

Actinide chemistry in environmental conditions, and Activity coefficient vs. surface complexation

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UMR 8587 Unité Mixte de Recherche **8587** :
CEA – Université d'Evry -CNRS

- Boltzmann - Poisson - Van der Waal calculi in spherical and planar geometries for Activity coefficients and Surface complexation respectively.
- Stoichiometries and thermodynamic stabilities of complexing and redox reactions for Actinides

Actinide chemistry in aqueous solutions for waste disposal and environmental studies



For the management of radioactive wastes, Equilibrium Speciation is studied in aqueous solutions: Chemistry of Actinides and other Radionuclides (critical reviewing and measuring thermodynamic data), also thermodynamics, methodologies...

Mass Action Law

in Nature

**in Laboratory (measuring equilibrium constants and stoichiometries)
...for Solid Solutions ...and Ionic Exchange Equilibria**

Activity coefficients

**SIT (and Pitzer) Formula = extended Debye and Hückel Formula
= Boltzmann – Poisson Calculus ...as for Surface Complexation Formula**

Consistency

**of thermochemical data
between different scientific fields, *i.e.* reference states...**

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Thermodynamics of solid solutions as published in text books



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Example: $\text{Na}_{2x-1}\text{NpO}_2(\text{CO}_3)_x$

or equivalently $\text{Na}_{2(1-y)}(\text{NpO}_2)_{2y}\text{CO}_3$ where $y = 1/(2x)$

the amount of CO_3^{2-} is the amount of solid matrix
while $\text{Na}^+/\text{NpO}_2^+$ cations are exchanged

Dissolution Reaction



Ionic Exchange Reaction



Mass Action Law for Reaction(2):

$$D = \frac{[\text{Na}^+(\text{s})] [\text{NpO}_2^+(\text{aq})]}{[\text{Na}^+(\text{aq})] [\text{NpO}_2^+(\text{s})]} = \frac{2(1-y)[\text{NpO}_2^+(\text{aq})]}{2y [\text{Na}^+(\text{aq})]}$$

$D = K_{s1} / K_{s0}$ is obtained by linear combinations of chemical potentials
where $K_{sy} = [\text{Na}^+(\text{aq})]^{2(1-y)} [\text{NpO}_2^+(\text{aq})]^{2y} [\text{CO}_3^{2-}(\text{aq})]$
are the solubility product of the endmembers for $y = 0$ or 1

Similarly $K_{sy} = K_{s0}^{1-y} K_{s1}^y (1-x)^{b(1-y)} x^{cy}$

which is **only similar to** Mass Action Law for Reaction(1)

Thermodynamics of solid solutions

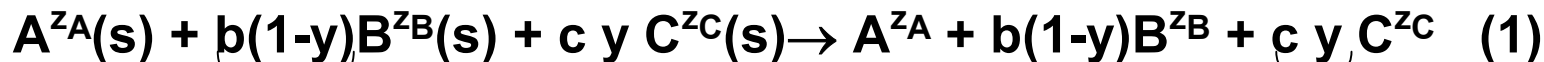
a reaction with 2 advancement variables

Advancement variable for Reaction 1 at constant y (n_X = number of mole for

Species X): $(dn_X)_y = v_X (dn_{A^{zA}})_y$ $v_A = 1$, $v_B = b(1-y)$, $v_C = c y$, $v_{X(s)} = -v_X$

$$b = -z_A/z_B, c = -z_A/z_C, \mathbf{A} \mathbf{B}_{b(1-y)} \mathbf{C}_{c y}(\mathbf{s}) = \mathbf{A}^{zA}(\mathbf{s}) + b(1-y) \mathbf{B}^{zB}(\mathbf{s}) + c y \mathbf{C}^{zC}(\mathbf{s})$$

Dissolution Reaction



It appears that: $\frac{dv_X}{dy} = v'_X$ are the stoichiometric coefficients for Reaction 2:

$$v'_A = 0 \quad v'_B = b, \quad v'_C = c, \quad v_{X(s)} = -v_X$$

Ionic Exchange Reaction



$$dn_X = d(v_X n_{A^{zA}}) = v_X (dn_{A^{zA}})_y$$

$$0 = \sum_X (\mu_X dn_X) = \left(\sum_X (\mu_X v_X) \right) (dn_{A^{zA}})_y$$

+

$$n_{A^{zA}} v'_X dy$$

+

$$n_{A^{zA}} \left(\sum_X (\mu_X v'_X) \right) dy$$

$$\frac{[\mathbf{A}^{zA}] [\mathbf{B}^{zB}]^{b(1-y)} [\mathbf{C}^{zC}]^{cy}}{(1-y)^{b(1-y)} y^{cy}} = K_{s0}^{1-y} K_{s1}^y \quad \text{and} \quad \frac{(1-y)^b [\mathbf{C}^{zC}]^c}{[\mathbf{B}^{zB}]^b y^c} = \frac{K_{s1}}{K_{s0}}$$

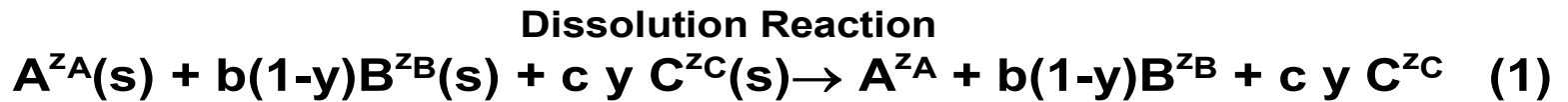
$0 < y < 1$



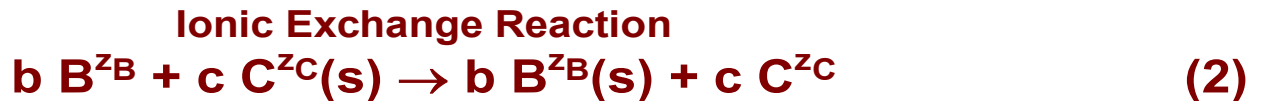
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Thermodynamics of solid solutions

Dissolution Reaction ↔ Ionic Exchange Reaction



Differentiating: $\frac{dv_x}{dy} = v'_x$ Integral calculus: $v_x = \int v'_x dy$



$K_{ex} = \frac{K_{s1}}{K_{s0}}$, where K_{ex} is the equilibrium constant for a **ionic exchange equilibrium**.



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Activity coefficients

using SIT formula at 25°C for Reaction $\text{Pu}^{4+} + \text{e}^- \rightarrow \text{Pu}^{3+}$

$$\lg K_{\text{Pu}^{4+}/\text{Pu}^{3+}} + 7 D = \lg K^\circ_{\text{Pu}^{4+}/\text{Pu}^{3+}} + \Delta\varepsilon_{\text{Pu}^{4+}/\text{Pu}^{3+}} m_{\text{ClO}_4^-}$$

$$D = \frac{0.509 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} \text{ at } 25^\circ\text{C}$$

Equilibrium constant K is constant in a given ideal system, typically a solution of high and constant ionic strength I.

here $m_{\text{ClO}_4^-} = I_m$,

I_m is the molal ionic strength (mol.kg^{-1})

Reference state $K^\circ = K(I \rightarrow 0)$



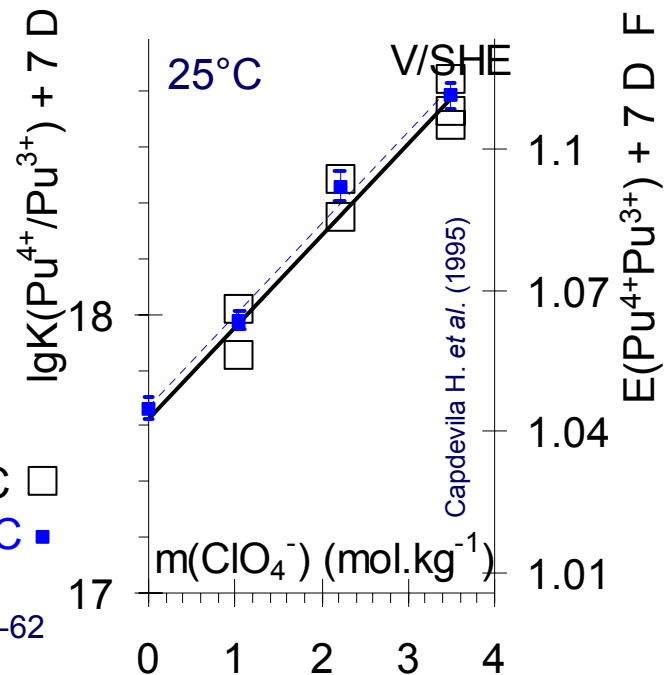
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$\Delta\varepsilon$ appears to be constant, which validates SIT Formula

$$\Delta_r G = -R T \ln K_{\text{Pu}^{4+}/\text{Pu}^{3+}} = -F E_{\text{Pu}^{4+}/\text{Pu}^{3+}}$$

R is the molar gas constant,

F the Faraday constant



measured at 25°C \square

interpolated at 25°C from data at 5 to 65°C \blacksquare

Capdevila H., Vitorge P. (1995) Radiochim. Acta 68, 1, 51-62
& CEA-N-2762 (1994)

Activity coefficients

SIT formula at 25°C for the highly charged species Pu⁴⁺

$$\lg \gamma_i = -z_i^2 D + \varepsilon_{i,j} m_j, \quad (j = \text{ClO}_4^- \text{ or } \text{Na}^+)$$

$$\Delta_r \lg \gamma = -\Delta_r z^2 D + \Delta_r \varepsilon m$$

$$\Delta_r \lg \gamma_i + \Delta_r z_i^2 D = \Delta_r \varepsilon_{i,j} m_j$$



$$\Delta \varepsilon_{\text{PuO}_2(\text{s})} = \varepsilon_{\text{Pu}^{4+}, \text{ClO}_4^-} + (4+n) a_{\text{H}_2\text{O}}/m - 4 \varepsilon_{\text{H}^+, \text{ClO}_4^-}$$



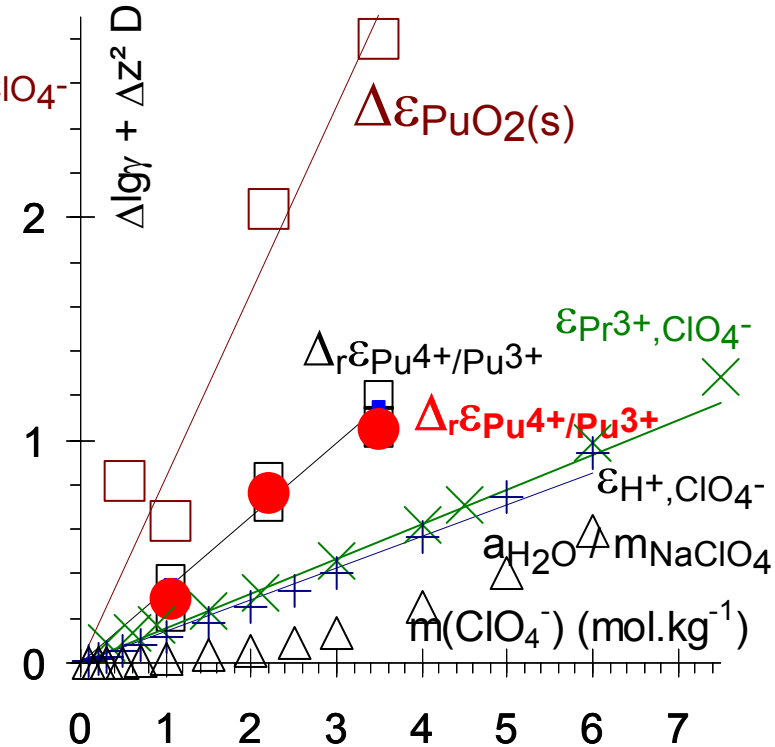
$$\Delta_r \varepsilon_{\text{Pu}^{4+}/\text{Pu}^{3+}} = \varepsilon_{\text{Pu}^{3+}, \text{ClO}_4^-} - \varepsilon_{\text{Pu}^{4+}, \text{ClO}_4^-}$$

Checking by using Thermodynamic Cycle

$$\Delta_r \varepsilon_{\text{Pu}^{4+}/\text{Pu}^{3+}} = \varepsilon_{\text{Pu}^{3+}} - \Delta \varepsilon_{\text{PuO}_2} - 4 \varepsilon_{\text{H}^+} \dots$$

Auxiliary data from isopiestic measurements

$$\varepsilon_{\text{Pr}^{3+}, \text{ClO}_4^-} \approx \varepsilon_{\text{Pu}^{3+}, \text{ClO}_4^-}$$



Capdevila H., Vitorge P. Radiochim. Acta 82, 11-16 (1998)

Activity coefficients at 25°C: conclusion



SIT Formula accounts for experimental data to surprisingly high ionic strength, even for highly charged species.

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However, this might very well be fortuitous; several linear effects might very well be empirically included in Ion Pair term ε .

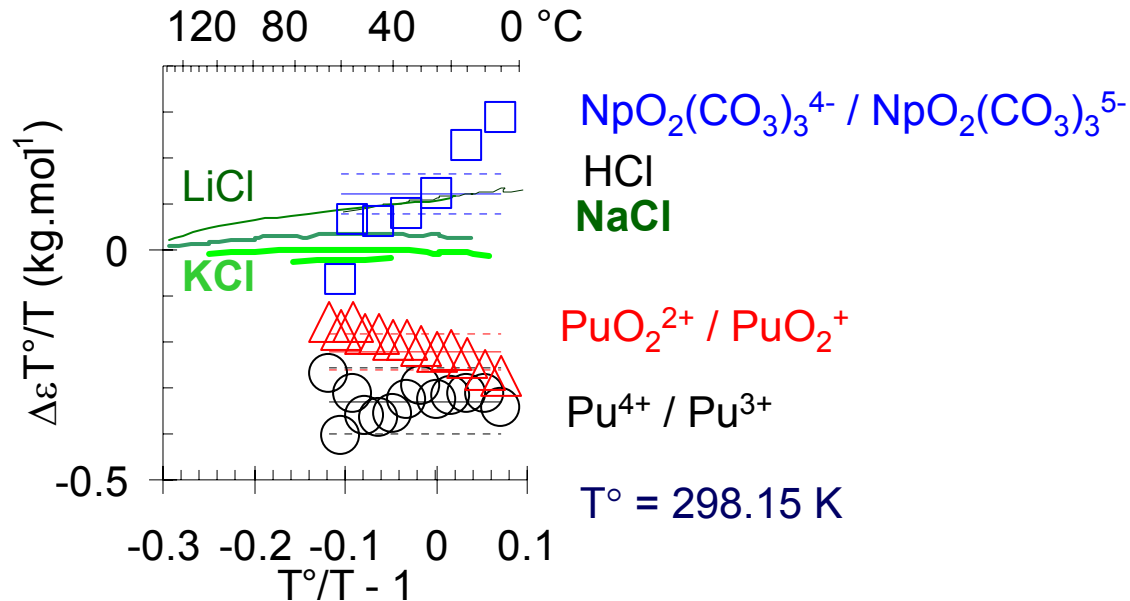
It is interesting to check whether SIT formula is also consistent with **temperature influence**, since it was proposed by using Statistical Physics as a result of temperature effect (disorder) and interactions (order).

Activity coefficients

temperature Influence on ε , the ion pair coefficient of SIT formula.



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It appears that

in several cases, (ε / T) does not depend on temperature, T .

Despite this corresponds to the model used to obtain SIT Formula, this was not specially expected.

As a consequence **the values of the activity coefficients, can be extrapolated from their values known at typically 25°C, i.e. without any new fitted parameter.**

Activity coefficients

comparison of SIT and Surface Complexation Formula.

SIT Formula

Ψ_{total}

-

Ψ_{Coulomb}

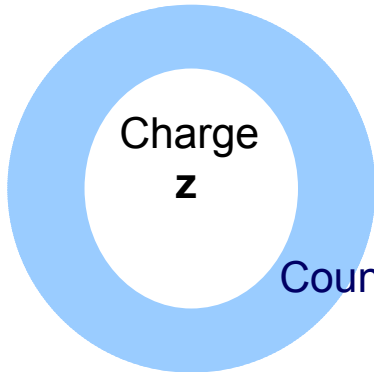
=

Ψ_{excess}

→

Debye-Hückel Formula
+ steric exclusion
+ ion pair interactions

Ψ = electrostatic potential



z

The model are different, however,
are the physical phenomena
actually different?

Debye distance = constant / (ionic strength)^{1/2}

Charges

z
z
z
z

Double layer

Surface Complexation Formula

Ψ_{total}

Gouy and Chapman Formula
+ supplementary layer(s)

Actinide carbonate complexes

Methodologies for estimating stoichiometries and stabilities



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Carbonate complexes of M^{3+} , a well known system(?)

Differences between Eu, Am and Cm are less than experimental accuracy.

Sensitivity analysis.

Limiting complex(es)

Comparison with sulfate complexes

Carbonate complexes of M^{4+}

Actinide carbonate complexes

Methodologies for estimating stoichiometries and stabilities

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**Maximum possible stabilities
for non well established stoichiometries**

Carbonate complexes of M^{3+}

Methodologies for estimating stoichiometries and stabilities

Introduction. For the management of radioactive wastes, Equilibrium speciation is studied in aqueous solutions for Actinides:

critical reviewing and measuring thermodynamic data,
(see typically NEA TDB reviews, and corresponding methodologies and thermodynamics basis)

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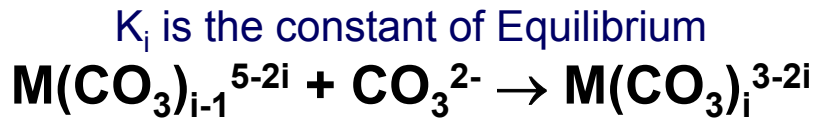
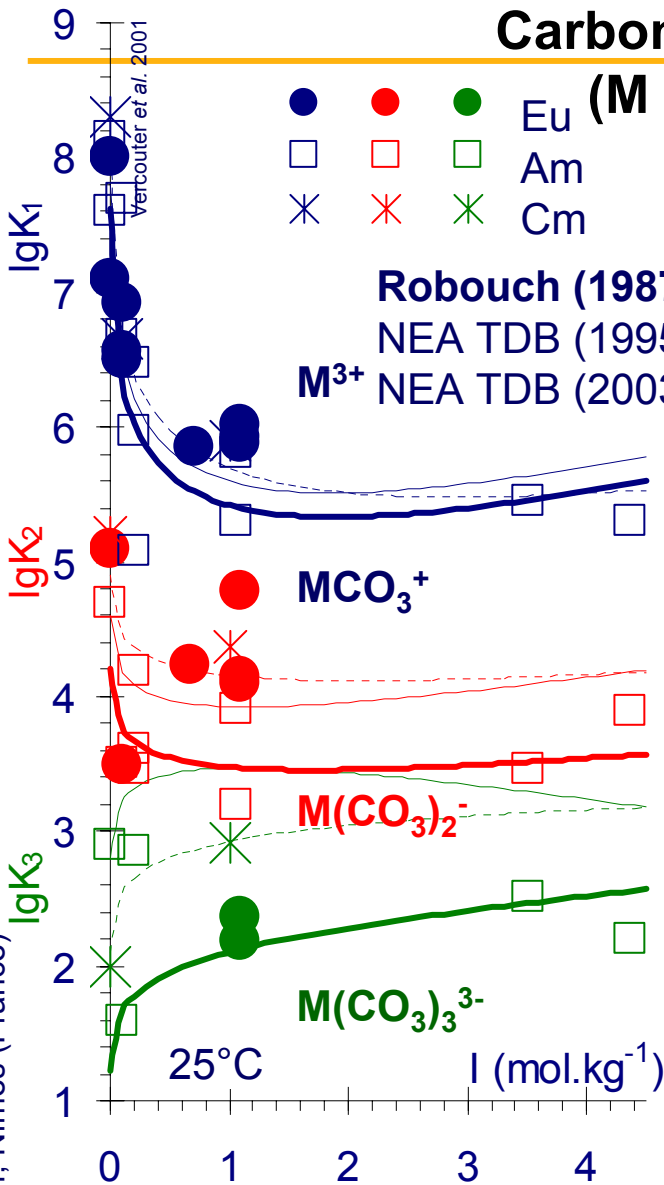
Comparison with sulfate complexes

Carbonate complexes of M^{4+}



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Carbonate complexes of M³⁺



→ Differences between Eu, Am and Cm are less than experimental accuracy

→ Consistency in stability data from different laboratories is obtained only for MCO₃⁺

Origins of differences in selected values:

- Giving more weight on selected measurements
- Experimental inconsistencies (typically activity coefficient, junction potentials)
- difficulty in decomposing the experimental observations into the contributions of each soluble the species *i.e.* in determining the **actual stoichiometries** (sensitivity analysis),

¹P.Robouch Thèse Université L.Pasteur, Strasbourg (France) 1987

²R.Silva *et al.* Chemical Thermodynamics of Americium NEA, Paris (France) 1995

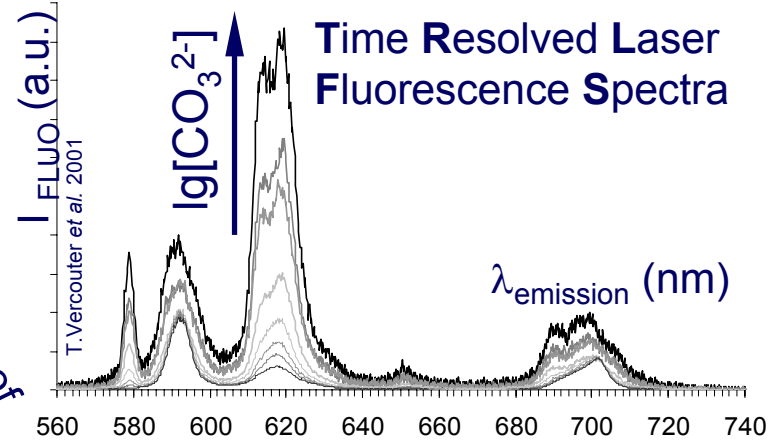
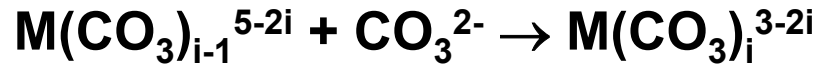
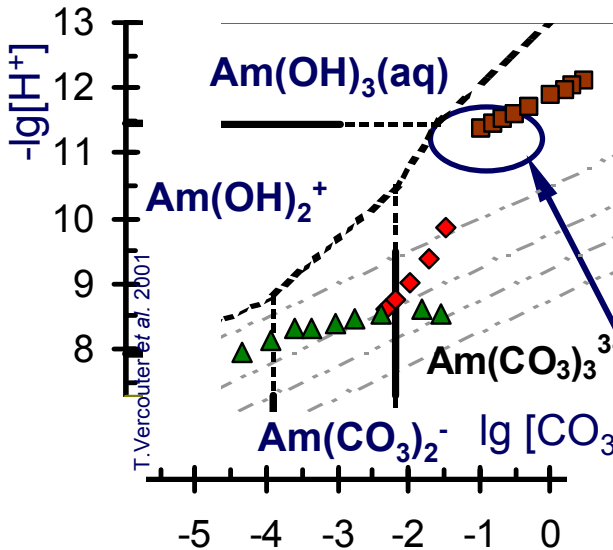
³R.Guillaumont *et al.* Update on the Chemical Thermodynamics of... NEA, Paris (France), Elsevier Ed. 2003



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T. Vercouter, P. Vitorge, C. Moulin.
Communication O22-02 ATALANTE
2004, Nîmes (France)

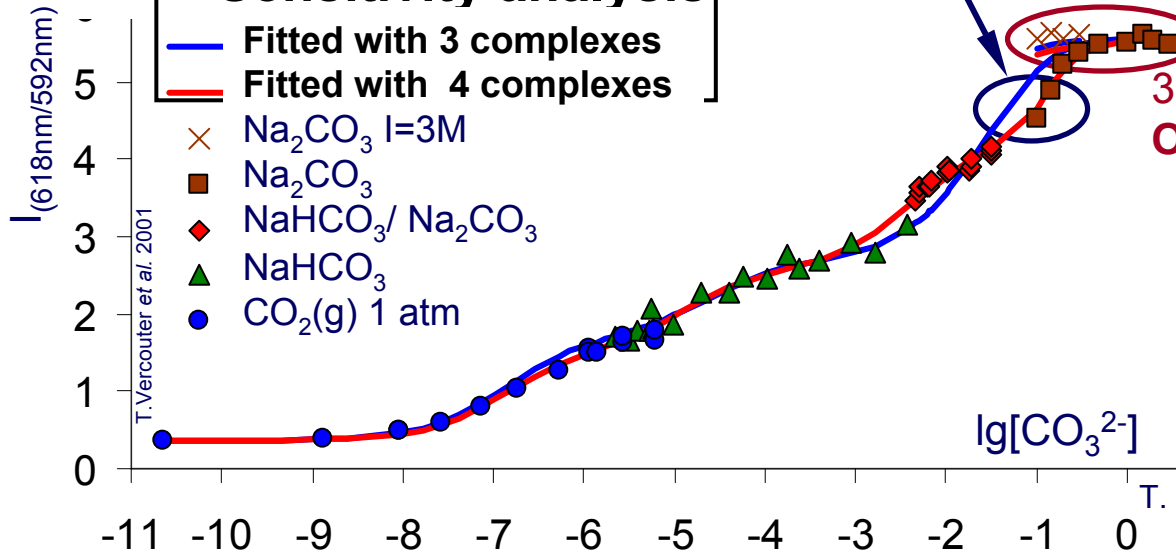
Carbonate complexes of Eu^{3+} a TRLFS study



Possible formation of $\text{Eu}(\text{OH})_2^+$ or $\text{Eu}(\text{CO}_3)_i(\text{OH})_{3-2i}^-$?

Sensitivity analysis

- Fitted with 3 complexes
- Fitted with 4 complexes
- × Na_2CO_3 $I=3\text{M}$
- Na_2CO_3
- ◆ $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$
- ▲ NaHCO_3
- $\text{CO}_2(\text{g})$ 1 atm



3M (high) ionic strength.
One single species

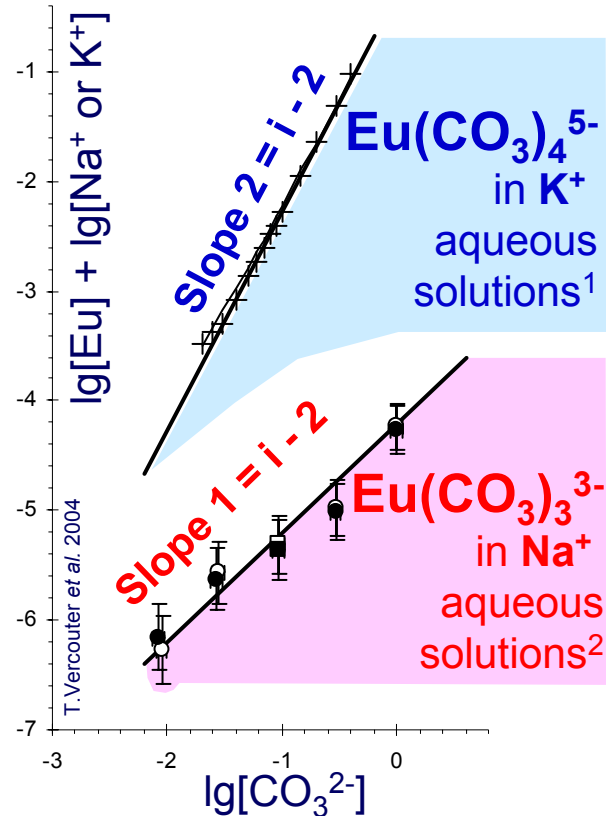
T. Vercouter, P. Vitorge, C. Moulin. Communication O22-02 ATALANTE 2004, Nîmes (France)

Carbonate complexes of Eu³⁺

Stoichiometries of the limiting complexes from solubility study



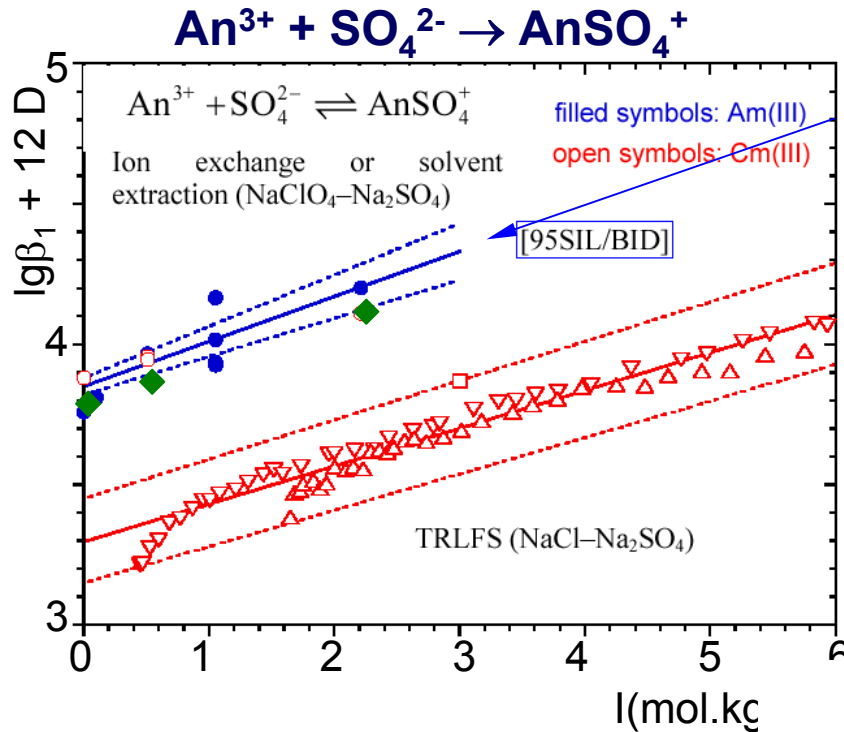
A⁺ = Na⁺ or K⁺



¹Faucherre *et al.*, *Rev. Chim. Minér.*, t3, 953 (1966)

²T. Vercouter, P. Vitorge, C. Moulin. Communication O22-02 ATALANTE 2004, Nîmes (France)

Comparison with sulfate complexes of M^{3+}



NEA 1995¹ Ion exchange or solvent extraction ($NaClO_4-Na_2SO_4$)

NEA 2003² from TRLF ($NaCl-Na_2SO_4$) data³

Inconsistency had been explained as follows: Spectroscopy would measure the stability of only **inner sphere complexes**, while other techniques would measure the stability of **in+outer sphere complexes**.

This is not consistent with Thermodynamics:
 $complex_{in} \rightarrow complex_{out} + n H_2O$

$$[complex_{out}] / [complex_{in}] = \text{Constant} (a_{H_2O})^n$$

Anyhow, our **TRLFS recent study⁴** rather confirms **NEA 1995 selection** for Eu ($NaClO_4-Na_2SO_4$)

¹R.Silva, G. Bidoglio, M.H. Rand, P.B. Robouch, H. Wanner, I. Puigdomenech. *Chemical thermodynamics of Am*. NEA Paris (France) 1995

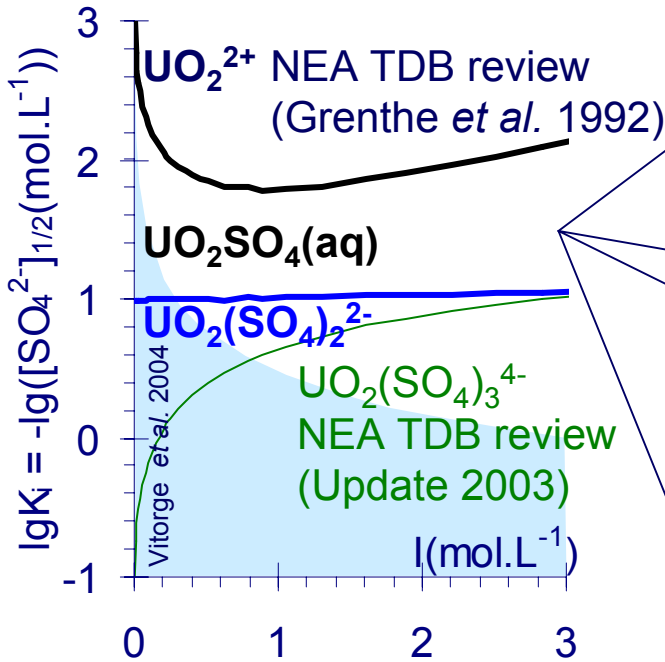
²R. Guillaumont, T. Fanghänel, V. Neck, J. Fuger, D.A. Palmer, I. Grenthe, M.H. Rand. *Update on the chemical thermodynamics of U, Np, Pu, Am and Tc*, Elsevier, Amsterdam, 2003

³P. Paviet, T. Fanghänel *et al.*, *Radiochim. Acta*, 74, 99-103 (1996) and V. Neck, T. Fanghänel *et al.*, Report, 1-108 (1998)

⁴T. Vercouter, P. Vitorge, C. Moulin. Communication O22-02 ATALANTE 2004, Nîmes (France)

Comparison with sulfate complexes of UO_2^{2+}

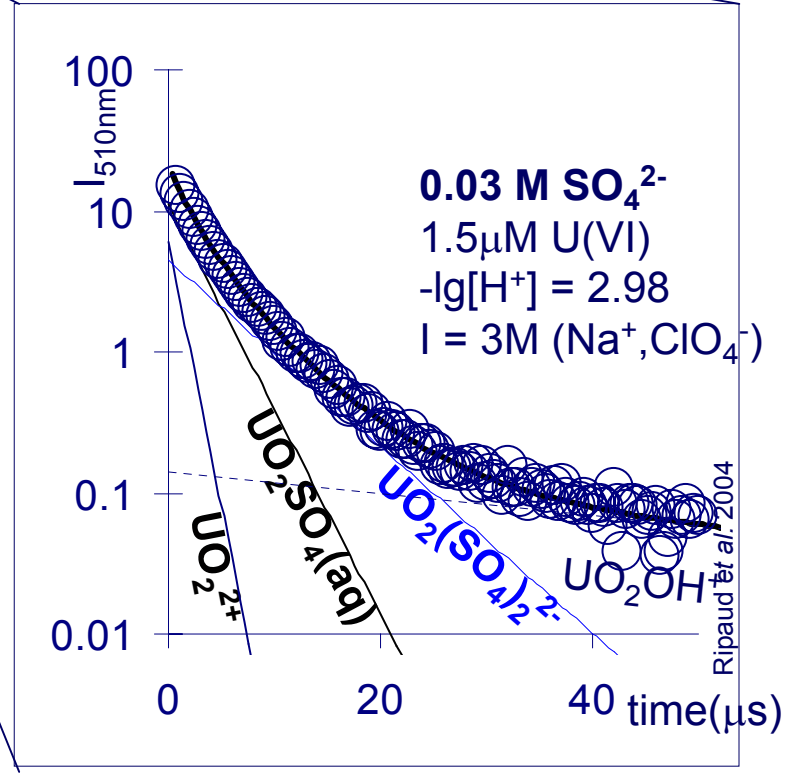
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a TRLFS study

Prediction: $\text{UO}_2\text{SO}_4(\text{aq}) + \text{UO}_2(\text{SO}_4)_2^{2-} + \text{UO}_2(\text{SO}_4)_3^{4-}$

$\text{UO}_2(\text{SO}_4)_3^{4-}$, was not evidenced by our TRLF measurements in these chemical conditions.



Conclusion

When **intermediary species** are **stable in narrow domains** of experimental conditions, it is difficult to measure independently their physical properties (as typically molar absorbance), and their contribution to measured signals. Beside other difficulties, this can often explain **differences in the values determined by different authors** for equilibrium constants.

Missing data on

Activity coefficients, specially for highly negative complexes,

Ion pairing? Structure of concentrated electrolytes?

Possible mixed complexes, *i.e.* $M(\text{CO}_3)_i(\text{OH})_j^{3-2i-j}$

(assuming no polynuclear complex).

Why no mixed complex have ever been evidenced?

Experimental difficulties?

Choice of experimental conditions?



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Carbonate complexes of M^{4+}

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Carbonate complexes of M^{3+} , a well known system(?)

Differences between Eu, Am and Cm are less than experimental accuracy.

Sensitivity analysis.

Limiting complex(es)

Comparison with sulfate complexes

Carbonate complexes of M^{4+}

$M(\text{CO}_3)_i^{4-2i}$ stoichiometries for $i = 4$ and 5 , for several An(IV) and Ln(IV).

However, $i = 6$ was also proposed Th(IV) and Ce(IV).

Maximum possible values are proposed for the formation constants of possible $M(\text{CO}_3)_i(\text{OH})_j^{4-2i-j}$ complexes based on published solubility data.

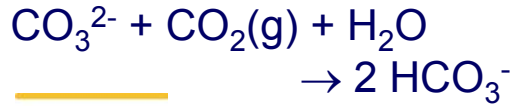


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Spectrophotometric study



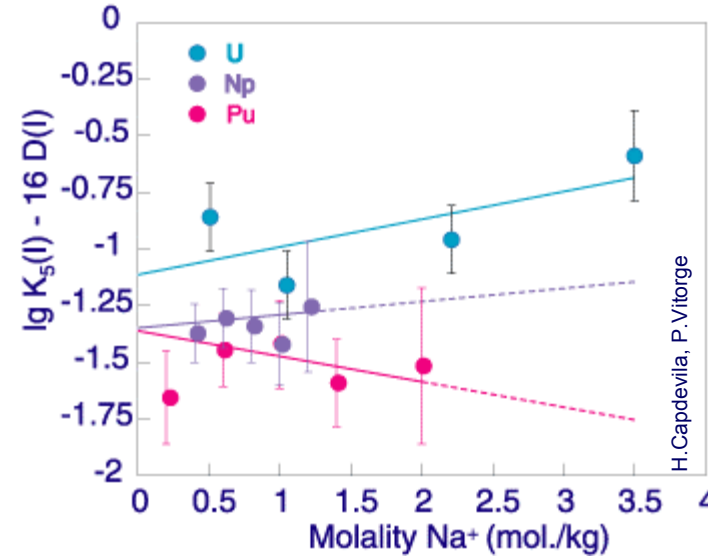
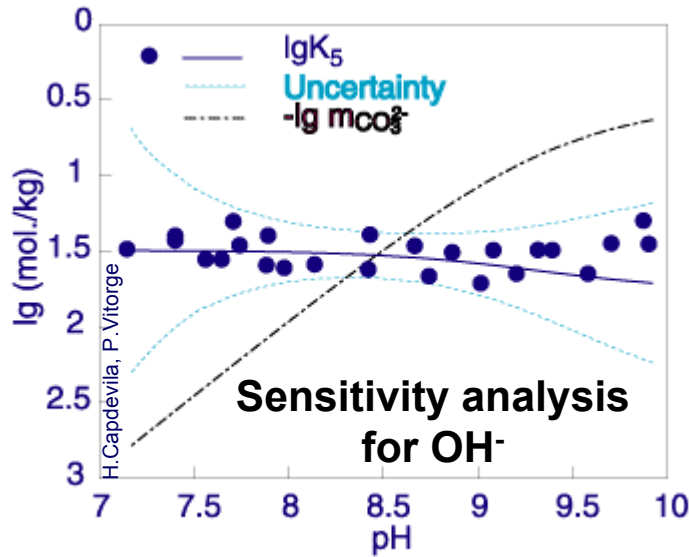
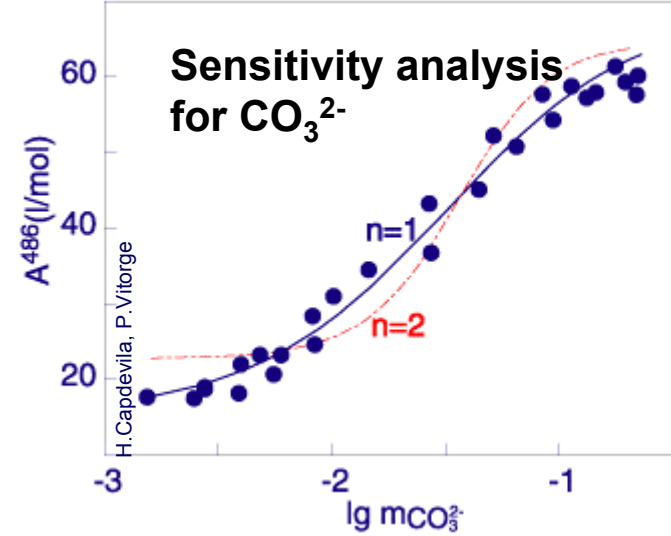
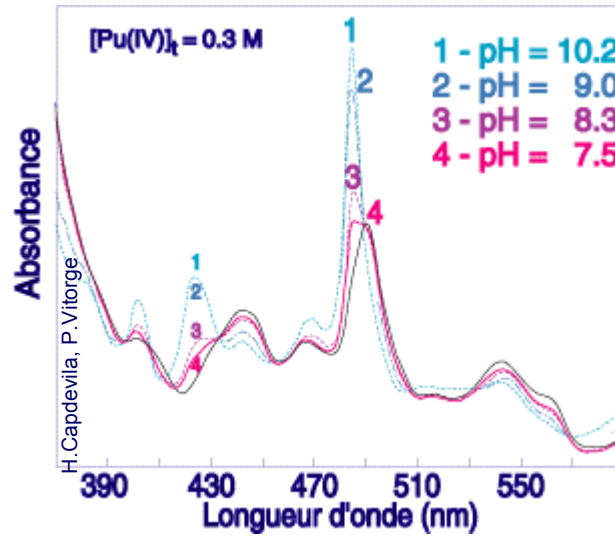
during titration



at 25°C



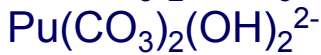
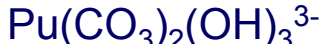
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H.Capdevila, P.Vitorge, E.Giffaut, L.Delmau. Radiochim. Acta 74, 93-98 (1996)

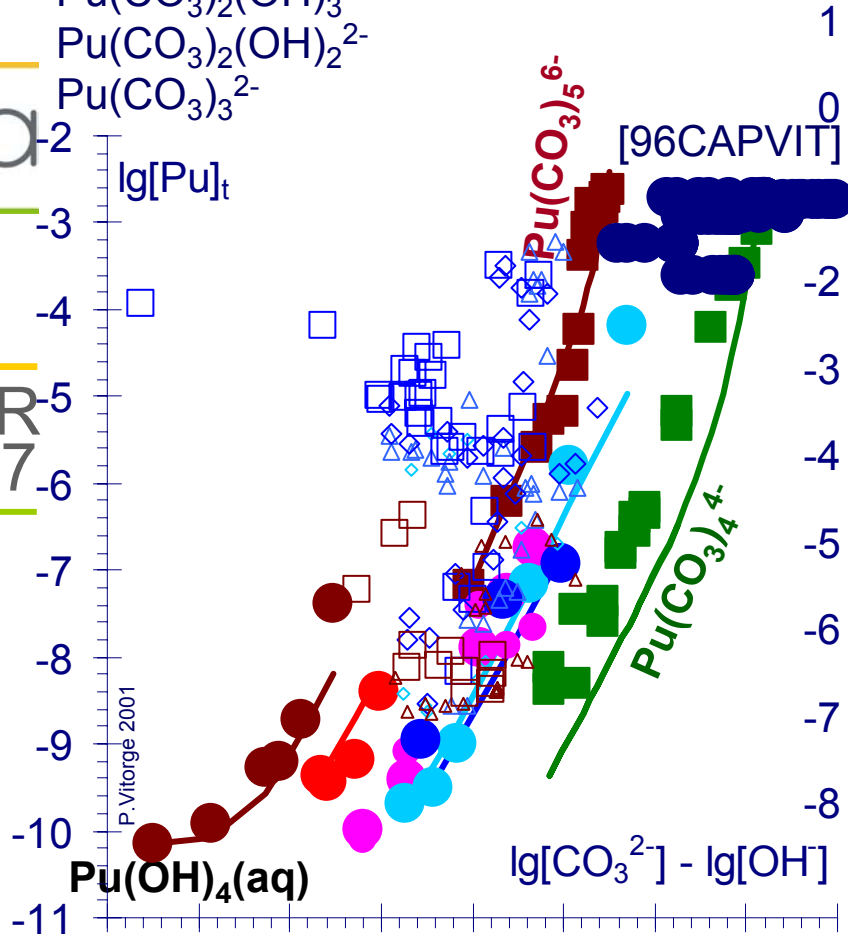
Pu(IV) solubility in carbonate media

Other possible species:

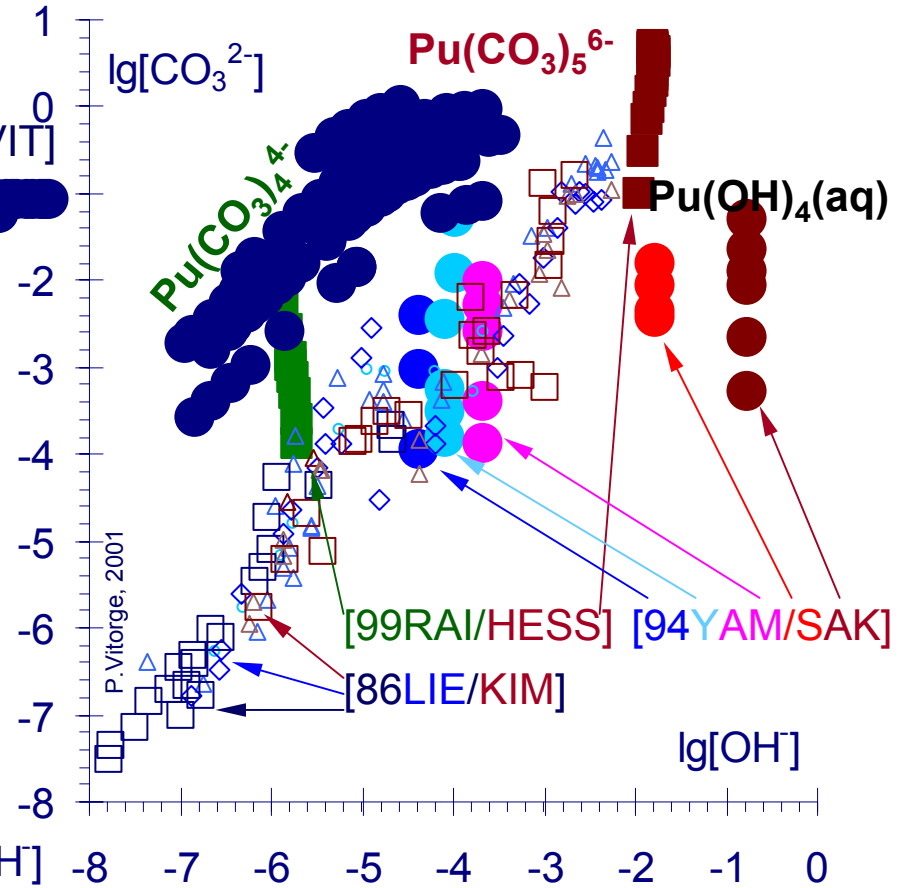


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Solubility

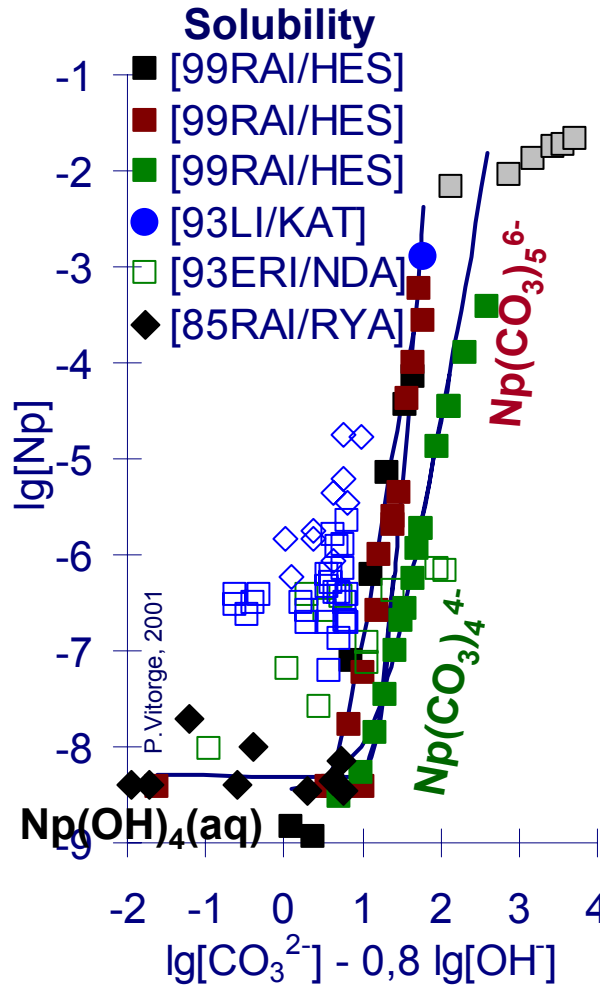


Experimental conditions



$\text{Pu}(\text{CO}_3)_5^{6-}$ + $\text{Pu}(\text{CO}_3)_4^{4-}$ are enough to account for experimental observation at high $\text{CO}_2(\text{g})$ partial pressure. Adding $\text{Pu}(\text{OH})_4(\text{aq})$ is enough to account for most of the other experimental data; however, **experimental solubilities are not consistent and activity coefficients were fitted.**

Np(IV) solubility in carbonate media



The way NEA TDB selected data

R.Lemire, J.Fuger, H.Nitsche, M.Rand, K.Spahiu, J.Sullivan, W.Ullman, P.Vitorge. *Chemical Thermodynamics of Neptunium and Plutonium*. Paris OCDE AEN, Elsevier (2001).

$\text{Np}(\text{CO}_3)_5^{6-} + \text{Np}(\text{CO}_3)_4^{4-}$ are enough to account for experimental observation at high $\text{CO}_2(\text{g})$ partial pressure. Adding $\text{Np}(\text{OH})_4(\text{aq})$ is enough to account for most of the other experimental data; however, **experimental solubilities are not consistent and activity coefficients were fitted.**



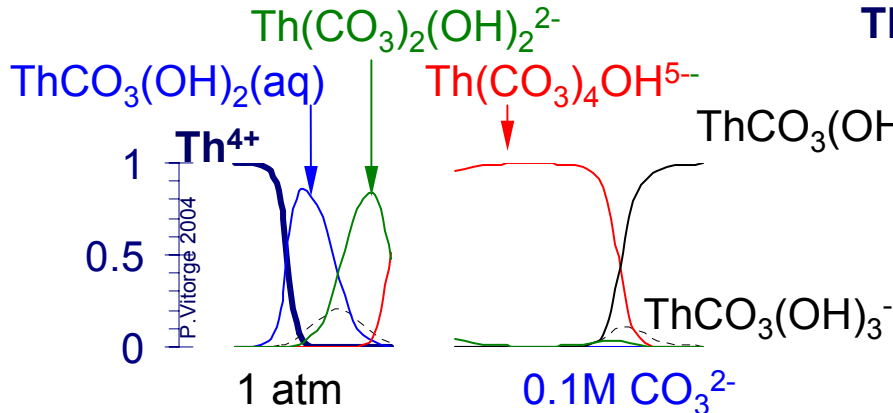
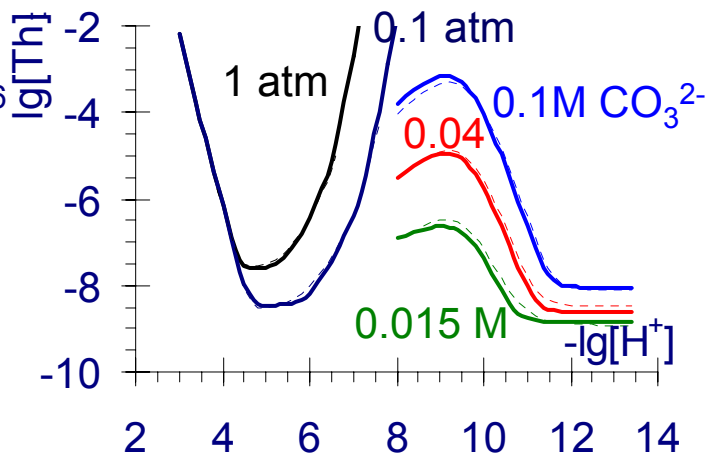
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Th solubility in carbonate media

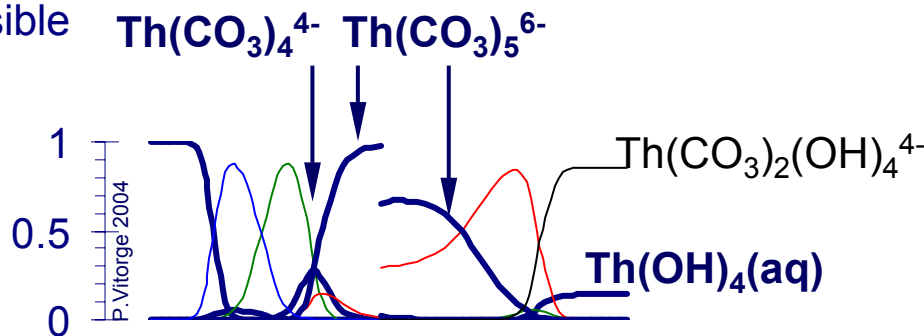
M. Altmaier, V. Neck, Th. Fanghänel NRC6 2004- O3



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Another possible interpretation



A possible interpretation; however: comparing with **other published data?**

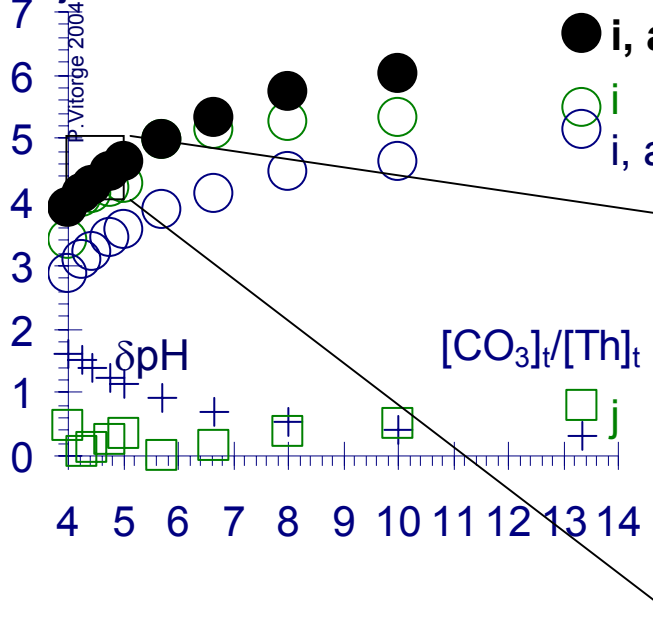
- D.Rai, D.Moore, C.Oakes, and M.Yui (2000)
- N.Hess, A.Felmy, D.Rai, and S.Conradson (1997).
- D.Rai, A.Felmy, D.Moore, M.Mason (1995)
- D.Rai, D.Moore, M.Yui (2000)
- D.Rai, N.Hess, A.Felmy, D.Moore, M.Yui (1999)
- D.Rai, L.Rao, H.Weger, A.Felmy, G.Choppin, and M.Yui (1999)
- D.Rai, A.Felmy, M.Mason, N.Hess (1996)

$\text{Th}(\text{CO}_3)_i^{4-2i}$ complexes are stable for $i = 4, 5$ (and 6?) at high I and $[\text{CO}_3^{2-}]$; $\text{ThCO}_3(\text{OH})_4^{2-}$ measured **activity coefficients** are needed for comparisons.

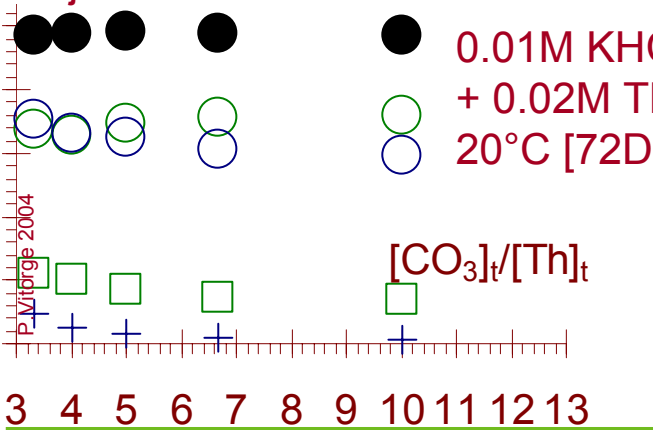
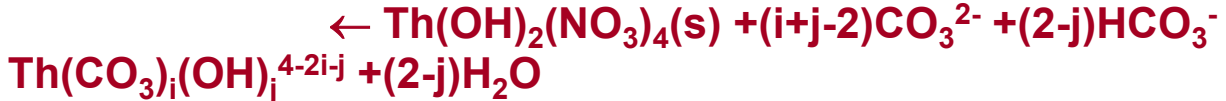
Evidence of $\text{Th}(\text{CO}_3)_5^{6-}$ in **0.16-0.3 M K_2CO_3** (2M Na^+), in **0.2-1 M KHCO_3** (2M Na^+), and in **0.1 M K_2CO_3 or KHCO_3** (0.08M K^+)
Dissociation into $\text{Th}(\text{CO}_3)_4^{4-}$? Also proposed at low ionic strength in 0.001 M K_2CO_3 , and in 0.01 M KHCO_3 + <0.01M K_2CO_3 aqueous solutions [72DER].



Th limiting carbonate complex



0.01M KHCO₃/K₂CO₃ 0.1M KNO₃
+ 0.02M Th(NO₃)₄
20°C [72DER]



0.01 M KHCO₃ + <0.01M K₂CO₃
aqueous solutions [72DER].

Th and Pu(IV) possible (hydroxo-)carbonate complexes

$M(\text{CO}_3)_i(\text{OH})_j^{(4-2i-j)+}$	$\lg\beta_{ij}^0(\text{Pu})^1$	$\lg\beta_{ij}(\text{Th})^2$	$\lg\beta_{ij}(\text{Th})^3$
M^{4+}			
MOH^{3+}	13.2		<8.7
$\text{M}(\text{OH})_4(\text{aq})$	< 47.9		27.4
$\text{MCO}_3(\text{OH})_2(\text{aq})$	<<42	27.0	26.9
$\text{MCO}_3(\text{OH})_3^-$	<<47.7	34.8	
$\text{M}(\text{CO}_3)_2\text{OH}^-$	<40.5		<25.6
$\text{MCO}_3(\text{OH})_4^{2-}$	<<51.8	37.4	<34
$\text{M}(\text{CO}_3)_2(\text{OH})_2^{2-}$	<46.2	33.3	33.3
$\text{M}(\text{CO}_3)_3^{2-}$	<37.6		<22.6
$\text{M}(\text{CO}_3)_2(\text{OH})_3^{3-}$	<50.5		<36.6
$\text{M}(\text{CO}_3)_3\text{OH}^{3-}$	<42		<31.4
$\text{M}(\text{CO}_3)_2(\text{OH})_4^{4-}$			38.4
$\text{M}(\text{CO}_3)_3(\text{OH})_2^{4-}$	<<41		<35.7
$\text{M}(\text{CO}_3)_4^{4-}$	37		27.4
$\text{M}(\text{CO}_3)_3(\text{OH})_3^{5-}$	<<40.5		<39.5
$\text{M}(\text{CO}_3)_4\text{OH}^{5-}$	<<39	34.4	34.1
$\text{M}(\text{CO}_3)_3(\text{OH})_4^{6-}$	<<38.5		<39.3
$\text{M}(\text{CO}_3)_4(\text{OH})_2^{6-}$	<<37		<36.4
$\text{M}(\text{CO}_3)_5^{6-}$	35.6		31.5

→ Maximum possible stabilities estimated for Pu complexes¹ are **consistent** with the values proposed or estimated for Th.

→ Depending on their stoichiometries, many possible mixed complexes would be more stable **in the experimental conditions of the Th study: corresponding estimation of the upper limits of their stability constants are closer to the actual value.**

→ **However not all published experimental data have been taken into account for Th.**

¹P.Vitorge, H.Capdevila. Radiochim. Acta 91, 623–631 (2003)

²M. Altmaier, V. Neck, Th. Fanghänel NRC6 2004- O3

³Another possible interpretation of experimental data from Ref.²



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**Maximum possible possible values for stabilities,
a conservative approach
a way for comparing published experimental data**



Actual stabilities

**Coordination chemistry
(including mixed hydroxo-carbonate complexes)**

**Bridging ligands?
(polynuclear complexes)**

**Activity coefficients
(ion pairing and structure of concentrated electrolytes)**

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