

Actinide(IV) in carbonate media

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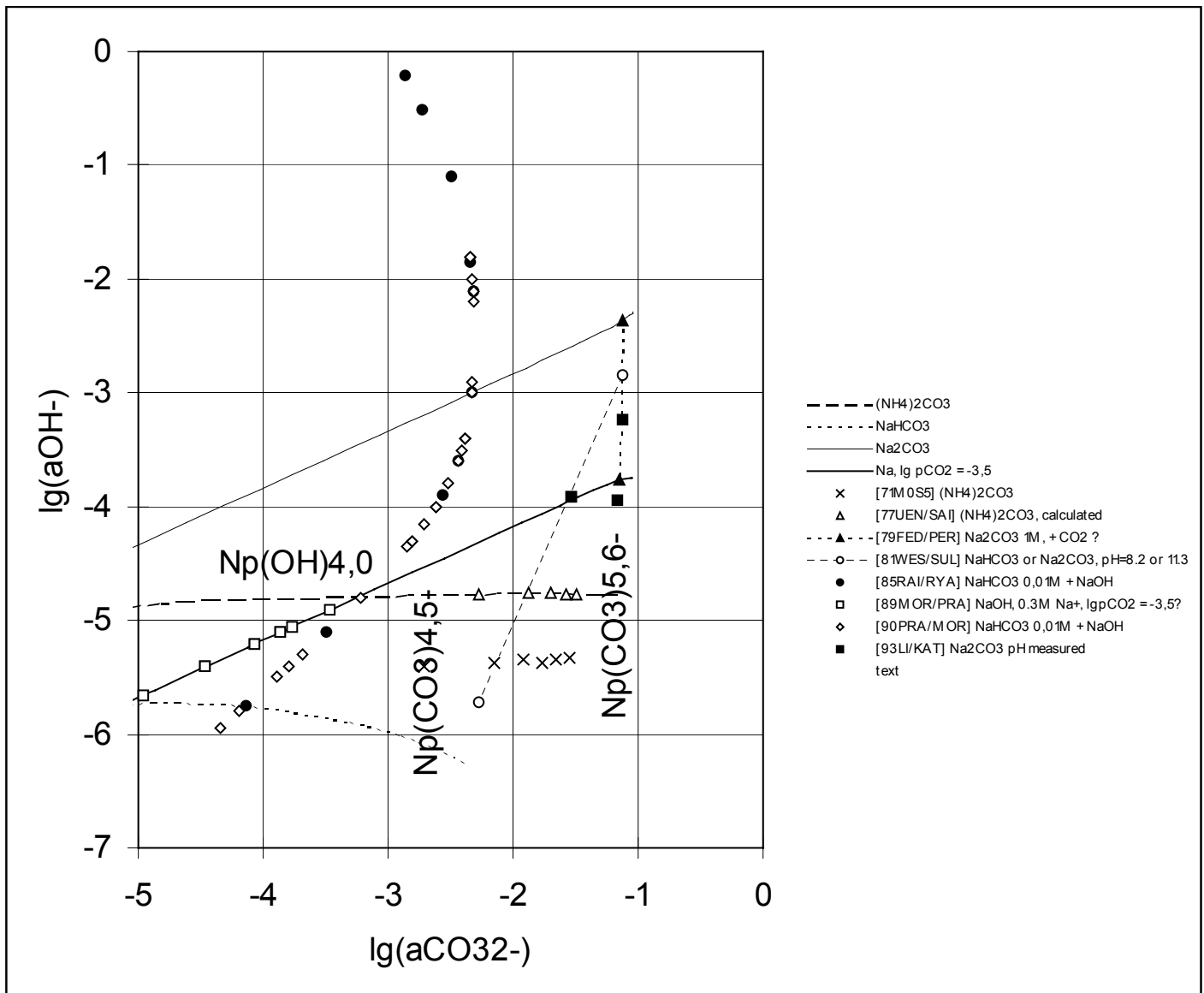
- **Critical review for the Thermodynamic Data Base of the Nuclear Energy Agency (OECD)** *Pierre Vitorge*
- **Electrochemical preparation and spectra of Np(IV) in carbonate media DEA (pre-PhD work)** *Laetitia Delmau*

Which soluble species of Np(IV) are formed in carbonate (natural) aqueous solutions ?

How to measure their stoichiometry and their stability ?

Comparison with other Actinide(IV).

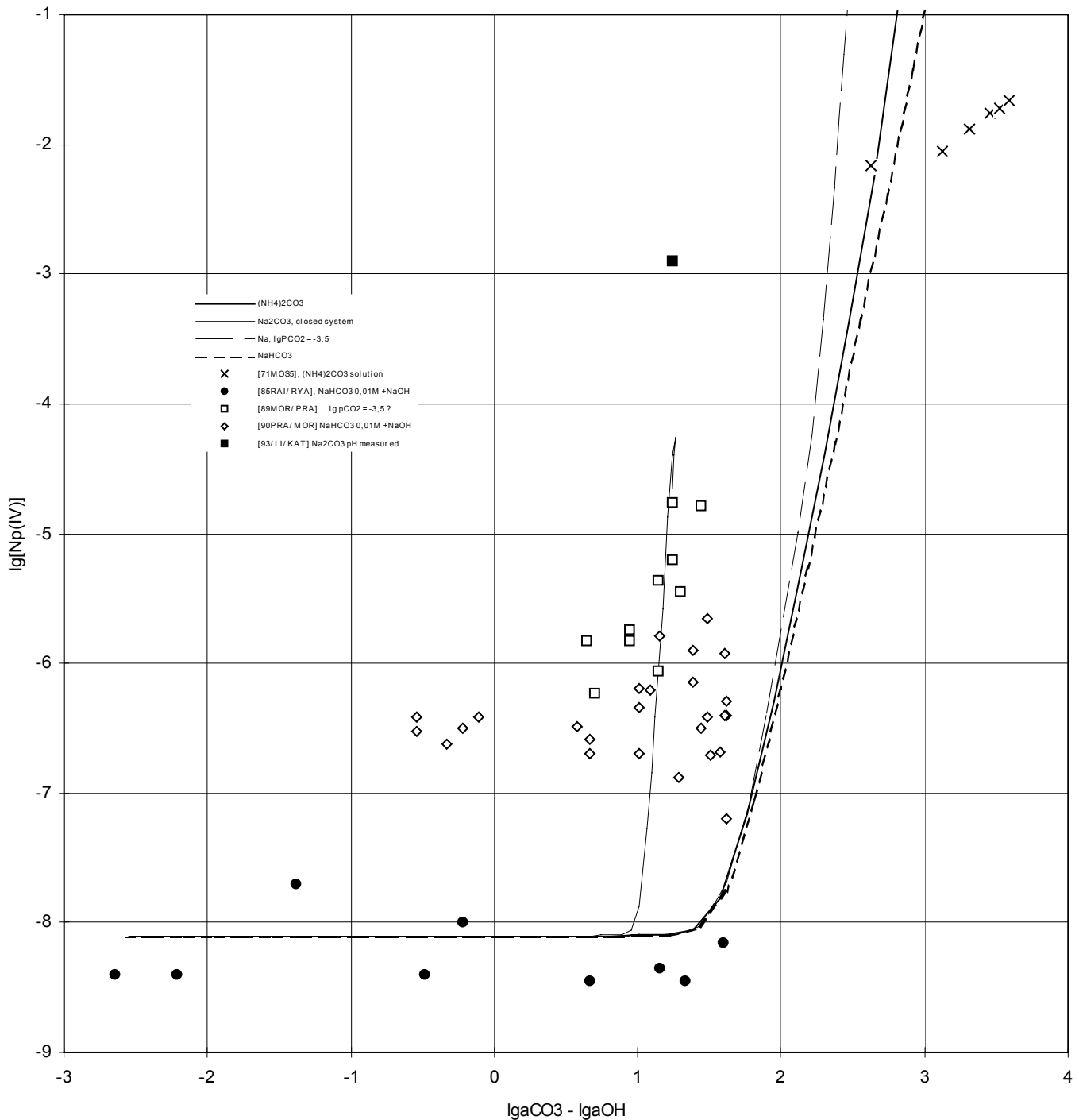
- 1 - Published works on Np(IV) solubility and solution chemistry: Comparison of the carbonate speciation (chemical conditions).**
- 2 - Published Np(IV) solubility: Testing their reproducibility and their interpretation**
- 3 - Published spectra: interpretation and experimental verification**
- 4 - Published Np(V)/Np(IV) redox potential: interpretation and experimental verification**



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 $\text{Np}(\text{OH})_4$, $\text{Np}(\text{CO}_3)_4^{4-}$ and $\text{Np}(\text{CO}_3)_5^{6-}$ 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 $\text{Np}(\text{CO}_3)_5^{6-}$, it is stabilised at high ionic strength, this reason, can explain, that it is obtained in concentrated carbonate or bicarbonate media. DATA.XLS



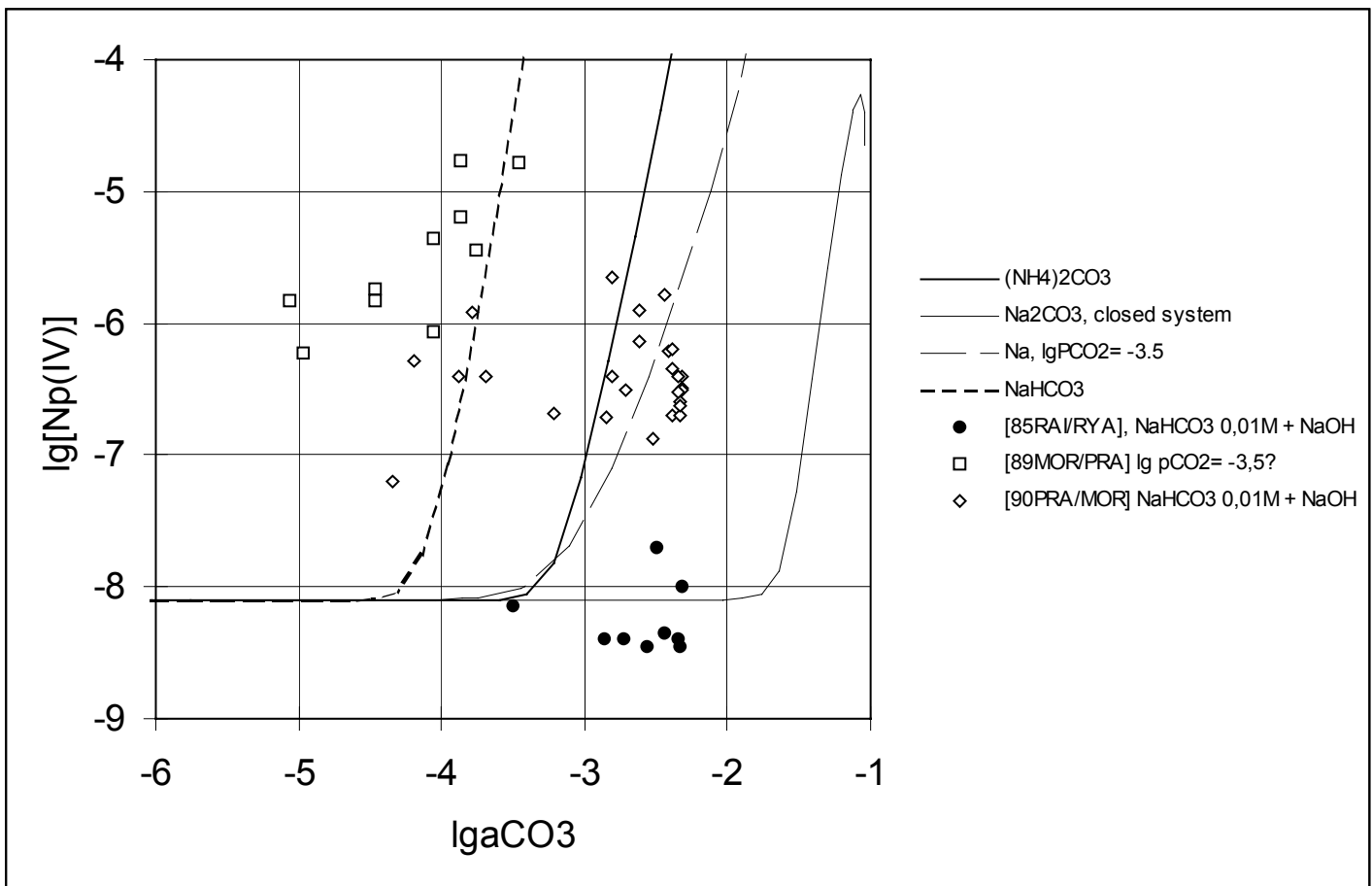
Np(IV) solubility in carbonate media.

The cited authors (experimental points in the figure) assume, that the solid phase is NpO_2s or $\text{Np}(\text{OH})_4\text{s}$. When the predominating soluble complex is $\text{Np}_k(\text{CO}_3)_i(\text{OH})_j^{4k-2i-j-}$, the Np(IV) solubility, S, is

$$\lg S = k \lg K_s^\circ + \lg \beta_{ijk} + i k (\lg a_{\text{CO}_3^{2-}} - (4/k - j) / i \lg a_{\text{OH}^-})$$

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 $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$ (proposed in [90PRA/MOR]) or $\text{Np}(\text{CO}_3)_4^{4-}$ (proposed in this review). The experimental data of Prapoto's thesis [89MOR/PA] [90PRA/MOR] are too scattered to make any conclusion.

Lines are drawn, assuming the formation of $\text{Np}(\text{OH})_4$, $\text{Np}(\text{CO}_3)_4^{4-}$ and $\text{Np}(\text{CO}_3)_5^{6-}$



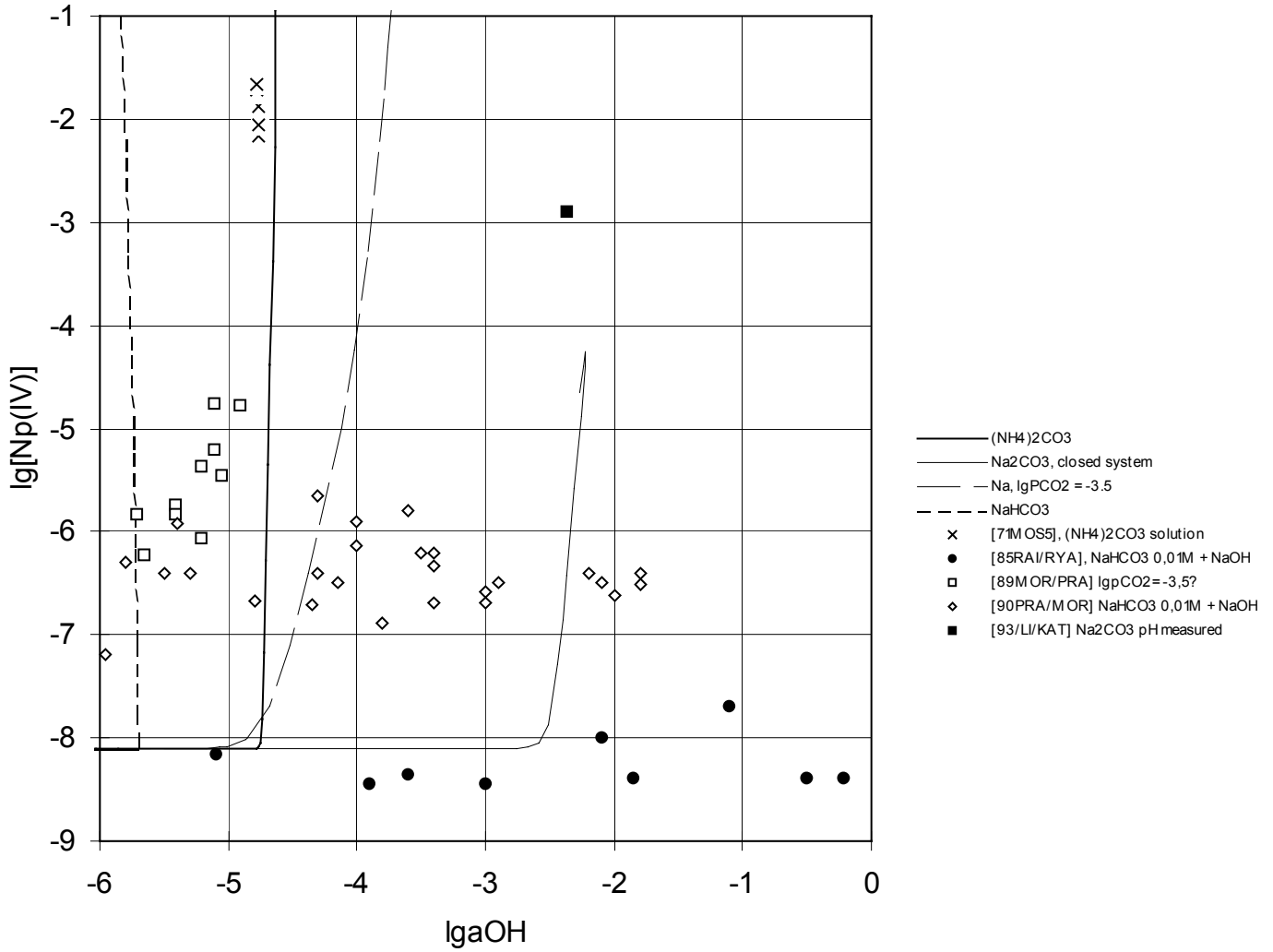
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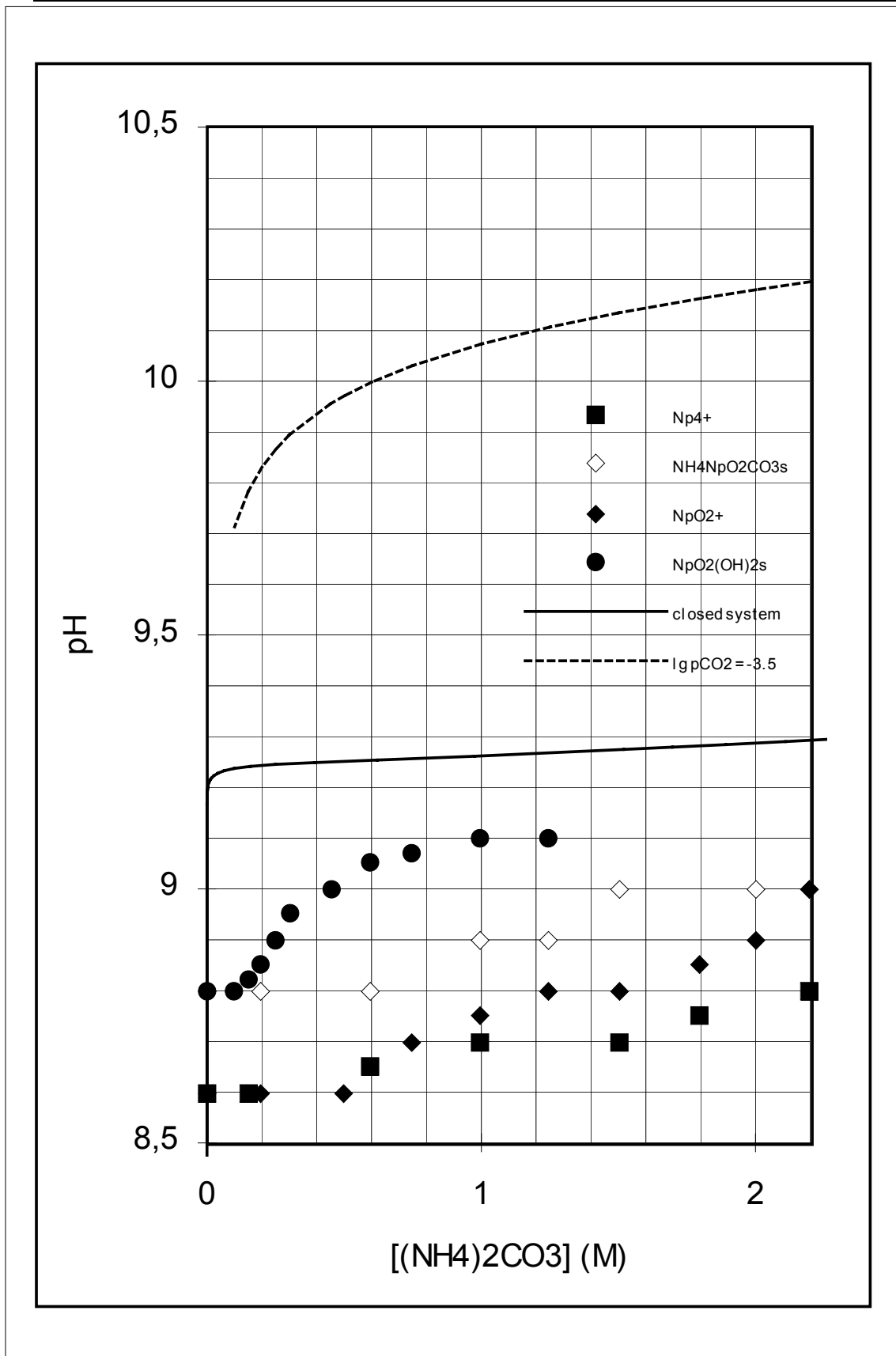
$$\log_{10} S = k \log_{10} K_s^\circ + \log_{10} \beta_{ijk} + i k (\log_{10} a_{\text{CO}_3^{2-}} - (4/k - j)/i \log_{10} a_{\text{OH}^-})$$

All the experimental points would then 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.

The spectrum of the supernatant solution, where $\lg[(\text{NH}_4)_2\text{CO}_3] = 0.18$, is also shown in [71MOS5]. It has also been observed later [77SAI/UEN], [81WES/SUL] and [93LI/KAT]: it is the spectrum of the Np(IV) carbonate limiting complex. It is consistent with the solubility calculation shown on the figure. For this calculation we assume, that this limiting complex is $\text{Np}(\text{CO}_3)_5^{6-}$. It would be dissociated into $\text{Np}(\text{CO}_3)_4^{4-}$ and $\text{Np}(\text{OH})_4^0$ concentration is negligible (less than 10^{-8} M). The calculations also indicate, that the solubility is not controlled by $\text{Np}(\text{OH})_4\text{(s)}$ solid phase. $(\text{NH}_4)_6\text{Np}(\text{CO}_3)_5 \cdot 12\text{H}_2\text{O}$ and other solid phases, where certainly slowly precipitating.

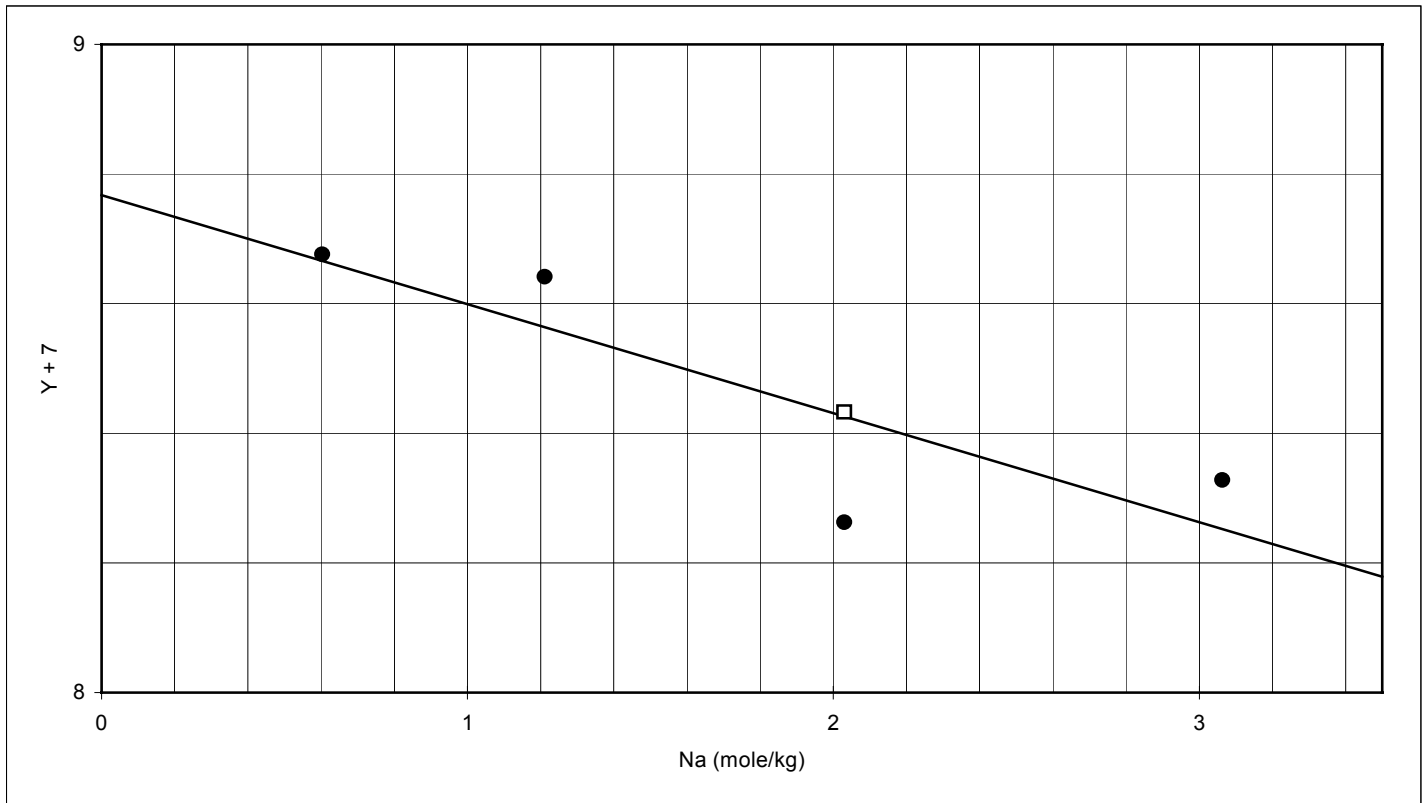


Np(IV) solubility in CO₃²⁻/HCO₃⁻ media.



pH measured by Moskvin

[71MOS5] during its solubility measurement of Np(IV, V and VI) in $(\text{NH}_4)_2\text{CO}_3$ solutions and calculated in this review. We assume, that there was either no exchange of carbonic gas with the air (solid line) or (dashed line) equilibrium with the air only for carbonic gas (not for ammoniac gas).



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 $E = E_m - 2 \times 0.05916 \log_{10} P_{CO_2}$. $Y = E / 0.05916 - 11 D$. The correction of E_m for the $[Np(V)] / [Np(IV)]$ ratio cannot be checked in [79FED/PER] (the square point) and has not yet been checked in [95DEL] (the other points). 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 $\Delta\varepsilon = -0.168$; $Y^\circ = 8.767$, 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 would then be higher by several orders of magnitudes. This is "unbelievable" [85RAY/RIAN]..DATA.XLS