

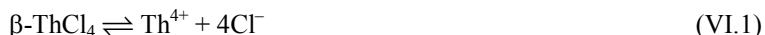
## VI The aqueous Th<sup>4+</sup> ion

There is no firm evidence for the stability of any valency state other than Th(IV) in aqueous media. Recently, Klappköté and Schulz [1997KLA/SCH] claimed to have identified Th<sup>3+</sup> in the reaction of Th<sup>4+</sup> with HN<sub>3</sub> in slightly acidic solutions (pH = *ca.* 3.5), by absorption and ESR spectra. However, as noted in Appendix A, Ionova *et al.* [1998ION/MAD] have seriously questioned both the value of  $E^\circ$  (Th<sup>3+</sup>/Th<sup>4+</sup>) chosen by [1997KLA/SCH] in their thermodynamic analysis and the validity of their conclusions, pointing out that the absorption bands observed by these authors could equally well be due to azide complexes of Th(IV), with or without Cl<sup>-</sup> ligands. Moreover, the stability of HN<sub>3</sub> in dilute aqueous solutions suggests that the proposed reduction of Th<sup>4+</sup> is unlikely to be thermodynamically controlled as suggested in [1997KLA/SCH]. Thus there seems no incontrovertible evidence for the existence of any stable ions in aqueous solutions other than Th(IV) and its derivatives.

### VI.1 Thermodynamic data for the Th<sup>4+</sup> ion

The enthalpy of formation of Th<sup>4+</sup> is derived from measurements of the enthalpy of solution in HCl solutions. Unless some fluorosilicate ion is present, this reaction leaves variable amounts of a black residue, probably an oxide hydride containing chloride and hydroxide ions, ThO(Cl,OH)H [1962KAT/KAP], [1973ACK/RAU3] (see Appendix A).

The standard enthalpy of formation of Th<sup>4+</sup>,  $\Delta_f H_m^\circ$  (Th<sup>4+</sup>, 298.15 K), is obtained from  $\Delta_f H_m^\circ$  (ThCl<sub>4</sub>,  $\beta$ , 298.15 K), and the extrapolation of the enthalpy of solution of ThCl<sub>4</sub> in HCl solutions to infinite dilution, according to reaction:



The enthalpy of formation of thorium tetrachloride itself (see Section VIII.2) involves the enthalpy of dissolution of thorium metal and of thorium tetrachloride in HCl solutions at various concentrations, the data for which are summarised in Table VI-1.

With the exception of the result from [1981BUR/KIJ2], which is cited for information only (see Appendix A), Figure VI-1 shows a plot of all the existing values for the enthalpy of solution of  $\beta$ -ThCl<sub>4</sub> as a function of the molality (*m*) of the HCl solutions, after correction ( $-1.25 \text{ kJ}\cdot\text{mol}^{-1}$ ) for the presence of Na<sub>2</sub>SiF<sub>6</sub> in some experiments. A linear extrapolation:

$$\Delta_{\text{sol}} H_m^\circ (\text{ThCl}_4, \beta) = -250.658 + 9.4002 m \quad \text{kJ}\cdot\text{mol}^{-1} \quad (\text{VI.2})$$

yields at zero ionic strength the selected value  $\Delta_{\text{sol}} H_m^\circ$  (ThCl<sub>4</sub>,  $\beta$ , 298.15 K) =  $-(250.7 \pm 1.8) \text{ kJ}\cdot\text{mol}^{-1}$ , the uncertainty being the  $2\sigma$  value from the linear regression; hence, using  $\Delta_f H_m^\circ$  (Cl<sup>-</sup>, 298.15 K) =  $-(167.080 \pm 0.100) \text{ kJ}\cdot\text{mol}^{-1}$  from [1989COX/WAG] and  $\Delta_f H_m^\circ$  (ThCl<sub>4</sub>,  $\beta$ , 298.15 K) =  $-(1186.3 \pm 1.3) \text{ kJ}\cdot\text{mol}^{-1}$  (see Section VIII.2),  $\Delta_f H_m^\circ$  (Th<sup>4+</sup>, 298.15 K) =  $-(768.7 \pm 2.3) \text{ kJ}\cdot\text{mol}^{-1}$ . This is very similar

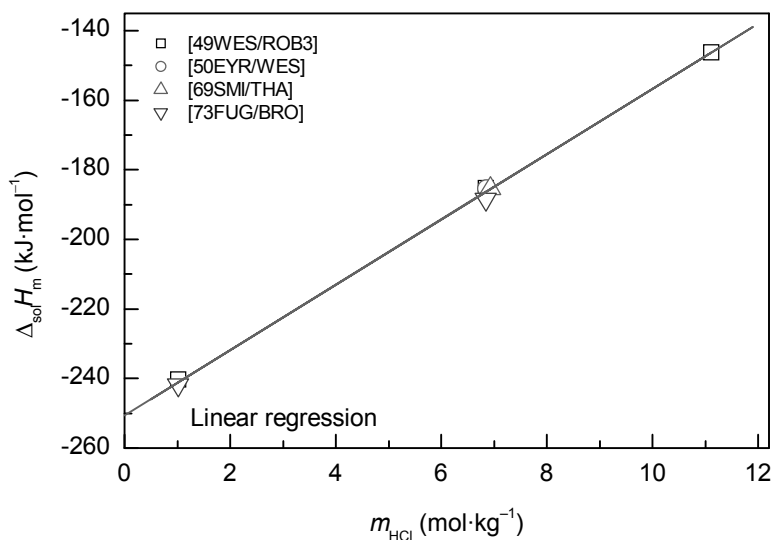
to the value obtained by [1975RAN] and [1976FUG/OET], using slightly different auxiliary data.

Table VI-1: Enthalpy of solution of  $\beta\text{-ThCl}_4$  in hydrochloric acid at various concentrations.

Medium		$\Delta_{\text{sol}}H_m$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )	Reference
HCl Molarity	HCl Molality		
1.000	1.0222	$-240.25 \pm 0.42$	[1949WES/ROB3]
1.00	1.0222	$-241.8 \pm 0.7$	[1973FUG/BRO]
1.00	1.0222	$-242.4 \pm 1.9$	[1981BUR/KIJ2]
6.000	6.8510	$-185.23 \pm 0.42$	[1949WES/ROB3]
6.00	6.8510	$-188.3 \pm 0.4$	[1973FUG/BRO]
6.004	6.8563	$-185.27 \pm 0.25$	[1950EYR/WES]
6.004 *	6.8563	$-186.52 \pm 0.33$	[1950EYR/WES]
6.06 *	6.9297	$-186.8 \pm 0.8$	[1969SMI/THA]
9.000	11.1107	$-146.15 \pm 0.42$	[1949WES/ROB3]

\*: containing 0.005M  $\text{Na}_2\text{SiF}_6$ . The influence of the fluorosilicate ion on the enthalpy of solution of  $\beta\text{-ThCl}_4$  in hydrochloric acid is discussed in Section VIII.2.1.3.1.

Figure VI-1: Enthalpy of solution of  $\beta\text{-ThCl}_4$  as a function of HCl molality.



In spite of its theoretical limitations, this linear extrapolation of the thorium data was adopted by [1975RAN] and [1976FUG/OET]. As pointed out by Wagman [1976WAG], a Debye-Hückel correction of the solution data, followed by an extrapolation against the ionic strength, yields an extrapolated value of  $\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{ThCl}_4, \beta) = -(260.7 \pm 4.2) \text{ kJ}\cdot\text{mol}^{-1}$  while a correction using Vasil'ev's method [1967VAS] as modified by Khodakovskiy [1975KHO] yielded  $\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{ThCl}_4, \beta) = -262.3 \text{ kJ}\cdot\text{mol}^{-1}$ . The extrapolation of thermal data to infinite dilution is discussed in some detail in [1997GRE/PLY2].

It was indeed noted by Wagman [1976WAG] that, although the more elaborate extrapolation was proper, the same situation occurs with the values for the dissolution of  $\text{UCl}_4(\text{cr})$  in HCl solutions. In that case also, substitution of a linear extrapolation by a more elaborate Debye-Hückel treatment would shift the enthalpy of formation of  $\text{U}^{4+}$  and several other values. Wagman noted that such a shift would result in a slightly poorer agreement in the various paths in the uranium ion network.

It is interesting to note that in both of the subsequent NBS assessments, [1977WAG/SCH] and the latest NBS Tables [1982WAG/EVA], the linear extrapolation was used to obtain the reported  $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{Th}^{4+}) = -769.0 \text{ kJ}\cdot\text{mol}^{-1}$ , using the then current auxiliary data.

In view of this situation, and also for consistency with other actinides, we will maintain in this review, as in [1976FUG/OET], the use of a linear extrapolation for the enthalpy of solution of  $\beta\text{-ThCl}_4$  to infinite dilution.

With  $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{ThCl}_4, \beta, 298.15 \text{ K}) = -(1186.3 \pm 1.3) \text{ kJ}\cdot\text{mol}^{-1}$  (see Section VIII.2), we thus obtain, from Reaction (VI.1):

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{Th}^{4+}, 298.15 \text{ K}) = -(768.7 \pm 2.3) \text{ kJ}\cdot\text{mol}^{-1}$$

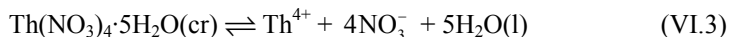
which is the selected value.

So-called "absolute" standard molar enthalpies of hydration of a number of individual ions, including  $\text{Th}^{4+}$ , have been obtained by using a combination of experimental data and estimates based on the extra-thermodynamic assumptions that  $\Delta_{\text{hyd}}H_{\text{m}}^{\circ}((\text{C}_6\text{H}_5)_4\text{As}^+) = \Delta_{\text{hyd}}H_{\text{m}}^{\circ}((\text{C}_6\text{H}_5)_4\text{P}^+) = \Delta_{\text{hyd}}H_{\text{m}}^{\circ}(\text{B}(\text{C}_6\text{H}_5)_4^-)$ . There is an extensive survey of the literature on the hydration of ions in the paper of Marcus [1987MAR2] and a claim that the "absolute" enthalpy of hydration of  $\text{H}^+$  is known with an accuracy of  $5 \text{ kJ}\cdot\text{mol}^{-1}$ . This value is then used to calculate the individual ion enthalpies of hydration listed therein; the value for  $\Delta_{\text{hyd}}H_{\text{m}}^{\circ}(\text{Th}^{4+})$  is  $-6057 \text{ kJ}\cdot\text{mol}^{-1}$ . As this value is based on extra-thermodynamic assumptions it is not accepted by this review.

Use of  $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{ThCl}_4, \beta, 298.15 \text{ K}) = -(1186.3 \pm 1.3) \text{ kJ}\cdot\text{mol}^{-1}$  and Equation (VI.2) leads to the values  $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{Th}^{4+}, 1.00 \text{ M HCl}) = -(769.877 \pm 1.600) \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{Th}^{4+}, 6.00 \text{ M HCl}) = -(758.957 \pm 1.600) \text{ kJ}\cdot\text{mol}^{-1}$ ; these values are used in later

assessments. They include the contributions from all the complex species present in 1.00 and 6.00 M HCl media.

The entropy of  $\text{Th}^{4+}$  was calculated by Morss and McCue [1976MOR/MCC], based on the measurement of the solubility and the enthalpy of solution of thorium nitrate pentahydrate, at infinite dilution, according to reaction:



which yielded  $\Delta_r H_m^\circ$  ((VI.3), 298.15 K) =  $-(19.807 \pm 0.250)$  kJ·mol<sup>-1</sup>. The uncertainty limits of the latter value are estimated by this review taking into account the uncertainties in the individual experimental results and the correction for hydrolysis. The measured entropy  $S_m^\circ(\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = (543.1 \pm 0.8)$  J·K<sup>-1</sup>·mol<sup>-1</sup> is from [1976CHE/WES]. This review has used these values, together with the solubility and activity coefficient data, to derive the standard entropy of  $\text{Th}^{4+}$ . The solubility of the salt at 298.15 K was taken by [1976MOR/MCC] as  $(3.7 \pm 0.1)$  mol·kg<sup>-1</sup> based on the values of 3.74 mol·kg<sup>-1</sup> reported by Appelblat *et al.* [1973APE/AZO] and 3.66 mol·kg<sup>-1</sup> obtained by [1976MOR/MCC]. The value of  $(3.7 \pm 0.1)$  mol·kg<sup>-1</sup> is also used in this review.

The activity coefficient data of thorium nitrate in saturated solution have been calculated by [1975WAG] (personal communication to the authors of [1976MOR/MCC]) based on the vapour pressure measurements of [1947ROB/LEV]. This calculation incorporated a Debye-Hückel treatment and yielded a mean activity coefficient,  $\gamma_{\pm}$ , of 0.377. The results of vapour pressure measurements of [1947ROB/LEV] are preferred to those of [1973APE/AZO2] because they are more consistent. For the calculation of the water activity, the molal osmotic coefficient,  $\phi$ , was taken as 1.673 from [1973APE/AZO2].

Use of selected auxiliary data for the entropies of the nitrate ion and of water leads to the value  $S_m^\circ(\text{Th}^{4+}, 298.15 \text{ K}) = -(423.1 \pm 2.3)$  J·K<sup>-1</sup>·mol<sup>-1</sup>. Noting that the use of the vapour pressure data of [1973APE/AZO2] would have led to an entropy value *ca.* 16 J·K<sup>-1</sup>·mol<sup>-1</sup> more negative, we will take more conservative uncertainty limits and adopt the value:

$$S_m^\circ(\text{Th}^{4+}, 298.15 \text{ K}) = -(423.1 \pm 16.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

Morss and McCue [1976MOR/MCC] reported a value of  $C_{p,m}^\circ(\text{Th}^{4+}, 298.15 \text{ K}) = -(1 \pm 11)$  J·K<sup>-1</sup>·mol<sup>-1</sup> based on their integral heats of dilution of  $\text{Th}(\text{NO}_3)_4$  at 288.15, 298.15 and 308.15 K. Apelblat and Sahar [1975APE/SAH] reported bulk heat capacity and heat of dilution of thorium nitrate solutions at 303.15 K.

More recently, Hovey [1997HOV] obtained the value  $C_{p,m}^\circ(\text{Th}^{4+}, 298.15 \text{ K}) = -(224 \pm 5)$  J·K<sup>-1</sup>·mol<sup>-1</sup>. This author also reviewed earlier attempts to estimate the partial molar heat capacity of the  $\text{Th}^{4+}$  ion. Using a more recent value for the heat capacity of the nitrate ion  $C_{p,m}^\circ(\text{NO}_3^-, 298.15 \text{ K}) = -72$  J·K<sup>-1</sup>·mol<sup>-1</sup>,

[1988HOV/HEP3], he recalculated the results of [1976MOR/MCC], obtaining  $C_{p,m}^{\circ}(\text{Th}^{4+}, 298.15 \text{ K}) = -(60 \pm 11) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . He also obtained  $C_{p,m}^{\circ}(\text{Th}^{4+}, 303.15 \text{ K}) = 111 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  from the data of [1975APE/SAH], using  $C_{p,m}^{\circ}(\text{NO}_3^-, 303.15 \text{ K}) = -63.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , from [1989HOV/HEP]. Reasons for the large discrepancy of the value deduced from the results of [1975APE/SAH] are briefly discussed in the comments on [1997HOV] in Appendix A. As the results of [1997HOV] arise from differential measurements, as compared to the integral enthalpy measurements by [1976MOR/MCC], and also because this author selected experimental conditions which minimised hydrolysis and complexation, his results are preferred. Nevertheless we feel that the differences from the earlier values noted above are so large that his estimated uncertainty of  $\pm 5 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  (assumed to be  $1\sigma$ ) is probably too small. In view of this, and the lack of comparative determinations for other tetravalent ions, the uncertainty has been increased to  $\pm 15 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ , and the selected value is

$$C_{p,m}^{\circ}(\text{Th}^{4+}, 298.15 \text{ K}) = -(224 \pm 15) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}.$$

The analysis of the results of [1997HOV] in Appendix A is essentially that from [2003GUI/FAN], as these results served as basis for the adoption of new values for the heat capacity of the U<sup>4+</sup> and U<sup>3+</sup> aqueous ions.

Combining the selected molar standard enthalpy of formation and entropy yields the selected molar standard Gibbs energy of formation:

$$\Delta_f G_m^{\circ}(\text{Th}^{4+}, 298.15 \text{ K}) = -(704.783 \pm 5.298) \text{ kJ}\cdot\text{mol}^{-1}.$$

This unusually large uncertainty arises mainly from the large uncertainty in the entropy, in turn arising from the uncertainty in the vapour pressure of saturated Th(NO<sub>3</sub>)<sub>4</sub> solution.

## VI.2 Hydration of the Th<sup>4+</sup> ion

As a result of its high charge and large ionic radius one expects a high coordination number for the Th<sup>4+</sup> ion. This has been confirmed by direct structure determinations using large angle X-ray scattering (LAXS) [1968JOH2], [1991JOH/MAG] and EXAFS data [1999MOL/DEN] and [2002ROT/DEN]. The first of these studies was made at a very high total concentration of Th(IV), 1.94 M. Johansson [1968JOH] reports a Th–O distance in the first shell equal to  $(2.51 \pm 0.03) \text{ \AA}$ , relating to coordinated water and additional features assigned to the coordination of four bidentate nitrate ligands, resulting in a coordination number of 12 for Th(IV). This assignment seems reasonable, as the data have been collected in solutions with a very high concentration of nitrate; however, the structural model proposed is not unique. In [1991JOH/MAG], the authors have collected three different sets of LAXS data from concentrated (1–2.5 m) Th(IV) solutions containing high concentrations (4–11 m) of perchlorate, chloride and nitrate, respectively. The perchlorate data indicate a coordination number of  $(8.5 \pm 0.5)$  with a

Th–OH<sub>2</sub> distance of 2.48 Å; the perchlorate ions are located in the second coordination sphere. The data from chloride solutions indicate a coordination number of 10.5, mainly coordinated water but with indications of some coordination of chloride (the model used is not unique). The large difference in coordination number is certainly an artefact due to experimental uncertainties and the difficulty in obtaining a unique structural model. The data from nitrate solution indicate very clearly bonding of nitrate, probably bidentate, in the first coordination sphere. The LAXS data suggests that the bonding of nitrate to Th(IV) is much stronger than that of perchlorate and chloride, in agreement with solution chemical data discussed in Sections VIII.2.2.1 and X.1.3.3. The EXAFS data were collected in perchlorate solutions with a much lower total concentration of thorium. In [1999MOL/DEN] the concentration of Th(IV) was 0.03 and 0.05 M in 1.5 M HClO<sub>4</sub> and these data are accordingly better suited to obtain information of the aquo ion. The reported bond distance Th–OH<sub>2</sub> is equal to  $(2.45 \pm 0.01)$  Å and the coordination number  $(10 \pm 1)$ . The second EXAFS study [2002ROT/DEN] was made using 0.055 M Th(IV) in 1.5 M HClO<sub>4</sub>, and gives a Th–OH<sub>2</sub> distance of 2.45 Å and a coordination number of 12.7. The uncertainty in the coordination number as determined from EXAFS data is in general large, while the bond distances are much more accurate as indicated above. The data above demonstrate that it is not possible to obtain an accurate value of the coordination number for the  $\text{Th}^{4+}$  ion from EXAFS data alone; it is also not possible to deduce a three-dimensional structure. Information of this type may be obtained by using quantum chemical methods as shown in [2001YAN/TSU], [2002YAN/TSU] and [2003OKA/MOC]. The authors suggest that the most stable geometry is obtained for the complex  $[\text{Th}(\text{OH}_2)_9]^{4+}$  with  $C_{4v}$  geometry. The calculated Th–OH<sub>2</sub> distance for this complex is 2.54 Å in fair agreement with the experimental EXAFS data. The calculations also indicate that the energy difference between complexes of different geometry is small (a few  $\text{kJ}\cdot\text{mol}^{-1}$ ), as is the energy difference between aquo ions with nine and ten coordinated water molecules.

The dynamics of water exchange between the water solvent and the  $\text{Th}^{4+}$  ion has been investigated using <sup>17</sup>O NMR [2000FAR/GRE] and these data indicate a rate constant at 25°C,  $k_{\text{ex}} > 5 \times 10^7 \text{ s}^{-1}$ , significantly larger than that for the corresponding  $\text{U}^{4+}$  ion,  $k_{\text{ex}} = 5.4 \times 10^6 \text{ s}^{-1}$ . Farkas *et al.* [2000FAR/GRE] discuss the mechanism of the exchange reaction and suggest that this is dissociative if the coordination number of the aqua ion is ten and associative if it is nine. This conclusion is supported by the quantum chemical studies of Yang *et al.* [2003TSU/YAN], [2003YAN/TSU].

Marcus [1991MAR2] has estimated the average hydration number of  $\text{Th}^{4+}$ ,  $n_{\text{hyd}} = 14.4$ , and the Gibbs energy of hydration,  $-5395 \text{ kJ}\cdot\text{mol}^{-1}$ , by using an empirical electrostatic model. The hydration number has also been estimated in [1972SAT], using compressibility data. For reasons given in Appendix A the data in these two studies have not been accepted by this review.

Based on the available experimental and quantum chemical data this review suggests that the coordination number in the Th<sup>4+</sup> ion is either nine or ten and that the energy difference between them is small, less than 10 kJ·mol<sup>-1</sup>.

### VI.3 Ion interaction coefficients of the Th<sup>4+</sup> ion

Experimental studies on the hydrolysis of the Th<sup>4+</sup> ion, its complexes with strong inorganic ligands, and the solubility of thorium oxides or hydroxides are usually performed with low concentrations of thorium in perchlorate, chloride, and nitrate media. There is no evidence for complex formation between Th<sup>4+</sup> and ClO<sub>4</sub><sup>-</sup>; however, chloride and nitrate form weak Th(IV) complexes as discussed in Sections VIII.2.2.1 and X.1.3.3, respectively. For the evaluation of equilibrium constants at zero ionic strength from data in chloride and nitrate media we have therefore the general problem to decide if the activity of Th<sup>4+</sup>,  $a_{\text{Th}^{4+}} = m_{\text{Th}^{4+}} \cdot \gamma_{\text{Th}^{4+}}$ , should be calculated using a complex formation or a strict ion interaction model.

#### ▪ Complex formation model

The formation of complexes between Th<sup>4+</sup> and X<sup>-</sup> = Cl<sup>-</sup> or NO<sub>3</sub><sup>-</sup> is described with the equilibrium constants  $\beta_n$  for the reactions:



The concentration of free Th<sup>4+</sup> is calculated from the total thorium concentration  $m_{\text{Th}}$  according to:

$$m_{\text{Th}^{4+}} = m_{\text{Th}} - \sum m_{\text{ThX}_n^{4-n}} = \frac{m_{\text{Th}}}{1 + \sum \beta_n (m_{\text{X}^-})^n} \quad (\text{VI.5})$$

The activity coefficients of Th<sup>4+</sup> and the complexes ThX<sub>n</sub><sup>4-n</sup> are calculated with the specific ion interaction theory, SIT, assuming that log<sub>10</sub>γ<sub>Th<sup>4+</sup></sub> and log<sub>10</sub>γ<sub>ThX<sub>n</sub><sup>4-n</sup></sub> in chloride or nitrate solution or in (H<sup>+</sup>/Na<sup>+</sup>)(X<sup>-</sup>/ClO<sub>4</sub><sup>-</sup>) mixtures are the same as in pure perchlorate solution of the same ionic strength, *i.e.*, with the simplifications  $\varepsilon(\text{Th}^{4+}, \text{X}^-) = \varepsilon(\text{Th}^{4+}, \text{ClO}_4^-)$  and  $\varepsilon(\text{ThX}_n^{4-n}, \text{X}^-) = \varepsilon(\text{ThX}_n^{4-n}, \text{ClO}_4^-)$ . Since no negatively charged ThCl<sub>n</sub><sup>4-n</sup> complexes are formed, the Th<sup>4+</sup> activity in chloride or nitrate solutions and in mixtures with perchlorate is given by:

$$\log_{10} a_{\text{Th}^{4+}} = \log_{10} m_{\text{Th}} - \log_{10} \{1 + \sum \beta_n (m_{\text{X}^-})^n\} - 16 D + \varepsilon(\text{Th}^{4+}, \text{ClO}_4^-) \cdot (m_{\text{X}^-} + m_{\text{ClO}_4^-}) \quad (\text{VI.6})$$

#### ▪ Ion interaction model

The weak Th(IV) chloride or nitrate complexes are not explicitly taken into account, *i.e.*, the simplification is made that  $m_{\text{Th}^{4+}} = m_{\text{Th}}$ . The decrease of the Th<sup>4+</sup> activity due to complex formation with X<sup>-</sup> is described by the specific ion interaction coefficient  $\varepsilon(\text{Th}^{4+}, \text{X}^-)$  which is therefore lower than  $\varepsilon(\text{Th}^{4+}, \text{ClO}_4^-)$ . The Th<sup>4+</sup> activity in chloride or nitrate solutions and in mixtures with perchlorate is thus given by:

$$\log_{10} a_{\text{Th}^{4+}} = \log_{10} m_{\text{Th}} - 16 D + \varepsilon(\text{Th}^{4+}, \text{X}^-) \cdot m_{\text{X}^-} + \varepsilon(\text{Th}^{4+}, \text{ClO}_4^-) \cdot m_{\text{ClO}_4^-} \quad (\text{VI.7})$$

SIT coefficients referring to this approach, mostly derived from osmotic coefficients in binary metal chloride or nitrate solutions [1980CIA], are reported in the previous NEA-TDB reviews. However, only the more recent reviews [2001LEM/FUG], [2003GUI/FAN] used the corresponding values of  $\varepsilon(\text{AnO}_2^+, \text{Cl}^-)$ ,  $\varepsilon(\text{An}^{3+}, \text{Cl}^-)$ , and  $\varepsilon(\text{An}^{4+}, \text{Cl}^-)$  to calculate equilibrium constants for the solubility, hydroxide and carbonate complexes of actinides from experimental data in chloride media.

In the following, the two models are illustrated using U(IV) as an analogue for Th(IV). Figure VI-2 shows a comparison between the complexation and ion interaction models for U(IV) as a trace component in nitrate and nitrate-perchlorate solution. The system U(IV)-NO<sub>3</sub><sup>-</sup> is chosen as an example because it is well studied by different authors using different methods at widely varying ionic strength, including spectroscopy (*cf.* [1992GRE/FUG]). In the NEA-TDB review on uranium [1992GRE/FUG], the available experimental data were well described with the nitrate complexation model. Figure VI-2 shows that the activity of the U<sup>4+</sup> ion and hence the equilibria in acidic nitrate solution and nitrate-perchlorate mixtures can be described with about same accuracy using the ion interaction approach.

The parameters used for the nitrate complexation model (all data from [1992GRE/FUG]) are:

$$\begin{aligned} \log_{10} \beta_1^\circ &= (1.47 \pm 0.13), \\ \Delta\varepsilon(\text{VI.4}, \text{X}^- = \text{NO}_3^-, n = 1) &= -(0.21 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1} \text{ in HClO}_4\text{-HNO}_3 \text{ solution}, \\ \log_{10} \beta_2^\circ &= (2.30 \pm 0.35), \\ \Delta\varepsilon(\text{VI.4}, \text{X}^- = \text{NO}_3^-, n = 2) &= -(0.41 \pm 0.13) \text{ kg} \cdot \text{mol}^{-1} \text{ in HClO}_4\text{-HNO}_3 \text{ solution}, \\ \varepsilon(\text{U}^{4+}, \text{NO}_3^-) &= \varepsilon(\text{U}^{4+}, \text{ClO}_4^-) = (0.76 \pm 0.06) \text{ kg} \cdot \text{mol}^{-1}. \end{aligned}$$

and the parameters used for the ion interaction model (fitted by this review) are:

$$\varepsilon(\text{U}^{4+}, \text{NO}_3^-) = (0.34 \pm 0.06) \text{ kg} \cdot \text{mol}^{-1} < \varepsilon(\text{U}^{4+}, \text{ClO}_4^-) = (0.76 \pm 0.06) \text{ kg} \cdot \text{mol}^{-1}.$$

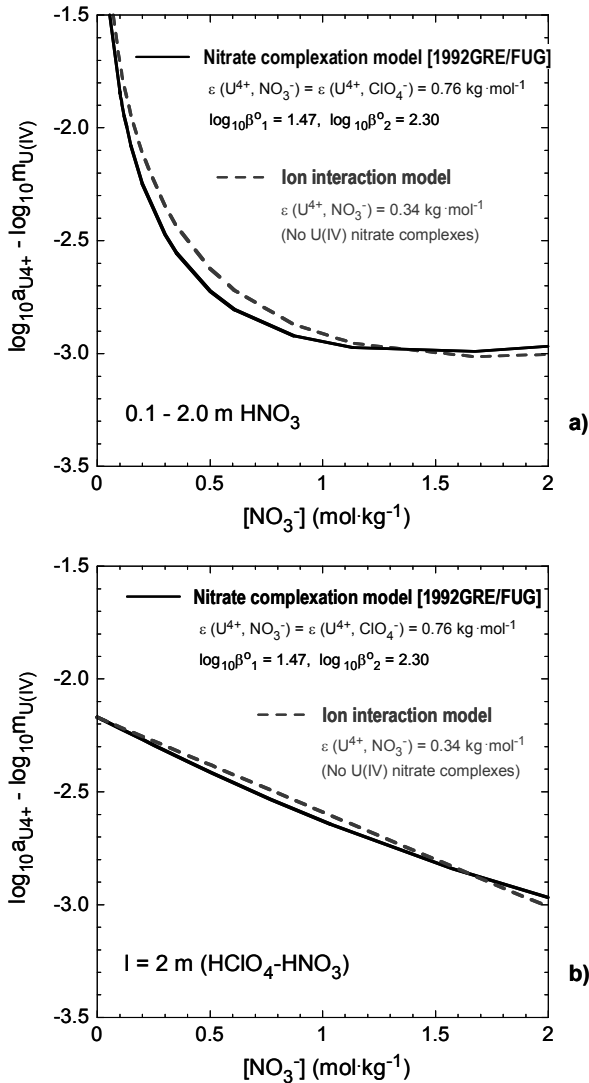
Similarly to the activity of U(IV) in nitrate solution, shown in Figure VI-2, that of Th<sup>4+</sup> in chloride and nitrate solution can be described equally well with either the complexation model or the ion interaction approach (*cf.* Appendix A reviews of [1952WAG/STO] and [2006NEC/ALT]). The application of the two models to thorium chloride and nitrate complexes is discussed in Sections VIII.2.2.1 and X.1.3.3, respectively.

The SIT coefficients used by this review for the determination of standard state solubility constants and equilibrium constants for hydroxide, fluoride, and carbonate complexes from experimental data in chloride and nitrate media refer to the strict ion interaction approach. They implicitly include the formation of weak Th(IV) complexes or ion pairs with nitrate and chloride ions. However, they must not be combined with



the formation constants of chloride and nitrate complexes discussed in Sections VIII.2.2.1 and X.1.3.3, where further comments are given.

Figure VI-2: Activity of  $\text{U}^{4+}$  relative to the total U(IV) concentration ( $\log_{10} a_{\text{U}^{4+}} - \log_{10} m_{\text{U(IV)}}$ ) at 25°C calculated with the complex formation model (solid lines) and the ion interaction model (dashed lines) for trace concentrations of U(IV) in (a) 0.1–2.0 m  $\text{HNO}_3$  and (b) 2.0 m  $\text{HClO}_4$ - $\text{HNO}_3$ .



The Pitzer coefficients used in the literature for actinide and other metal ions (*e.g.* in [1973PIT/MAY], [1991PIT], [1991FEL/RAI], [1997RAI/FEL], [1999FEL/RAI], [2000RAI/MOO], [1995NEC/FAN], [1998NEC/FAN], [1998FAN/KIM]) usually also refer to an ion interaction approach where the formation of weak complexes is included in the interaction coefficients.

### VI.3.1 SIT coefficients

The interaction coefficients  $\varepsilon(\text{Th}^{4+}, \text{NO}_3^-) = (0.11 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}$  and  $\varepsilon(\text{Th}^{4+}, \text{Cl}^-) = (0.25 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ , listed in the previous NEA-TDB reviews [1992GRE/FUG] to [2005HUM/AND], were calculated by Ciavatta [1980CIA]. They are based on isopiestic measurements and osmotic coefficients for Th(NO<sub>3</sub>)<sub>4</sub> and ThCl<sub>4</sub> solutions up to rather high concentrations from [1947ROB/LEV], [1955ROB], [1965ROB/STO]. However, these data are not well established [1955ROB]. Activity coefficients calculated for the Th<sup>4+</sup> ion as trace component in chloride solution with the ion interaction Pitzer parameters reported in [1992ROY/VOG] (based on emf data in ThCl<sub>4</sub>-HCl mixtures, also at rather high Th concentrations) and [1997RAI/FEL] deviate considerably from those calculated with the SIT, *cf.* discussion in Section VI.3.2.

There are no experimental studies available from which  $\varepsilon(\text{Th}^{4+}, \text{ClO}_4^-)$  can be deduced. A value of  $\varepsilon(\text{Th}^{4+}, \text{ClO}_4^-) = (0.67 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$  has been estimated in [2001NEC/KIM] assuming a linear correlation between the values of  $\varepsilon(\text{U}^{4+}, \text{ClO}_4^-) = (0.76 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$  [1992GRE/FUG],  $\varepsilon(\text{Np}^{4+}, \text{ClO}_4^-) = (0.82 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$  [1992GRE/FUG] and  $\varepsilon(\text{Pu}^{4+}, \text{ClO}_4^-) = (0.83 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$  [1998CAP/VIT] and the ionic radii of the tetravalent actinide ions, *cf.* Figure VI-3. In the later NEA-TDB reviews slightly different SIT coefficients were selected for Np<sup>4+</sup> and Pu<sup>4+</sup>, ( $\varepsilon(\text{Np}^{4+}, \text{ClO}_4^-) = (0.84 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$ ,  $\varepsilon(\text{Pu}^{4+}, \text{ClO}_4^-) = (0.82 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$  [2001LEM/FUG], [2003GUI/FAN]). With these values, the correlation *vs.* the ionic radius of the An<sup>4+</sup> ions (for coordination number CN = 8, [1994CHO/RIZ]) *cf.* Figure VI-3, leads to a slightly different value of:

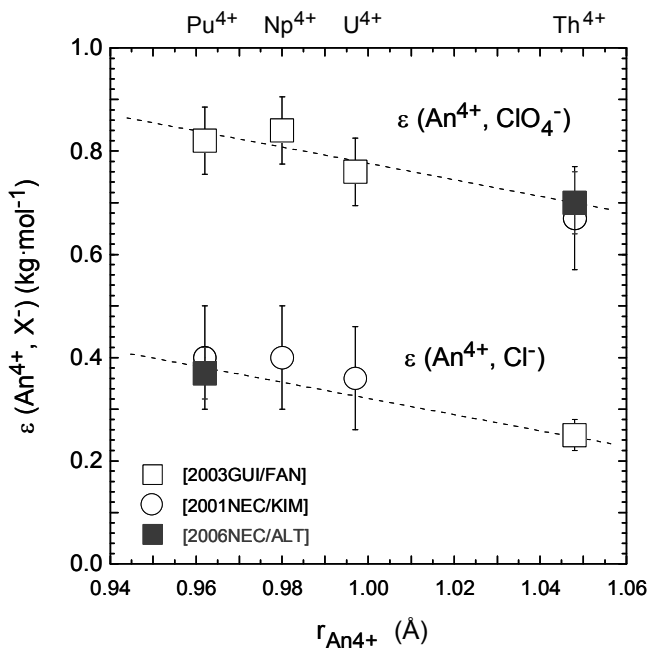
$$\varepsilon(\text{Th}^{4+}, \text{ClO}_4^-) = (0.70 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1},$$

which is selected in the present review.

The SIT coefficient  $\varepsilon(\text{Pu}^{4+}, \text{Cl}^-) = (0.37 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$  included in Figure VI-3 is calculated from the redox potentials  $E^\circ(\text{Pu}^{4+}/\text{Pu}^{3+})$  at  $I = 0$  and in 1.0 M HCl at 25°C, *i.e.* from the equilibrium constants  $\log_{10} K_{\text{IV/III}}(\text{Pu}^{4+} + e^- \rightleftharpoons \text{Pu}^{3+})$ . The values of  $E^\circ(\text{Pu}^{4+}/\text{Pu}^{3+}) = (1.047 \pm 0.003) \text{ V}$  and  $\log_{10} K_{\text{IV/III}}^\circ = (17.69 \pm 0.04)$  at  $I = 0$  selected by [2001LEM/FUG] are based on the redox potential  $E^\circ(\text{Pu}^{4+}/\text{Pu}^{3+}) = (0.9821 \pm 0.0005) \text{ V}$  ( $\log_{10} K_{\text{IV/III}} = (16.603 \pm 0.01)$ ) determined by Rabideau and Lemons [1951RAB/LEM] in 1.0 M HClO<sub>4</sub> at 25°C. Using the same experimental equipment, [1951RAB/LEM] also determined the redox potential in 1.0 M HCl at 25°C:  $E^\circ(\text{Pu}^{4+}/\text{Pu}^{3+}) = (0.9703 \pm 0.0005) \text{ V}$ , ( $\log_{10} K_{\text{IV/III}} = (16.404 \pm 0.01)$ ). Lemire *et al.* [2001LEM/FUG] used the SIT coefficients  $\varepsilon(\text{Pu}^{4+}, \text{ClO}_4^-) = (0.82 \pm 0.07) \text{ kg}\cdot\text{mol}^{-1}$  and  $\varepsilon(\text{Pu}^{3+}, \text{ClO}_4^-) =$

( $0.49 \pm 0.05$ ) kg·mol<sup>-1</sup> [2001LEM/FUG], [2003GUI/FAN] for the extrapolation of  $\log_{10} K_{IV/III}$  from 1.05 m HClO<sub>4</sub> to  $I = 0$ . The equilibrium constants at  $I = 0$  and in 1.02 m HCl yield  $\Delta\epsilon(\log_{10} K_{IV/III}$  in HCl solution) =  $-(0.14 \pm 0.04)$  kg·mol<sup>-1</sup>, and with  $\epsilon(\text{Pu}^{3+}, \text{Cl}^-) = \epsilon(\text{Am}^{3+}, \text{Cl}^-) = (0.23 \pm 0.02)$  kg·mol<sup>-1</sup> [2003GUI/FAN], we obtain  $\epsilon(\text{Pu}^{4+}, \text{Cl}^-) = (0.37 \pm 0.05)$  kg·mol<sup>-1</sup>. A very similar value,  $\epsilon(\text{Pu}^{4+}, \text{Cl}^-) = (0.4 \pm 0.1)$  kg·mol<sup>-1</sup>, was estimated by [2001NEC/KIM] from analogies and correlations between the tetravalent actinide ions (Figure VI-3) which confirms the possibility of estimating interaction coefficients in the series of the tetravalent actinide ions from the systematic dependence on the ionic radius.

Figure VI-3: SIT coefficients  $\epsilon(\text{An}^{4+}, \text{ClO}_4^-)$  and  $\epsilon(\text{An}^{4+}, \text{Cl}^-)$  of tetravalent actinide aquo ions as a function of the ionic radius ( $r_{\text{An}^{4+}}$  for coordination number 8, taken from [1994CHO/RIZ]).



As the ion interaction coefficients for the Th<sup>4+</sup> ion are important parameters for the evaluation of standard state equilibrium constants from experimental data in perchlorate, nitrate and chloride media, an additional experimental study was undertaken [2006NEC/ALT] where trace activity coefficients of the Th<sup>4+</sup> ion in dilute to concentrated NaClO<sub>4</sub>, NaNO<sub>3</sub> and NaCl solutions ( $[\text{H}^+] = 0.01-0.02$  M) were determined at 22°C from liquid-liquid distribution equilibria between aqueous

$(1-8) \times 10^{-3}$  M  $\text{Th}^{4+}$  solutions and organic phases consisting of 10–50 vol% tri-*n*-butyl phosphate (TBP) in *n*-dodecane.

In the liquid-liquid extraction study with  $\text{Th}^{4+}$  by Neck *et al.* [2006NEC/ALT], the distribution coefficients  $D_{\text{Th}}$  at  $m_{\text{NaCl}} < 3 \text{ mol}\cdot\text{kg}^{-1}$  were too low to evaluate SIT coefficients by linear regression, but the equilibrium constants in 2.5–5.0 m NaCl were found to be compatible with the SIT coefficients selected in the NEA-TDB review [2003GUI/FAN],  $(\varepsilon(\text{Th}^{4+}, \text{Cl}^-) + 4\varepsilon(\text{Na}^+, \text{Cl}^-) = (0.37 \pm 0.04) \text{ kg}\cdot\text{mol}^{-1})$ . The results obtained in 0.05–1.5 m  $\text{NaClO}_4$  and 0.05–3 m  $\text{NaNO}_3$ , combined with  $\varepsilon(\text{Na}^+, \text{NO}_3^-) = -(0.04 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$  and  $\varepsilon(\text{Na}^+, \text{ClO}_4^-) = (0.01 \pm 0.01) \text{ kg}\cdot\text{mol}^{-1}$ , yield the following interaction coefficients for the  $\text{Th}^{4+}$  ion [2006NEC/ALT]:  $\varepsilon(\text{Th}^{4+}, \text{NO}_3^-) = (0.31 \pm 0.12) \text{ kg}\cdot\text{mol}^{-1}$  and  $\varepsilon(\text{Th}^{4+}, \text{ClO}_4^-) = (0.70 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$ .

The interaction coefficient  $\varepsilon(\text{Th}^{4+}, \text{ClO}_4^-) = (0.70 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$  [2006NEC/ALT] confirms the value estimated from the correlation between  $\varepsilon(\text{An}^{4+}, \text{ClO}_4^-)$  and the ionic radii of the  $\text{An}^{4+}$  ions (Figure VI-3). The interaction coefficient  $\varepsilon(\text{Th}^{4+}, \text{NO}_3^-) = (0.31 \pm 0.12) \text{ kg}\cdot\text{mol}^{-1}$  [2006NEC/ALT] is close to the value of  $\varepsilon(\text{U}^{4+}, \text{NO}_3^-) = (0.34 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$  calculated in the present review if the ion interaction model is applied to the U(IV)-nitrate system. However, it differs considerably from  $\varepsilon(\text{Th}^{4+}, \text{NO}_3^-) = (0.11 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}$  [1980CIA] adopted in the previous NEA-TDB reviews. Figure VI-4 strongly supports the ion interaction coefficient determined in [2006NEC/ALT]. It shows a linear correlation between known values of  $\varepsilon(\text{M}^{Z+}, \text{NO}_3^-)$  and  $\varepsilon(\text{M}^{Z+}, \text{ClO}_4^-)$  or  $\varepsilon(\text{M}^{Z+}, \text{Cl}^-)$  and  $\varepsilon(\text{M}^{Z+}, \text{ClO}_4^-)$  for numerous cations  $\text{M}^{Z+}$  with  $Z = 1-4$ . All values, including  $\varepsilon(\text{Th}^{4+}, \text{Cl}^-) = (0.25 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ ,  $\varepsilon(\text{U}^{4+}, \text{NO}_3^-) = (0.34 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$  and those determined in [2006NEC/ALT],  $\varepsilon(\text{Th}^{4+}, \text{NO}_3^-) = (0.31 \pm 0.12) \text{ kg}\cdot\text{mol}^{-1}$  and  $\varepsilon(\text{Th}^{4+}, \text{ClO}_4^-) = (0.70 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$  (filled points in Figure VI-4), fall on, or close to the correlation line, whereas the value of  $\varepsilon(\text{Th}^{4+}, \text{NO}_3^-) = (0.11 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}$  is far out indicating that it is considerably in error.

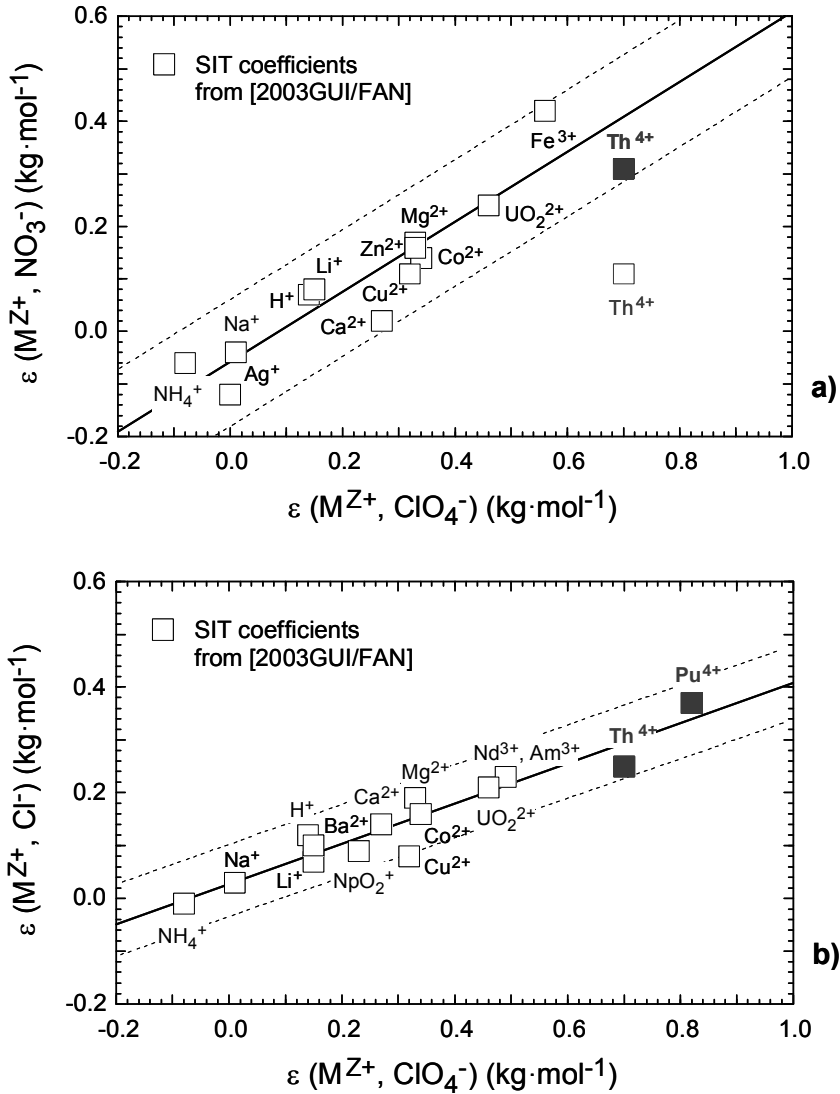
In summary this review selects the following interaction coefficients:

$$\varepsilon(\text{Th}^{4+}, \text{Cl}^-) = (0.25 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$$

$$\varepsilon(\text{Th}^{4+}, \text{ClO}_4^-) = (0.70 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$$

$$\varepsilon(\text{Th}^{4+}, \text{NO}_3^-) = (0.31 \pm 0.12) \text{ kg}\cdot\text{mol}^{-1}.$$

Figure VI-4: Correlations between SIT coefficients of non-complexed cations  $\text{M}^{Z+}$ . (a)  $\varepsilon(\text{M}^{Z+}, \text{NO}_3^-)$  and  $\varepsilon(\text{M}^{Z+}, \text{ClO}_4^-)$ , (b)  $\varepsilon(\text{M}^{Z+}, \text{Cl}^-)$  and  $\varepsilon(\text{M}^{Z+}, \text{ClO}_4^-)$ . Open points are taken from the NEA-TDB [2003GUI/FAN], filled points from [2006NEC/ALT].



### VI.3.2 Pitzer coefficients

Throughout the present review the SIT is used for ionic strength corrections. However, numerous computer codes for geochemical model calculations, in particular for calculations in concentrated chloride solutions, are based on the ion interaction equations of Pitzer [1991PIT]. Pitzer parameters reported in the literature to calculate activity coefficients for the Th<sup>4+</sup> ion in chloride solutions are briefly discussed and summarised in Table VI-2.

Table VI-2: Ion interaction Pitzer parameters for the Th<sup>4+</sup> ion at 25°C.

Binary interaction parameters Th <sup>4+</sup> -Cl <sup>-</sup>					
$\beta^{(0)}$ / (kg·mol <sup>-1</sup> )	$\beta^{(1)}$ / (kg·mol <sup>-1</sup> )	$\beta^{(2)}$ / (kg·mol <sup>-1</sup> )	$C^{\phi}$ / (kg <sup>2</sup> ·mol <sup>-2</sup> )	data source	Reference
1.014	13.33		-0.1034	a	[1973PIT/MAY]
1.092	13.7	-160	-0.112	b	[1992ROY/VOG], [1997RAI/FEL]
	( $\alpha_1 = 2 \text{ kg}^{1/2}\cdot\text{mol}^{-1/2}$ )	( $\alpha_2 = 12 \text{ kg}^{1/2}\cdot\text{mol}^{-1/2}$ )			
Ternary interaction parameters					
$\theta_{\text{Th}^{4+}/\text{H}^+} = 0.60 \text{ kg}\cdot\text{mol}^{-1}$		$\Psi_{\text{Th}^{4+}/\text{H}^+/\text{Cl}^-} = 0.37 \text{ kg}^2\cdot\text{mol}^{-2}$		b	[1992ROY/VOG]
$\theta_{\text{Th}^{4+}/\text{Na}^+} = 0.42 \text{ kg}\cdot\text{mol}^{-1}$		$\Psi_{\text{Th}^{4+}/\text{Na}^+/\text{Cl}^-} = 0.21 \text{ kg}^2\cdot\text{mol}^{-2}$		c	[1997RAI/FEL]
$\theta_{\text{Th}^{4+}/\text{Mg}^{2+}} = 0.60 \text{ kg}\cdot\text{mol}^{-1}$		$\Psi_{\text{Th}^{4+}/\text{Mg}^{2+}/\text{Cl}^-} = 0.21 \text{ kg}^2\cdot\text{mol}^{-2}$		c	[1997RAI/FEL]

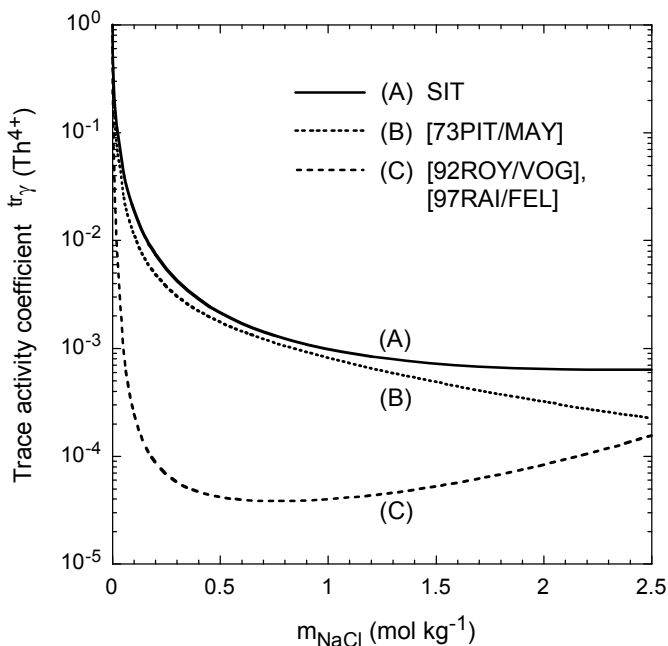
a: Isopiestic data for ThCl<sub>4</sub> [1955ROB].

b: HCl activities in aqueous HCl-ThCl<sub>4</sub> mixtures [1992ROY/VOG].

c: Solubility of ThO<sub>2</sub>(am, hyd) at pH 3.5–5.5 in NaCl and MgCl<sub>2</sub> solutions [1997RAI/FEL], in combination with the binary parameters of Roy *et al.* [1992ROY/VOG].

Pitzer and Mayorga [1973PIT/MAY] calculated binary parameters from Robinson's isopiestic data for ThCl<sub>4</sub> solutions [1955ROB] which were also used by Ciavatta [1980CIA] to calculate the SIT coefficient  $\epsilon(\text{Th}^{4+}, \text{Cl}^-) = (0.25 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$  adopted in the NEA-TDB review [1992GRE/FUG]. Roy *et al.* [1992ROY/VOG] performed emf ( $a_{\text{HCl}}$ ) measurements in aqueous HCl-ThCl<sub>4</sub> mixtures of various compositions at 25°C, including data at low H<sup>+</sup> concentrations (pH ≥ 3), where hydrolysis of the Th<sup>4+</sup> ion was considered as negligible. Roy *et al.* [1992ROY/VOG] introduced a binary parameter  $\beta^{(2)}$  to account for strong interactions between Th<sup>4+</sup> and Cl<sup>-</sup>. If this  $\beta^{(2)}$  parameter is used in the expression for the trace activity coefficient of Th<sup>4+</sup> in NaCl solution, this leads to activity coefficients  $\gamma_{\text{Th}^{4+}}$  which deviate considerably from the Debye-Hückel law (at low ionic strength) and also from the SIT and [1973PIT/MAY] models (at higher ionic strength) (Figure VI-5).

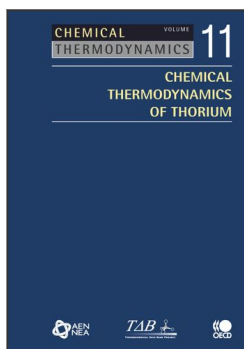
Figure VI-5: Trace activity coefficients of  $\text{Th}^{4+}$  in NaCl solution at 25°C, calculated with the SIT coefficient  $\varepsilon(\text{Th}^{4+}, \text{Cl}^-) = (0.25 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}$  [1980CIA], [1992GRE/FUG] (A) and with the different sets of the Pitzer parameters reported by Pitzer and Mayorga [1973PIT/MAY] (B) and by Roy *et al.* [1992ROY/VOG] and Rai *et al.* [1997RAI/FEL] (C).



Felmy *et al.* [1991FEL/RAI] proposed a Pitzer model for the solubility of  $\text{ThO}_2(\text{am, hyd})$  in 0.6–3.2 m NaCl solution. This model was refined in [1997RAI/FEL] where the solubility studies were extended up to 6 m NaCl and 3 m  $\text{MgCl}_2$  solutions. Based on the binary parameters of [1992ROY/VOG], Rai *et al.* [1997RAI/FEL] fitted ternary parameters for the systems  $\text{Na}^+ - \text{Th}^{4+} - \text{Cl}^-$  and  $\text{Mg}^{2+} - \text{Th}^{4+} - \text{Cl}^-$  to the solubility data for  $\text{ThO}_2(\text{am, hyd})$  at pH 3.5–5.5 in NaCl and  $\text{MgCl}_2$  solutions.  $\text{Th}(\text{IV})$  hydroxide complexes are not included in this model. The Pitzer model used by Rai *et al.* [1997RAI/FEL] is appropriate to fit solubility data of  $\text{ThO}_2(\text{am, hyd})$  in dilute to concentrated NaCl and  $\text{MgCl}_2$  media. However it is not compatible with the selections in the present review because the underlying chemical model (without hydrolysis species) is completely different. The solubility and hydrolysis constants selected by this review must not be combined with the Pitzer parameters used by Rai *et al.* [1997RAI/FEL] for the  $\text{Th}^{4+}$  ion and *vice versa*, the solubility constants given in [1997RAI/FEL], [2000RAI/MOO] must not be combined with the SIT coefficients and hydrolysis constants evaluated in the present review.

As illustrated in Figure VI-5, the different approaches and ion interaction coefficients can lead to appreciably discrepant activity coefficients for the  $\text{Th}^{4+}$  ion. For instance the values of  $\gamma_{\text{Th}^{4+}}$  in 0.1 or 0.5 m NaCl and hence the solubility constants calculated in [2000RAI/MOO] and [2003NEC/ALT] with the Pitzer model and SIT respectively for microcrystalline  $\text{ThO}_2(\text{cr})$  at low pH, where hydrolysis is actually negligible, differ by about two orders of magnitude.





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