

Neptunium Chemistry in Environmental Conditions. 1 : Survey of Np(V) soluble complexes in OH-CO₃-HCO₃-CO₂ media

PIERRE.VITORGE, INGMAR GRENTHE⁽¹⁾.

CEN-FAR, CEA DCC/DSD/SCS/SGC LAT, BP6 92265 FONTENAY-AUX-ROSES CEDEX, FRANCE
⁽¹⁾ROYAL INSTITUTE OF TECHNOLOGY, DT INORGANIC CHEMISTRY, S-100 44, STOCKHOLM, SWEDEN

Summary

A quick preliminary discussion indicates that in much natural waters Np(V) major soluble species should be NpO₂⁺ and some carbonate complexes. In reducing conditions Np(IV) is stable : a few indication are given to select thermodynamic data on Np redox potential and Np(IV) chemistry. The present paper mainly propose Np(V) formation constants in OH-CO₃-HCO₃-CO₂ conditions : NpO₂(CO₃)_i¹⁻²ⁱ (i=1, 2, 3) and NpO₂(CO₃)₂(OH)₂⁻⁵ complexes are formed. Published data are reviewed and data selected, they are then corrected for ionic strength effects using the SIT (Single Interaction Theory) : standard formation constants are deduced and activity coefficients (specific interaction coefficients) measured to finally obtain a set of thermodynamic data. The proposed values are consistent with previous [89RIG] published ones where Np environmental chemistry is also discussed. The main scopes of the present papers are to show that the selected Np(V) data are consistent with all published experimental works and to present several experimental data treatments for sensitivity analysis (see part 2).

Introduction

The 2.14 million years half life ²³⁷Np isotope that have can be a major contributor to nuclear waste or spent fuel radiotoxicity. NpO₂⁺, one of the most stable Neptunium aqueous species, is usually quite soluble and poorly trapped in natural environment. Chemical equilibrium in groundwaters between most soluble species is usually achieved before significant migration. EQ3/6, PHREEQE, MINEQL or other codes that solve chemical thermodynamic equations are then extensively used for radioactivity migration predictions. Increasing interest is now being focussed on the quality of the data bases used by the codes : chemists have to select (or reinterpret or measure) stability constants used by scientists and engineers involved in safety assessment with different scientific backgrounds who need to predict which chemical species could predominate. Np migration in natural system usually involves physical and chemical interactions of aqueous soluble species with natural surfaces or particles ("pseudo-colloïdes") ; Np speciation to study this processes should be calculated using a set of soluble species stability constants selected independantly and before this multielement work.. A reference data base (TDB) is being built by OECD-NEA for U [92GRE/LEM], Np [93LEM/NIT] and other actinides.

We present heresome Np(V) stability constants in OH-CO₃-HCO₃-CO₂ aqueous solutions that are in discussion (for TDB selection). We also give a few indications to select (before the end of Np TDB work) Np data for environmental chemistry predictions. In part 2 we give some experimental details of unpublished experimental work and interpret it to justify our interpretations, sensitivity analysis, data selections and calculation procedures [90CAC]. The same type of calculations is performed here on published work, and we also discuss the conclusions of these (re)interpretations.

Np(III, IV, V, VI and VII) can be stable in some aqueous solutions. Np(VII) would be reduced by, at least, the water in environmental conditions and Np³⁺ oxydised before hydroxide complexation (hyrolisis) when increasing pH. Np speciation prediction hence essentially rely on Np(IV, V, VI) thermodynamic data : redox potential are reviewed [89RIG], Np(IV and VI) formation constants and activity coefficient are (as a first approximation) not much different from those selected for Uranium [92GRE/LEM] and there is anyhow much more published experimental data for this element. Since there is no Np(V) natural analog, we will focus on Np(V) carbonate chemistry. We already determined the stability of such complexes and gave indications about consistency with the other published experimental works [86GRE/ROB], and the data set presented here will be also quite consistent with some previous work [89RIG] where Np and some other actinides chemistry in aqueous carbonate-hydroxide solutions were deduced : predominance diagrams (E=f(pH) or pH=f(pCO₃)) were presented.

To compare published Np(V) experimental work and to propose consistent equilibrium constant set need a common thermodynamic reference state : we use the chemist standard infinite dilution condition (0 ionic strength). Ionic strength corection are performed using activity coefficients calculated according to the SIT, this type of corrections are discussed in [87RIG/VIT] and described in NEA Thermodynamic Data Base [92GRE/LEM]. Uncertainties assignement and experimental data (re)interpretation methodologies are presented in part 2 for our own experimental results : we use the same treatment of data for published work reinterpretation. Pentavalent Neptunium chemical reactivity is quite weak ; most of the inorganic ligand usual concentrations in natural waters are too low to complex NpO₂⁺, exsept CO₃²⁻ [83MAY] [85BID/TAN] [85LIE/TRE] [RIG89]. Most tri, tetra and hexavalent actinides are mainly hydrolysed in near neutral solutions equilibrated with the air ;

but Np(V) soluble complexes are hardly detected and carbonate complexes predominate in these conditions. NpO₂⁺ coordination chemistry is still consistent with this chemical reactivity (see part 2).

Ionic strength corrections

Activity coefficients of an ion, i ,

$$\lg \gamma_i = -z_i^2 D(I) + \varepsilon_{i1} m_1 + \varepsilon_{i2} m_2 \quad (8)$$

are calculated according to the SIT [87RIG/VIT] [92GRE/LEM] approach,

where z_i is ion i charge,
 $D(I) = 0.511(I)^{1/2}/(1 + 1.5(I)^{1/2})$,
 m_n is ion n molality,
 ε_{in} is a fitted parameter relative to the ions i and n of opposite charges
 I is the ionic strength mainly due to m_1 , m_2 and the molality of their counterions.

Equilibrium constant ionic strength correction is then (with straightforward notations) :

$$\lg K = -\Delta z^2 D(I) + \Delta \varepsilon_1 m_1 + \Delta \varepsilon_2 m_2 \quad (9)$$

In (8) and (9), molal unit are used, e unit is then kg/mole, usual molar (mole/l) equilibrium constant are then converted to molal units for "SIT regressions" (figures 1).

Np(V) hydrolysis

Np(V) hydrolysis has been studied with potentiometric titration, solubility and spectrophotometric techniques.

Np(V)-OH solubility studies

Solubility measurements [48KRA/NEL] were first interpreted with the formation of NpO₂OH_(s) solid, NpO₂OH° and soluble species with OH/Np ratio greater than 1 ; but since NpO₂OH_(s) precipitation was the main hydrolysis reaction, NpO₂OH° formation constant measurement are not consistent. It was found later [85LIE/TRE] [85EWA/HOW] that NpO₂OH_(s) precipitation is the main Np(V) hydrolysis product up to at least pH=10.8 (figure 2), where Np(V) solubility is around 10⁻⁶ M : potentiometric [48KRA/NEL] [76SEV/KHA] or pulse radiolysis [80SCH/GOR] techniques are then not sensitive enough to detect soluble Np(V) hydrolysis species (up to at least pH=11) and soluble hydroxide formation constant determinations from these types of works are therefore probably incorrect.

Np(V)-OH solubility products

Reliable data on Np(V) hydrolysis come therefore only from solubility measurements. NpO₂OH_(s) solid precipitated easily in NaOH solutions (but NaOH<0.02 M) and its X-ray diffraction pattern showed an amorphous structure [84VOL/KAP]. The calculated NpO₂OH_(s) thermodynamic stability indicates that one should verify that (through agging) it is not transformed to Np(IV) and/or Np(VI), hydroxide(s) or oxide(s) : this might induce uncertainties on Np(V) solubility measurements. Still, most of the NpO₂OH_(s) solubility product determinations (figure 2) [48KRA/NEL] [71MOS3] [76SEV/KHA] [85LIE/TRE] are not widely scattered, only 3 solubility products are significantly smaller : this could be due to ionic strength [78MUS] or to agging of the solid [88NAK/ARI] [85EWA/HOW]. There are not any details about glass electrode calibration (including junction potentials) : to avoid to include this possible systematic error in the activity coefficient calculations, we use published [89RIG] [92GRE/LEM] specific interaction coefficients to compare (figures 1) the solubility product determinations at different ionic strengths.

Soluble hydroxide stability deduced from solubility measurements

There are 3 experimental solubility data sets at sufficiently high pH to produce soluble hydroxide species. In one of them [88NAK/ARI] Np(V) measured solubility in neutral and basic solution is much higher than in the other ones and the experimental procedure allowed equilibration with air : unwanted carbonate complexation was certainly the main reaction we then cannot accept Np(V)-OH formation constants measured in this work. In the second one [85EWA/HOW] the solubility product law is poorly verified and there is no Np(V) hydrolysis soluble species evidence up to pH=12.9. An anionic species is clearly formed [85LIE/TRE] at pH=11.3 : the authors proposed NpO₂(OH)₂⁻. This is the most reliable study ; but its interpretation is still questionable since other anionic (eventually polynuclear) species formation was also possible. Carbonate complexation from the air can also be suspected (typically when stirring the solution for pH measurement) : if NpO₂OH_(s) was then partially transformed into NaNpO₂CO_{3(s)}, we calculate that NpO₂⁺ would be transformed to NpO₂CO₃⁻ at pH>10.8, to NpO₂(CO₃)₂³⁻ at pH 12.7, and to NpO₂(OH)₂(CO₃)₂⁵⁻ at pH>12.5 and it is enough to explain the experimental data (figure 2) without assuming any pure hydroxide complex.

Np(V)-OH Spectrophotometric studies

Spectrophotometry [76KEV/KHA] and electromigration [76KEV/KHA] [87ROE/MIL] were interpreted with Np(V) hydrolysis that would have started when pH were greater than 8 or 9 ; but we cannot accept these conclusions : Np(V) carbonate complexation starts when [CO₃²⁻] reaches about 10⁻⁵ M hence pH reaches 8 in a

solution equilibrated with air : this might have been the main chemical reaction during these experiments. The absorption band attributed to NpO_2OH^0 is quite similar to the 991 nm $\text{NpO}_2\text{CO}_3^-$ one [89RIG].

Other Np(V)-OH studies

NpO_2OH^0 formation constant fitted from experimental data [83MAY] [85BID/TAN] essentially used for Np(V) carbonate complexation do not significantly improve the fit (as in our own work : see part 2).

Np(V)-OH binary system conclusions

There is (figure 2) no clear evidence of Np(V)-OH soluble complex : the relative great affinity of CO_3^{2-} ligand toward Np(V) (compared to OH^- ligand) disturbs its formation constant measurement. Careful experimental work is needed ; it would be necessary to control very low $[\text{CO}_3^{2-}]$ in concentrated basic solutions ; this could be achieved from solubility measurements with 2 solid phases such as $\text{NpO}_2\text{OH}_{(s)}$ (or $\text{NaNpO}_2(\text{OH})_{2(s)}$) and $\text{NaNpO}_2\text{CO}_{3(s)}$ (or $\text{Na}_3\text{NpO}_2(\text{CO}_3)_{2(s)}$) or such as $\text{Ca}(\text{OH})_{2(s)}$ and $\text{CaCO}_{3(s)}$ (in cement or lime water for this latter example). In concentrated $\text{NaOH} + \text{Na}_2\text{CO}_3$ solutions there is clear evidence of mixed Np(V)-OH- CO_3^- complex [84VAR/BEG] [84VAR/HOB] [89RIG] and $\text{NpO}_2(\text{CO}_3)_2(\text{OH})_2^{-5}$ stoichiometry is proposed (see part 2) : if OH^- ligand can coordinate central NpO_2^+ cation in a mixed complex, NpO_2OH^0 or/and $\text{NpO}_2(\text{OH})_2^-$ should also be stable in some pure NaOH media, we then propose to accept NpO_2OH^0 and $\text{NpO}_2(\text{OH})_2^-$ formation constants deduced from [85LIE/TRE] assuming that they might be overestimated (table 1a). Published $\text{NpO}_2\text{OH}_{(s)}$ solubility corrected for ionic strength effects (figure 1a) are consistent and a standard value is proposed (table 1a).

Np(V) carbonate complexation

Np(V) carbonate complexation evidence has been discovered quite recently [63MOS/GEL] [66GOR/ZEN] [71MOS5] [75UEN/SAI] [77SIM] [79MOS/POZ] [81BIL], and was clearly demonstrated only in 1983 Maya's publication [83MAY] that is consistent with our experimental work : CO_3^{2-} ligand affinity for Np(V) is nearly as great as for Am(III). This is quite an exception : Np(V) reactivity toward oxygen or electronegative "hard" donors is usually much lower than the reactivity of tri, hexa and tetravalent actinides. The most reliable experimental techniques used to study Np(V) complexation in carbonate media are solubility and spectrophotometry. We correlate the published results using the SIT (figures 1). Since there are not many experimental determinations of formation constants, we use nearly all of them (eventually increasing uncertainty estimations and remeasuring equilibrium constants). In all the examined publications there are not really enough experimental points to perform a good statistical analysis of the errors : most of the uncertainties are therefore usually deduced from propagation error laws rather than from standard deviations computed from curve fitting algorithms.

Np(V)- CO_3 solubility studies

Np(V)- CO_3 solid phases

A careful examination of the $\text{NaNpO}_2\text{CO}_{3(s)}$ X-ray diffraction patterns has been done in a series of 10 publications that are discussed in [81VOL/VIS3] : this solid is quite poorly crystallised, probably because Na^+ , $2\text{H}_2\text{O}$ and NpO_2^+ can be exchanged in the proposed structure, a small domain of non stoichiometry might then be stable or at least metastable. K_s determinations were then not so precise. NpO_2^+ , ClO_4^- specific interaction coefficient deduced from the SIT correlation (figure 1b) are still in very good agreement with the value determined [89RIG/ROB] from redox measurements and Np(VI)-U(VI) analogy ; but it is not more precise, we therefore keep the previous value.

Np(V)- CO_3 soluble complex stabilities deduced from solubility measurements

The above discussion indicates that $\text{NaNpO}_2\text{CO}_{3(s)}$ solubility product, K_{s1} , experimental determinations could systematically vary with $[\text{CO}_3^{2-}]$ which could induce unprecise b_1 determinations. To avoid this systematic error, we correlate (figures 1b to 1e) experimental results at different ionic strengths using the SIT for $\lg(K_{s1}b_1)$. Extrapolations (for $i=0, 1, 2$ and 3) to standard conditions (0 ionic strength) from Maya's [83MAY] and the present work (describe in part 2) are consistent with all the other published ones as previously shown [86GRE/ROB]. These 2 works used the same methodology and they are the only ones that give sufficient indication on their pH and junction potential measurements, still Maya's solid phase evocation is not much consistent with the present work but he did not published the X-ray diffraction patterns mentioned in his work.

Np(V)- CO_3 spectrophotometric studies

Other informations on Np(V) carbonate complexation are mainly deduced from spectrophotometric techniques. $\text{NpO}_2(\text{CO}_3)_2^{3-}$ molar absorptivity cannot be directly measured, it is a fitted parameter [89RIG], which could induce systematic errors on k_2 and k_3 ($k_i = \beta_i / \beta_{i-1}$ are directly measured in spectrophotometric studies : see part 2) stepwise formation constant determinations : to avoid error propagation, we correlate experimental results at different ionic strengths using the SIT for stepwise formation constants (figures 1g, 1h, 1i). k_1 has been measured very precisely [89RIG] and all the other determinations of this constants (eventually recalculated) lead to consistent $\text{NpO}_2\text{CO}_3^-, \text{Na}^+$ interaction coefficient (figures 1). This correlation is also in fair

agreement with solubility results. k_2 and k_3 have been measured using spectrophotometry at different ionic strengths [89RIG]. Systematic errors are involved in global curve fitting ; graphic reinterpretation minimise this problem and finally leads to consistent $\text{NpO}_2(\text{CO}_3)_2^{3-}$ and $\text{NpO}_2(\text{CO}_3)_3^{5-}, \text{Na}^+$ interaction coefficients (figures 1, tables 1b and 1c), hence we do not consider [89RIG] curve fitting results. Spectrophotometric and solubility determinations of k_1 [89RIG] and present work (part 2) are not $[\text{Np}]_t$ dependent (and $[\text{Np}]_t$ varied by at least one order of magnitude) : there are then no polynuclear complex evidence. These results are also in fair agreement with the above solubilities correlations and all the other published eventually reinterpreted results. Complexation constant that are consistent with all the published works are then proposed (table 1). The other published works have been reinterpreted and are consistent with the proposed standard equilibrium constants (table 1b and figures 1) and activity coefficients (table 1c and figures 1).

Np(V)-CO₃ liquid-liquid extraction studies

Liquid-liquid extraction techniques [85BID/TAN] [85INO/TOC] results are usually consistent with solubility measurements (figures 1) ; but it is not always easy or possible to take into account precisely all the side chemical reactions involved in this type of study.

M₃NpO₂(CO₃)_{2(s)} solubility product

Our non-(or poorly) interpreted published works reanalysing on Np(V) solubility in concentrated Na_2CO_3 solutions [75UEN/SAI] [77SIM] is consistent with K_{s_i} ($i=1$ and 2) and k_3 (table 1b and figures 1) values. We then also deduce solubility products from other works published in K_2CO_3 [66GOR/ZEN] and $(\text{NH}_4)_2\text{CO}_3$ [71MOS5] (table 1b, figure 1f) solutions.

Np(V)-CO₃ binary system conclusions

$\text{NpO}_2(\text{CO}_3)_i^{1-2i}$ ($i=0, 1, 2, 3$) are formed in carbonate media, their standard formation constants (table 1b) and activity coefficients (table 1c) are computed from all published work (including part 2) some of which have been reinterpreted (table 1b). Specific interaction coefficients (needed to calculate activity coefficients) numerical values (table 1c) are fitted from experimental works performed by different authors where systematic errors can be bigger than ionic medium effects. Since our fitted specific interaction coefficients (figures 1, table 1c) are within the order of magnitude of previous estimated [86GRE/ROB] or measured [89RIG] values, and of other actinides having the same charges [92GRE/LEM], we believe that our "SIT correlation" are consistent with their activity coefficient physical meaning. As previously proposed [86GRE/ROB], $\text{NpO}_2(\text{CO}_3)_i^{1-2i}$ standard formation constants and activity coefficients can also be deduced from only two solubility works ([83MAY] and [86GRE/ROB] with more details in part 2 of present work) the results of this simplest procedure are quite consistent with present ones.

Np(V)-OH-CO₃ ternary system and other complexes

The conclusions of part 2 of the present work are not discussed here but they are included in tables 1 ; namely $\text{NpO}_2(\text{CO}_3)_2(\text{OH})_2^{-5}$ spectrophotometric evidence, and HCO_3^- or mixed complex maximum stability deduced from sensitivity analysis.

Conclusion

The data selection is in tables 1. Extra experimental work is needed to validate the Np(V)-OH soluble complex formation constants (an experimental procedure is suggested) because pure hydroxide complexes are quite difficult to obtain, hence they should not be important in environmental conditions.

Acknowledgment :

Patrick Tran The made the figures This work is part of CEA-SKB collaboration, and is a join CEA DCC-ANDRA program.

Table 1 : Recommended and published Np(V) formation constants, solubility products and activity coefficients.

First line of each table bloc indicates the name of the constant published and reinterpreted (in this work) decimal log of constants and their uncertainties (+/-) are tabulated. Experimental method of measurement are : electromigration (el.mig), literature review (lit), potentiometry (pot), pulse radiolysis (p.rad), solubility (sol), spectrophotometry (sp). Recommended values (recom) are the standard values deduced in the present work (p.w.) from SIT extrapolation (SIT) to 0 ionic strength (figures 1), they are on the same line as the name of the constant in "reinterpreted column", when (SIT) is not indicated in the "method" column (of this first line) recommended value is not proposed (see text).

$$*\beta_i = [\text{NpO}_2(\text{OH})_i]^{1-i} [\text{H}^+]^i / [\text{NpO}_2^+]$$

$$*K_{s_i} = [\text{M}^+]^i [\text{NpO}_2^+] / [\text{H}^+]^{i+1} \text{ is } M_i \text{NpO}_2(\text{OH})_{i+1(s)} \text{ solubility product}$$

$$*k_{s_i} = *K_{s_i} / *K_{s_{i-1}} = [\text{M}^+] / [\text{H}^+]$$

$$\beta_i = [\text{NpO}_2(\text{CO}_3)_i]^{1-2i} / [\text{NpO}_2^+] [\text{CO}_3^{2-}]^i$$

$$K_{s_i} = [\text{M}^+]^{2i-1} [\text{NpO}_2^+] [\text{CO}_3^{2-}]^i \text{ is } M_{2i-1} \text{NpO}_2(\text{CO}_3)_i(s) \text{ solubility product}$$

$$*\beta_{i,j} = [\text{NpO}_2(\text{CO}_3)_i(\text{OH})_j]^{1-2i-j} [\text{H}^+]^j / [\text{NpO}_2^+] [\text{CO}_3^{2-}]^i$$

Table 1a : Hydrolysis.

		reinterpreted					
+/-		+/-		I	medium	method	ref
lg*β₁		<-11		0		lit	p.w.
-8.9	0.1	<-9		0.1	Cl ⁻	pot	[48KRA/NEL]
-10.1		<-10			diluted	sol	[71MOS3]
-8.92	0.04	<-9		0.02	HNO ₃	pot	[76SEV/KHA]
-8.9	0.1	NpO ₂ CO ₃ ⁻				spec	
-8.94	0.05	<-9		0.02	HClO ₄	pot	
-8.7	1.0	<-9		0.01	EtOH	p.rad	[80SCH/GOR]
		<-13 ?		0 to 0.1	NaOH	sol	[85EWA/HOW]
-11.7	0.62	<-11.3		1	NaClO ₄	sol	[85LIE/TRE]
-10.45	0.25	?		0.1	NaClO ₄	el.mig	[87ROE/MIL]
-8.3		<-8		0.01	NaNO ₃	sol	[88NAK/ARI]
lg*β₂		<-23		0		lit	p.w.
-23.11	0.05	NpO ₂ -CO ₃ ?		1	NaClO ₄	sol	[85LIE/TRE]
-21.95	0.35	?		0.1	NaClO ₄	el.mig	[87ROE/MIL]
-19.4		NpO ₂ -CO ₃		0.01	NaNO ₃	sol	[88NAK/ARI]
lg*K_{s0}		5.12	0.34				p.w.
4.8	0.3	4.8	0.5	0.00032		sol	[48KRA/NEL]
4.97	0.07	5.0	0.3		diluted	sol	[71MOS3]
5.08	0.04	5.1	0.3		HNO ₃ dilut.	sol	[76SEV/KHA]
3.8		3.9	1.2	9	NaOH + ?	sol	[78MUS]
				0.02 to 2.1	NaOH	prep	[84VIS/VOL]
		4.6	0.4	0 to 0.1	NaOH	sol	[85EWA/HOW]
5.19	0.05	5.0	0.3	1	NaClO ₄	sol	[85LIE/TRE]
3.3		3.3	0.5	0.01	NaNO ₃	sol	[88NAK/ARI]
lg*ks₁							
		13.4	1.1	2.1 to 15	NaOH	prep.	[84VIS/VOL]
		13.6	1.2	3.5 to 9	KOH	prep.	
lg*ks₂							
		13.5	1.5	15	NaOH	sol	[84VIS/VOL]
		15.5	1.3	9	KOH	sol	
lg(*K_{s2}/*K_{s0})							
		13.8	1.1	2	LiOH	sol	[84VIS/VOL]

Table 1b : Carbonate complexes and solid phases.

		reinterpreted		I	medium	method	ref
+/-		+/-					
β_1		4,70	0,10	0		SIT	p.w (recom)
		5.5	0.5	0.02		sp	[81BIL]
4.49	0.06	4.56	0.3	1	NaClO ₄	sol	[83MAY]
4.13	0.03	3.9	0.5	0.2	NaClO ₄	ext	[85BID/TAN]
4.14	0.01	4.14	0.5	1	NaClO ₄	ext	[85INO/TOC]
		5.34	0.13	3	NaClO ₄	sol	[86GRE/ROB] and p.w
4.62				0			[86GRE/ROB]
4.39	0.04	4.39	0.2	0.5	NaClO ₄	sp	[89RIG]
4.3	0.1						
β_2		6,39	0,21	0		SIT	p.w (recom)
7.11	0.07	7.13	0.2	1	NaClO ₄	sol	[83MAY]
7.06	0.05	7.06	0.5	0.2	NaClO ₄	ext	[85BID/TAN]
6.78	0.01	6.78	0.5	1	NaClO ₄	ext	[85INO/TOC]
		8.13	0.6	3	NaClO ₄	sol	[86GRE/ROB] and p.w
6.93				0			[86GRE/ROB]
β_3		5,52	0,33	0		SIT	p.w (recom)
8.53	0.09	8.54	0.3	1	NaClO ₄	sol	[83MAY]
		10.56	0.18	3	NaClO ₄	sol	[86GRE/ROB] and p.w
5.86				0			
$\beta_{2;2}$				3	Na ₂ CO ₃ 0.1 to 1, spec NaOH 0.1 to 1 (NaClO ₄)		p.w (part.2)
-17.0	0.6						
k_2		1,38	0,32	0		SIT	p.w (recom)
		2.5	0.5	0.1	NaHCO ₃ < 0.13	copr	[79MOS/POZ]
		2.5	0.5	0.01		sp	[81BIL]
2.62	0.13	2.57	0.5	1	NaClO ₄	sol	[83MAY]
2.93	0.08	3.16	1	0.2	NaClO ₄	ext	[85BID/TAN]
2.64	0.02	2.64	1	1	NaClO ₄	ext	[85INO/TOC]
		2.79	0.6	3	NaClO ₄	sol	[86GRE/ROB] and p.w
2.31				0			[86GRE/ROB]
		2.75	0.5	3	Na ₂ CO ₃ 0.02 to	sp	[89RIG]
2.54	0.07	2.5	0.3	2	0.4		
2.05	0.07	2.45	0.15	2	(NaClO ₄)		
2.38	0.07	2.05	0.5	1			
2.23	0.07	2.1	0.6	0.5			
1.51	0.15			0			
		1.4	0.3	0.03	Na ₂ CO ₃		
k_3		-0,86	0,13	0		SIT	p.w (recom)
		0.7	0.2	0.2	(NH ₄) ₂ CO ₃	sol	[71MOS5]
		1.2	0.3	0.06	Na ₂ CO ₃	sol	[75UEN/SAI]
		1.4	1	0.2		sp	[81BIL]
1.42	0.16	1.41	0.5	1	NaClO ₄	sol	[83MAY]
		2.43	0.6	3	NaClO ₄	sol	[86GRE/ROB] and p.w
-1.07				0			[86GRE/ROB]
2.47	0.07			2	Na ₂ CO ₃ 0.02 to	sp	[89RIG]
1.86	0.07			1	0.4		
1.60	0.07	1.91	0.11	1	(NaClO ₄)		
1.37	0.07			0.5			
-0.86	0.15			0			

-0.98	0.15			0			
		1.00	0.04	0.1	Na ₂ CO ₃		
β_{2;22/β₃}		-27.5	0.5	3	Na ₂ CO ₃ 0.1 to 1. spec NaOH 0.1 to 1 (NaClO ₄)	p.w	
Ks₁		-11.00	0.22	0		SIT	p.w (recom)
-10.14	0.04	-10.13	0.12	1	NaClO ₄	sol	[83MAY]
		-11.11	0.09	3	NaClO ₄	sol	[86GRE/ROB]+pw
Ks₁ β₁		-6.06	0.18	0		SIT	p.w (recom)
-5.65	0.06	-5.57	0.50	1	NaClO ₄	sol	[83MAY]
		-5.77	0.09	3	NaClO ₄	sol	[86GRE/ROB]+pw
Ks₁ β₂		-4.31	0.29	0		SIT	p.w (recom)
-3.03	0.07	-3.00	0.15	1	NaClO ₄	sol	[83MAY]
		-2.98	0.59	3	NaClO ₄	sol	[86GRE/ROB]+pw
Ks₁ β₃		-5.60	0.23	0		SIT	p.w (recom)
		-2.3	0.3	0.16	K ₂ CO ₃	sol	[66GOR/ZEN]
		-3.3	0.3	0.3	(NH ₄) ₂ CO ₃	sol	[71MOSS5]
		-2.5	0.3	0.1	Na ₂ CO ₃	sol	[75UEN/SAI]
		-1.6	0.3	0.6			
-1.61	0.09	-1.59	0.20	1	NaClO ₄	sol	[83MAY]
		-0.55	0.14	3	NaClO ₄	sol	[86GRE/ROB]+pw
Ks₂ β₃							
		-2.9	0.3	1	K ₂ CO ₃	sol	[66GOR/ZEN]
		-3.4	0.3	0.7	(NH ₄) ₂ CO ₃	sol	[71MOSS5]
		-1.5	0.3	3	NaNO ₃	sol	[77SIM]
*β_{0;1}		<-9		3	NaClO ₄	sol	[86GRE/ROB]+pw
-9.12	0.15	<-10		1	NaClO ₄	sol	[83MAY]
-9.84		<-9		0.2	NaClO ₄	ext	[85BID/TAN]
*β_{1;-1}		<10		3	NaClO ₄	sol	[86GRE/ROB]+pw
8.1							[63MOS/GEL]
7.9				0			
11.7				0.25	NaHCO ₃	copr	[79MOS/POZ]
12.52				0			
*β_{1;1}		<<-9		3	NaClO ₄	sol	[86GRE/ROB]+pw
-9.18	0.12			0 to 2.2	(NH ₄) ₂ CO ₃	sol	[71MOSS5]
*β_{1;2}		<<0					[86GRE/ROB]+pw
*β_{2;-1}		<15					[86GRE/ROB]+pw
*β_{2;1}		<-3		3	NaClO ₄	sol	[86GRE/ROB]+pw
-9.26	0.05			0 to 2.2	(NH ₄) ₂ CO ₃	sol	[71MOSS5]
*β_{3;-1}		<21					[86GRE/ROB]+pw
β₄		<10					[86GRE/ROB]+pw

Table 1c : specific interaction coefficients

Slope result is $\Delta\varepsilon$ calculated from linear regression (figures 1) on the equilibrium constant, K. E refers to redox measurements [89RIG/ROB]). Calculated ε is deduced from calculated $\Delta\varepsilon$ and published ε [89RIG] [92GRE/LEM] (in recom. column with no other value on the same line). Different ε determinations are compared to propose a recommended value (recom.) which is then use to deduce calculated $\Delta\varepsilon$. These coefficients are in NaClO₄ medium.

K	slope result		calculated				recom.		
	$\Delta\varepsilon$	+/-	$\Delta\varepsilon$	+/-	ε	+/-	ε	+/-	
OH ⁻							0.04	0.01	
ClO ₄ ⁻							0.01	0.01	
CO ₃ ²⁻							-0.05	0.03	
H ⁺							0.14	0.02	
Li ⁺							0.15	0.01	
Na ⁺							0.01	0.01	
K ⁺							0.01	0.02	
UO ₂ ²⁺ (NpO ₂ ²⁺)							0.46	0.03	
NpO ₂ ⁺	E	0.21	0.03			0.26	0.08	0.26	0.08
	*K _{s0}			0.24	0.08				
	K _{s1}	0.28	0.10	0.22	0.12	0.32	0.14		
NpO ₂ OH ⁰	*K _{s1}			0.00			0.00		
NpO ₂ (OH) ₂ ⁻	*K _{s2}								
NpO ₂ CO ₃ ⁻	K _{s1} β ₁	0.00	0.06	-0.06	0.08	-0.01	0.07	-0.07	0.07
	K ₁	-0.40	0.03	-0.28	0.18	-0.19	0.14		
NpO ₂ (CO ₃) ₂ ³⁻	K _{s1} β ₂	-0.12	0.07	-0.15	0.13	-0.18	0.11	-0.21	0.09
	k ₂	-0.13	0.03	-0.09	0.19	-0.25	0.13		
NpO ₂ (CO ₃) ₃ ⁵⁻	K _{s1} β ₃	-0.29	0.04	-0.25	0.15	-0.40	0.11	-0.36	0.08
	k ₃	-0.04	0.02	-0.06	0.20	-0.30	0.14		
NpO ₂ (CO ₃) ₂ (OH) ₂ ⁵⁻	*β _{2:2} / β ₃	0.85	0.50	0.88	1.19			-0.36	0.20

Figures 1 : Ionic strength dependence of Np(V)-OH-CO₃ equilibrium constants

Published data are examined, eventually (re)interpreted, the uncertainties are usually increased (see text). Published equilibrium constants, $K(I)$, are converted in molal units, then corrected for ionic strength, I , effect with $D=0.511VI/(1+1.5VI)$ term : standard value, $K(0)$, is deduced from linear correlation (SIT). The slope is $\Delta\epsilon$ (see text), the activity of water correction is included in $\Delta\epsilon$ [89RIG]. In a set of figures, only solubility constants are compared in CO₃ media. In another set, all stepwise constants (in CO₃ media) are compared. The results of the 2 sets are consistent (within uncertainties) and are used (tables 1) to propose "recommended values". These recommended values are then used to recalculate $K(0)$ and $\Delta\epsilon$ (as in table 1c) which are written in parenthesis on each figure.

Figures 7 : Published Np(V) solubility results in OH media

Curves are our reinterpretations with (eventually) carbonate complexation perturbation due to carbonic gas

(from the air) penetration in solutions.

This figure is not available.