solutions below 10^{-5} mol/l in 0.1 M $\text{DClO}_4\text{-NaClO}_4$, the intensity of the 723 nm absorption band remains constant even up to $\log [\text{D}^+] = -2.5$ (c.f. Sect. 3.2, Fig. 7). However, at the Np(IV) concentrations of 2.7×10^{-4} and 1.04×10^{-3} mol/l, the molar absorbance decreases already at higher acidities of $\log [\text{H}^+] > -1.5$, i.e. below the solubility limit of Np(IV) hydroxide or hydrous oxide. This effect is enhanced by increasing Np(IV) concentrations: at $\log [\text{H}^+] = -1.5$, the ratio of $A/A^\circ = 1$ at $[\text{Np(IV)}] = 1.12 \times 10^{-4}$ mol/l decreases to $A/A^\circ = 0.8$ at $[\text{Np(IV)}] = 2.7 \times 10^{-4}$ mol/l and $A/A^\circ = 0.6$ at $[\text{Np(IV)}] = 1.04 \times 10^{-3}$ mol/l (c.f. Table 2). These results unambiguously demonstrate that the observed decrease of the Np(IV) absorption bands depends on both, H^+ and Np concentration. Con-

sequently, it is clearly ascribed to polynucleation but not to mononuclear hydrolysis as assumed in the literature [1–3] (In the latter case it should be independent of the Np concentration). At Np(IV) concentrations above 10^{-4} mol/l, polynuclear aqueous species or small colloids are formed even at low pH.

- 3) The molar extinction coefficients determined in the present study for 10^{-3} to 10^{-4} M Np(IV) solutions in 0.1 M HClO_4 and $\leq 10^{-4}$ M Np(IV) solutions in 0.1 M $\text{HClO}_4\text{-NaClO}_4$ of pH 1–2 vary in the range $\epsilon_{723} = 130 \pm 5 \text{ L mol}^{-1} \text{ cm}^{-1}$. The corresponding values in 1.0 M HClO_4 are found to be somewhat higher, $139 \pm 5 \text{ L mol}^{-1} \text{ cm}^{-1}$. If the acidity is decreased from 1.0 M to 0.1 M HClO_4 , the molar absorption decreases by 3%–6% at $[\text{Np(IV)}] = 10^{-4}$ mol/l and about 10% at a Np(IV) concentration of 1.04×10^{-3} mol/l. This might be caused either by a certain degree of polynucleation, even in 0.1 M HClO_4 , or by slightly different spectroscopic properties of the predominant mononuclear species. In 1.0 M HClO_4 the fraction of the Np^{4+} aquo ion is 73% (according to the hydrolysis constants in [4]), whereas at pH 1–2 the hydroxo complex Np(OH)_2^{2+} is expected as the major species. It is to note that a comparable decrease of the 723 nm band is not observed in the LPAS spectra of Np(IV) solutions in 1.0 to 0.01 M DClO_4 (c.f. Table 2 and Fig. 6). In undersaturated solutions with Np(IV) concentrations below 10^{-4} mol/l, the intensity of the molar LPAS signal remains constant (within $\pm 3\%$) for acidities varying from $\log [\text{D}^+] = 0$ to -2.5 . Therefore, even with respect to the somewhat higher molar absorption coefficient for Np^{4+} in 1.0 M HClO_4 , the molar absorption for mononuclear hydrolysis species can be considered as constant within an uncertainty less than 10%. The value of $\epsilon_{723} = 130 \pm 10 \text{ L mol}^{-1} \text{ cm}^{-1}$ may hence be used over the whole pH range investigated for the spectrophotometric determination of the mononuclear Np(IV) concentration.

3.2 LPAS in $\text{DClO}_4\text{-NaClO}_4$ solution

The laser-induced photoacoustic spectroscopy (LPAS) is applied to extend the spectroscopic study to lower Np(IV) concentrations and acidities. As the sensitivity of LPAS is mainly limited by the background absorption [19, 20], the sensitivity is increased by replacing the solvent H_2O by D_2O , which shows significantly less absorption in the spectral range of 680–760 nm. At 723 nm the background signal of D_2O is about 20 times smaller than that of H_2O . This leads to an increase of the sensitivity for Np(IV) down to 2×10^{-7} mol/l. In LPAS spectra of 3.0×10^{-5} M Np(IV) solutions in 1.0, 0.1 and 0.01 M DClO_4 , recorded with a resolution of 0.15 nm, the absorption maxima of the multiplet (at 712.4, 723.3 and 740.7 nm) are in accord with UV/VIS spectra in HClO_4 solution. Moreover, the LPAS spectra in 1.0 and 0.01 M DClO_4 are nearly identical (Fig. 6). The absorption maxima remain at the same position and the intensity of the LPAS signals at 723.3 nm differs only by about 3%. In 0.001 M DClO_4 the intensity of the LPAS signal is considerably decreased, and the background signal is increased by light scattering caused by colloidal particles.

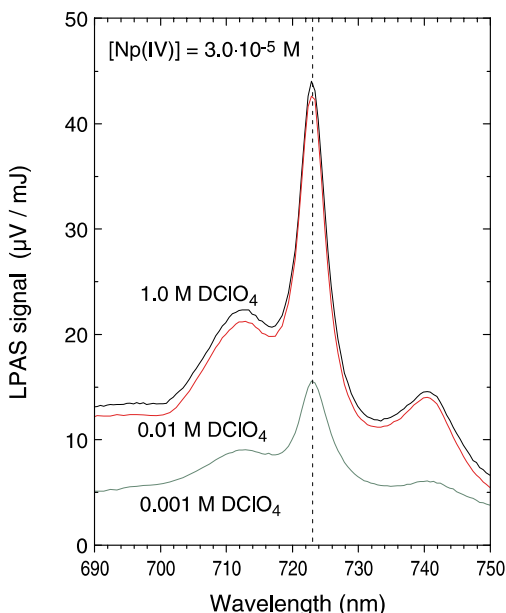


Fig. 6. LPAS spectra of 3.0×10^{-5} M Np(IV) solutions in 1.0, 0.01 and 0.001 M DClO₄.

In analogy to the UV/VIS study described above, four series of Np(IV) solutions are prepared at constant ionic strength (0.1 M DClO₄-NaClO₄) and varying D⁺ concentration. The Np(IV) concentration in these series ranges from 5.2×10^{-4} down to 2.0×10^{-6} mol/l. The intensity change of the molar LPAS signal at 723 nm (I/I° = intensity I of the LPAS signal relative to I° in 0.1 M DClO₄) is shown in Fig. 7a, in comparison with the solubility of Np(OH)₄(am) in 0.1 M HClO₄-NaClO₄ (dashed line). At the lowest Np(IV) concentrations of 4.8×10^{-6} and 2.0×10^{-6} mol/l, the intensity of the molar LPAS signal is constant up to $\log [D^+] = -2.5$. In each of these series the intensity of the Np(IV) absorption band at 723 nm decreases if the solubility limit is exceeded. The formation of colloidal Np(IV) particles is confirmed by LIBD measurements in 3.1×10^{-5} M Np(IV) solutions, where an increase of the breakdown probability is observed between $\log [D^+] = -2.3$ and -2.5 (Fig. 7b).

3.3 Comparison of the present results with thermodynamic data for the hydrolysis of Np(IV) and the solubility product of Np(OH)₄(am)

The spectroscopic and LIBD studies are further used to determine the solubility of Np(IV). As shown in our recent papers [7,8], the pH of initial colloid formation at a given Np(IV) concentration refers to the solubility of the corresponding solid (in this case small colloidal particles). In the present LIBD study the initial colloid formation in 3.1×10^{-5} M Np(IV) solutions is observed at $\log [H^+] = -2.20 \pm 0.05$ and at $\log [D^+] = -2.40 \pm 0.10$. When the solubility limit is exceeded in the spectroscopic studies, the formation of colloidal particles is accompanied by a significant decrease of the Np(IV) absorption band at 723 nm. The Np(IV) concentration measured in these solutions after one day by UV/VIS spectroscopy or LPAS can be considered as solubility determined from oversaturation. The data given in Table 2 represent the mononuclear Np(IV) concentration upon small solid particles of freshly precipitated

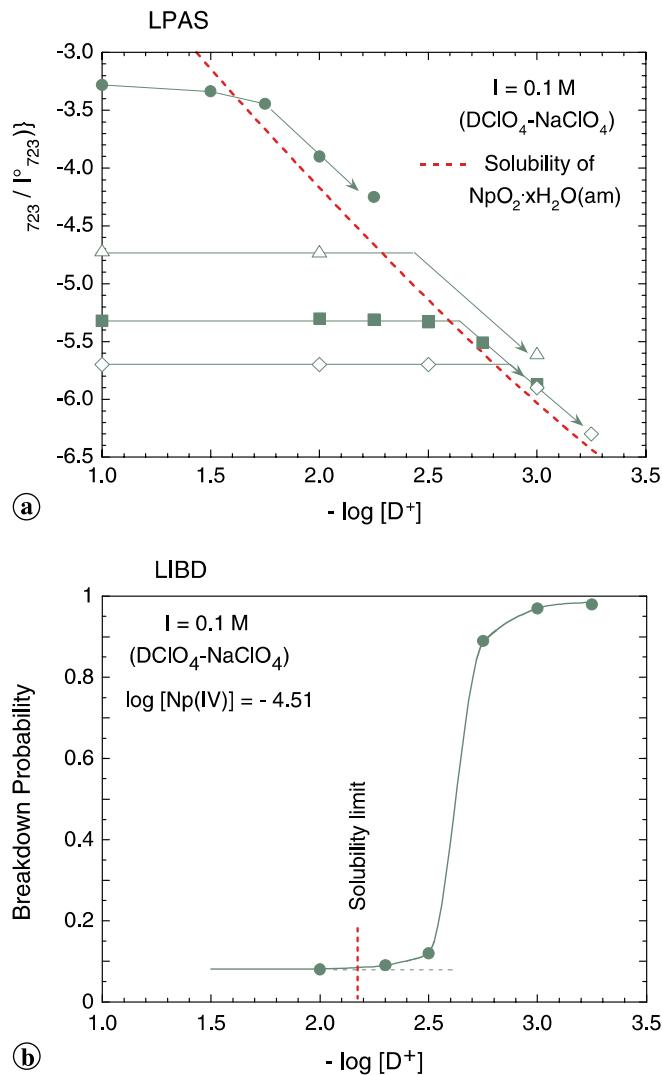


Fig. 7. (a) Decrease of the molar LPAS signal at 723 nm (measured after 1 day) as a function of the D⁺ concentration. The different symbols refer to four series at initial Np(IV) concentrations of 5.2×10^{-4} , 1.9×10^{-5} , 4.8×10^{-6} , and 2.0×10^{-6} mol/l in 0.1 M DClO₄-NaClO₄. (b) Colloid detection by LIBD: breakdown probability measured in 3.1×10^{-5} M Np(IV) solutions as a function of the D⁺ concentration in 0.1 M DClO₄-NaClO₄.

Np(OH)₄(am), because colloidal contributions are removed either numerically by deconvolution as shown in Fig. 3 or by filtration of the solution:

$$[Np(IV)]_{eq} = (K'_{sp}/[OH^-]^4) \left(1 + \sum \beta'_n [OH^-]^n\right). \quad (5)$$

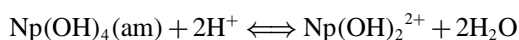
As an equilibration time of 1 day appears rather short, one of the experiments has been continued for several days. At an initial Np(IV) concentration of $\log [Np(IV)]^\circ = -3.57$ and $\log [H^+] = -2.0$, the spectroscopically determined Np(IV) concentration decreased from $\log [Np(IV)] = -3.99$ after 1 day to -4.05 and -4.06 after 3 and 7 days, respectively. With respect to a possible alteration of the solid particles, this decrease of $\log [Np(IV)]$ is relatively small, in particular, if compared to the usual scattering of solubility data for tetravalent actinides. The Np(IV) concentration measured after one day may hence be considered as an upper limit for the thermodynamic solubility of amorphous Np(IV) hydroxide or hydrous oxide.

Table 2. Decrease of the 723 nm band of Np(IV) as a function of the acidity at different initial Np(IV) concentrations.

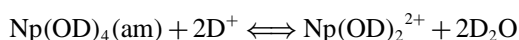
a) UV/VIS spectroscopy in HClO ₄ -NaClO ₄ -H ₂ O solution			
Solution ^a	- log [H ⁺]	(A/A ^o) ^b	log [Np(IV)] _{eq} ^c
log [Np(IV)] ^o = -2.98			
1.0 M HClO ₄	0.00	1.09 ± 0.02	
I = 0.1 M	0.99	1	
	1.30	0.81 ± 0.02	
	1.50	0.61 ± 0.02	
	1.70	0.38 ± 0.02	-3.40 ± 0.03
	2.05	0.10 ± 0.02	-3.98 ± 0.09
log [Np(IV)] ^o = -3.57			
I = 0.1 M	0.98	1	
	1.46	0.81 ± 0.02	
	1.73	0.60 ± 0.02	
	1.98	0.37 ± 0.02	-3.99 ± 0.03
(3 days)	2.00	0.33 ± 0.02	-4.05 ± 0.03
(7 days)	2.00	0.32 ± 0.02	-4.06 ± 0.03
	2.23	0.26 ± 0.02	-4.16 ± 0.04
log [Np(IV)] ^o = -3.95			
I = 0.1 M	1.00	1	
	1.48	0.98 ± 0.02	
	1.97	0.98 ± 0.02	
	2.42	0.28 ± 0.02	-4.51 ± 0.10
	2.68	0.054 ± 0.02	-5.23 ± 0.19
b) LPAS in DClO ₄ -NaClO ₄ -D ₂ O solution			
Solution ^a	- log [D ⁺]	(I/I ^o) ^b	log [Np(IV)] _{eq} ^c
log [Np(IV)] ^o = -4.52			
1.0 M DClO ₄	0.0	1.01 ± 0.02	
0.1 M DClO ₄	1.0	1	
0.01 M DClO ₄	2.0	0.98 ± 0.02	
0.001 M DClO ₄	3.0	0.31 ± 0.02	
(after 1–2 hours)			
log [Np(IV)] ^o = -3.28			
I = 0.1 M	1.0	1	
	1.5	0.88 ± 0.02	
	1.75	0.69 ± 0.02	
	2.0	0.24 ± 0.02	-3.90 ± 0.04
	2.25	0.11 ± 0.02	-4.25 ± 0.09
log [Np(IV)] ^o = -4.71			
I = 0.1 M	1.0	1	
	2.0	0.98 ± 0.02	
	3.0	0.13 ± 0.02	-5.60 ± 0.07
log [Np(IV)] ^o = -5.32			
I = 0.1 M	1.0	1	
	2.0	1.02 ± 0.03	
	2.25	1.02 ± 0.03	
	2.5	0.98 ± 0.03	
	2.75	0.63 ± 0.03	-5.52 ± 0.02
	3.0	0.27 ± 0.03	-5.89 ± 0.05
log [Np(IV)] ^o = -5.70			
I = 0.1 M	1.0	1	
	2.0	0.99 ± 0.03	
	2.5	0.99 ± 0.03	
	3.0	0.62 ± 0.03	-5.91 ± 0.02
	3.25	0.25 ± 0.03	-6.30 ± 0.06

a: The solutions are equilibrated for 1 day except otherwise stated;
b: The ratios A/A^o and I/I^o represent the absorbances A and LPAS signal intensities I at 723.4 nm relative to A^o and I^o in 0.1 M HClO₄ and DClO₄, respectively. In order to minimize uncertainties arising from baseline fluctuations, the values at 723.4 nm are determined versus the plateaus at 695 and 760 nm and the local minimum at 717 nm. Colloidal contributions are removed either numerically (by deconvolution as shown in Fig. 3) or by filtration of the solution;
c: Mononuclear Np(IV) concentration in equilibrium with solid (colloidal) particles of Np(OH)₄(am) (see text).

The solubility data determined by LIBD and spectroscopy in 0.1 M HClO₄-NaClO₄ or DClO₄-NaClO₄ are shown in Fig. 8a. In the investigated ranges of log [H⁺] and log [D⁺], the equilibrium concentration log [Np(IV)]_{eq} decreases with a slope of -2. This dependence is consistent with the hydrolysis constants of Duplessis and Guillaumont [4], which predict the predominance of the species Np(OH)₂²⁺ in the pH range of 1.5 to 3 (c.f. Fig. 8b). There is no evidence for a significant or systematic deviation between the data in H₂O and D₂O solution, suggesting that the solubility at higher pH will be similar to the low Np(IV) concentrations measured by LPAS in D₂O solution. The agreement between the Np(IV) solubilities in H₂O and D₂O solution might be fortuitous, if contrary isotope effects in deprotonation, hydrolysis and solubility constants compensate one another in the reactions



and



but this question is not further investigated. Applying Eq. (5) and the hydrolysis constants in Table 1 (from Refs. [4, 6]),

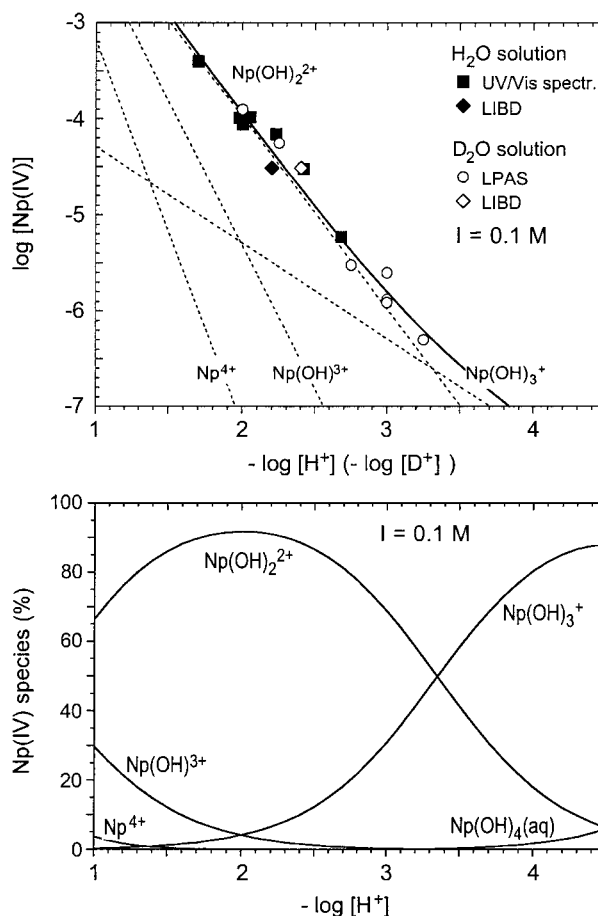


Fig. 8. Experimental Np(IV) solubility data measured upon freshly formed solid particles of Np(OH)₄(am) as a function of the H⁺ or D⁺ concentration in 0.1 M perchlorate solution (above). The solid curve and the dashed speciation lines are calculated with log K_{sp} = -54.4 (at I = 0.1 M) and the hydrolysis constants from Refs. [4, 6] (Table 1). The corresponding Np(IV) species distribution in 0.1 M HClO₄-NaClO₄ is shown below.

the solubility product for colloidal $\text{Np}(\text{OH})_4(\text{am})$ particles is calculated from the data in 0.1 M HClO_4 - NaClO_4 to be

$$\log K'_{\text{sp}} = -54.4 \pm 0.4$$

and

$$\log K^{\circ}_{\text{sp}} = -56.5 \pm 0.4$$

if converted to $I = 0$ with the SIT. This value is in good agreement with $\log K^{\circ}_{\text{sp}} = -56.7 \pm 0.5$ [6] accordingly calculated from the experimental solubility data of Rai *et al.* [9], which were also measured from oversaturation direction, in suspensions of $\text{Np}(\text{IV})$ hydrous oxide equilibrated for 14 days.

4. Conclusions

As the UV/VIS and LPAS spectra recorded over a wide range of pH and $\text{Np}(\text{IV})$ concentration show no significant displacement of the characteristic $\text{Np}(\text{IV})$ absorption bands, no direct speciation is possible. However, the present study clearly demonstrates that the decrease of the molar absorption, if the Np concentration is increased at constant pH or if pH is increased at constant Np concentration, is caused by polynucleation and colloid formation. In addition, the present results confirm the thermodynamic data selected recently [6]. The mononuclear $\text{Np}(\text{IV})$ hydrolysis constants of Duplessis and Guillaumont [4], which predict the predominance of $\text{Np}(\text{OH})_2^{2+}$ at low Np concentrations in the pH range of 1.5 to 3, are confirmed indirectly by the pH-dependence of the mononuclear $\text{Np}(\text{IV})$ concentration upon colloidal suspensions of solid $\text{Np}(\text{OH})_4(\text{am})$ particles. These solubility data are consistent with those reported by Rai *et al.* [9] for amorphous $\text{Np}(\text{IV})$ hydrous oxide.

Acknowledgment. This work was partially supported by ANDRA (contract No. 008790) and by the European commission, in the frame of the ACTAF program within the 5th R&D framework program (contract No. FIKW-CT-2000-00035). A portion of the work at Argonne National Laboratory was performed under the auspices of the Office of Basic Energy Science, Division of Chemical Science, U.S. Department of Energy under contract W-31-109-ENG-38.

References

- Sullivan, J. C., Hindman, J. C.: The Hydrolysis of Neptunium(IV). *J. Phys. Chem.* **63**, 1332 (1959).
- Paul, M. Th.: Die Komplexbildung vierwertiger Actiniden mit Pyridin- und α -Aminopolycarbonsäuren. Report KFK 1210, Kernforschungszentrum Karlsruhe (1970).
- Fedoseev, A. M., Peretrukhin, V. F., Orlova, M. M., Krot, N. N.: Spectrophotometric Study of the Hydrolysis of Tetravalent Neptunium in Aqueous Organic Solutions. *Soviet Radiochem.* **20**, 686 (1978).
- Duplessis, J., Guillaumont, R.: Hydrolyse du Neptunium tetravalent. *Radiochem. Radioanal. Lett.* **31**, 293 (1977).
- Metivier, H., Guillaumont, R.: Hydrolyse du Plutonium tetravalent. *Radiochem. Radioanal. Lett.* **10**, 27 (1972).
- Neck, V., Kim, J. I.: Solubility and Hydrolysis of Tetravalent Actinides. Report FZKA 6350, Forschungszentrum Karlsruhe, 1999 and *Radiochim. Acta* **89**, 1 (2001).
- Knopp, R., Neck, V., Kim, J. I.: Solubility, Hydrolysis and Colloid Formation of Plutonium(IV). *Radiochim. Acta* **86**, 101 (1999).
- Bundschuh, T., Knopp, R., Müller, R., Kim, J. I., Neck, V., Fanghänel, Th.: Application of LIBD to the determination of the solubility product of thorium(IV)-colloids. *Radiochim. Acta* **88**, 625 (2000).
- Rai, D., Swanson, J. L., Ryan, J. L.: Solubility of $\text{NpO}_2 \cdot x\text{H}_2\text{O}$ in the Presence of $\text{Cu}(\text{I})/\text{Cu}(\text{II})$ Redox Buffer. *Radiochim. Acta* **42**, 35 (1987).
- Rai, D., Ryan, J. L.: Neptunium(IV) Hydrous Oxide Solubility under Reducing and Carbonate Conditions. *Inorg. Chem.* **24**, 247 (1985).
- Eriksen, T. E., Ndalamba, P., Cui, D., Bruno, J., Caceci, M., Spahiu, K.: Solubility of the Redox-Sensitive Radionuclides ^{99}Tc and ^{237}Np Under Reducing Conditions in Neutral to Alkaline Solutions. Effect of Carbonate. SKB Technical Report, TR 93-18, Stockholm (1993).
- Nakayama, S., Yamaguchi, T., Sekine, K.: Solubility of $\text{Np}(\text{IV})$ Hydrous Oxide in Aqueous Solutions. *Radiochim. Acta* **74**, 15 (1996).
- Ciavatta, L.: The specific ion interaction theory in evaluating ionic equilibria. *Ann. Chim. (Rome)* **70**, 551 (1980).
- Grenthe, I., Fuger, J., Konings, R. J. M., Lemire, R. J., Muller, A. B., Nguyen-Trung, C., Wanner, H. (OECD, NEA-TDB): Chemical Thermodynamics Vol. 1. Chemical Thermodynamics of Uranium, Elsevier Science Publ., North-Holland, Amsterdam (1992).
- Hindman, J. C., Magnusson, L. B., LaChapelle, T. J.: In: *The Transuranium Elements*. (Seaborg, G. T., Katz, J. J., Manning, W. M. eds.), Natl. Nucl. Energy Ser. Div. IV, Vol. 14B, paper 15.2 (1949), p. 1039.
- Sjoblom, R., Hindman, J. C.: Spectrophotometry of Neptunium in Perchloric Acid Solutions. *J. Am. Chem. Soc.*, **73**, 1744 (1951).
- Gainar, I., Sykes, K. W.: The Spectra and Stability of Some of Neptunium Complex Ions in Water and Methanol. *J. Chem. Soc.* 4452 (1964).
- Hagan, P. G., Cleveland, J. M.: The Absorption Spectra of Neptunium Ions in Perchloric Acid Solution. *J. Inorg. Nucl. Chem.* **28**, 2905 (1966).
- Kim, J. I., Stumpe, R., Klenze, R.: Laser-induced Photoacoustic Spectroscopy for the Speciation of Transuranic Elements in Natural Aquatic Systems. *Topics in Current Chemistry* (Springer-Verlag) **157**, 131 (1990).
- Tam, A. C., Patel, C. K. N.: Optical absorptions of light and heavy water by laser photoacoustic spectroscopy. *Appl. Opt.* **18**, 3348 (1979).
- Kitamori, T., Yokose, K., Suzuki, K., Sakagami, M., Goshi, Y.: Laser Breakdown Acoustic Effect to Ultrafine Particles in Liquids and its Application to Particle Counting. *Jpn. J. Appl. Phys.* **27**, L983 (1988).
- Kitamori, T., Yokose, K., Sakagami, M., Sawada, T.: Detection and Counting of Ultrafine Particles in Ultrapure Water Using Laser Breakdown Acoustic Method. *Jpn. J. Appl. Phys.* **28**, 1195 (1989).
- Scherbaum, F., Knopp, R., Kim, J. I.: Counting of Particles in Aqueous Solution by Laser Induced Photoacoustic Breakdown Detection (LIBPD). *Appl. Phys. B* **63**, 299 (1996).
- Bundschuh, T., Knopp, R., Kim, J. I.: Laser-induced breakdown detection (LIBD) of aquatic colloids with different laser systems. *Colloids Surf. A* **177**, 47 (2001).
- Bundschuh, T., Kim, J. I.: Entwicklung und Anwendung der Laser-induzierten Breakdown-Detektion zur Quantifizierung aquatischer Kolloide und Actinidenkolloide. Report FZKA 6273, Forschungszentrum Karlsruhe (1999).