

Actinide(IV) in carbonate media

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Abstract

To predict the geochemical behaviour of Neptunium and Plutonium, or to design sorption or migration experiments with these radioelements, one needs to know their speciation in reducing aqueous solutions at pH 6 to 11, containing some carbonate ions. Their solubility is very low (10^{-8} to less than 10^{-10} mol./l), and is quite difficult to measure. The solid seems to be an amorphous Actinide(IV) hydroxide, that slowly transforms to a more crystalline phase, probably the Actinide(IV) oxide. Aqueous speciation is strongly dependent on the redox conditions. Most of the interpretations of the published Np(IV) or Pu(IV) solubility measurements are then questionable. Rai and Ryan (1985) already discussed this, and showed, that $[\text{CO}_3^{2-}]$ must probably be more than 0.01 mol./l to complex Np(IV). The limiting carbonate complex of U(IV) is (Grenthe et al. 1992) $\text{U}(\text{CO}_3)_5^{6-}$ and it dissociates into $\text{U}(\text{CO}_3)_4^{4-}$. This highly charged anion has also been identified in Ce(IV), Th(IV), and probably Np(IV) and Pu(IV) solid phases; but there are not enough correct experimental measurements to determine the stoichiometry of the soluble carbonate complexes of these elements. As stated above, precise experiments are difficult. The aim of this work is then mainly to confirm, that all these f transition elements at the +4 oxidation state, have the same behaviour in concentrated carbonate media.

Assuming the formation of $\text{An}(\text{OH})_4$, $\text{An}(\text{CO}_3)_4^{4-}$ and $\text{An}(\text{CO}_3)_5^{6-}$ (An= Np, Pu or Am), the speciation is calculated and it is enough to explain most of the published work (solubility, spectrophotometric and electrochemical behaviour of these elements). Still a few published solubility data are higher than the calculated ones. This is probably an evidence for other soluble hydroxocarbonate complexes. As stated above, this increase of solubility might also often be attributed to experimental artefacts, any conclusion on the stoichiometry and stability of such complex would then be very poorly reliable.

Np(IV) and Pu(IV) are prepared by electrochemical reduction in concentrated Na_2CO_3 solutions. The titration into NaHCO_3 by bubbling CO_2 gas, is followed by spectrophotometry. As for U(IV), the spectral changes are consistent with the lost of one CO_3^{2-} anion, (and no OH^-) over several pH units. These experiments are performed mainly in bicarbonate solutions. In too alkaline carbonate solutions, solubility is too low to use this methodology. All this confirms the U-Np-Pu-Am(IV) analogy for the stability of their limiting complex. The equilibrium constants are extrapolated to standard conditions by using the SIT and are used to discuss the preparation conditions of Am(IV) in bicarbonate/carbonate media (1983 Bourges et al.), and other actinide(IV) published results. It is finally shown, that the measurement of the Np(V)/Np(IV) and Pu(VI)/Pu(IV) redox potential can be used to determine the stoichiometry of these actinide(IV) limiting complexes.

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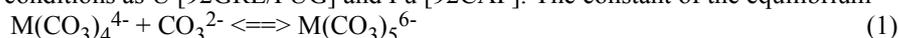
Critical review

The following review will be discussed within the TDB, the idea of this pre-publication is to obtain comments before the TDB publication. The detail of the calculations will appear this year as a CEA Note Bibliographique, that should be sent to the authors cited in it.

There is not any published work from which the stoichiometry of the limiting carbonate complex of Np(IV) can be deduced. Rai and Ryan [85RAI/Ryan] pointed out, that the only published work before 1985 [71MOS5], that proposed the stoichiometry and formation constant of a Np(IV) carbonate complex, is "completely erroneous", "unbelievable". This review agrees with Rai and Ryan comments. Unfortunately Moskvin's or other incorrect complexation constants are still being used [88NAG/TAN] [89MOR/PRA] [89PRA/MOR] [89TAN/NAG] [90PRA/MOR] [91ITA/TAN] [91PRA/YAM] [93PRA/YAM]. The stoichiometry and the stability of the limiting complex of U(IV) are well established [92GRE/FUG]. All the published work on lanthanide and actinide(IV) in concentrated carbonate aqueous solutions or in carbonate solids can be interpreted as confirmation of the analogous behaviour of the f element series. To test this hypothesis, we shall then first assume, that the limiting complex of Np(IV) is $\text{Np}(\text{CO}_3)_5^{6-}$. The dissociated one will then be $\text{Np}(\text{CO}_3)_4^{4-}$.

Spectrophotometric measurements.

The first experimental evidence of carbonate complexation of neptunium is the absorption spectrum of Np(IV) in carbonate media [71MOS5], that been confirmed later [77SAI/UEN] [81WES/SUL] [84VAR/HOB] [93LIT/KAT] [95DEL] (figure 1). These spectra clearly show, that the limiting complex of Np(IV) is stable in 1 M NaHCO_3 solution and in Na_2CO_3 ones with concentration more than 0.3 M (figure 1 to 3). This behaviour is similar to the U [92GRE/FUG] and Pu [92CAP] one. It is consistent with Ray and Ryan [85RAY/Ryan] solubility measurement. The limiting complex is dissociated when decreasing the ionic strength or the free carbonate concentration: our interpretation of [93LI/KAT] (figure 1) and our experimental confirmation (figure 2). One carbonate ion and no hydroxide ion is exchanged between the limiting and the dissociated complex (see below). This occurs in similar conditions as U [92GRE/FUG] and Pu [92CAP]. The constant of the equilibrium

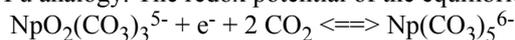


is (table I) $\log_{10} k_5 = 0.98$. $\varepsilon(\text{Np}(\text{CO}_3)_5^{6-}, \text{Na}^+) - \varepsilon(\text{Np}(\text{CO}_3)_4^{4-}, \text{Na}^+) = -0.39$ kg/mole. Assuming that $\varepsilon(\text{Np}(\text{CO}_3)_4^{4-}, \text{Na}^+) \approx \varepsilon(\text{U}(\text{CO}_3)_4^{4-}, \text{Na}^+) = 0.09 \pm 0.10$ kg/mole [92GRE/FUG], $\varepsilon(\text{Np}(\text{CO}_3)_5^{6-}, \text{Na}^+) \approx -0.30$ kg/mole. This value is in reasonable agreement with the one deduced from redox measurements (figure 5).

Measurement of the redox couple of Np(V)/Np(IV).

Since the limiting complex of Np(V) and the standard potential of the $\text{NpO}_2^+/\text{Np}^{4+}$ redox couple are well known; studying the Np(V)/Np(IV) redox couple could give useful information on the stoichiometry of the limiting complex of Np(IV). Unfortunately there are some experimental difficulties [95DEL] [79FED/PER], and the authors, that tried to use this

methodology (*table III*) either did not succeed to measure the potential [84VAR/HOB], or only propose a very rough value [79FED/PER], or do not give enough information to check their interpretation [95DEL]. Our calculation (on [79FED/PER], *figure 4*) again is consistent with U-Np-Pu analogy. The redox potential of the equilibrium



is then $E^\circ(P_{\text{CO}_2} = 10^{-3.5} \text{ atm}) = 0.1 \pm 0.15 \text{ V/SHE}$ in 1 M Na_2CO_3 solution equilibrated with the air. $E^\circ(P_{\text{CO}_2} = 1 \text{ atm}) = 0.105 \text{ V/SHE}$. From SIT regression [95DEL], $\varepsilon(\text{Np}(\text{CO}_3)_5^{6-}, \text{Na}^+) - \varepsilon(\text{NpO}_2(\text{CO}_3)_3^{5-}, \text{Na}^+) = -0.17 \text{ kg/mole}$. Using the $\varepsilon(\text{NpO}_2(\text{CO}_3)_3^{5-}, \text{Na}^+)$ selected in this review (-0.36 ± 0.08), $\varepsilon(\text{Np}(\text{CO}_3)_5^{6-}, \text{Na}^+) = -0.53 \text{ kg/mole}$.

The reduction of water seems to be a limitation to study the redox couple of Np(IV)/Np(III).

Solubility measurements.

Rai and Ryan [85RAI/Ryan] have shown a good methodology to performed solubility measurement in neutral or low concentrated carbonate media (*figures 3 and 4*). They conclude, that there is no evidence of any carbonate complexation in these conditions. The present review completely agrees, that there is no evidence of any Np(IV) carbonate complex when the total carbonate concentration is less than 0.01 M at low ionic strength. Pratopo et col. published two papers [90PRA/MOR] [89MOR/PRA] were they tried to reproduce Rai and Ryan measurements; but they did not succeed, certainly because they did not use a proper methodology to handle Np(IV) in near neutral solutions. They end up with a set of solubility data, that is hardly correlated to any chemical parameters (*figures 4*), that are obtained in quite a narrow domain of chemical conditions. They still proposed some curve fitting results from these very scattered solubility data: this has no meaning at all. This type of questionable results is now widely cited and used. To avoid this, the idea of Rai and Ryan [85RAI/Ryan] is very good: they calculated an "upper limit" of certain equilibrium constants corresponding to the formation of complexes, that probably do not exist. We use (*table II*) a similar procedure.

The highly charged $\text{Np}(\text{CO}_3)_5^{6-}$ anion can be precipitated by many cations; but the work published on this subject [71MOS5] [77SAI/UEN] cannot be used to determine the stoichiometry of the Np(IV) limiting complex.

Conclusion of the bibliography

The U-Np-Pu analogy seems to be enough to explain all published data. Hence $\text{Np}(\text{CO}_3)_5^{6-}$, $\text{Np}(\text{CO}_3)_4^{4-}$ and $\text{Np}(\text{OH})_4^0$ complexes are probably formed in carbonate media. There is no evidence of other complexes, that does not mean, that they do not exist. We have estimated the formation constants of these Np complexes (*table I to III*).

Experimental results and discussion

To check the above interpretations we performed two types of experiments. All details and results will appear in [95DEL]. Our results are in *table I to II*. The extrapolation to zero ionic strength is performed by using the SIT according to the published [92GRE/FUG] methodology. As already pointed out [92CAP] the highly negatively charged carbonate complexes probably form ion pairs, that would explain the value of the specific interaction coefficients, ε , used to calculate the activity coefficients.

First we prepare Np(IV) media by reducing a Np(V) solution in concentrated carbonate, as already published [79FED/PER], this method was not [93LI/KAT] or was hardly [84VAR/BEG] reproduced later probably because its key points was not well understood. For the first time, we obtain quite a stable measurement of the solution potential (up to 21 days at room temperature). For this the initial Hg pool is taken of the solution and a platinum electrode is used instead (only for E measurement, not for electrolysis). We also control, that we are in the proper chemical conditions (*figure 3*) to avoid $\text{Np}(\text{OH})_4$ precipitation and other unwanted side reactions. Our results are in reasonable agreement with the [79FED/PER] previous published one (*figure 5*). More data in various well controlled chemical conditions are still needed to check the interpretation (*table III*).

This result are used to calculate the formation constant of the limiting complex of Np(IV) (*table I*). Using the U(VI)/U(IV) couple in carbonate media and other known equilibria, the same methodology has been used to deduce the formation constant of U [92GRE/FUG]. In the same way, to calculate the formation constant of the limiting complex of Pu, β_5 , we made preliminary measurements [92CAP] of the redox potential of the Pu(VI)/Pu(IV), E(VI/IV), and of the disproportionation constant of Pu(V) in carbonate media, K_V . We are using E(VI/IV) to estimate β_5 (*table I*); but this value is questionable [92CAP]: it leads to overestimate K_V by 2.8 order of magnitude, β_5 might then be smaller by 1.4 lg unit (than the value proposed for Pu in *table I*). We conclude (*table I*), that, using the existing published data, all these results lead to similar value for the formation constant of the limiting complex of U, Np and Pu; this has to be confirmed, and even the stoichiometry of Np or Pu limiting complex is not clearly proved. The same conclusion seems to be valid for Am [87ROB]. We also use this interpretation to understand the best condition to prepare Np, Pu or Am at different oxidation states in carbonate media solutions: it is consistent with the fact, that too high pH leads to Np(IV) precipitation, Am(IV) and Am(V) should be prepared in carbonate-bicarbonate mixtures [83BOU/GUI], Pu(VI) reduction produce Pu(IV) in bicarbonate solution, and Pu(V) in carbonate one [92CAP].

A spectrophotometric study of the dissociation of the limiting complex was performed when decreasing $[\text{CO}_3^{2-}]$ by bubbling CO_2 gas in the solution. The methodology is explained elsewhere for a similar study on plutonium [92CAP]. The interpretation of the data clearly shows, that during the dissociation the limiting complex loose only one CO_3^{2-} and no OH^- anion over nearly three pH unit. Very similar results are again found for U, Np and Pu (*table I*).

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Table I: Possible complexes of Np(IV) in concentrated carbonate media

$M^{4+} + 4 CO_3^{2-} \leftrightarrow M(CO_3)_4^{4-}$							K ^o is K at I=0, ε is SIT coefficient	
M	ref	lg K	±	kg K ^o	±	method	conditions	
U	[92GRE/FUG]			34.0	0.9	rev	I = 0	
Np	[85RAI/Ryan]	<	38.5			sol	0.01 M (HCO ₃ + CO ₃), Na	
Np	*[85RAI/Ryan]	<	38		37.9	*sol	0.01 M (HCO ₃ + CO ₃), Na	
Np	[89MOR/PRA]		41.1	1.4	39.35	sol	NaHCO ₃ in contact with air	
Pu	*[92CAP] ?				32.2	1.0	*rev	I = 0
$M(CO_3)_4^{4-} + CO_3^{2-} \leftrightarrow M(CO_3)_5^{6-}$								
M	ref	lg K	±	kg K ^o	±	method	conditions	
Np	*[93LI/KAT]	<	1.3	0.5	-1.45	*sp	0.2 M Na ₂ CO ₃ , pH 10.8	
Np	[95DEL]		1.5		-0.994	sp	I = 0.394 0.4 m Na ⁺ , HCO ₃ , air?	
Np	[95DEL]		1.63		-1.002	sp	I = 0.583 0.6 m Na ⁺ , HCO ₃ , air?	
Np	[95DEL]		1.80		-0.92	sp	I = 0.756 0.8 m Na ⁺ , HCO ₃ , air?	
Np	[95DEL]		1.79		-1.018	sp	I = 0.976 1.0 m Na ⁺ , HCO ₃ , air?	
Np	[95DEL]		2.2		-0.606	sp	I = 1.146 1.2 m Na ⁺ , HCO ₃ , air?	
							I = 0, SIT regression	
U	[92GRE/FUG]	Δε	±	kg K ^o	±		TDB review	
Np	[95DEL]	0.44	0.05	-0.98	0.15		from [95DEL] data	
Pu	[92CAP]	0.9	0.1	-1.0	0.2		from [92CAP] data	
Pu	[95CAP/VIT]	0.26	0.1	-1.36	0.2		from [92CAP] data	
$M^{4+} + 5 CO_3^{2-} \leftrightarrow M(CO_3)_5^{6-}$								
M	ref	lg K	±	kg K ^o	±	method	conditions	
U	[92GRE/FUG]			34	0.9		I = 0	
Np	*[79FED/PER]		41.5	3.4	39.1	3.7	red	1 M Na ₂ CO ₃
Np	*[79FED/PER]		39.7	1.7	36.5	3.1	red	1 M K ₂ CO ₃
Np	*[84VAR/HOB]		39.4	1.7	36.1	3.1	red	1 M K ₂ CO ₃
Np	*[84VAR/HOB]		38.2	1.7	35.2	3.8	red	2 M Na ₂ CO ₃
Pu	*[92CAP] ?				32.2	2		I = 0

* calculated or estimated in this review

Table II: No evidence of the following complexes

$Np^{4+} + 2 OH^- + 2 CO_3^{2-} \leftrightarrow Np(OH)_2(CO_3)_2^{2-}$							
	ref	lg K	±			method	conditions
	*[85RAI/Ryan]	<	42			sol	0.01 M (HCO ₃ + CO ₃), Na
	[90PRA/MOR]		45.69	0.44		sol	0.01 M (HCO ₃ + CO ₃), Na
$Np^{4+} + 4 OH^- + CO_3^{2-} \leftrightarrow Np(OH)_4CO_3^{2-}$							
	*[85RAI/Ryan]	<	46			sol	0.01 M (HCO ₃ + CO ₃), Na
	[90PRA/MOR]		53.05	0.02		sol	0.1 to 2.2 M (NH ₄) ₂ CO ₃
$Np^{4+} + 4 OH^- + 2 CO_3^{2-} \leftrightarrow Np(OH)_4(CO_3)_2^{4-}$							
	*[85RAI/Ryan]	<	48			sol	0.01 M (HCO ₃ + CO ₃), Na
	[90PRA/MOR]		53.07	0.44		sol	0.01 M (HCO ₃ + CO ₃), Na
$Np^{4+} + 4 CO_3^{2-} \leftrightarrow Np(CO_3)_4^{4-}$							
	[85RAI/Ryan]	<	33,2			sol	0.01 M (HCO ₃ + CO ₃), Na
	*[85RAI/Ryan]	<	36			sol	0.01 M (HCO ₃ + CO ₃), Na
	[89MOR/PRA]		37	1.2		sol	NaOH, lgpCO ₂ = -3,5

* calculated or estimated in this review

Table III: Redox potentials of Np in carbonate media

Np(V)/Np(IV)							
	ref	E	±	ΔS	±	method	conditions
	[79FED/PER]	0.1	*0.2			red	1 M Na ₂ CO ₃
	[95DEL]	0.51		-272	50	red	I = 0, 1 atm carbonic gas ?
	[95DEL]	0.247				red	0.3 M Na ₂ CO ₃ , pH 10.22 ?
	[95DEL]	0.234		-133		red	0.6 M Na ₂ CO ₃ , pH = 10.28 ?
	[95DEL]	0.244		-169		red	1 M Na ₂ CO ₃ , pH = 10.10 ?
	[95DEL]	0.228		-136		red	1.5 M Na ₂ CO ₃ , pH = 11.54 ?
	*[95DEL]	*0.10	*0.06			red	I = 0, air conditions
	*[95DEL]	*0.52	*0.06			red	I = 0, 1 atm carbonic gas
Np(IV)/Np(III)							
	ref	E	±	ΔS	±	method	conditions
	[79FED/PER]	-1.32	0.1			vlt	1 M K ₂ CO ₃
	[84VAR/HOB]	-1.3	0.1			vlt	1 M K ₂ CO ₃
	[84VAR/HOB]	-1.2	0.1			vlt	2 M Na ₂ CO ₃

* calculated or estimated in this review

Figure 1: Np(IV) spectra in concentrated carbonate media. The spectrum of the limiting complex is obtained in 1.5 M [71MOS5] or 1 M [77SAI/UEN] $(\text{NH}_4)_2\text{CO}_3$, 1 M Na_2CO_3 or NaHCO_3 [81WES/SUL], 2 M [84VAR/HOB] or 1 M Na_2CO_3 [93LIT/KAT]. It is dissociated in 0.2 M Na_2CO_3 [93LIT/KAT].

Figure 2: Np(IV) spectra in concentrated carbonate media.

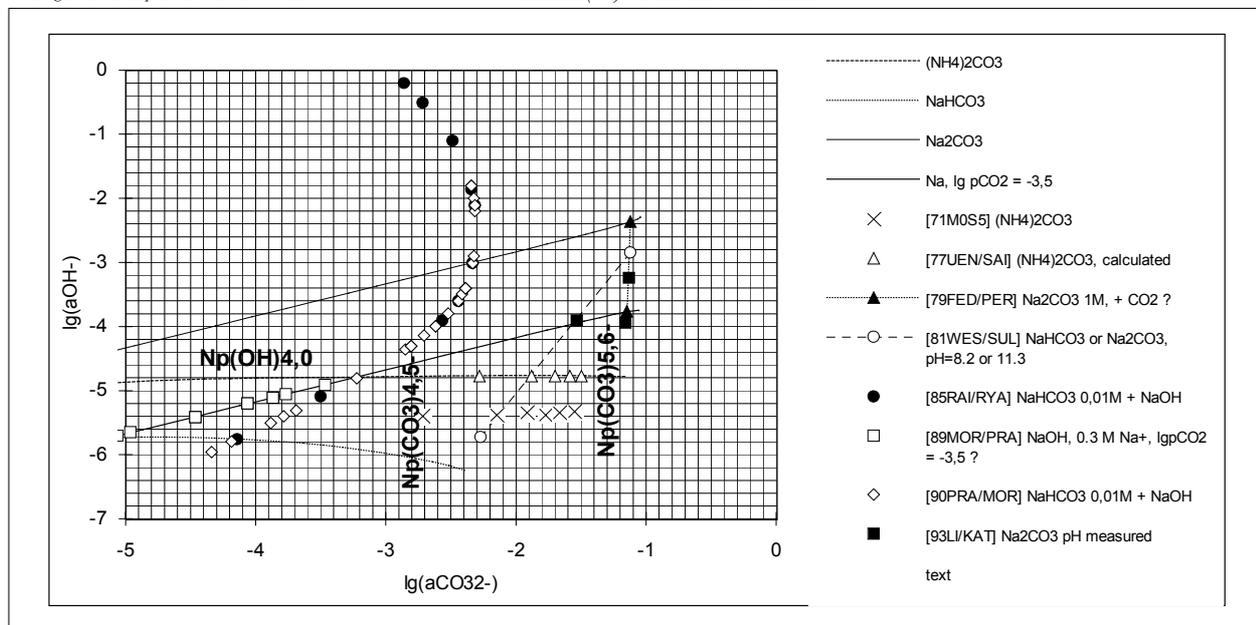


Figure 3: Comparison of the carbonate speciation used in the published works on Np(IV) solubility and solution chemistry in carbonate media. Only the works of [85RAI/RYAN], [89MOR/PRA] and [90PRA/MOR] were performed in similar chemical conditions, and can then be easily compared. If only $Np(OH)_4$, $Np(CO_3)_4^{4-}$ and $Np(CO_3)_5^{6-}$ soluble complexes are formed, a predominance diagram is suggested (by the places, where the name of these species are written). If the limiting complex is $Np(CO_3)_5^{6-}$, it is stabilised at high ionic strength, this reason, can explain, that it is obtained in concentrated carbonate or bicarbonate media.

Np(IV) Solubility in CO3 or HCO3 solutions

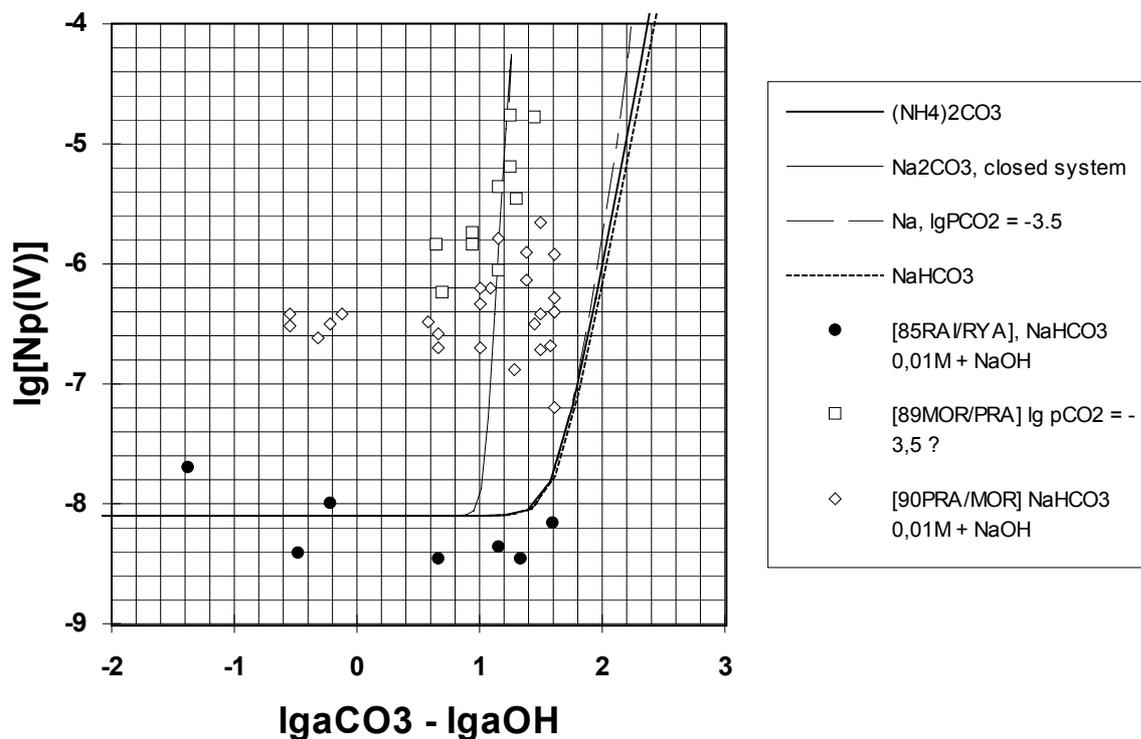


Figure 4a: Np(IV) solubility in carbonate media. The cited authors (experimental points in the figure) assume, that the solid phase is NpO_2s or $Np(OH)_4s$. When the predominating soluble complex is $Np_k(CO_3)_i(OH)_j^{4k-2i-j-}$, the Np(IV) solubility, S, is $\log_{10}S = k \log_{10}K_s^\circ + \log_{10}\beta_{ijk} + i k(\log_{10}a_{CO_3^{2-}} - (4 / k - j) / i \log_{10}a_{OH^-})$. All the experimental points would then have fallen on the same line, if the major soluble complex had the stoichiometry $i = 4 / k - j$, typically $Np(CO_3)_2(OH)_2^{2-}$ (proposed in [90PRA/MOR]) or $Np(CO_3)_4^{4-}$ (proposed in this review). The experimental data of Prapoto's thesis [89MOR/PA] [90PRA/MOR] are too scattered to make a conclusion.

Np(IV) Solubility in CO₃ or HCO₃ solutions

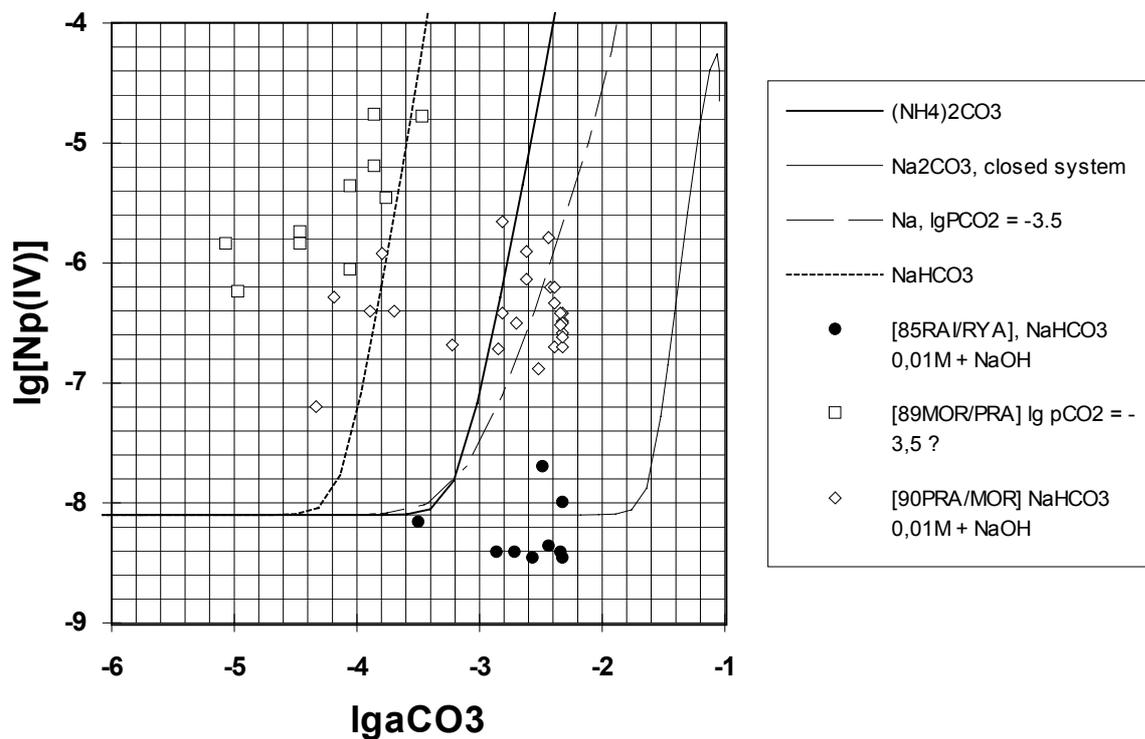


Figure 4b: Np(IV) solubility in carbonate media. All the experimental points would now have fallen on the same line, if the major soluble complex had the stoichiometry $4 = k j$, typically $\text{Np}(\text{OH})_4^0$, $\text{Np}(\text{OH})_4\text{CO}_3^{2-}$ (proposed in [71MOS5]) or $\text{Np}(\text{OH})_4(\text{CO}_3)_2^{4-}$ (proposed in [90PRA/MOR]). The experimental data of Prapoto's thesis [89MOR/PA] [90PRA/MOR] are too scattered to make a conclusion.

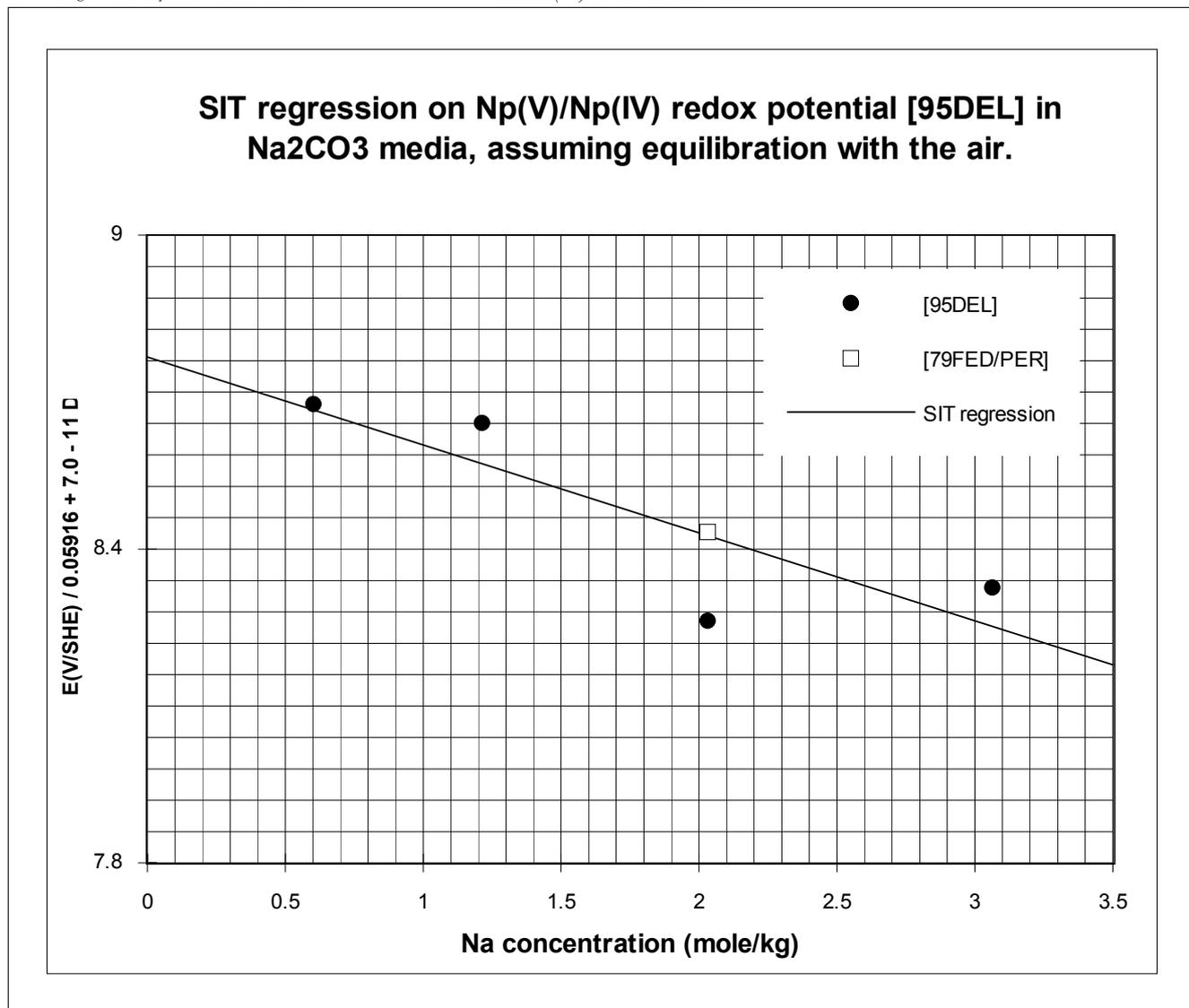


Figure 5: SIT regression on the redox potential of the Np(V)/Np(IV) couple in Na₂CO₃ media. The measured potential E_m , is corrected for P_{CO_2} assuming equilibration with the air $E = E_m - 2 \times 0.05916 \log_{10} P_{CO_2}$. $Y = E / 0.05916 - 11 D$, where D is a Debye-Hückel term [92GRE/FUG]. [95DEL] is not yet published, its reviewing is not yet finished. The correction of E_m for the [Np(V)] / [Np(IV)] ratio cannot be checked in [79FED/PER] and has not yet been checked in [95DEL]. The junction potential and the calibration of the reference electrode cannot be checked in [79FED/PER]; they seem to be correct in [95DEL]. SIT regression (m_{Na^+} , Y) gives $\Delta\epsilon = -0.168$; $Y^\circ = 8.767$, then $E^\circ(P_{CO_2} = 10^{-3.5} \text{ atm}) = 0.519 \text{ V/SHE}$, is a formal potential in standard conditions except for P_{CO_2} . $E^\circ(P_{CO_2} = 1 \text{ atm}) = E^\circ(P_{CO_2} = 10^{-3.5} \text{ atm}) - 7 \times 0.05916 = 0.105 \text{ V/SHE}$. Equilibration with the air was not checked in these works. $\log_{10} P_{CO_2}$ could then be smaller than -3.5 . This would lower E and then E° by several orders of magnitude. The formation constant of the $Np(CO_3)_5^{6-}$ estimated from this type of measurement (*tables I and II*) would then be higher by several orders of magnitudes. This is "unbelievable" [85RAY/RIAN].