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Ion interaction (SIT) coefficients for the Th^{4+} ion and trace activity coefficients in $NaClO_4$, $NaNO_3$ and NaCl solution determined by solvent extraction with TBP

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Summary. Trace activity coefficients of the Th^{4+} ion in dilute to concentrated $NaClO_4$, $NaNO_3$ and NaCl solutions ($[H^+] = 0.01–0.02$ M) have been determined at 22 °C from liquid-liquid phase equilibria with 10–50 vol. % TBP in *n*-dodecane. Using the specific ion interaction theory (SIT) to describe these equilibria as a function of the medium electrolyte concentration, the following ion interaction coefficients are calculated: $\varepsilon(Th^{4+}, ClO_4^-) = 0.70 \pm 0.06$ kg/mol and $\varepsilon(Th^{4+}, NO_3^-) = 0.31 \pm 0.12$ kg/mol. The latter value differs considerably from $\varepsilon(Th^{4+}, NO_3^-) = 0.11 \pm 0.02$ kg/mol used in the NEA-TDB. The low distribution coefficients at $m_{NaCl} < 3$ mol/kg do not allow the linear SIT extrapolation to $I = 0$, but the equilibrium constants in 2.5–5.0 m NaCl are compatible with the NEA-TDB value of $\varepsilon(Th^{4+}, Cl^-) = 0.25 \pm 0.03$ kg/mol.

The SIT coefficients determined for the Th^{4+} ion follow the linear correlations between known values of $\varepsilon(M^{Z+}, NO_3^-)$, $\varepsilon(M^{Z+}, Cl^-)$ and $\varepsilon(M^{Z+}, ClO_4^-)$ for non-complexed cations M^{Z+} with $Z = 1 - 4$, including $\varepsilon(Pu^{4+}, ClO_4^-) = 0.82 \pm 0.07$ kg/mol and $\varepsilon(Pu^{4+}, Cl^-) = 0.37 \pm 0.05$ kg/mol calculated from data accepted in the NEA-TDB. The interaction coefficients in the series of the tetravalent actinide ions show a slight systematic dependence on the ionic radius.

1. Introduction

In the thermochemical database of the OECD Nuclear Energy Agency (NEA-TDB), *e.g.* [1–3], the specific ion interaction theory (SIT) [4] is used for ionic strength corrections to evaluate standard state equilibrium constants. The ion interaction (SIT) coefficients for the Th^{4+} ion are therefore basic parameters within the current NEA-TDB III project on the "Chemical thermodynamics of thorium". The interaction coefficients $\varepsilon(Th^{4+}, NO_3^-) = 0.11 \pm 0.02$ kg/mol and $\varepsilon(Th^{4+}, Cl^-) = 0.25 \pm 0.03$ kg/mol [1] hitherto used to calculate trace activity coefficients of Th^{4+} were calculated by Ciavatta [4] from osmotic coefficients of rather concentrated $Th(NO_3)_4$ and $ThCl_4$ solutions [5]. The formation of Th(IV) complexes with nitrate and chloride ions is included in these interaction coefficients. It is not yet ascertained whether the activity coefficient of the Th^{4+} ion at $I < 0.5$ mol/kg follows the extended Debye–Hückel term in the SIT equation. Activity coefficients in chloride solution calculated with the set of Pitzer parameters used by Rai *et al.* [6, 7] (based on emf data in $ThCl_4$-HCl mixtures [8], also at rather high Th concentrations) deviate considerably from those calculated with the SIT, c.f. discussion in [9]. Experimental studies on the interaction coefficient $\varepsilon(Th^{4+}, ClO_4^-)$ are not available. Neck and Kim [10] estimated a value of $\varepsilon(Th^{4+}, ClO_4^-) = 0.67 \pm 0.10$ kg/mol from a correlation between the increasing values of $\varepsilon(U^{4+}, ClO_4^-) = 0.76 \pm 0.06$ kg/mol [1], $\varepsilon(Np^{4+}, ClO_4^-) = 0.82 \pm 0.05$ kg/mol [1] and $\varepsilon(Pu^{4+}, ClO_4^-) = 0.83 \pm 0.10$ kg/mol [11] and the ionic radii of the tetravalent actinide ions.

The objective of the present work is to derive ion interaction coefficients for the Th^{4+} ion from trace activity coefficients in perchlorate, nitrate and chloride media. For this purpose we have studied the liquid-liquid phase equilibria between aqueous, $1–8 \times 10^{-3}$ M Th^{4+} solutions in dilute to concentrated $NaClO_4$, $NaNO_3$ and NaCl containing 0.01 or 0.02 M H^+ to avoid hydrolysis of the Th^{4+} ion and organic phases consisting of 10–50 vol. % tri-*n*-butyl phosphate (TBP) in *n*-dodecane. In a recent study [12] we successfully used this method to determine trace activity coefficients of the UO_2^{2+} ion in dilute to concentrated $NaClO_4$, $NaNO_3$ and chloride solutions (NaCl, $MgCl_2$, $CaCl_2$). The evaluated SIT coefficients, $\varepsilon(UO_2^{2+}, ClO_4^-) = 0.40 \pm 0.07$ kg/mol, $\varepsilon(UO_2^{2+}, NO_3^-) = 0.25 \pm 0.06$ kg/mol and $\varepsilon(UO_2^{2+}, Cl^-) = 0.21 \pm 0.03$ kg/mol, are in excellent agreement with those of the NEA-TDB (0.46 ± 0.03, 0.24 ± 0.03 and 0.21 ± 0.02 kg/mol, respectively [1–3]).

1.1 Liquid-liquid phase equilibria

The properties of tri-*n*-butyl phosphate (TBP) and its use for liquid-liquid extraction are well known [13–15]. The extraction of Th^{4+} from the aqueous phase into organic mixtures of TBP and an inert diluent is given by the reaction

$$Th^{4+}(aq) + 4X^-(aq) + n\mathrm{TBP}(org) \Leftrightarrow ThX_4(\mathrm{TPB})_n(org) \quad (1)$$

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with $X^- = ClO_4^-$, NO_3^- and Cl^- and the following conditional equilibrium constants K' and $^*K'$ for a given aqueous ionic medium

$$K' = \frac{[ThX_4(TPB)_n(org)]}{[Th^{4+}][X^-]^4[TBP(org)]^n} \tag{2}$$

$$^*K' = K'[TBP(org)]^n = \frac{[ThX_4(TPB)_n(org)]}{[Th^{4+}][X^-]^4} \tag{3}$$

$[Th^{4+}] = [Th]_{aq}$ includes nitrate or chloride complexes which are not explicitly formulated, $[X^-] = [NaX] + [HX]$ is given by the background electrolyte concentration in the aqueous phase and $[ThX_4(TPB)_n(org)] = [Th]_{org}$. The free TBP equilibrium concentration in the organic phase, [TBP(org)], is given by the initial TBP concentration $[TBP(org)]^\circ$, if the TBP consumed by complex formation with thorium, HX and NaX in the organic phase are small:

$$[TBP(org)] = [TBP(org)]^\circ - n[ThX_4(TPB)_n(org)] - p[HX(TPB)_p(org)] - q[NaX(TPB)_q(org)] \tag{4}$$

The total thorium concentrations used in the present study and hence $[Th]_{org}$ are very low compared to $[TBP(org)]^\circ$ (0.365–1.83 mol/L). However, as the studies have to be performed at H^+ concentrations high enough to exclude hydrolysis of the Th^{4+} ion and up to rather high NaX concentrations, the co-extraction of acids and sodium salts must be taken into account:

$$H^+(aq) + X^-(aq) + pTBP(org) \Leftrightarrow HX(TPB)_p(org) \tag{5}$$

$$Na^+(aq) + X^-(aq) + qTBP(org) \Leftrightarrow NaX(TPB)_q(org) \tag{6}$$

The equilibrium constants K' and $^*K'$ for HX and NaX are defined analogous to those for the extraction of thorium (c.f., Eq. (2) and Eq. (3)).

The number of TBP ligands for the extraction of Th and acids, n and p, are often derived from the slopes of the plots log $^*K$ or log D for a constant aqueous ionic medium *versus* log [TBP] [16–22]. (The distribution coefficients of Th and HX are defined by $D_{Th} = [Th]_{org}/[Th]_{aq}$ and $D_{HX} = [HX]_{org}/[H^+]_{aq}$, respectively.) However, usually this does not lead to a clear-cut value, because the activity coefficients of the neutral organic species TBP(org), $ThX_4(TPB)_n(org)$ and $HX(TPB)_p(org)$ varies with the TBP concentration [15]. The slope also depends on the concentration scale used for [TBP(org)] (vol.%, mol/L or mol/kg dodecane). The extraction studies with aqueous nitrate and chloride media and other methods indicate the formation of complexes with two TBP ligands bound to Th^{4+} and UO_2^{2+} ions and one TBP molecule coordinated to mineral acids HX [13–15]. In the case of extraction from perchlorate solution, the observed slopes are considerably higher, $n = 5$–6 for Th and $p = 3$–4 for $HClO_4$; analogous results were reported for the extraction of $HReO_4$ and $HTcO_4$, *e.g.* in [20–22]. The additional TBP molecules are bound to the oxyanions in the organic complexes *via* H_2O-bridges [20, 21].

Because of the uncertainties concerning the values of n, we consider only the equilibrium constants log $^*K'$ at a fixed TBP concentration in the organic phase (n = constant). This requires that the free TBP(org) concentration remains constant (*i.e.*, $[ThX_4(TPB)_n(org)] + [HX(TPB)_p(org)] + [NaX(TPB)_q(org)] < 0.01[TBP(org)]^\circ$) under the experimental conditions (NaX, HX and TBP concentrations) studied.

1.2 Activity coefficients and ion interaction (SIT) coefficients

According to the specific ion interaction theory (SIT) [1–4] the activity coefficients γ_i of the ions in the aqueous phase are given by

$$\log \gamma_i = -z_i^2 D + \sum \varepsilon_{ij}\, m_j \tag{7}$$

where z_i is the charge of ion i, ε_{ij} is the interaction parameter for ion i and an oppositely charged ion j and m_j (mol/kg H_2O) is the molal concentration of ion j, D is the Debye–Hückel term at 25 °C: $D = 0.509\sqrt{I_m}/(1 + B\mathring{a}\sqrt{I_m})$, with $B\mathring{a} = 1.5$ and I_m (mol/kg H_2O) is the molal ionic strength. The equilibrium constants determined in the present study, $^*K'$ (for a given concentration of NaX in the aqueous phase and a constant concentration [TBP(org)]) and $^*K^\circ$ (for $I = 0$ in the aqueous phase and [TBP(org)] = const.) are related by

$$^*K^\circ = \frac{[ThX_4(TPB)_n(org)]}{[Th^{4+}]\gamma_{Th^{4+}}[X^-]^4(\gamma_{X^-})^4} \tag{8}$$

and

$$\log {^*K^0} = \log {^*K'} + 20D - \varepsilon(Th^{4+}, X^-)m_{X^-} - 4\varepsilon(Na^+, X^-)m_{Na^+} \tag{9}$$

The corresponding equilibrium constants for the extraction of HX are related by

$$\log {^*K^\circ_{HX}} = \log {^*K'_{HX}} + 2D - \varepsilon(H^+, X^-)m_{X^-} - \varepsilon(Na^+, X^-)m_{Na^+} \tag{10}$$

For a given composition of the organic phase ([TBP(org)] = const.) the activity coefficients of the neutral species in the organic phase and also the numbers n and p of TBP ligands are constant, *i.e.*, independent of the aqueous phase. The water content in the equilibrated organic phase is proportional to the water activity in the aqueous phase [15] and hence dependent on the concentration of NaX. This may have a certain effect on the activity coefficients of organic species with TBP coordinated to water *via* $\cdots H{-}O{-}H \cdots O{=}P(O{-}C_4H_9)_3$ bridges. *Vice versa*, the low solubility of TBP in aqueous solution (1.5×10^{-3} M in pure water [13]) does not affect the activity coefficients in the aqueous phase.

2. Experimental

Aqueous solutions were prepared with solid *p.a.* materials $NaClO_4 \cdot H_2O$, $NaNO_3$, NaCl, and $HClO_4$ (71%), HNO_3 (65%) and HCl (0.1 M, Titrisol) from Merck. The concentration of diluted acid standard solution was controlled by titration with a 0.1 M NaOH standard (Titrisol). Thorium stock solutions were prepared from $Th(NO_3)_4 \cdot 5H_2O$ (Merck, *p.a.*) or by dissolving previously prepared $ThO_2 \cdot xH_2O(am)$ [23]

in 1 M $HClO_4$ and HCl. The aqueous phases for the liquid-liquid extraction experiments, 0.05–3.0 M $NaNO_3$, 0.05–3.0 M $NaClO_4$, and 1.0–5.0 M NaCl, contained 0.01 or 0.02 M $HClO_4$, HNO_3 or HCl, respectively. The initial Th concentrations were in the range 0.001–0.002 M in nitrate and perchlorate solutions and up to 0.008 M in chloride solutions. All aqueous solutions were prepared with purified water from a Milli-Q-academic apparatus (Millipore).

The organic phases consisting of 10–50 vol. % extractant TBP (Merck, *p.a.*) and diluent *n*-dodecane (Merck, *p.a.*) were prepared from weighed amounts of TBP and *n*-dodecane. The mixtures were purified by washing several times with 0.01 M NaOH and pure water.

Extractions were performed batchwise at 22 ± 2 °C, shaking vigorously equal volumes (2 mL) of aqueous and organic phase for 20 minutes. The organic TBP/*n*-dodecane phases were pre-equilibrated with the corresponding aqueous phases (without Th). Phase separation was achieved by centrifugation for 10 minutes at 2500 g. Thorium concentrations were determined in both phases by ICP-MS (ELAN 6100, Perkin Elmer). Depending on the electrolyte concentration in the aqueous phases the aliquots for ICP-MS analysis have to be diluted at least 1 : 100 and acidified (2% HNO_3). Accordingly, at a background of 0.001–0.002 ppb Th-232, the detection limit for thorium in the original solutions varies from 10^{-10} to 10^{-9} mol/L. The Th concentration in the organic phase was measured after back-extraction from 1 mL organic phase with 1 mL 0.001 M HCl. The extraction from chloride solutions was performed with 10 mL organic phase (back-extraction from 8 mL organic phase) because of the low concentrations in the organic phase.

The phase equilibria of HNO_3 and $HClO_4$ between the corresponding sodium salt media and TBP/*n*-dodecane were investigated in extraction experiments with 5 mL organic phase and 5 mL aqueous phase containing 0.01 M HX. The concentration of $HX(TPB)_p(org)$ is determined after back-extraction of 4 mL organic phase with 4 mL pure water. A ROSS electrode calibrated against Merck buffer solutions was used to measure the pH of these dilute back-extraction aqueous phases and pH was converted into H^+ concentration by calculating the activity coefficient γ_{H^+} with Eq. (7). Under the conditions of the present study, the extraction of HCl was found to be negligible. The extraction of the sodium salts was investigated in analogous tests measuring $[Na^+]$ by ICP-MS.

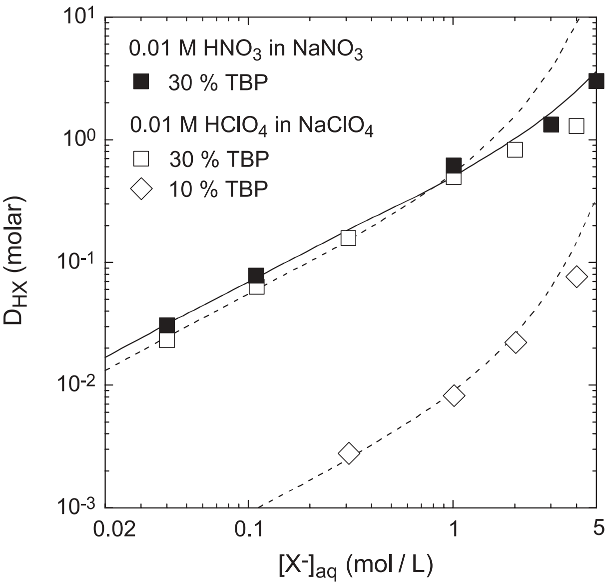

Fig. 1. Distribution coefficients D_{HX} between 0.01 M HNO_3 and $HClO_4$ in dilute to concentrated sodium nitrate and perchlorate solutions, respectively, and 10 or 30 Vol. % TBP in *n*-dodecane. The calculated lines are based on the equilibrium constants $\log {}^*K^\circ_{HX}$ given in Table 1 and SIT coefficients $\varepsilon(H^+, X^-)$ and $\varepsilon(Na^+, X^-)$ from the NEA-TDB [1–3].

Table 1. Equilibrium constants $\log {}^*K^\circ$ for the extraction of HX and ThX_4 with TBP/*n*-dodecane from nitrate, perchlorate and chloride solution ($I = 0$, 20–25 °C); present results and values calculated from literature data (uncertainties are given as 2σ).

TBP (vol.%)^a	$\log {}^*K^\circ$ (HX) (molar)^b	$\log {}^*K^\circ$ (ThX_4) (molar)^b	(molal)^c
	HNO_3	$Th(NO_3)_4$	
10	-0.91 ± 0.10^d	2.84 ± 0.05	3.01 ± 0.05
30	0.05 ± 0.14	3.91 ± 0.03	4.19 ± 0.03
	-0.10 ± 0.15^d	3.86^e	
100	0.74 ± 0.11^d		
	$HClO_4$	$Th(ClO_4)_4$	
10	-1.84 ± 0.11	-0.03 ± 0.07	0.14 ± 0.07
20		1.97 ± 0.06	2.20 ± 0.06
30	-0.06 ± 0.05	2.92 ± 0.03	3.20 ± 0.03
100	1.86 ± 0.13^d		
	HCl	$ThCl_4$	
20	-3.35 ± 0.23^d		
50	-2.15 ± 0.16^d	-3.7 ± 0.4	-3.3 ± 0.4
100	-1.13 ± 0.15^d		

a: The molar and molal TBP concentrations are calculated from the molecular weights and densities of TBP ($M = 266.32$ g/mol, $d = 0.973$ g/cm^3 at 25 °C) and *n*-dodecane ($M = 170.34$ g/mol, $d = 0.745$ g/cm^3 at 25 °C), except for 100 vol. % TBP, which contains appreciable amounts of water after equilibration (60 g/L, mole ratio TBP: $H_2O \approx 1:1$) [13, 14].
10 vol. % TBP = 0.365 mol/L = 0.545 mol/kg $C_{12}H_{26}$
20 vol. % TBP = 0.731 mol/L = 1.226 mol/kg $C_{12}H_{26}$
30 vol. % TBP = 1.096 mol/L = 2.10 mol/kg $C_{12}H_{26}$
50 vol. % TBP = 1.827 mol/L = 4.90 mol/kg $C_{12}H_{26}$
100 vol. % TBP = 3.44 mol/L [13];

b: All concentrations in the aqueous and organic phase: c_i (mol/L);

c: Aqueous phase: m_i (mol/kg H_2O), organic phase: m_i (mol/kg $C_{12}H_{26}$);

d: Calculated in [22] from distribution coefficients for HNO_3 [16–18], $HClO_4$ [17, 18] and HCl [17–19];

e: Calculated from the distribution coefficient of 0.01 M $Th(NO_3)_4$ in 0.5 M KNO_3 at $pH_c < 2$ [24].

3. Results and discussion

The evaluation of equilibrium constants $\log {}^*K'$ and the application of Eq. (9) to determine ion interaction coefficients for the Th^{4+} ion, requires experimental conditions where the co-extraction of HX and NaX does not affect the free TBP concentration. Therefore, in a first step, the possible ranges of aqueous electrolyte concentrations where this prerequisite is fulfilled was determined for the different TBP concentrations used. The liquid-liquid extraction of HNO_3, $HClO_4$ and HCl from binary aqueous solutions was investigated in numerous studies, *e.g.* in [16–20], for different TBP concentrations and usually for high acid concentrations. As these conditions are not comparable with those in the present study, we have determined the equilibrium constants for the systems $HClO_4$/10 and 30 vol. % TBP and HNO_3/30 vol. % TBP using aqueous phases of 0.01 M HX in dilute to concentrated NaX. The experimental results (Fig. 1) indicate that for extraction studies with 30 vol. % TBP the aqueous nitrate and perchlorate concentration ranges have to be restricted to $[\mathrm{NaX}] < 1.5\,\mathrm{M}$ to maintain $[\mathrm{HX(TPB)}_p(\mathrm{org})] < 0.01[\mathrm{TBP(org)}]^\circ$, while the studies with 10 vol. % TBP can be extended to higher electrolyte concentrations. The evaluated equilibrium constants $\log {}^*K^0_{\mathrm{HX}}$ are given in Table 1 together with values calculated in [22] from distribution coefficients D_{HX} at low and moderate acid concentrations. The extraction of HCl is negligible in the present study with 50 vol. %TBP. This is consistent with the low $\log {}^*K^0_{\mathrm{HCl}}$ values calculated from the distribution coefficients in [17–19].

The solubilities of NaCl and $NaNO_3$ in undiluted TBP (4.2×10^{-3} and 5.4×10^{-2} mol/L, respectively, at 25 °C [13]) are very low. Accordingly the co-extracted amounts of NaCl and $NaNO_3$ are negligible under the conditions of the present study. However, the rather high solubility of $NaClO_4 \cdot xH_2O$ in undiluted TBP (1.04 mol/L at 25 °C [13]) indicates that the co-extracted $NaClO_4$ might decrease the free TBP(org) concentration. This is actually the case; we measured the following concentrations of $\mathrm{NaClO_4(TBP \cdot H_2O)}_q(\mathrm{org})$ in equilibrium with 0.5, 1.0, 1.5, 2.0 and 3.0 M aqueous $NaClO_4$ solutions containing 0.02 M $HClO_4$: $[\mathrm{Na}]_{\mathrm{org}} = 2.6 \times 10^{-4}$, 8.3×10^{-4}, 1.9×10^{-3}, 3.4×10^{-3} and 8.7×10^{-3} mol/L for 10 vol. % TBP (0.365 mol/L) and $[\mathrm{Na}]_{\mathrm{org}} = 4.8 \times 10^{-3}$, 1.5×10^{-2}, 2.9×10^{-2}, 5.0×10^{-2} and 9.6×10^{-2} mol/L for 30 vol. % TBP (1.10 mol/L). The equilibrium constants for the extraction of $NaClO_4$ are not explicitly determined in the present study, but the effect on the liquid-liquid equilibria of $Th(ClO_4)_4$ and $HClO_4$ will be discussed in the evaluation of the experimental data.

3.1 Equilibrium constants and SIT coefficients for the Th^{4+} ion

The experimental results of the TBP extraction studies are listed in Table 2. The thorium concentration in the organic phase, $[\mathrm{Th}]_{\mathrm{org}} = [\mathrm{ThX_4(TPB)}_n(\mathrm{org})]$, is always very low compared to $[\mathrm{TBP(org)}]^\circ$ and does not affect the free TBP concentration. For NaCl concentrations below 3 mol/L, the values of $[\mathrm{Th}]_{\mathrm{org}}$ are very low. They can still be measured by ICP-MS, however, the corresponding distribution coefficients of $D_{\mathrm{Th}} < 10^{-5}$ are not reliable, because they can easily be affected by trace impurities in the organic phase or by sorption effects. These data are not further considered.

For the calculation of conditional equilibrium constant $\log {}^*K'$ from $[\mathrm{NaX}]_{\mathrm{aq}}$, $[\mathrm{HX}]_{\mathrm{aq}}$, $[\mathrm{Th}]_{\mathrm{aq}}$ and $[\mathrm{Th}]_{\mathrm{org}}$ given in Table 2, the molar concentrations in the aqueous phases are transformed into molal values m_i (mol/kg H_2O) with the conversion factors given in the NEA-TDB [1–3]. The concentrations $[\mathrm{Th}]_{\mathrm{org}}$ are also expressed as molalities m_i (mol/kg dodecane) with $m_i/c_i = 1.491$, 1.678, 1.918 and 2.685 L mixture/kg dodecane for 10, 20, 30 and 50 vol. % TBP, respectively. The SIT Eq. (10) can be rewritten as

$$\log {}^*K' + 20D = \log {}^*K^0 - \Delta\varepsilon_{\mathrm{X}} I_{\mathrm{m}} \tag{11}$$

Table 2. Equilibrium concentrations in the liquid-liquid extraction experiments at 22 °C, all data given as molar concentrations c_i(mol/L).

$[\mathrm{NaClO_4}]$	$[\mathrm{HClO_4}]$	$[\mathrm{Th}]_{\mathrm{aq}}$	$[\mathrm{Th}]_{\mathrm{org}}$
10 vol. % TBP			
0.80	0.02	1.21×10^{-3}	3.25×10^{-7}
1.25	0.02	1.23×10^{-3}	1.93×10^{-6}
1.50	0.02	1.26×10^{-3}	3.59×10^{-6}
2.00	0.02	1.29×10^{-3}	1.24×10^{-5}
2.50	0.02	1.24×10^{-3}	3.64×10^{-5}
3.00	0.02	1.20×10^{-3}	8.77×10^{-5}
0.50	0.01	1.24×10^{-3}	5.69×10^{-8}
1.00	0.01	1.25×10^{-3}	7.24×10^{-7}
3.00	0.01	1.30×10^{-3}	8.27×10^{-5}
20 vol. % TBP			
0.30	0.02	1.23×10^{-3}	1.78×10^{-6}
0.50	0.02	1.22×10^{-3}	7.04×10^{-6}
0.70	0.02	1.21×10^{-3}	1.84×10^{-5}
1.00	0.02	1.20×10^{-3}	5.30×10^{-5}
1.25	0.02	1.20×10^{-3}	1.07×10^{-4}
1.50	0.02	1.13×10^{-3}	1.56×10^{-4}
30 vol. % TBP			
0.05	0.02	1.13×10^{-3}	3.18×10^{-7}
0.10	0.02	1.22×10^{-3}	1.29×10^{-6}
0.20	0.02	1.25×10^{-3}	6.14×10^{-6}
0.40	0.02	1.22×10^{-3}	3.42×10^{-5}
0.60	0.02	1.11×10^{-3}	9.05×10^{-5}
0.80	0.02	1.06×10^{-3}	1.84×10^{-4}
1.00	0.02	9.74×10^{-4}	2.90×10^{-4}
0.50	0.01	1.17×10^{-3}	5.17×10^{-5}
$[\mathrm{NaNO_3}]$	$[\mathrm{HNO_3}]$	$[\mathrm{Th}]_{\mathrm{aq}}$	$[\mathrm{Th}]_{\mathrm{org}}$
10 vol. % TBP			
0.30	0.02	1.94×10^{-3}	1.15×10^{-5}
0.50	0.02	1.91×10^{-3}	3.52×10^{-5}
0.70	0.02	1.86×10^{-3}	7.37×10^{-5}
1.00	0.02	1.76×10^{-3}	1.69×10^{-4}
1.50	0.02	1.50×10^{-3}	4.32×10^{-4}
2.00	0.02	1.15×10^{-3}	8.02×10^{-4}
2.50	0.02	7.97×10^{-4}	1.19×10^{-3}
3.00	0.02	5.05×10^{-4}	1.46×10^{-3}
0.50	0.01	1.17×10^{-3}	2.28×10^{-5}
3.00	0.01	3.31×10^{-4}	1.03×10^{-3}
30 vol. % TBP			
0.05	0.02	1.98×10^{-3}	4.88×10^{-6}
0.075	0.02	1.90×10^{-3}	9.64×10^{-6}
0.10	0.02	2.00×10^{-3}	1.66×10^{-5}
0.20	0.02	1.90×10^{-3}	6.15×10^{-5}
0.40	0.02	1.70×10^{-3}	2.50×10^{-4}
0.60	0.02	1.47×10^{-3}	5.15×10^{-4}
0.80	0.02	1.13×10^{-3}	8.25×10^{-4}
0.50	0.01	1.03×10^{-3}	2.15×10^{-4}
1.00	0.01	5.65×10^{-4}	6.72×10^{-4}
[NaCl]	[HCl]	$[\mathrm{Th}]_{\mathrm{aq}}$	$[\mathrm{Th}]_{\mathrm{org}}$
50 vol. % TBP			
3.00	0.01	6.00×10^{-4}	1.86×10^{-9}
5.00	0.01	6.31×10^{-4}	1.63×10^{-7}
1.90	0.01	8.48×10^{-3}	7.93×10^{-9}
2.38	0.01	8.58×10^{-3}	1.05×10^{-8}
2.86	0.01	8.28×10^{-3}	2.35×10^{-8}
3.33	0.01	8.38×10^{-3}	5.53×10^{-8}
3.81	0.01	8.43×10^{-3}	1.26×10^{-7}
4.29	0.01	8.31×10^{-3}	3.51×10^{-7}
4.76	0.01	7.77×10^{-3}	1.01×10^{-6}

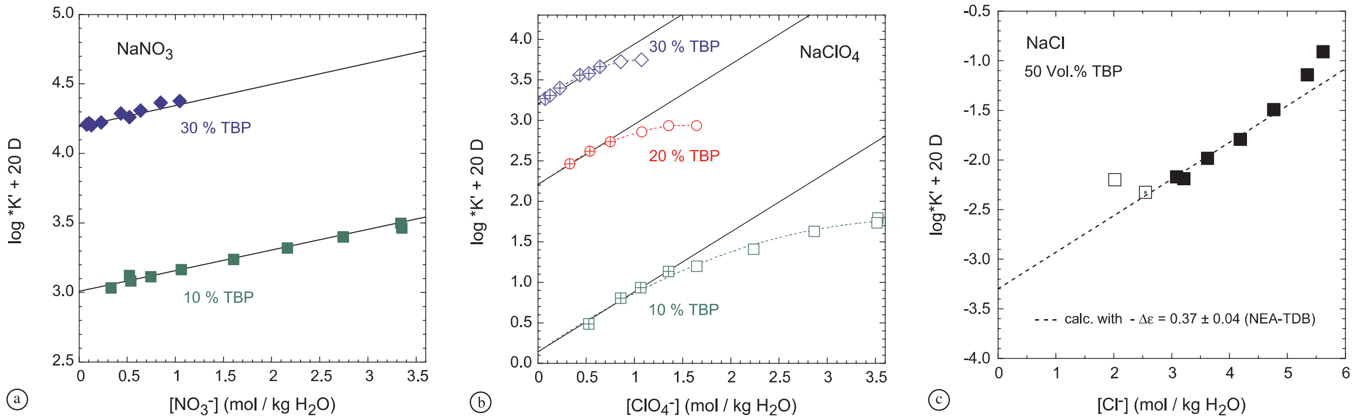

Fig. 2. Application of the linear SIT regression to equilibrium constants log $^*K'$ for the liquid-liquid extraction of Th^{4+} with TBP from nitrate (*a*), perchlorate (*b*) and chloride (*c*) media. The linear regression in Fig. 2b (solid line) is restricted to the data points marked with crosses inside, the data at higher perchlorate concentrations require a polynomial fit (dashed lines). The data at $m_{\mathrm{NaCl}} < 3$ mol/kg (open points in Fig. 2c) are not considered to be reliable because of the extremely low distribution coefficients (see text).

with $-\Delta\varepsilon_{\mathrm{X}} = \varepsilon(\mathrm{Th}^{4+}, \mathrm{X}^-) + 4\varepsilon(\mathrm{Na}^+, \mathrm{X}^-)$, $I_{\mathrm{m}} = m_{\mathrm{NaX}} + m_{\mathrm{HX}} + 10m_{\mathrm{ThX}_4}$ and $D = (0.509\sqrt{I_{\mathrm{m}}})/(1 + 1.5\sqrt{I_{\mathrm{m}}})$.

The linear extrapolation to $I = 0$ according to Eq. (11) is illustrated in Figs. 2a, 2b and 2c for nitrate, perchlorate and chloride media, respectively. The simultaneous evaluation of the experimental series at different TBP concentrations leads to the log $^*K^0$ values summarized in Table 1 and the following $\Delta\varepsilon_{\mathrm{X}}$ values (corresponding to the slopes in Figs. 2a and 2b):

$$-\Delta\varepsilon_{\mathrm{NO}_3} = \varepsilon(\mathrm{Th}^{4+}, \mathrm{NO}_3{}^-) + 4\varepsilon(\mathrm{Na}^+, \mathrm{NO}_3{}^-) = 0.15 \pm 0.02\ \mathrm{kg/mol}$$

$$-\Delta\varepsilon_{\mathrm{ClO}_4} = \varepsilon(\mathrm{Th}^{4+}, \mathrm{ClO}_4{}^-) + 4\varepsilon(\mathrm{Na}^+, \mathrm{ClO}_4{}^-) = 0.74 \pm 0.04\ \mathrm{kg/mol}$$

With $\varepsilon(\mathrm{Na}^+, \mathrm{NO}_3{}^-) = -0.04 \pm 0.03$ kg/mol and $\varepsilon(\mathrm{Na}^+, \mathrm{ClO}_4{}^-) = 0.01 \pm 0.01$ kg/mol [1–3], the following interaction coefficients are obtained for the Th^{4+} ion:

$$\varepsilon(\mathrm{Th}^{4+}, \mathrm{NO}_3{}^-) = 0.31 \pm 0.12\ \mathrm{kg/mol}$$
$$\varepsilon(\mathrm{Th}^{4+}, \mathrm{ClO}_4{}^-) = 0.70 \pm 0.06\ \mathrm{kg/mol}$$

The interaction coefficient with nitrate differs considerably from the NEA-TDB value of $\varepsilon(\mathrm{Th}^{4+}, \mathrm{NO}_3{}^-) = 0.11 \pm 0.02$ kg/mol, whereas the interaction coefficient with perchlorate is in excellent agreement with $\varepsilon(\mathrm{Th}^{4+}, \mathrm{ClO}_4{}^-) = 0.67 \pm 0.10$ kg/mol [10] estimated from the correlation between $\varepsilon(\mathrm{An}^{4+}, \mathrm{ClO}_4{}^-)$ and the ionic radii of the An^{4+} ions (c.f., Table 3). The lack of data at low NaCl concentrations does not allow an accurate evaluation of $\Delta\varepsilon_{\mathrm{Cl}}$ by extrapolation to $I = 0$, because the strict validity range of the linear SIT equation is limited to $I_{\mathrm{m}} < 4$ mol/kg H$_2$O [1–4], but the equilibrium constants in 2.5–5.6 m NaCl are compatible with the SIT coefficients of the NEA-TDB (c.f. dashed line in Fig. 2c):

$$-\Delta\varepsilon_{\mathrm{Cl}} = \varepsilon(\mathrm{Th}^{4+}, \mathrm{Cl}^-) + 4\varepsilon(\mathrm{Na}^+, \mathrm{Cl}^-) = 0.37 \pm 0.04\ \mathrm{kg/mol}\ [1\text{–}3].$$

Table 3. SIT coefficients $\varepsilon_{\mathrm{j,k}}$ (kg/mol) used and discussed in the present study.

j/k	ClO$_4^-$	Cl$^-$	NO$_3^-$
H$^+$	0.14 ± 0.01^a	0.12 ± 0.01^a	0.07 ± 0.01^a
Na$^+$	0.01 ± 0.01^a	0.03 ± 0.01^a	−0.04 ± 0.03^a
Th^{4+}	0.67 ± 0.10^b 0.70 ± 0.06^c	0.25 ± 0.03^a	0.11 ± 0.02^a 0.31 ± 0.12^c
U^{4+}	0.76 ± 0.06^a	0.36 ± 0.10^b	
Np^{4+}	0.84 ± 0.06^a	0.40 ± 0.10^b	
Pu^{4+}	0.82 ± 0.07^a	0.40 ± 0.10^b 0.37 ± 0.05^c	

a: NEA-TDB [3];
b: Estimated by Neck and Kim [10];
c: Present work.

The equilibrium constants in perchlorate solutions (Fig. 2b) deviate from the linear SIT regression at aqueous NaClO$_4$ concentrations above 0.7–1.5 mol/kg. This deviation is not due to an ionic strength dependence of $\varepsilon(\mathrm{Th}^{4+}, \mathrm{ClO}_4{}^-)$, but caused by the co-extraction of HClO$_4$(TBP)(TBP·H$_2$O)$_{p-1}$(org) and NaClO$_4$(TBP·H$_2$O)$_q$ (org). The calculated activity coefficients, *i.e.*, the sums $(\log\gamma_{\mathrm{Th}^{4+}} + 4\log\gamma_{\mathrm{X}^-})$ and $(\log\gamma_{\mathrm{H}^+} + \log\gamma_{\mathrm{X}^-})$ given by the differences $(\log {}^*K' - \log {}^*K^\circ)$ and $(\log {}^*K'_{\mathrm{HX}} - \log {}^*K^\circ_{\mathrm{HX}})$, respectively, are shown in Fig. 3a and b, where the terms

$$\log\gamma_{\mathrm{Th}^{4+}} + 4\log\gamma_{\mathrm{X}^-} + 20D = \left\{\varepsilon(\mathrm{Th}^{4+}, \mathrm{X}^-) + 4\varepsilon(\mathrm{Na}^+, \mathrm{X}^-)\right\} I_{\mathrm{m}} \qquad (12)$$

and

$$\log\gamma_{\mathrm{H}^+} + \log\gamma_{\mathrm{X}^-} + 2D = \left\{\varepsilon(\mathrm{H}^+, \mathrm{X}^-) + \varepsilon(\mathrm{Na}^+, \mathrm{X}^-)\right\} I_{\mathrm{m}} \qquad (13)$$

are plotted *versus* I_{m}. The deviation from linearity depends not only on the aqueous perchlorate concentration. With increasing concentration of TBP(org) the effect from co-extracted perchlorate (and water) on the free concentration and activity of TBP(org) becomes more and more pronounced, for both Th(ClO$_4$)$_4$ (Fig. 3a) and HClO$_4$ (Fig. 3b). Therefore only the data points marked with crosses inside (Figs. 2b and 3a) are used to calculate $-\Delta\varepsilon_{\mathrm{ClO}_4} = \varepsilon(\mathrm{Th}^{4+}, \mathrm{ClO}_4{}^-) + 4\varepsilon(\mathrm{Na}^+, \mathrm{ClO}_4{}^-)$.

On the other hand, Fig. 3a clearly shows that the trace activity coefficients of the Th^{4+} ion in nitrate and perchlorate solution follow the extended Debye–Hückel equation

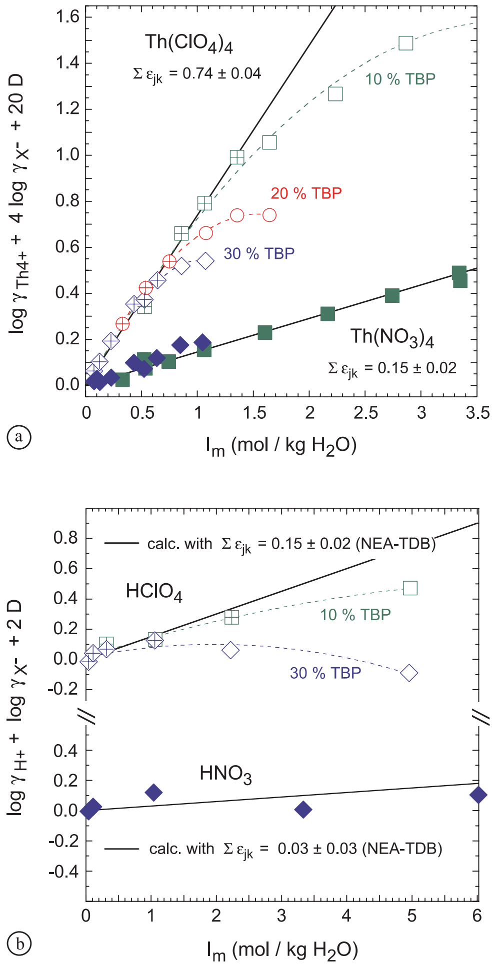

Fig. 3. Activity coefficients derived for a) $Th(ClO_4)_4$ and $Th(NO_3)_4$ and b) $HClO_4$ and HNO_3 as trace components in $NaClO_4$ and $NaNO_3$ media, respectively. The data are plotted according to Eq. (12) and Eq. (13). The deviation from linearity (dashed line: polynominal fit including open points without crosses inside) is caused by the co-extraction of $NaClO_4$.

of the SIT down to ionic strengths below 0.1 mol/kg. It is further to note that the activity coefficients derived from the TBP extraction studies with HNO_3 (in 0.1–6 m $NaNO_3$) and $HClO_4$ (in 0.1–1.5 m $NaClO_4$) are consistent with the SIT coefficients of the NEA-TDB, *i.e.*, with $\varepsilon(H^+, X^-) + \varepsilon(Na^+, X^-) = 0.03 \pm 0.03$ and 0.15 ± 0.02 kg/mol for $X^- = NO_3^-$ and ClO_4^-, respectively (Fig. 3b). This agreement confirms that the study of liquid-liquid phase equilibria with TBP is an appropriate method to determine the activity coefficients in the aqueous phase.

3.2 Discussion of the SIT coefficients of the Th^{4+} ion and conclusions from the comparison with SIT coefficients of other metal ions

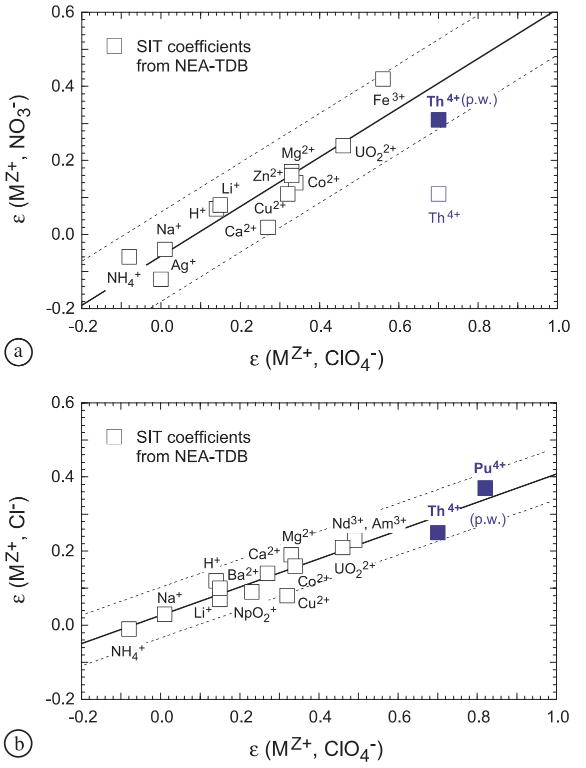

Fig. 4. Linear correlations (±2σ) between SIT coefficients of non-complexed cations M^{Z+}. (a) $\varepsilon(M^{Z+}, NO_3^-)$ and $\varepsilon(M^{Z+}, ClO_4^-)$, (b) $\varepsilon(M^{Z+}, Cl^-)$ and $\varepsilon(M^{Z+}, ClO_4^-)$.

Figure 4 shows ion interaction coefficients $\varepsilon(M^{Z+}, NO_3^-)$, $\varepsilon(M^{Z+}, Cl^-)$ and $\varepsilon(M^{Z+}, ClO_4^-)$ selected in the NEA-TDB [3] for various for non-complexed cations M^{Z+} with $Z = 1–4$, including the values for the comparable Pu^{4+} ion, $\varepsilon(Pu^{4+}, ClO_4^-) = 0.82 \pm 0.07$ kg/mol and $\varepsilon(Pu^{4+}, Cl^-) = 0.37 \pm 0.05$ kg/mol. The latter value is calculated in the present work from data accepted in the NEA-TDB [2] (see Appendix). There is an obvious linear correlation between $\varepsilon(M^{Z+}, NO_3^-)$ and $\varepsilon(M^{Z+}, ClO_4^-)$ or $\varepsilon(M^{Z+}, Cl^-)$ and $\varepsilon(M^{Z+}, ClO_4^-)$ with all values lying in a narrow range. The SIT coefficients for the Th^{4+} ion, $\varepsilon(Th^{4+}, Cl^-) = 0.25 \pm 0.03$ kg/mol [1–3] and those determined in the present work, $\varepsilon(Th^{4+}, NO_3^-) = 0.31 \pm 0.12$ kg/mol and $\varepsilon(Th^{4+}, ClO_4^-) = 0.70 \pm 0.06$ kg/mol (filled points in Fig. 4), follow these linear correlations. This is considered as a confirmation of these values, whereas the NEA-TDB value of $\varepsilon(Th^{4+}, NO_3^-) = 0.11 \pm 0.02$ kg/mol [1–3] is far out of this range (Fig. 4a).

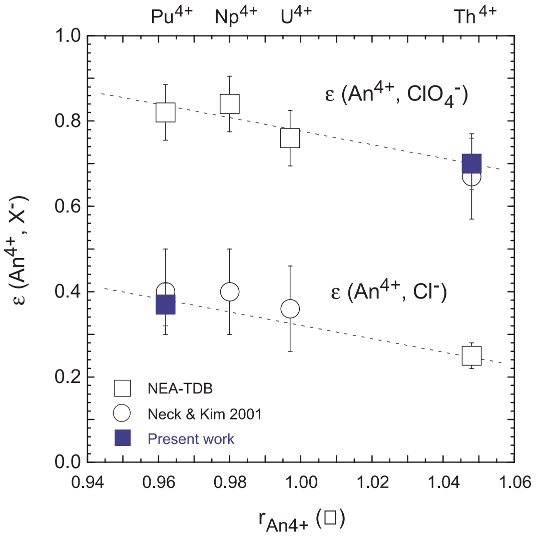

Fig. 5. Linear correlations between SIT coefficients $\varepsilon(An^{4+}, ClO_4^-)$ and $\varepsilon(An^{4+}, Cl^-)$ of tetravalent actinide aquo ions and $1/r_{An^{4+}}$ ($r_{An^{4+}}$ = ionic radius for coordination number CN = 8, from [25]).

The interaction coefficients $\varepsilon(\mathrm{Th}^{4+}, \mathrm{ClO_4}^-) = 0.70 \pm 0.06$ kg/mol and $\varepsilon(\mathrm{Th}^{4+}, \mathrm{Cl}^-) = 0.25 \pm 0.03$ kg/mol [1–3] are further confirmed by the correlation between known values $\varepsilon(\mathrm{An}^{4+}, \mathrm{ClO_4}^-)$ and $\varepsilon(\mathrm{An}^{4+}, \mathrm{Cl}^-)$ for other tetravalent actinide aquo ions and their ionic radii [25] (c.f., Fig. 5). It is to note that the effect of complex formation with chloride ions is included in these ion interactions coefficients $\varepsilon(\mathrm{An}^{4+}, \mathrm{Cl}^-)$.

Appendix: Ion interaction (SIT) coefficient $\boldsymbol{\varepsilon}(\mathbf{Pu}^{4+}, \mathbf{Cl}^-)$

The SIT coefficient $\varepsilon(\mathrm{Pu}^{4+}, \mathrm{Cl}^-)$ is calculated from the redox potentials $E^{\circ\prime}(\mathrm{Pu}^{4+}/\mathrm{Pu}^{3+})$ at $I = 0$ and in 1.0 M HCl at 25 °C, *i.e.*, from the equilibrium constants $\log K_{\mathrm{IV/III}}$ for the reaction

$$\mathrm{Pu}^{4+} + \mathrm{e}^- \Leftrightarrow \mathrm{Pu}^{3+}\,.$$

The NEA-TDB selections of $E^\circ(\mathrm{Pu}^{4+}/\mathrm{Pu}^{3+}) = 1.047 \pm 0.003$ V and $\log K^\circ_{\mathrm{IV/III}} = 17.69 \pm 0.04$ at $I = 0$ [2] is based on the redox potential $E^{\circ\prime}(\mathrm{Pu}^{4+}/\mathrm{Pu}^{3+}) = 0.9821 \pm 0.0005$ V ($\log K_{\mathrm{IV/III}} = 16.603 \pm 0.01$) determined by Rabideau and Lemons [26] in 1.0 M $HClO_4$ at 25 °C. Using the same experimental equipment these authors [26] also determined the redox potential in 1.0 M HCl at 25 °C: $E^{\circ\prime}(\mathrm{Pu}^{4+}/\mathrm{Pu}^{3+}) = 0.9703 \pm 0.0005$ V($\log K_{\mathrm{IV/III}} = 16.404 \pm 0.01$).

Lemire *et al.* [2] used the SIT coefficients $\varepsilon(\mathrm{Pu}^{4+}, \mathrm{ClO_4}^-) = 0.82 \pm 0.07$ and $\varepsilon(\mathrm{Pu}^{3+}, \mathrm{ClO_4}^-) = 0.49 \pm 0.05$ [2, 3] for the extrapolation of $\log K_{\mathrm{IV/III}}$ from 1.05 m $HClO_4$ to $I = 0$. The equilibrium constants at $I = 0$ and in 1.02 m HCl yield $\Delta\varepsilon(\log K_{\mathrm{IV/III}}$ in HCl solution$) = -0.14 \pm 0.04$, and with $\varepsilon(\mathrm{Pu}^{3+}, \mathrm{Cl}^-) = \varepsilon(\mathrm{Am}^{3+}, \mathrm{Cl}^-) = 0.23 \pm 0.02$ [3], we obtain

$$\varepsilon(\mathrm{Pu}^{4+}, \mathrm{Cl}^-) = 0.37 \pm 0.05\ \mathrm{kg/mol}\,.$$

This value agrees well with $\varepsilon(\mathrm{Pu}^{4+}, \mathrm{Cl}^-) = 0.4 \pm 0.1$ kg/mol estimated by Neck and Kim [10] from analogies and correlations between the tetravalent actinide ions.

References

1. Grenthe, I., Fuger, J., Konings, R. J. M., Lemire, R. J., Muller, A. B., Nguyen-Trung, C., Wanner, H. (OECD, NEA-TDB): Chemical Thermodynamics. Vol. 1. *Chemical Thermodynamics of Uranium*. Elsevier, North-Holland, Amsterdam (1992).
2. Lemire, R. J., Fuger, J., Nitsche, H., Potter, P., Rand, M. H., Rydberg, J., Spahiu, K., Sullivan, J. C., Ullman, W. J., Vitorge, P., Wanner, H. (OECD, NEA-TDB): Chemical Thermodynamics. Vol. 4. *Chemical Thermodynamics of Neptunium and Plutonium*. Elsevier, North-Holland, Amsterdam (2001).
3. Guillaumont, R., Fanghänel, Th., Fuger, J., Grenthe, I., Neck, V., Palmer, D. A., Rand, M. H. (OECD, NEA-TDB): Chemical Thermodynamics Vol. 5. *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*. Elsevier, North Holland, Amsterdam (2003).
4. Ciavatta, L.: The specific interaction theory in evaluating ionic equilibria. Ann. Chim. (Rome) **70**, 551 (1980).
5. Robinson, R. A., Stokes, R. M.: *Electrolyte Solutions*. Revised 2nd edn., Butterworths, London (1965).
6. Rai, D., Felmy, A. R., Sterner, S. M., Moore, D. A., Mason, M. J., Novak, C. F.: The solubility of Th(IV) and U(IV) hydrous oxides in concentrated NaCl and $MgCl_2$ solutions. Radiochim. Acta **79**, 239 (1997).
7. Rai, D., Moore, D. A., Oakes, C. S., Yui, M.: Thermodynamic model for the solubility of thorium dioxide in the Na^+-Cl^--OH^--H_2O system at 23 °C and 90 °C. Radiochim. Acta **88**, 297 (2000).
8. Roy, R. N., Vogel, K. M., Good, C. E., Davis, W. B., Roy, L. N., Johnson, D. A., Felmy, A. R., Pitzer, K. S.: Activity coefficients in electrolyte mixtures: $HCl + ThCl_4 + H_2O$ for 5–55 °C. J. Phys. Chem. **96**, 11065 (1992).
9. Neck, V., Altmaier, M., Müller, R., Bauer, A., Fanghänel, Th., Kim, J. I.: Solubility of crystalline thorium dioxide. Radiochim. Acta **91**, 253 (2003).
10. Neck, V., Kim, J. I.: Solubility and hydrolysis of tetravalent actinides. Radiochim. Acta **89**, 1 (2001).
11. Capdevila, H., Vitorge, P.: Solubility product of $Pu(OH)_4$(am). Radiochim. Acta **82**, 11 (1998).
12. Altmaier, M., Neck, V., Fanghänel, Th.: to be published.
13. McKay, H. A. C., Healy, T. V.: Tri-*n*-butyl orthophosphate (TBP) as an extracting solvent. In: Progr. Nucl. Energy. Series III, *Process Chemistry* (Bruce, F. R., Fletcher, J. M., Hyman, H. H., eds.) Pergamon Press, London (1958) Vol. 2, p. 546.
14. Marcus, Y., Kertes, A. S.: *Ion Exchange and Solvent Extraction of Metal Complexes*. Wiley, London, New York (1969).
15. Marcus, Y.: *Critical Evaluation of Some Equilibrium Constants Involving Organophosphorus Extractants*. IUPAC Add. Publ., Butterworths, London (1974).
16. Davies Jr., W.: Thermodynamics of extraction of nitric acid by tri-*n*-butyl phosphate-hydrocarbon diluent solutions. I. Distribution studies with TBP in Amsco 125-82 at intermediate and low acidities. Nucl. Sci. Eng. **14**, 159 (1962).
17. Hesford, E., McKay, H. A. C.: The extraction of mineral acids by tri-*n*-butyl phosphate (TBP). J. Inorg. Nucl. Chem. **13**, 156 (1960).
18. Naito, K., Suzuki, T.: The mechanism of the extraction of several proton acids by tri-*n*-butyl phosphate. J. Phys. Chem. **66**, 983 (1962).
19. Irving, H., Edgington, D. N.: The extraction of some metal chlorides into tri-*n*-butyl phosphate. J. Inorg. Nucl. Chem. **10**, 306 (1959).
20. Whitney, D. G., Diamond, R. M., The extraction of acids by basic organic solvents. I. Tributyl phosphate – $HClO_4$ and tributyl phosphate – $HReO_4$. J. Phys. Chem. **67**, 209 (1963).
21. Pruett, D. J.: The solvent extraction behavior of technetium. Part I. The nitric acid – tri-*n*-butyl phosphate system and Part II. The hydrochloric acid – tri-*n*-butyl phosphate system. Radiochim. Acta **28**, 153 (1981) and **29**, 107 (1981).
22. Neck, V.: Thermodynamische Untersuchungen zur Solvatation von Ionen und ihrer Konsequenzen für Extraktionsvorgänge. Thesis, Techn. Univ. Karlsruhe, Germany (1988).
23. Neck, V., Müller, R., Bouby, M. Altmaier, M., Rothe, J., Denecke, M. A., Kim, J. I.: Solubility of amorphous Th(IV) hydroxide – application of LIBD to determine the solubility product and EXAFS for aqueous speciation. Radiochim. Acta **90**, 485 (2002).
24. Nakashima, T., Zimmer, E.: Hydrolysis of $Th(NO_3)_4$ and its extractability by TBP. Radiochim. Acta **37**, 165 (1984).
25. Choppin, G. R., Rizkalla, E. N.: Solution Chemistry of Actinides and Lanthanides. In: *Handbook on the Physics and Chemistry of Rare Earths*. (Gschneidner Jr., K. A., Eyring, L., eds.) North Holland, Amsterdam (1994) Vol. 18, Chap. 128, p. 559.
26. Rabideau, S. W, Lemons, J. F.: The potential of the Pu(III)-Pu(IV) couple and the equilibrium constants for some complex ions of Pu(IV). J. Am. Chem. Soc. **73**, 2895 (1951).