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SOLUBILITY AND HYDROLYSIS BEHAVIOR OF NEPTUNIUM(V)

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Solubility and Hydrolysis Behaviour of Neptunium(V)

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Neptunium(V) / Solubility / Hydrolysis / Ionic strength-dependence

Abstract

The hydrolysis behaviour of the NpO_2^+ ion has been investigated at 25°C by solubility experiments in the pH range 7 to 14 in 0.1 M, 1.0 M and 3.0 M NaClO_4 solutions under pure Ar atmosphere. By measuring the time dependent equilibrium concentration of Np(V) , the chemical state of Np(V) hydroxide precipitates in each solution is confirmed. In 0.1 M NaClO_4 the precipitate remains amorphous over several months, while in 1.0 M NaClO_4 the precipitate changes from an amorphous to a more stable aged state within a relatively short time. In 3.0 M NaClO_4 the aged modification of NpO_2OH is formed from the beginning. Applying specific ion interaction theory (SIT), the thermodynamic constants at $I=0$ are found to be: $\log K_{sp} = -8.76 \pm 0.05$ for amorphous $\text{NpO}_2\text{OH(s)}$, $\log K_{sp} = -9.44 \pm 0.10$ for aged $\text{NpO}_2\text{OH(s)}$, $\log \beta_1 = 2.7 \pm 0.2$ for the hydrolysis species NpO_2OH and $\log \beta_2 = 4.35 \pm 0.15$ for $\text{NpO}_2(\text{OH})_2^-$.

1. Introduction

Because of its long half life and relatively large abundance in nuclear waste, neptunium is an element of particular interest concerning the migration behaviour of radionuclides. Among numerous geochemical reactions that govern the migration behaviour of the actinides in aquifer systems, hydrolysis, carbonate complexation, redox reactions, humate complexation and colloid generation appear to be the most important reactions. Since in natural aquatic solutions all these reactions may occur simultaneously as concurrent reactions, a better understanding of the migration behaviour requires accurate knowledge on each of these reactions. The present paper investigates the solubility and hydrolysis behaviour of Np(V) , which is the stable oxidation state under natural aerobic conditions as in non-complexing perchlorate solutions of atmospheric contact [1, 2, 3].

In carbonate-free solution with OH^- as the only complexing ion, solubility of Np(V) is determined by the solubility product of $\text{NpO}_2\text{OH(s)}$ and by the concentration of the hydroxo complexes NpO_2OH and $\text{NpO}_2(\text{OH})_2^-$ [1–13]. In spite of the large number of publications [1, 5–13], current knowledge on solubility product and hydrolysis constants is not at all satisfactory. Table 1 shows the data reported in the literature, including methods of determination and experimental conditions (medium, temperature, ionic

strength). The solubility product reported for NpO_2OH varies from $\log K_{sp} = -8.8$ [1] to $\log K_{sp} = -10.7$ [5] and hydrolysis constants determined by different authors [1, 5–13] vary over several orders of magnitude. Since all values have been determined at 20–25°C and $I \leq 1$ M, the large discrepancies cannot be ascribed to the influence of temperature and ionic strength. Since all investigations on Np(V) hydrolysis have been carried out in neutral to alkaline solutions, the sensitive absorption of CO_2 , which causes carbonate complexation and thus influences hydrolysis experiments, could be a possible source of errors. In the case of the spectrophotometric determination of $\log \beta_1$ by Sevost'yanova and Khalurin [11], it was demonstrated that carbonate contamination had caused erroneous results [2, 14]. Bidoglio *et al.* [8] and Maya [9] evaluated the first hydrolysis constant from Np(V) carbonate complexation experiments, in which the influence of hydrolysis was almost negligible. Lierse *et al.* [1] and Kraus [13] are the only authors who mentioned the use of CO_2 -free inert gas atmosphere throughout their experiments. However, Kraus evaluated the first hydrolysis constant by potentiometric titration without accounting for the formation of the anionic complex $\text{NpO}_2(\text{OH})_2^-$. Moskvín [12] calculated β_1 from only one solubility value at pH = 8.6, assuming Np(V) to be totally hydrolyzed as NpO_2OH . Extremely different hydrolysis constants have been obtained from solubility experiments of Lierse *et al.* [1] and Nakayama *et al.* [5] and from electrophoresis studies of Nagasaki *et al.* [6] and Rösch *et al.* [7].

The objective of the present work is to gain reliable information on Np(V) hydrolysis reactions from the pH-dependent solubility experiments in 0.1 M, 1 M and 3 M NaClO_4 solutions under well controlled argon atmosphere.

2. Experimental

2.1. Solubility measurement

The solubility of Np(V) has been determined in radiometric titration cells thermostated at 25°C. All experiments have been performed under CO_2 -free argon atmosphere. The radiochemically pure Np-237, 10–30 mg dissolved as NpO_2ClO_4 in $\text{HClO}_4/\text{NaClO}_4$ solution, has been precipitated by adding CO_2 -free NaOH (Baker Co.); pH was varied by adding CO_2 -

Table 1. Literature data on solubility products and hydrolysis constants of Np(V)

Ref.	Method	$\log K_{sp}(\text{NpO}_2\text{OH})$	$\log \beta_1$	$\log \beta_2$	Medium	$T(^{\circ}\text{C})$	$I(\text{M})$
Lierse <i>et al.</i> [1]	solubility	- 8.81	2.33	4.89	NaClO_4	25	1.0
Nakayama <i>et al.</i> [5]	solubility	-10.7	5.7	8.6	NaNO_3	RT	0.01
Nagasaki <i>et al.</i> [6]	electrophoresis		6.0	9.9		RT	0.1
			5.7	9.2			0.005
Rösch <i>et al.</i> [7]	electrophoresis		3.33	5.61	NaClO_4	25	0.1
Bidoglio <i>et al.</i> [8]	solvent extraction		4.16		$\text{NaClO}_4/$ NaHCO_3	25	0.2
Maya [9]	solubility		4.68		$\text{NaClO}_4/$ NaHCO_3	25	1.0
Schmidt <i>et al.</i> [10]	pulse radiolysis		5.2			25	0.001
Sevost'yanova and Khaturn [11]	solubility titration spectrophotometry	- 9.73	5.1		$\text{NaNO}_3, \text{NaClO}_4$	23	0.02
			5.1		NaNO_3	20	0.002
Moskvin [12]	solubility	- 9.02	3.92			20	0.02
Kraus [13]	titration	- 9.2	4.9		NaCl	RT	0.1

RT = room temperature.

free NaOH or $\text{HClO}_4/\text{NaClO}_4$ maintaining ionic strength constant at 0.1 M, 1.0 M and 3.0 M, respectively. Stirring the solution by a magnetic stirrer or by bubbling argon through, solubility equilibria were attained after 1–2 days. In order to monitor oversaturation or undersaturation effects, the neptunium concentration has been determined over a period of 4–10 days. When freshly precipitated green NpO_2OH in 1 M NaClO_4 was changed into a white precipitate by aging and thus resulting in a lower solubility, the experiment was continued for 2–4 weeks until the final solubility equilibrium was achieved.

The equilibrium concentration of Np-237 was determined radiometrically by α -liquid scintillation counting (Beckman LS 6800). Filtered (Sartorius filter of 220 nm pore size) and unfiltered aliquots showed no difference in activity, suggesting no adsorption effects on the filter surface.

Absorption spectra in the UV/VIS/IR wavelength regions were recorded with a Lambda 9 spectrometer (Perkin-Elmer Co.) using quartz cuvettes with a thickness layer of 1 cm.

2.2. Determination of pH and OH^- concentration

pH was measured with a combination glass electrode (type ROSS, Orion Co.) calibrated against pH buffer standards (pH = 1–13, Merck Co.), using 3.0 M NaCl as a junction electrolyte to avoid KClO_4 precipitation. Due to the difference in liquid junction potential between the calibration against buffer standards and pH-measurement in NaClO_4 solutions, the observed pH (pH_{obs}) can be shifted as given by

$$\text{pH}_{\text{obs}} = \text{pH} + \Delta\text{pH}. \quad (1)$$

The ΔpH value has been determined by measuring

$\text{NaClO}_4/\text{HClO}_4$ and $\text{NaClO}_4/\text{NaOH}$ solutions of known H^+ and OH^- concentration (0.001 M–0.1 M) and pH buffer standards containing NaClO_4 :

$$\begin{aligned} \Delta\text{pH} &= 0 \pm 0.04 && \text{at } I = 0.1 \text{ M} \\ \Delta\text{pH} &= -0.33 \pm 0.05 && \text{at } I = 1.0 \text{ M} \\ \Delta\text{pH} &= -0.69 \pm 0.10 && \text{at } I = 3.0 \text{ M}. \end{aligned}$$

The correct pH value corresponding to the H^+ ion activity is then given by

$$\text{pH} = -\log(\text{H}^+) = \text{pH}_{\text{obs}} - \Delta\text{pH}. \quad (2)$$

The concentration of the OH^- ion is related to pH by the ion product of water K_w and the activity coefficient γ_{H^+} at given ionic strength:

$$\begin{aligned} \log[\text{OH}^-] &= \log K_w - \log[\text{H}^+] \\ &= \log K_w + \text{pH} + \log \gamma_{\text{H}^+}. \end{aligned} \quad (3)$$

The mean activity coefficient of H^+ and OH^- ions, $\gamma_{\pm}(\text{H}^+, \text{OH}^-)$, is obtained by

$$\gamma_{\pm}(\text{H}^+, \text{OH}^-) = \left(\frac{K_w}{K_w^*} \cdot a_w \right)^{1/2} \quad (4)$$

where a_w = rational activity of water

$K_w = (\text{H}^+)(\text{OH}^-)/a_w$ thermodynamic ion product of water

$K_w^* = [\text{H}^+][\text{OH}^-]$ ion product at given ionic strength.

() = activity, [] = concentration.

Ion products and activities of water in 0.1 M, 1.0 M and 3.0 M NaClO_4 and mean activity coefficients of H^+ and OH^- ions calculated by Eq. (4) are summarized in Table 2. Introducing these data into Eq. (3), the concentration of OH^- ions becomes

Table 2. Ion products, activities of water and mean activity coefficients of H^+ and OH^- in $NaClO_4$ solution at 25°C (molar scale)

I (M)	$\log K_w^a$	a_w^b	$\log \gamma_{\pm}(H^+, OH^-)$
0	-13.999	1	0
0.1	-13.78	0.997	-0.110
1.0	-13.80	0.966	-0.107
3.0	-14.20	0.885	+0.074

^a from Refs. [15, 16]

^b from Refs. [17, 18].

$$\log[OH^-] = pH + A, \quad (5)$$

with $A = -13.89$ in 0.1 M $NaClO_4$; $A = -13.91$ in 1.0 M $NaClO_4$; $A = -14.13$ in 3.0 M $NaClO_4$.

3. Results and discussion

In carbonate-free $NaClO_4$ solution, the concentration of the NpO_2^+ ion is related to the solubility product of $NpO_2(OH)(s)$:

$$K_{sp} = [NpO_2^+][OH^-]. \quad (6)$$

At higher OH^- concentration, the total concentration of $Np(V)$ depends further on the formation constants of the hydrolysis species NpO_2OH and $NpO_2(OH)_2^-$ [1-13]:

$$\beta_1 = [NpO_2OH]/[NpO_2^+][OH^-] \quad (7)$$

$$\beta_2 = [NpO_2(OH)_2^-]/[NpO_2^+][OH^-]^2. \quad (8)$$

K_{sp} and β' , representing concentration products and quotients, respectively, are apparent constants for given ionic strength. The total $Np(V)$ concentration in equilibrium solution is given by

$$\begin{aligned} [Np(V)]_t &= [NpO_2^+] + [NpO_2OH] + [NpO_2(OH)_2^-] \\ &= \frac{K_{sp}}{[OH^-]} (1 + \beta_1[OH^-] + \beta_2[OH^-]^2). \quad (9) \end{aligned}$$

Fig. 1a shows the pH-dependent solubility of green amorphous NpO_2OH , determined in 0.1 M $NaClO_4$. At $pH = 7-10$, the solubility shows a linear relationship with pH as expected according to the solubility product of NpO_2OH . At $pH > 11$, the formation of hydrolysis complexes becomes evident and the solubility increase at $pH > 12$ clearly indicates the formation of an anionic hydrolysis species. In 0.1 M $NaClO_4$ the aging process of the precipitate was not observed even over a period of three months. The neptunium concentration in equilibrium solution remained unchanged at each pH, suggesting the same solid state of NpO_2OH involved throughout the experiment.

From the experiment at $I = 1.0$ M, two solubility curves have been obtained as shown in Fig. 1b. Both curves are identical in shape and the systematic difference in solubility remains the same over the whole pH range investigated. Therefore, the solid phases in equilibrium must be different. The upper solubility

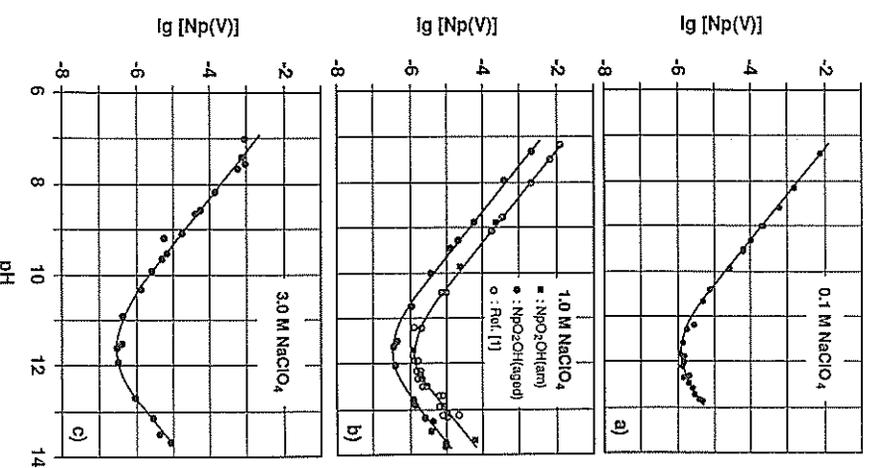


Fig. 1. Solubility of NpO_2OH in carbonate-free $NaClO_4$ solution at 25°C. a) $I = 0.1$ M, b) $I = 1.0$ M, c) $I = 3.0$ M.

curve in equilibrium with freshly precipitated green amorphous NpO_2OH is confirmed to be identical to the results of Lieser *et al.* [1]. However, after some days, the amorphous NpO_2OH is aged into a grey-white precipitate, which results in a solubility decrease from the upper to the lower curve (Fig. 2). The solubility of aged NpO_2OH indicates the formation of a thermodynamically more stable modification of a neptunyl hydroxide. Similar observations have been reported by Schindler and Feitknecht [19-21] for a large number of hydroxides, e.g. $Zn(OH)_2$ and $Fe(OH)_3$. According to these authors, the aging process to reach the final solid state depends on temperature, ionic strength and on the amount of solid involved. Lieser *et al.* [1] did not observe the aging of amorphous NpO_2OH , but it must be taken into consideration that a total amount of 1 g $Np-237$ used in their experiment possibly required much longer time for complete aging than 10-30 mg NpO_2OH used in the present work.

On the other hand, in 3 M $NaClO_4$ only the grey-white precipitate, the aged modification of NpO_2OH , has been obtained. Fig. 1c shows the corresponding solubility as a function of pH. It seems that, because of the high ionic strength, the precipitation of neptunyl hydroxide undergoes directly the formation of the more stable solid state which then appears unchanged over the entire experimental period.

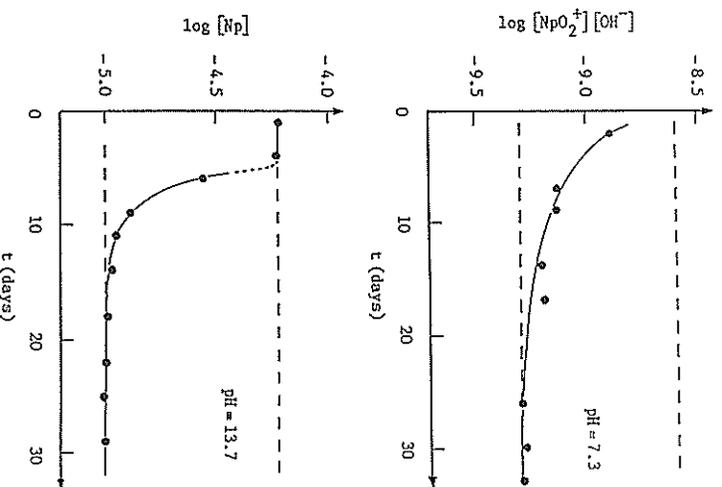


Fig. 2. Change of solubility during the aging process of NpO₂OH at $I=1.0$ M. a) final pH = 7.3, b) pH = 13.7.

Table 3. Solubility products of NpO₂OH and hydrolysis constants of Np(V) at various ionic strength (NaClO₄) and 25°C (molar scale)

I (M)	$\log K'_{sp}$	$\log \beta'_1$	$\log \beta'_2$
	NpO ₂ OH (am.)	NpO ₂ OH (aged)	
0.1	-8.56 ± 0.05	2.44 ± 0.16	4.10 ± 0.12
1.0^a	-8.59 ± 0.07	2.11 ± 0.62	4.45 ± 0.18
1.0		-9.30 ± 0.06	2.67 ± 0.20
		-9.85 ± 0.17	3.18 ± 0.33
3.0			5.15 ± 0.26

^a Data from Lierse *et al.* [1], corrected as described in the text.

Applying Eq. (9), solubility products K'_{sp} and formation constants β'_1 and β'_2 have been evaluated using a non-linear least squares program (SIMPLEX algorithm). The results are shown in Table 3. The ranges of error include statistical errors as well as uncertainties arising from pH and Np concentration measurements. Lierse *et al.* [1, 22] measured pH in 1.0 M NaClO₄ with the same pH measuring system as used in the present work, but they neglected the correction of ΔpH in the calculation of the OH⁻ concentration from pH_{obs}. The reported solubility product and hydrolysis constants have therefore been corrected appropriately for the purpose of comparison. After introducing such corrections, their results agree very well with the data from the present work.

The thermodynamic constants K_{sp} , β_1 and β_2 at $I=0$ can be further calculated from the ionic strength dependent constants by the following relations:

$$\log K_{sp} = \log K'_{sp} + \log(\gamma_{NpO_2^+} \cdot \gamma_{OH^-}) \quad (10)$$

$$\log \beta_1 = \log \beta'_1 + \log(\gamma_{NpO_2OH} / \gamma_{NpO_2^+} \cdot \gamma_{OH^-}) \quad (11)$$

$$\log \beta_2 = \log \beta'_2 + \log(\gamma_{NpO_2(OH)_2} / \gamma_{NpO_2^+} \cdot \gamma_{OH^-}^2) \quad (12)$$

Since the activity coefficients of individual ions concerned can not be assessed precisely in NaClO₄ solutions of higher ionic strength, we applied Brønsted-Guggenheim-Scatchard approach [23] for the evaluation of thermodynamic data. This specific ion interaction theory (SIT) is often used as a semi-empirical method to describe the ionic strength dependence of solution equilibria [14, 24]. According to the SIT activity coefficients of ions in a given NaClO₄ medium are estimated by

$$\log \gamma_i = -z_i^2 \frac{0.5107 m^{1/2}}{1 + 1.5 m^{1/2}} + \epsilon_{ij} \cdot m \quad (13)$$

where m = NaClO₄ concentration in mol/kg

z_i = ionic charge

ϵ_{ij} = specific ion interaction coefficient, with $j = Na^+$ and ClO₄⁻, respectively.

Replacing the individual activity coefficients in Eqs. (10)–(12) by Eq. (13), we obtain

$$\log K_{sp}(m) = \log K_{sp}(I=0) + 2D - A \cdot m \quad (14)$$

$$\log \beta'_1(m) = \log \beta'_1(I=0) - 2D + A \cdot m \quad (15)$$

$$\log \beta'_2(m) = \log \beta'_2(I=0) - 2D - B \cdot m \quad (16)$$

where D represents the Debye-Hückel term $(0.5107 m^{1/2} / 1 + 1.5 m^{1/2})$ and A, B are given by

$$A = \epsilon(NpO_2^+, ClO_4^-) + \epsilon(OH^-, Na^+) \quad (17)$$

$$B = \epsilon(NpO_2(OH)_2^-, Na^+) - \epsilon(NpO_2^+, ClO_4^-) - 2\epsilon(OH^-, Na^+) \quad (18)$$

The parameters A , B and the thermodynamic constants are then calculated by linear least squares regression from the experimental values at $I=0.1$ M, 1.05 M and 3.5 M (in molal scale):

$$A = +0.23 \pm 0.04 \quad \log K_{sp} = -8.76 \pm 0.05$$

$$B = -0.34 \pm 0.06 \quad \log K_{sp} = -9.44 \pm 0.10$$

(am. NpO₂OH)
(aged NpO₂OH)

$$\log \beta_1 = 2.7 \pm 0.2$$

$$\log \beta_2 = 4.35 \pm 0.15.$$

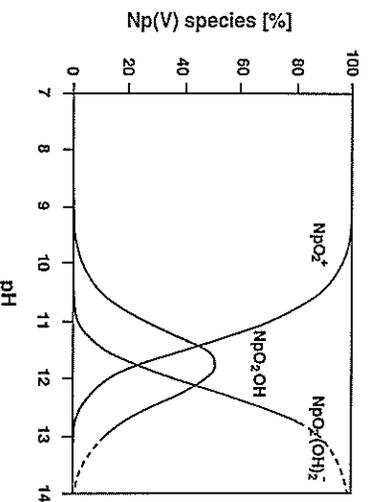
Applying Eqs. (14)–(16) derived from SIT, the solubility products and hydrolysis constants of Np(V) have been calculated in the range $I=0$ –3 M (Table 4).

The pH-dependent speciation of Np(V), based on the data at $I=0.1$ M, is illustrated in Fig. 3. At pH < 10 hydrolysis reactions are negligible. The formation of the first hydrolysis species (NpO₂OH) is significant in the solubility minimum region. At higher pH the anionic species (NpO₂(OH)₂⁻) becomes predominant.

In order to verify the calculated species distribution, aliquots taken from the solubility experiment

Table 4. Solubility products and hydrolysis constants of Np(V); experimental values (in brackets) and calculated values applying SIT

I (mol/kg)	0	0.10	0.20	0.51	1.05	2.2	3.5
$\log K_{sp}$ (am. NpO_2OH)	-8.76	-8.56 (-8.56)	-8.53	-8.53	-8.58 (-8.55)	-8.77	-9.06
$\log K_{sp}$ (aged NpO_2OH)	-9.44	-9.24	-9.21	-9.21	-9.27 (-9.26)	-9.46	-9.74 (-9.72)
$\log \beta_1$	2.70	2.50 (2.44)	2.47	2.47	2.53 (2.65)	2.71	3.00 (3.11)
$\log \beta_2$	4.35	4.16 (4.10)	4.14	4.17	4.30 (4.39)	4.63	5.03 (5.02)
I (mol/l)	0	0.1	0.2	0.5	1.0	2.0	3.0
$\log K_{sp}$ (am. NpO_2OH)	-8.76	-8.56 (-8.56)	-8.54	-8.55	-8.62 (-8.59)	-8.85	-9.19
$\log K_{sp}$ (aged NpO_2OH)	-9.44	-9.24	-9.22	-9.23	-9.31 (-9.30)	-9.54	-9.87 (-9.85)
$\log \beta_1$	2.70	2.50 (2.44)	2.48	2.48	2.55 (2.67)	2.75	3.07 (3.18)
$\log \beta_2$	4.35	4.16 (4.10)	4.15	4.19	4.34 (4.43)	4.71	5.16 (5.15)

Fig. 3. Np(V) species distribution in carbonate-free NaClO_4 solution at $I=0.1$ M and 25°C .

at $I=0.1$ mol/l have been investigated by spectroscopy under exclusion of CO_2 . In the pH region 1–10, the absorption spectrum of the NpO_2^+ ion with the characteristic absorption maximum at 982 nm and the molar extinction coefficient $\epsilon_{\text{max}}=395 \pm 5 \text{ l mol}^{-1} \text{ cm}^{-1}$ is not affected by the variation of pH (Fig. 4). Constant molar extinctions at 982 nm further indicate the absence of colloids and oligomeric species. However, the low solubility at $\text{pH} > 11$ did not allow the spectroscopic characterization of the hydrolysis species. Fig. 4b demonstrates the influence of carbonate contamination on the absorption spectrum of Np(V). The first spectrum shows a saturated Np(V) solution at $\text{pH}=9.9$ under inert argon atmosphere. When the quartz cuvette was opened, atmospheric CO_2 entered the solution immediately. Simultaneously the NpO_2^+ peak at 982 nm decreased and a new band at 993 nm arised. In fact, the absorption band at 993 nm

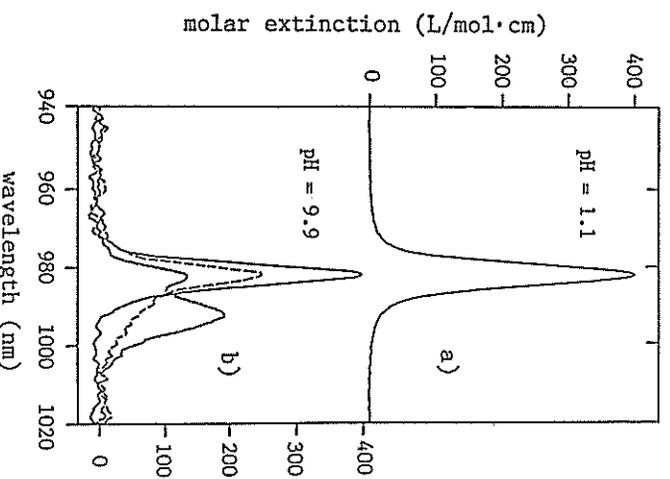


Fig. 4. Absorption spectra of Np(V). a) $\text{pH}=1.1$, $c_{\text{Np}}=6.7 \cdot 10^{-4}$ M in 0.1 M HClO_4 . b) $\text{pH}=9.9$, $c_{\text{Np}}=3.3 \cdot 10^{-5}$ M in 0.1 M NaClO_4 . — cuvette under CO_2 -free Ar atmosphere; --- cuvette opened for 5 min; cuvette opened for 10 h.

is not caused by hydrolysis reactions as claimed by Sevost'yanova and Khaturin [11], but obviously by Np(V) carbonate complexation.

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