

INFO #: 18845448

LOS ALAMOS NATIONAL LABORATORY
Jean-Francois Lucchini

Entered: 11/5/2008 12:13:00PM

NB 11/12/2008
12:00 AM PT
A

SHIP VIA: **Ariel**

Ariel

FILLED ON: 11/06/2008

Infotrieve, Inc.

1888 Century Park East, Ste 600

Los Angeles, CA 90067

Phone 800-422-4633 or 203-423-2175

Fax



Holdings

Send article only if in the Library collection

NB 11/12/2008
12:00 AM PT
A

SHIP TO: 14288 / 2205718

LOS ALAMOS NATIONAL LABORATORY
Jean-Francois Lucchini
A141

Please contact us if you have questions or comments regarding this article.

Email: service@infotrieve.com

Phone: (800) 422-4633

CUSTOMER INFO
PHONE: +1.575.234.5556
FAX: +1.575.887.3051
TEAM: T8-14288
COURIER:

ARTICLE INFORMATION

ARIEL:

0033-8230

NOTES:

RADIOCHIMICA ACTA

69(3):169 176 1995

Main 1962-1993
Publisher 2000-2002 Online

THERMODYNAMICS OF NEPTUNIUM(V) IN CONCENTRATED SALT-SOLUTIONS .2. ION-IN
Send article only if in the Library collection

CCD 0
SHIP VIA Ariel
ORDER #
BILLING REF
ORDERED ON 11/05/2008
FILLED ON 11/06/2008
NEED BY 11/12/2008
ATTENTION Jean-Francois Lucchini
INFO # 18845448

This document is protected by U.S. and International copyright laws. No additional reproduction is authorized. Complete credit should be given to the original source.

Thermodynamics of Neptunium(V) in Concentrated Salt Solutions: II. Ion Interaction (Pitzer) Parameters for Np(V) Hydrolysis Species and Carbonate Complexes

By Th. Fanghänel¹, V. Neck¹ and J. I. Kim^{1,2}

¹ Forschungszentrum Karlsruhe, Institut für Nukleare Entsorgungstechnik, Postfach 3640, D-76021 Karlsruhe, FRG

² Technische Universität München, Institut für Radiochemie, D-85747 Garching, FRG

(Received May 9, 1995)

*Neptunium(V)/Pitzer parameters / Hydrolysis /
Carbonate complexation / Solubility / Ionic strength*

Abstract

A comprehensive set of ion interaction parameters of the Pitzer model, including the relevant thermodynamic constants and standard chemical potentials, is evaluated for the hydrolysis reactions and carbonate complexation of Np(V) in NaClO₄ and NaCl solutions. Based on the hitherto available solubility products, hydrolysis constants and carbonate complexation constants, the binary Pitzer parameters $\beta^{(0)}$ and $\beta^{(1)}$ for the interaction of the Np(V) complex species with Na⁺ are evaluated. The affinity of the NpO₂⁺ ion and its complexed species for the Cl⁻ ion is treated as a strong ion-ion interaction by taking into account mixing parameters θ_{ij} . With these parameters, equilibrium constants for the hydrolysis reactions and carbonate complexation of Np(V) are calculated in a wide range of ionic strength, up to 6.5 m NaClO₄ and 5.6 m NaCl. Solubilities of various Np(V) solid phases are calculated for different NaClO₄ and NaCl concentrations in both carbonate-free solutions and systems with a constant CO₂ partial pressure, and the results are compared with experimental values.

1. Introduction

The predictive geochemical modelling of the aquatic behaviour of Np(V) requires a fundamental database consisting of chemical potentials (thermodynamic equilibrium constants) for all species involved and model parameters for calculating the excess Gibbs energy of the aqueous solution. The predominant geochemical reaction of Np(V), beside its weak chloride complexation [1] and hydrolysis [2–11], is the carbonate complexation [11–21]. In saline solution, the aqueous Np(V) species are in equilibrium with different solid phases [1–3, 11–16, 22, 23], depending on the salt concentration, pH and CO₂ partial pressure. The activity coefficients of the species involved in these equilibrium reactions can be calculated by semi-empirical models comprising the specific ion interaction theory (S.I.T.) [24] and the ion interaction model of Pitzer [25]. The S.I.T. has been applied frequently to describe the ionic strength dependence of solid-liquid equilibria of Np(V) in NaClO₄ solution [3, 12, 19, 20]. However, the applicability of the S.I.T. is confined to ionic strength less than 3.5 mol/kg [12]. The

Pitzer model with its extended parameters for ion-ion interactions can be applied from zero to high ionic strength in systems of unlimited complexity.

The binary Pitzer parameters $\beta^{(0)}$, $\beta^{(1)}$ and C^ϕ for the interaction of NpO₂⁺ with ClO₄⁻ and Cl⁻ have been evaluated recently [1] from NpO₂⁺ trace activity coefficients determined by solvent extraction with NaDNNS in 0.2–5 M NaClO₄ and in 0.2–5 M NaCl, respectively. The different behaviour of the NpO₂⁺ ion in NaClO₄ and NaCl solutions has been described successfully by considering the interaction between NpO₂⁺ and Cl⁻ as a strong ion-ion interaction without invoking Np(V) chloro complex species. Together with the known Pitzer parameters in the systems Na⁺/H⁺/OH⁻/HCO₃⁻/CO₃²⁻/ClO₄⁻(Cl⁻)/H₂O at 25 °C [25–30], including recently evaluated parameters θ_{ij} and Ψ_{ijk} for $i = \text{OH}^-, \text{HCO}_3^-, \text{CO}_3^{2-}$; $j = \text{ClO}_4^-$; $k = \text{Na}^+$ [30], the solubility products of the Np(V) hydroxide and carbonate solid phases have been predicted accurately as a function of the NaClO₄ or NaCl concentration [1].

The present study is aimed to determine appropriate parameters for the Np(V) hydrolysis and carbonate species. In carbonate-free solution, the hydrolysis species NpO₂OH⁰ and NpO₂(OH)₂ are formed at pH ≥ 10 [2, 3, 11]. In carbonate solution, the formation of three monomeric complexes NpO₂(CO₃)_n¹⁻²ⁿ ($n = 1, 2, 3$) is predominant [11–21]. Under atmospheric conditions (pCO₂ = 10^{-3.5} atm) in the pH range 6–11, neither hydrogencarbonate nor mixed hydroxocarbonate complexes of the NpO₂⁺ ion are formed to a significant extent, and the hydrolysis becomes much inferior to the carbonate complexation. The formation of mixed Np(V) chlorocarbonato species has been assumed previously [11, 13] in order to explain considerable differences observed for the solubilities in concentrated NaCl and NaClO₄ solutions. In the present work, the differences between NaCl and NaClO₄ solutions are considered as caused by strong ion-ion interactions between the Np(V) complex species and Cl⁻, similar to the case of the aquo NpO₂⁺ ion [1].

2. Determination of Pitzer ion interaction parameters for the Np(V) hydrolysis species and carbonate complexes

The experimental input data for the determination of the desired model parameters, i.e. the formation con-

Table 1. Pitzer ion interaction parameters used for the present calculation

Binary parameters	$\beta^{(0)}$	$\beta^{(1)}$	C°	Ref.
Na ⁺ /Cl ⁻	0.0765	0.2664	0.00127	[25, 26]
Na ⁺ /ClO ₄ ⁻	0.0554	0.2755	-0.00118	[25, 26]
Na ⁺ /OH ⁻	0.0864	0.253	0.0044	[25, 26]
H ⁺ /Cl ⁻	0.1775	0.2945	0.00080	[25, 26]
H ⁺ /ClO ₄ ⁻	0.1747	0.2931	0.00819	[25, 26]
Na ⁺ /CO ₃ ²⁻	0.0362	1.510	0.0052	[25, 28]
Na ⁺ /HCO ₃ ⁻	0.028	0.044	0	[25, 28]
NpO ₂ ⁺ /Cl ⁻ *	0.1415	0.281	0	[1]
NpO ₂ ⁺ /ClO ₄ ⁻ *	0.257	0.180	0.0081	[1]

Ternary parameters <i>i/j/k</i>	Θ_{ij}	Ψ_{ijk}	Ref.
H ⁺ /Na ⁺ /Cl ⁻	0.036	-0.004	[25, 27]
OH ⁻ /Cl ⁻ /Na ⁺	-0.050	-0.006	[25, 27]
CO ₃ ²⁻ /Cl ⁻ /Na ⁺	-0.02	0.0085	[25, 29]
HCO ₃ ⁻ /Cl ⁻ /Na ⁺	0.03	-0.015	[25, 29]
H ⁺ /Na ⁺ /ClO ₄ ⁻	0.036	-0.016	[25, 27]
OH ⁻ /ClO ₄ ⁻ /Na ⁺	-0.032	0	[30]
CO ₃ ²⁻ /ClO ₄ ⁻ /Na ⁺	0.21	-0.024	[30]
HCO ₃ ⁻ /ClO ₄ ⁻ /Na ⁺	0.095	-0.010	[30]
OH ⁻ /CO ₃ ²⁻ /Na ⁺	0.10	-0.017	[25, 29]
HCO ₃ ⁻ /CO ₃ ²⁻ /Na ⁺	-0.04	0.002	[25, 29]

* $\Theta_{\text{Na}^+/\text{NpO}_2^+}$, $\Psi_{\text{Na}^+/\text{NpO}_2^+/\text{ClO}_4^-}$ and $\Psi_{\text{Na}^+/\text{NpO}_2^+/\text{Cl}^-}$ are set equal to 0.

stants of the species $(\text{NpO}_2)_x(\text{OH})_y(\text{CO}_3)_z^{x-y-2z}$ at given NaClO₄ and NaCl concentrations, are defined by:

$$\beta'_{xyz} = \frac{[(\text{NpO}_2)_x(\text{OH})_y(\text{CO}_3)_z]^{x-y-2z}}{[\text{NpO}_2^+]^x[\text{OH}^-]^y[\text{CO}_3^{2-}]^z} \quad (1)$$

The hydrolysis constants ($\log \beta'_{1n0}$) used for the present calculations are taken from our solubility studies in 0.1–3 M NaClO₄ [2, 3] and in 5 M NaCl [11]. Some literature data [4–10], which scatter several orders of magnitude because of experimental artefacts involved [3], are disregarded. The carbonate complexation constants ($\log \beta'_{10n}$) reported by different authors [11–21] agree quite well with one another, independent of the applied experimental method. However, some data are found to deviate up to 0.4 log units from a general tendency of ionic strength dependence. Therefore, the results from our solubility experiments [11–13] are weighed in double for calculation.

The hydrolysis and carbonate complexation constants in a given medium are related to the thermodynamic constants at $I = 0$ according to Eqs. (2) and (3), respectively:

$$\log \beta'_{1n0} = \log \beta_{1n0}^{\circ} + \log \gamma_{\text{NpO}_2^+} \quad (2)$$

$$+ n \log \gamma_{\text{OH}^-} - \log \gamma_{\text{NpO}_2(\text{OH})_n^{n-}}$$

$$\log \beta'_{10n} = \log \beta_{10n}^{\circ} + \log \gamma_{\text{NpO}_2^+} \quad (3)$$

$$+ n \log \gamma_{\text{CO}_3^{2-}} - \log \gamma_{\text{NpO}_2(\text{CO}_3)_n^{2-n}}$$

The trace activity coefficients $\gamma_{\text{NpO}_2^+}$, γ_{OH^-} and $\gamma_{\text{CO}_3^{2-}}$ are calculated with the Pitzer parameters summarized in Table 1. The Pitzer ion interaction parameters, which

Table 2. Thermodynamic formation constants/standard chemical potentials for the Np(V) hydrolysis species and carbonate complexes at 25 °C evaluated in the present work

	Thermodynamic formation constants	Standard chemical potentials* μ° (kJ/mol)
Hydrolysis species	$\log \beta'_{1n0}$	
NpO ₂ OH ⁰	2.69 ± 0.13	-1087.60
NpO ₂ (OH) ₂ ⁻	4.46 ± 0.06	-1254.95
Carbonate complexes	$\log \beta'_{10n}$	
NpO ₂ CO ₃ ⁻	5.03 ± 0.06	-1471.52
NpO ₂ (CO ₃) ₂ ²⁻	6.47 ± 0.14	-2007.55
NpO ₂ (CO ₃) ₃ ³⁻	5.37 ± 0.36	-2529.08

* Calculated according to:

$$\mu_{(\text{NpO}_2)_x(\text{OH})_y(\text{CO}_3)_z}^{\circ} = -RT \ln \beta_{xyz}^{\circ} + x\mu_{\text{NpO}_2^+}^{\circ} + y\mu_{\text{OH}^-}^{\circ} + z\mu_{\text{CO}_3^{2-}}^{\circ}$$

with

$$\mu_{\text{NpO}_2^+}^{\circ} = -915.0 \pm 5.4 \text{ kJ/mol [32]},$$

$$\mu_{\text{OH}^-}^{\circ} = -157.244 \text{ kJ/mol [33]}, \mu_{\text{CO}_3^{2-}}^{\circ} = -527.81 \text{ kJ/mol [33]}.$$

Table 3. Pitzer ion interaction parameters for the Np(V) hydrolysis species and carbonate complexes at 25 °C evaluated in the present work^a

$\lambda_{\text{NpO}_2\text{OH}^0/\text{Na}^+}$	0 ± 0.07 ^b	$\beta_{\text{NpO}_2\text{CO}_3^-}^{(0)}/\text{Na}^+$	0.10 ± 0.03
$\lambda_{\text{NpO}_2\text{OH}^0/\text{Cl}^-}$	-0.19 ± 0.05 ^b	$\beta_{\text{NpO}_2\text{CO}_3^-}^{(1)}/\text{Na}^+$	0.34 ^c
		$\Theta_{\text{NpO}_2\text{CO}_3^-/\text{Cl}^-}$	-0.21 ± 0.03 ^d
$\beta_{\text{NpO}_2(\text{OH})_2^-}^{(0)}/\text{Na}^+$	0 ± 0.05	$\beta_{\text{NpO}_2(\text{CO}_3)_2^{2-}}^{(0)}/\text{Na}^+$	0.48 ± 0.05
$\beta_{\text{NpO}_2(\text{OH})_2^-}^{(1)}/\text{Na}^+$	0 ^c	$\beta_{\text{NpO}_2(\text{CO}_3)_2^{2-}}^{(1)}/\text{Na}^+$	4.4 ± 0.8
$\Theta_{\text{NpO}_2(\text{OH})_2^-/\text{Cl}^-}$	-0.24 ± 0.03 ^d	$\Theta_{\text{NpO}_2(\text{CO}_3)_2^{2-}/\text{Cl}^-}$	-0.26 ± 0.03 ^d
		$\beta_{\text{NpO}_2(\text{CO}_3)_3^{3-}}^{(0)}/\text{Na}^+$	1.80 ± 0.06
		$\beta_{\text{NpO}_2(\text{CO}_3)_3^{3-}}^{(1)}/\text{Na}^+$	22.7 ± 1.5
		$\Theta_{\text{NpO}_2(\text{CO}_3)_3^{3-}/\text{Cl}^-}$	-0.26 ± 0.02 ^d

^a C° and Ψ_{ijk} are set equal to 0 for all Np(V) hydrolysis and carbonate species.

^b λ_{ij} is set equal to 0 for $j = \text{ClO}_4^-$ (see text).

^c Fixed value (see text).

^d All Θ_{ij} values are set equal to 0 for $j = \text{ClO}_4^-$ (see text).

are necessary for calculating the activity coefficients of the complex Np(V) species, and the thermodynamic constants $\log \beta^{\circ}$ are evaluated simultaneously by a non-linear least squares procedure minimizing the differences between calculated and experimental $\log \beta'$ values in both NaClO₄ and NaCl solutions. The evaluated thermodynamic formation constants and Pitzer parameters are summarized in Tables 2 and 3.

Due to the limited number of available experimental data and their inherent uncertainties, it is found impossible to determine all hitherto unknown ion interaction parameters in the system Np(V)/Na⁺/H⁺/OH⁻/CO₃²⁻/ClO₄⁻/Cl⁻/H₂O. Therefore, the following simplifications have been made:

(1) All parameters accounting for the interaction between two or three different trace components and terms involving a product of molalities of trace components are set to zero.

(2) The parameters accounting for triple ion interactions of Np(V) hydrolysis species and carbonate com-

plexes (C_{ij}^{ϕ} and Ψ_{ijk} , with $i = \text{Np(V) complex species}$) are also set to zero.

(3) When there is no accurate measurement available at low ionic strength, the parameter $\beta^{(1)}$ has to be estimated. We recommend to fix $\beta^{(1)}$ to a certain value rather than to set it equal to zero. Setting $\beta^{(1)} = 0$ is an oversimplification in particular for higher charge type electrolytes (other than 1:1 electrolytes) and leads to systematic deviations in the concentration dependence of activity coefficients. It has been demonstrated recently [31] that the binary parameters $\beta^{(1)}$ specific for the interaction of complex species with the ionic medium can be estimated from a correlation between $\Delta\beta^{(1)}$ and Δz^2 . For 1:1 electrolytes the following correlation has been derived [31]:

$$\Delta\beta^{(1)} \approx 0.34 \Delta z^2 \quad (4)$$

where z_i is the ionic charge, $\Delta z^2 = \sum z_i^2(\text{products}) - \sum z_i^2(\text{educts})$ and $\Delta\beta^{(1)} = \sum \beta^{(1)}(\text{products}) - \sum \beta^{(1)}(\text{educts})$. Applying the $\beta^{(1)}$ parameters for $\text{NpO}_2^+/ \text{ClO}_4^-$, $\text{Na}^+ / \text{OH}^-$ and $\text{Na}^+ / \text{CO}_3^{2-}$ given in Table 1, the following values are estimated:

$$\beta_{\text{NpO}_2^+ \text{CO}_3^{2-} / \text{Na}^+}^{(1)} \approx 0.34$$

$$\beta_{\text{NpO}_2(\text{OH})_2^- / \text{Na}^+}^{(1)} \approx 0.$$

For electrolytes of charge type higher than 2:1 it is difficult to derive a similar correlation because of the limited number of available experimental data. However, from a general correlation of $\beta^{(1)}$ with corresponding charge type electrolytes, the values of about 4.3 for $\beta_{\text{NpO}_2(\text{CO}_3)_2^- / \text{Na}^+}^{(1)}$ and about 23 for $\beta_{\text{NpO}_2(\text{CO}_3)_3^{3-} / \text{Na}^+}^{(1)}$ are estimated. The best fitted value of $\beta_{\text{NpO}_2(\text{CO}_3)_2^- / \text{Na}^+}^{(1)} = 4.4$ is in good agreement with the estimated value and the best fitted value of $\beta_{\text{NpO}_2(\text{CO}_3)_3^{3-} / \text{Na}^+}^{(1)} = 22.7$ is close to known values for the fivefold negative ion $\text{P}_3\text{O}_{10}^{5-}$ ($\beta_{\text{P}_3\text{O}_{10}^{5-} / \text{Na}^+}^{(1)} = 21.7$ and $\beta_{\text{P}_3\text{O}_{10}^{5-} / \text{K}^+}^{(1)} = 23.8$ [25]). In the case of the second hydrolysis species, the parameter $\beta_{\text{NpO}_2(\text{OH})_2^- / \text{Na}^+}^{(1)}$ is found to be not significant and thus set equal to zero.

(4) The parameter $\beta^{(0)}$ for the interaction of negatively charged Np(V) hydrolysis species and carbonate complexes with Na^+ and the parameter θ for the interaction with ClO_4^- or Cl^- can not be determined separately. This would require further experimental data in the binary electrolyte system, which are however not available. The activity coefficients of negatively charged Np(V) species ($\gamma_{\text{Np(V)}^-}$) in pure NaClO_4 or NaCl solution are related to these parameters by

$$\ln \gamma_{\text{Np(V)}^-} = z_i^2 F + 2m_{\text{NaClO}_4}(\beta_{\text{Np(V)}^- / \text{Na}^+}^{(0)} + \theta_{\text{Np(V)}^- / \text{ClO}_4^-}) + \dots \quad (5a)$$

or

$$\ln \gamma_{\text{Np(V)}^-} = z_i^2 F + 2m_{\text{NaCl}}(\beta_{\text{Np(V)}^- / \text{Na}^+}^{(0)} + \theta_{\text{Np(V)}^- / \text{Cl}^-}) + \dots \quad (5b)$$

where the term F depends only on the ionic strength (see Pitzer equations [25]). Therefore, the parameters $\beta_{\text{Np(V)}^- / \text{Na}^+}^{(0)}$, $\theta_{\text{Np(V)}^- / \text{ClO}_4^-}$ and $\theta_{\text{Np(V)}^- / \text{Cl}^-}$ given in Table 3 are not independent of each other. The parameter $\beta^{(0)}$

Table 4. Formation constants of Np(V) hydrolysis and carbonate species in NaClO_4 and NaCl solutions at 25°C; experimental data and values calculated by the Pitzer model

Species	Medium	I_m (mol/kg)	$\log \beta'$ (exp.)	Ref., method*	$\log \beta'$ (calc.)
$\text{NpO}_2\text{OH}^\circ$	NaClO_4	0.1	2.44±0.16	[3], sol	2.48
		1.05	2.65±0.20	[3], sol	2.45
		3.5	2.09±0.62	[2, 3], sol	
	NaCl	3.5	3.11±0.33	[3], sol	2.92
		5.6	3.61±0.22	[11], sol	3.61
$\text{NpO}_2(\text{OH})_2^-$	NaClO_4	0.1	4.10±0.12	[3], sol	4.27
		1.05	4.37±0.14	[3], sol	4.33
		3.5	4.41±0.18	[2, 3], sol	
	NaCl	3.5	5.02±0.26	[3], sol	4.97
		5.6	5.88±0.19	[11], sol	5.88
$\text{NpO}_2\text{CO}_3^-$	NaClO_4	0.1	4.58±0.04	[12], sol	4.58
			4.38±0.04	[12], spec	
			4.34±0.04	[19], spec	
			4.52±0.02	[21], sol	
		0.2	4.13±0.03	[17], ex	4.48
		0.51	4.29±0.1	[20], spec	4.36
		1.05	4.48±0.04	[12], sol	4.32
			4.47±0.06	[15], sol	
			4.12±0.01	[18], ex	
	NaCl	3.5	4.69±0.04	[12], sol	4.57
			5.02	[16], sol	
		6.5	4.89±0.05	[12], sol	5.08
		0.1	4.68±0.03	[11], spec	4.57
		1.02	4.31±0.07	[11], sol	4.24
		3.2	4.64±0.07	[11], spec	4.32
		5.6	4.63	[13], sol	4.69
			4.66±0.04	[11], sol	
			4.67±0.13	[11], spec	
$\text{NpO}_2(\text{CO}_3)_2^-$	NaClO_4	0.1	6.60±0.07	[12], sol	6.58
			6.4±0.3	[12], spec	
		0.2	7.05±0.05	[17], ex	6.62
		0.51	6.48±0.2	[20], spec	6.72
		1.05	6.92±0.06	[12], sol	6.89
			7.07±0.02	[15], sol	
	NaCl	3.5	6.74±0.01	[18], ex	
			7.56±0.07	[12], sol	7.59
			8.02	[16], sol	
		6.5	8.06±0.09	[12], sol	8.16
		1.02	6.47±0.09	[11], sol	6.65
		5.6	7.13	[13], sol	7.32
	7.44±0.05	[11], sol			
	7.53±0.19	[11], spec			
$\text{NpO}_2(\text{CO}_3)_3^{3-}$	NaClO_4	0.51	7.87±0.2	[20], spec	8.11
		1.05	8.61±0.09	[12], sol	8.60
		3.5	8.47±0.10	[15], sol	
	NaCl	3.5	10.10±0.09	[12], sol	10.23
			10.26	[16], sol	
		6.5	11.13±0.08	[12], sol	11.05
		1.02	8.40±0.06	[11], sol	8.15
		5.6	9.58	[13], sol	9.55
			9.48±0.05	[11], sol	

* sol: solubility experiment; spec: spectroscopy; ex: solvent extraction.

includes $\theta_{\text{Np(V)}^- / \text{ClO}_4^-}$, which has been arbitrarily set equal to zero, and the given $\theta_{\text{Np(V)}^- / \text{Cl}^-}$ value actually represents the difference of $\theta_{\text{Np(V)}^- / \text{Cl}^-} - \theta_{\text{Np(V)}^- / \text{ClO}_4^-}$.

The same problem arises for the neutral hydrolysis species $\text{NpO}_2\text{OH}^\circ$. The parameters λ for the interaction of the neutral species $\text{NpO}_2\text{OH}^\circ$ with Na^+ and

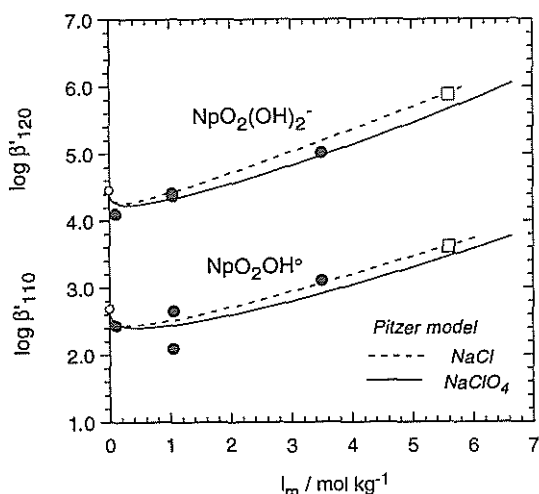


Fig. 1. Formation constants of the Np(V) hydrolysis species; experimental data in NaClO₄ (●) and NaCl (□) solutions and the ionic strength dependence predicted by the Pitzer model. The symbol (○) represents log β° at I = 0 (see Table 5).

ClO₄⁻ (in NaClO₄ solution) or Cl⁻ (in NaCl solution) are not available independently:

$$\ln \gamma_{\text{NpO}_2\text{OH}^-} = m_{\text{NaClO}_4} (\lambda_{\text{NpO}_2\text{OH}^-/\text{Na}^+} + \lambda_{\text{NpO}_2\text{OH}^-/\text{ClO}_4^-}) \quad (6a)$$

or

$$\ln \gamma_{\text{NpO}_2\text{OH}^-} = m_{\text{NaCl}} (\lambda_{\text{NpO}_2\text{OH}^-/\text{Na}^+} + \lambda_{\text{NpO}_2\text{OH}^-/\text{Cl}^-}). \quad (6b)$$

Since $\ln \gamma_{\text{NpO}_2\text{OH}^-}$ shows no significant dependence on the NaClO₄ concentration, both $\lambda_{\text{NpO}_2\text{OH}^-/\text{Na}^+}$ and $\lambda_{\text{NpO}_2\text{OH}^-/\text{ClO}_4^-}$ are set equal to zero, i.e. $\gamma_{\text{NpO}_2\text{OH}^-} = 1$ in NaClO₄ solution. The parameter $\lambda_{\text{NpO}_2\text{OH}^-/\text{Cl}^-}$ merely describes the different behaviour of NpO₂OH⁰ in NaCl and NaClO₄ solutions.

Table 4 shows that the log β' values calculated with the parameters from the present work agree well (in most cases within ±0.2 log units) with the experimental data in both NaClO₄ and NaCl solutions. Some values of log β'_{101} and log β'_{102} in 0.2 and 3.5 m NaClO₄ [16, 17] deviate up to ±0.4 log units from the calculated ionic strength dependence. Comparisons of calculated values with experimental hydrolysis and carbonate complexation constants are illustrated in Figs. 1 and 2 as a function of the NaClO₄ and NaCl concentrations.

The formation constants of the two hydrolysis species and the first carbonate complex show no notable difference between NaClO₄ and NaCl solutions. For these species, the interaction with Cl⁻ must be comparable to the interaction between NpO₂²⁺ and Cl⁻ ions. In contrast to that, with increasing ionic strength the formation constants of NpO₂(CO₃)₂³⁻ and NpO₂(CO₃)₃⁵⁻ become considerably larger in NaClO₄ than the corresponding values in NaCl solution. Due to the high charge of the complex NpO₂(CO₃)₃⁵⁻, log β'_{103} shows a considerable dependence on ionic strength and increases several orders of magnitude from the value at I = 0 (Fig. 2).

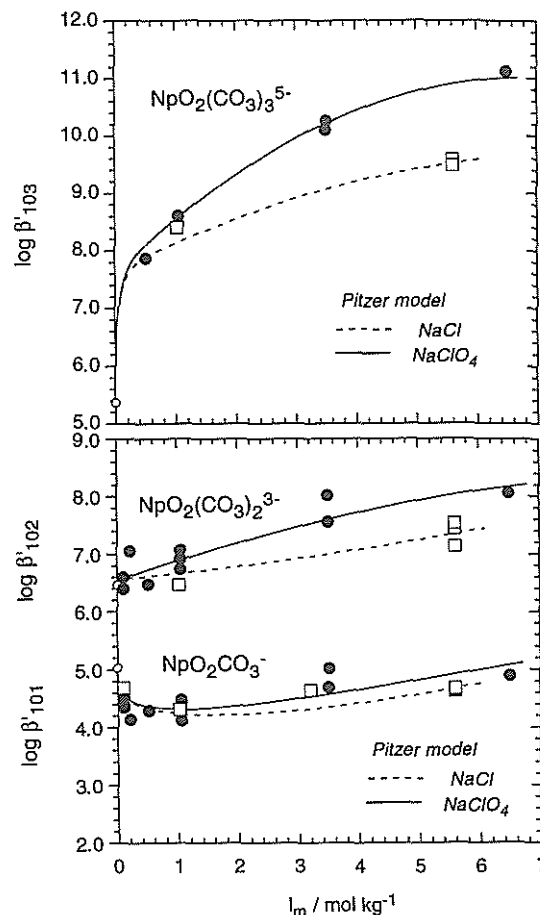


Fig. 2. Formation constants of the Np(V) carbonate complexes; experimental data in NaClO₄ (●) and NaCl (□) solutions and the ionic strength dependence predicted by the Pitzer model. The symbol (○) represents log β° at I = 0 (see Table 5).

3. Solubility of Np(V) hydroxide and carbonate solid phases

In order to demonstrate the predictive capability of the present model, the solubility of Np(V) is calculated for the different hydroxide and carbonate solid phases as a function of [H⁺] or [CO₃²⁻] at different NaClO₄ and NaCl concentrations. In carbonate-free solution the amorphous and aged NpO₂OH · nH₂O have been reported as equilibrium solid phases [2, 3, 23]. In carbonate solution two solid phases are formed, either NaNpO₂CO₃ · nH₂O [11–16, 21, 22] or Na₃NpO₂(CO₃)₂ · nH₂O [11, 14, 16, 22], depending on the carbonate concentration and ionic strength. The calculation of the solubility depends, to a certain extent, on whether the crystal water of the solid phase is considered or not [1], because the water activity *a_w* decreases considerably at high electrolyte concentrations. However, the number of crystal water molecules has been determined only for amorphous NpO₂OH (n = 2.5 [23]) and for NaNpO₂CO₃ (n = 3.5 [15, 22]). For the latter solid phase, the solubility is calculated with and without taking account of the crystal water. The solubility of amorphous NpO₂OH has been determined at I ≤ 1 mol/L, where the ac-

tivity of water does not differ very much from $a_w = 1$ ($a_w = 0.966$ in 1 M NaClO_4) and hence the water content of the solid phase has been neglected.

The solubility of Np(V) is related to the solubility product K'_{sp} of a given equilibrium solid phase by Eqs. (7–9). In carbonate-free solution, with amorphous or aged NpO_2OH (amorphous $\text{NpO}_2\text{OH} \cdot 2.5 \text{H}_2\text{O}$) as equilibrium solid phases, the total Np(V) concentration is a function of the OH^- concentration:

$$[\text{Np(V)}]_t = \frac{{}^1K'_{sp}}{[\text{OH}^-]} (1 + \sum \beta'_{1n0} [\text{OH}^-]^n) \quad (7)$$

with

$${}^1K'_{sp} = {}^1K_{sp}^{\circ} / \gamma_{\text{NpO}_2^+} \gamma_{\text{OH}^-} \quad ({}^1K'_{sp} = {}^1K_{sp}^{\circ} / \gamma_{\text{NpO}_2^+} \gamma_{\text{OH}^-} (a_w)^{2.5}).$$

In carbonate solution, the solubility of $\text{NaNpO}_2\text{CO}_3$ ($\text{NaNpO}_2\text{CO}_3 \cdot 3.5\text{H}_2\text{O}$) is a function of the CO_3^{2-} concentration:

$$[\text{Np(V)}]_t = \frac{{}^{II}K'_{sp}}{[\text{Na}^+][\text{CO}_3^{2-}]} (1 + \sum \beta'_{10n} [\text{CO}_3^{2-}]^n) \quad (8)$$

with

$${}^{II}K'_{sp} = {}^{II}K_{sp}^{\circ} / \gamma_{\text{Na}^+} \gamma_{\text{NpO}_2^+} \gamma_{\text{CO}_3^{2-}}$$

$$({}^{II}K'_{sp} = {}^{II}K_{sp}^{\circ} / \gamma_{\text{Na}^+} \gamma_{\text{NpO}_2^+} \gamma_{\text{CO}_3^{2-}} (a_w)^{3.5}).$$

The solubility of $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2$ is given by

$$[\text{Np(V)}]_t = \frac{{}^{III}K'_{sp}}{[\text{Na}^+]^3[\text{CO}_3^{2-}]^2} (1 + \sum \beta'_{10n} [\text{CO}_3^{2-}]^n) \quad (9)$$

with

$${}^{III}K'_{sp} = {}^{III}K_{sp}^{\circ} / \gamma_{\text{Na}^+}^3 \gamma_{\text{NpO}_2^+} \gamma_{\text{CO}_3^{2-}}^2.$$

The predicted solubilities of amorphous and aged NpO_2OH , $\text{NaNpO}_2\text{CO}_3$ and $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2$ are shown in Figs. 3 and 4 as a function of ionic strength and $[\text{H}^+]$ or $[\text{CO}_3^{2-}]$ in comparison with the experimental data. The calculated solubilities of Np(V) agree well with the experimental data in both media, although the differences of the solubilities in NaClO_4 and NaCl solutions become large at high ionic strength. When the solubility products of $\text{NaNpO}_2\text{CO}_3 \cdot 3.5\text{H}_2\text{O}$ are calculated taking account of the crystal water (dashed lines in Fig. 4), the solubilities can be calculated very accurately (within ± 0.2 log units).

Recently, Novak and Roberts [34] determined another set of Pitzer parameters for the modeling of Np(V) solubilities in the system $\text{Na}^+/\text{H}^+/\text{OH}^-/\text{CO}_3^{2-}/\text{ClO}_4^-/\text{Cl}^-$ at 25 °C. Table 5 shows a comparison of the parameters from the present work with those of Novak and Roberts. They used the same experimental data (NpO_2^+ trace activity coefficients determined by solvent extraction [13]) for the evaluation of the interaction parameters between NpO_2^+ and ClO_4^- or Cl^- . They also used the formation constants from our solubility studies in NaClO_4 solution [3, 12, 13] for the parametrization of the Np(V) hydrolysis and carbonate species. With their one parameter approach (the parameters $\beta^{(1)}$, C^ϕ , θ_{ij} and Ψ_{ijk} for the NpO_2^+ ion and other

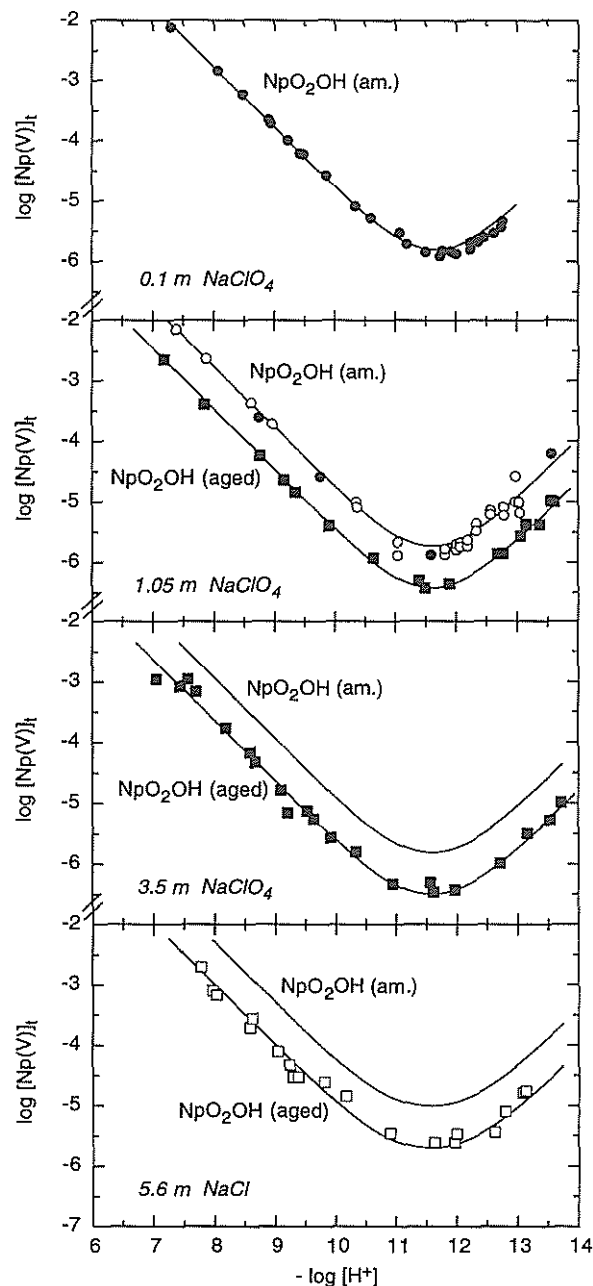


Fig. 3. Experimental and calculated solubilities of amorphous and aged NpO_2OH as a function of the H^+ concentration in NaClO_4 and NaCl solutions (molal scale, 25 °C): ●, ■: Neck *et al.* [3], ○: Lierse *et al.* [2], □: Runde [11], — calculated with the present model parameters.

Np(V) species have been set equal to zero), the solubility and solvent extraction behaviour of Np(V) could be described well for many conditions. However, the parameters of Novak and Roberts appeared to be less satisfactory for NaClO_4 solutions of higher carbonate concentrations, for which the discrepancies between the calculated and experimental solubility data increase up to 0.5 log units. In concentrated NaCl , the solubility curve predicted for $\text{NaNpO}_2\text{CO}_3$ deviates even up to one order of magnitude from the experimental data. Furthermore, some of the thermodynamic constants calculated by Novak and Roberts differ con-

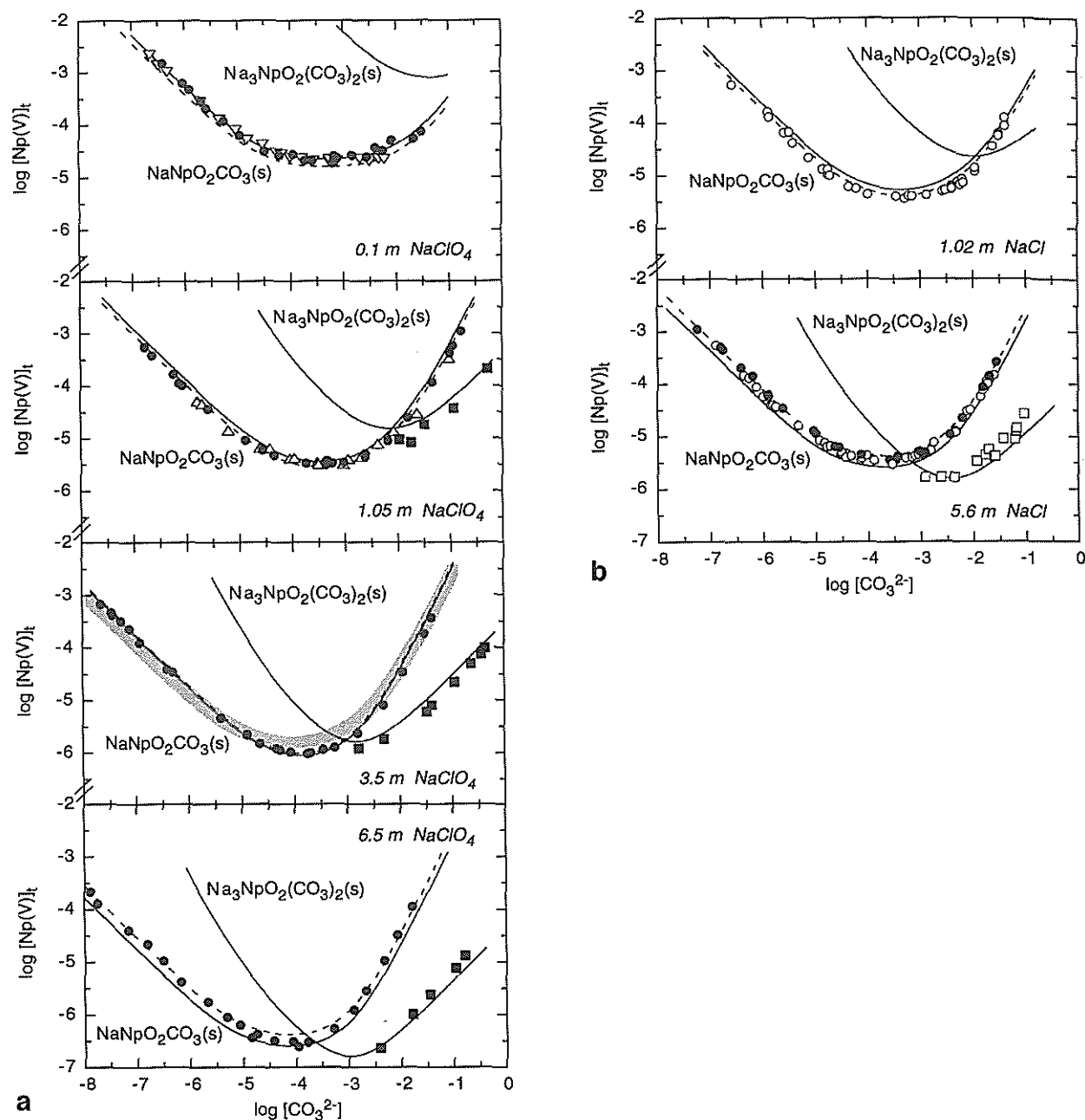


Fig. 4. Experimental and calculated solubilities of Np(V) as a function of the carbonate concentration a) in 0.1–6.5 m NaClO₄ and b) in 1.0 and 5.6 m NaCl (molal scale, 25 °C): NaNpO₂CO₃(s): ●: Neck *et al.* [12, 13], ▽: Meinrath [21], △: Maya [15], ○: Runde [11], ■: Grenthe *et al.* [16], — calculated with the present model parameters, - - - calculated for NaNpO₂CO₃ · 3.5 H₂O. Na₃NpO₂(CO₃)₂(s): ■: Neck *et al.* [14], □: Runde [11], — calculated with the present model parameters.

siderably from the values obtained by the S.I.T. formalism (Table 5). Since both Pitzer equations and S.I.T. have the same limiting law (Debye-Hückel) and are related to the same standard state, the extrapolation to $I = 0$ is expected to lead to similar values.

The problems in modeling Np(V) solubilities in carbonate solution arise primarily from the calculation of the trace activity coefficient $\gamma_{\text{CO}_3^{2-}}$ in NaClO₄ solution. For the NaCl system, a complete set of well established binary and ternary Pitzer parameters [25–29] can be applied to calculate $\gamma_{\text{CO}_3^{2-}}$, and γ_{OH^-} . For the NaClO₄ system, Novak and Roberts used the binary parameters published by Harvie *et al.* [29] and set the

ternary parameters $\theta_{\text{CO}_3^{2-}/\text{ClO}_4^-}$ and $\psi_{\text{Na}^+/\text{CO}_3^{2-}/\text{ClO}_4^-}$ equal to zero. However, with increasing NaClO₄ concentration these parameters considerably affect the calculation of $\log \gamma_{\text{CO}_3^{2-}}$, up to 0.6 log units in 6.5 m NaClO₄ [30]. (When the ternary interaction parameters for the OH⁻ ion are neglected, the errors in $\log \gamma_{\text{OH}^-}$ remain relatively small, below 0.2 log units [30].) Since Novak and Roberts evaluated their model parameters mainly from experimental data in NaClO₄ solutions (with $\theta_{\text{CO}_3^{2-}/\text{ClO}_4^-} = \psi_{\text{Na}^+/\text{CO}_3^{2-}/\text{ClO}_4^-} = 0$), they obtained somewhat erroneous $\log K_{sp}^\circ$ (NaNpO₂CO₃) and $\log \beta_{10n}^\circ$ values. Using these values, the solubilities in NaCl solutions cannot be predicted accurately. Furthermore,

Table 5. Comparison of the present model parameters with the model parameters of Novak and Roberts [34] for the system Np(V)/Na⁺/H⁺/OH⁻/CO₃²⁻/ClO₄⁻/Cl⁻/H₂O at 25 °C

a) Thermodynamic equilibrium constants			
Solid phase	log K _{sp} ^o (Pitzer model)		log K _{sp} ^o (S.I.T.) ¹
	Neck <i>et al.</i> [1] ²	Novak, Roberts [34] ¹	
NpO ₂ OH(amorphous) (NpO ₂ OH · 2.5H ₂ O)	-8.78±0.05 (-8.80±0.05)	-8.72	-8.76±0.05 [3]
NpO ₂ OH(aged)	-9.48±0.07	-9.32	-9.44±0.10 [3]
NaNpO ₂ CO ₃ (NaNpO ₂ CO ₃ · 3.5 H ₂ O)	-10.93±0.17 (-11.09±0.11)	-11.3	-10.94±0.08 [1] (-10.94±0.08 [1])
Na ₂ NpO ₂ (CO ₃) ₂	-14.18±0.13	n.d.	-14.32±0.15 [1]
Solution species			
	log β ^o (Pitzer model)		log β ^o (S.I.T.) ¹
	This work ²	Novak, Roberts [34] ¹	
NpO ₂ OH ^o	2.69±0.13	2.58	2.7±0.2 [3]
NpO ₂ (OH) ₂ ⁻	4.46±0.06	4.27	4.35±0.15 [3]
NpO ₂ CO ₃ ⁻	5.03±0.06	5.39	4.83±0.15 [12]
NpO ₂ (CO ₃) ₂ ²⁻	6.47±0.14	5.81	6.55±0.23 [12]
NpO ₂ (CO ₃) ₃ ³⁻	5.37±0.36	5.19	5.54±0.09 [12]

¹ Calculated using experimental data in NaClO₄ solution.
² Calculated using all experimental data in both NaClO₄ and NaCl solutions.

b) Pitzer ion interaction parameters at 25 °C					
	This work	Novak, Roberts [34]		This work	Novak, Roberts [34]
β _{NpO₂^o/ClO₄} ⁽⁰⁾	0.257	0.312	β _{NpO₂CO₃⁻/Na⁺} ⁽⁰⁾	0.10	0.161
β _{NpO₂^o/ClO₄} ⁽¹⁾	0.180	0	β _{NpO₂CO₃⁻/Na⁺} ⁽¹⁾	0.34	0
C _{NpO₂^o/ClO₄} ⁽⁰⁾	0.0081	0	Θ _{NpO₂CO₃⁻/Cl⁻}	-0.21	n.d.
β _{NpO₂^o/Cl⁻} ⁽⁰⁾	0.1415	0.169	β _{NpO₂(CO₃)₂²⁻/Na⁺} ⁽⁰⁾	0.48	0.407
β _{NpO₂^o/Cl⁻} ⁽¹⁾	0.281	0	β _{NpO₂(CO₃)₂²⁻/Na⁺} ⁽¹⁾	4.4	0
C _{NpO₂^o/Cl⁻} ⁽⁰⁾	0	0	Θ _{NpO₂(CO₃)₂²⁻/Cl⁻}	-0.26	n.d.
λ _{NpO₂OH/Na⁺}	0	0	β _{NpO₂(CO₃)₃³⁻/Na⁺} ⁽⁰⁾	1.80	1.97
λ _{NpO₂OH/ClO₄}	0	0	β _{NpO₂(CO₃)₃³⁻/Na⁺} ⁽¹⁾	22.7	16
λ _{NpO₂OH/Cl⁻}	-0.19	n.d.	Θ _{NpO₂(CO₃)₃³⁻/Cl⁻}	-0.26	n.d.
β _{NpO₂OH₂⁻/Na⁺} ⁽⁰⁾	0	0			
β _{NpO₂OH₂⁻/Na⁺} ⁽¹⁾	0	0			
Θ _{NpO₂OH₂⁻/Cl⁻}	-0.24	n.d.			

n.d. = not determined.

calculations at higher chloride and carbonate concentrations require parameters accounting for the interaction between Cl⁻ and Np(V) carbonate complexes.

4. Conclusions

Using the Pitzer approach with the ion interaction parameters evaluated in the present work, the activity coefficients of the NpO₂^o ion, hydrolysis species and carbonate complexes and thus equilibrium constants can

be described accurately from dilute solutions to high NaClO₄ and NaCl concentrations. However, the evaluation of the present set of Pitzer ion interaction parameters is based on a number of simplifications, i.e. some of the model parameters had to be fixed or neglected. The solubilities of different Np(V) solid phases are predicted as a function of pH, carbonate concentration and ionic strength within a maximum uncertainty of ±0.3 logarithmic units in both NaClO₄ and NaCl solutions.

References

- Neck, V., Fanghänel, Th., Rudolph, G., Kim, J. I.: Thermodynamics of Neptunium(V) in Concentrated Salt Solutions: Chloride Complexation and Ion Interaction (Pitzer) Parameters of the NpO₂^o Ion. *Radiochim. Acta* **69**, 39 (1995).
- Lierse, Ch., Treiber, W., Kim, J. I.: Hydrolysis Reactions of Neptunium(V). *Radiochim. Acta* **38**, 27 (1985).
- Neck, V., Kim, J. I., Kanellakopoulos, B.: Solubility and Hydrolysis Behaviour of Neptunium(V). *Radiochim. Acta* **56**, 25 (1992).
- Itagaki, H., Nakayama, S., Tanaka, S., Yamawaki, M.: Effects of Ionic Strength on the Solubility of Neptunium(V) Hydroxide. *Radiochim. Acta* **58/59**, 61 (1992).
- Nakayama, S., Arimoto, H., Yamada, N., Moriyama, H., Higashi, K.: Column Experiments on the Migration Behaviour of Neptunium(V). *Radiochim. Acta* **44/45**, 179 (1988).
- Nagasaki, S., Tanaka, S., Takahashi, Y.: Speciation and Solubility of Neptunium in Underground Environmentals by Paper Electrophoresis. *J. Radioanal. Nucl. Chem.* **124**, 383 (1988).
- Rösch, F., Milanov, M., Kim, H. T., Ludwig, R., Buklanov, G. V., Khalkin, V. A.: Electromigration of Carrier-free Radionuclides. 5. Ion Mobilities and Hydrolysis of Np(V) in Aqueous Perchlorate Solutions. *Radiochim. Acta* **42**, 43 (1987).
- Sevost'yanova, E. P., Khalturin, G. V.: Hydrolytic Behaviour of Neptunium(V). *Soviet Radiochem.* **18**, 738 (1976).
- Moskvin, A. I.: Hydrolytic Behaviour of Neptunium(IV, V, VI). *Soviet Radiochem.* **13**, 700 (1971).
- Kraus, K. A.: Hydrolytic Behaviour of the Heavy Elements. *Proc. Int. Conf. Peaceful Use Atom. Energy, Geneva*, Vol. 7 (1956), 245.
- Runde, W., Kim, J. I.: Chemisches Verhalten von drei- und fünfwertigem Americium in salinen NaCl-Lösungen. Report RCM 01094, Inst. für Radiochemie, Technische Universität München, 1994.
- Neck, V., Runde, W., Kim, J. I., Kanellakopoulos, B.: Solid-Liquid Equilibrium Reactions of Neptunium(V) in Carbonate Solution at Different Ionic Strength. *Radiochim. Acta* **65**, 29 (1994).
- Neck, V., Kim, J. I., Kanellakopoulos, B.: Thermodynamisches Verhalten von Neptunium(V) in konzentrierten NaCl- und NaClO₄-Lösungen. Report KfK 5301, Forschungszentrum Karlsruhe (1994).
- Neck, V., Runde, W., Kim, J. I.: Solid-Liquid Equilibria of Neptunium(V) in Carbonate Solutions of Different Ionic Strength (Part II), Proceedings of the 2nd Int. Conf. on f-Elements. Helsinki, Aug. 1994. *J. Alloys and Compounds* (1995).
- Maya, L.: Hydrolysis and Carbonate Complexation of Dioxoneptunium(V) in 1.0 M NaClO₄ at 25 °C. *Inorg. Chem.* **22**, 2093 (1983).
- Grenthe, I., Robouch, P., Vitorge, P.: Chemical Equilibria in Actinide Carbonate Systems. *J. Less-Common Met.* **122**, 225 (1986).
- Bidoglio, G., Tanet, G., Chatt, A.: Studies on Neptunium(V) Carbonate Complexes under Geologic Repository Conditions. *Radiochim. Acta* **38**, 21 (1985).

Na₂CO₃ and NaHCO₃ in H₂O.

equal concentrations of NaClO₄ or the main anions are not determined and log NaCl more,

18. Inoue, Y., Tochiyama, O.: Studies on the Complexes of Np(V) with Inorganic Ligands by Solvent Extraction with Thenoyltrifluoro-Acetone and 1,10-Phenanthroline. *Bull. Chem. Soc. Jap.* **58**, 588 (1985).
19. Nitsche, H., Standifer, E. M., Silva, R. J.: Neptunium(V) Complexation with Carbonate. *Lanth. and Act. Res.* **3**, 203 (1990).
20. Riglet, C.: Chimie du Neptunium et autres Actinides en milieu carbonate. Rapport CEA-R-5535, CEN Fontenay aux Roses, France 1990.
21. Meinrath, G.: Np(V) Carbonates in Solid State and Aqueous Solution. *J. Radioanal. Nucl. Chem. Lett.* **186**, 257 (1994).
22. Volkov, Yu. F., Visyashcheva, G. I., Kapshukov, I. I.: Study of Carbonate Compounds of Pentavalent Actinides with Alkali Metal Cations. V. Production and Identification of Hydrate Forms of Sodium Monocarbonatoneptunate. *Soviet Radiochem.* **19**, 263 (1977).
23. Merli, L., Fuger, J.: Thermochemistry of a Few Neptunium and Neodymium Oxides and Hydroxides. *Radiochim. Acta* **66/67**, 109 (1994).
24. Ciavatta, L.: The Specific Interaction Theory in Evaluating Ionic Equilibria. *Ann. Chim. (Rome)* (1980), 551.
25. Pitzer, K. S.: *Activity Coefficients in Electrolyte Solutions*. CRC Press, Boca Raton, Florida, 1991.
26. Pitzer, K. S., Mayorga, G.: Thermodynamics of Electrolytes. II. Activity and Osmotic Coefficients for Strong Electrolytes with One or Both Ions Univalent. *J. Phys. Chem.* **77**, 2300 (1973).
27. Pitzer, K. S., Kim, J. J.: Thermodynamics of Electrolytes. IV. Activity and Osmotic Coefficients for Mixed Electrolytes. *J. Am. Chem. Soc.* **96**, 5701 (1974).
28. Peiper, J. C., Pitzer, K. S.: Thermodynamics of aqueous carbonate solutions including mixtures of carbonate, bicarbonate, and chloride. *J. Chem. Thermodyn.* **14**, 613 (1982).
29. Harvie, C. F., Møller, N., Weare, J. H.: The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₂-H₂O System to High Ionic Strengths at 25°C. *Geochim. Cosmochim. Acta* **48**, 723 (1984).
30. Neck, V., Fanghänel, Th., Kim, J. I.: Dissoziationskonstanten von H₂O und H₂CO₃ in NaClO₄-Lösung und Pitzer-Parameter im System Na⁺/H⁺/OH⁻/HCO₃⁻/CO₃²⁻/ClO₄⁻/H₂O, 25°C, Report FZKA 5599, Forschungszentrum Karlsruhe, 1995.
31. Plyasunov, A. V., Fanghänel, Th., Grenthe, I.: Evaluation of the Pitzer Parameters for Aqueous Complex Species of Uranium at 298.15 K; in preparation.
32. Fuger, J., Oetting, F. L.: *The Chemical Thermodynamics of Actinide Elements and Compounds, Part 2. The Actinide Aqueous Ions*, Int. Atomic Energy Agency, Vienna, Austria, 1976.
33. Wagmann, D. D., Evans, W. H., Parker, V. B., Schumm, R. H., Halow, L., Bailey, S. M., Churney, K. L., Nuttall, R. L.: The NBS tables of chemical thermodynamic properties. *J. Phys. Chem. Ref. Data* **11**, (1982), Suppl. No. 2.
34. Novak, C. F., Roberts, K. E.: Thermodynamic Modeling of Neptunium(V) Solubility in Concentrated Na-CO₃-HCO₃-Cl-ClO₄-H-OH-H₂O Systems, presented at the 18. Int. Symp. on the Scient. Basis for Nucl. Waste Management, Kyoto, Japan (1994); to be published in *Mater. Res. Soc. Proc.* (1995).