Studies on the Complexation Behavior of Thorium(IV). 1. Hydrolysis Equilibria

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The stability constants of thorium(IV) hydrolysis species have been measured at 15, 25, and 35°C (in 1.0 mol dm^{-3} NaClO$_4$) using both potentiometry and solvent extraction. The results indicate the presence of the monomeric species Th(OH)$^{3+}$, Th(OH)$_2^{2+}$, Th(OH)$_3^+$, and Th(OH)$_4$, in addition to the polymeric species Th$_4$(OH)$_8^{8+}$ and Th$_6$(OH)$_{15}^{9+}$. The polymeric species were found to be important, although the total thorium concentration was limited to 0.01–0.1 mmol-dm^{-3}. The solvent extraction measurements required the use of acetylacetone. As such, the stability constants of thorium(IV) with acetylacetone were also measured using both potentiometry and solvent extraction. All logarithms of the stability constants were found to be linear functions of the reciprocal absolute temperature indicating that $\Delta H°$ and $\Delta S°$ of reaction are both independent of temperature (over the temperature range examined in the study).

KEY WORDS: Thorium; hydrolysis; potentiometry; solvent extraction; temperature; thermodynamics.

1. INTRODUCTION

The solution chemistry of actinides, particularly hydrolysis, is of major importance in the design of nuclear waste repositories and in relation to nuclear fuel reprocessing cycles.[1,2] Hydrolytic reactions in aqueous solution can limit an actinide metal's solubility, can lead to precipitation or adsorption, and/or reduce complexation by other ligands in the waste waters.[1]

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In aqueous solution, thorium exists only in the tetravalent state. Thorium is the largest of the tetravalent cations and, as such, has the least susceptibility to hydrolyze. Even though the hydrolysis of thorium(IV) has been studied for over 30 years[2–11] it is still poorly understood. The hydrolytic behavior of the ion is known to be extremely complex because of the presence of extensive polymerization reactions, which occur in a narrow pH range. As a result, there has been little agreement on the magnitude of the various stability constants but, more importantly, there has also been less agreement about the hydrolysis species that have been postulated to form. In addition to monomeric species, dimeric,[4,6,8,9,11] trimeric,[4,8,9] tetrameric,[4,6,9–11] hexameric,[4,6,9–11] and decameric[4] species have been proposed. The most extensive work is that of Baes $et\ al.$,[6] which indicated the presence of the species $Th(OH)^{3+}$, $Th(OH)_2^{2+}$, $Th_2(OH)_2^{6+}$, $Th_4(OH)_8^{8+}$, and $Th_6(OH)_{15}^{9+}$ (in 1.0 mol-kg^{-1} NaClO$_4$) at 0, 25 [based on the earlier data of Kraus and Holmberg[7]] and 95°C. In an attempt to elucidate the thorium(IV) hydrolysis species that form, the present study has examined the Th–H$_2$O system using both potentiometry and solvent extraction at 15, 25, and 35°C in an ionic medium of 1.0 mol-dm^{-3} NaClO$_4$.

2. EXPERIMENTAL

2.1. Reagents

The source of thorium was Th(NO$_3$)$_4$ · 6H$_2$O (BDH Analar; 99.9% purity) or ThO$_2$ (Cerac Pro analysi). The base was NaOH (Merck Suprapur or Merck G.R, Pro analysi). Sodium perchlorate (NaClO$_4$ · H$_2$O), used as the ionic medium, was either BDH Analar or Merck G.R. Pro analysi. Sodium chloride, used as a filling solution for the pH electrodes, was Merck Suprapur. The NaCl-filled electrodes were calibrated with potassium hydrogen phthalate (Merck; batch A848865). Perchloric acid was BDH Analar. Acetylacetone was SIGMA (batch A-3511), on which no pretreatment was performed. All solutions were made up to volume with MilliQ water.

2.2. Potentiometric Measurements (First Series)

The titration equipment was similar to that previously described.[12–14] In summary, it consisted of a Radiometer pH meter (PHM84), a Radiometer ABU80 Autoburette (2.5 cm^3 burette, resolution 0.1 mm^3), and a conventional stirred–gas reaction vessel. Radiometer GK2401C glass electrodes were used. However, since NaClO$_4$ was used as the ionic medium, KCl could not be used as the filling solution, because of the potential for precipitation of KClO$_4$. Therefore, the filling solution was changed to saturated NaCl, as previously described.[15] These electrodes have negligible drift over extended

periods[12] (*ca.* 0.002 pH units per 24 h), an important feature since the titrations were up to 24 h in duration. The titrant (nominally 0.01 mol-dm^{-3} NaOH) was delivered *via* a Teflon needle (Hamilton, bore 0.025 cm) dipping about 1 cm below the solution surface. Measurements were carried out under an argon atmosphere at 15.0, 25.0, and 35.0±0.1°C and at a total ionic strength of 1.0 mol-dm^{-3}, using NaClO$_4$. The temperature was regulated by a Thermoline Unistat 140 immersion heater and Thermoline TIC-580-T immersion cooler. The equipment was controlled using a personal computer control interface.[16] Titrant was added in constant increments (for a given titration) every 5 min; the pH was recorded every minute to verify that equilibrium had been attained and that colloids were not forming in the reaction vessel. Each titration was terminated when the change in pH over the 5-min period exceeded 0.002 units. The measured titration data for 15°C are given in the Appendix; full details are available on request.

2.3. Potentiometric Measurements (Second Series)

All titrations were carried out in a temperature-controlled plastic vessel under a nitrogen atmosphere. The titration equipment consisted of a Radiometer ABU91 (1.0 cm^3 burette, resolution: 0.1 mm^3) automatic burette and measuring system, which was controlled by a personal computer. The electrodes used were a Radiometer glass electrode (Radiometer PHG201) and an open junction electrode (Radiometer K102-K) filled with 1.0 mol-dm^{-3} NaClO$_4$ The electrode response was calibrated on the basis of the method developed by Gran.[17,18] The program used was a modified version of that supplied by the manufacturer, as previously described.[19] The number of measurements and the time between additions were defined by the user. In addition, the temperature was recorded for each measurement. The experimental conditions were the same as described for the first series of potentiometric titrations.

2.4. Solvent Extraction Measurements

Generally, studies of extraction and distribution between two immiscible liquids are performed batchwise and then, after separation, by taking samples from each phase. This method is cumbersome if many samples are desired and, therefore, the AKUFVE technique was developed.[20–23] The apparatus consists mainly of two parts: a mixing chamber and a centrifuge, which separates the different phases. Connected to the solvent extraction apparatus are pumps to withdraw samples from the flow as it passes from the centrifuge to the mixing chamber. This circulation flow is also used for pH measurements and temperature control. The apparatus used in the experiments has been described by Albinsson *et al.*,[24] except that to increase the precision of the
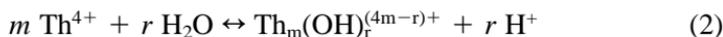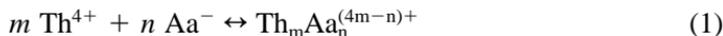
temperature measurement, the temperature in the present study was also measured on the outgoing flow from the centrifuge.[25]

To avoid carbonate in the system, all experiments were started at low pH (below pH 2) and were performed under a high-purity nitrogen atmosphere obtained by introducing nitrogen into the mixing chamber as well as into the centrifuge ventilation tube. The thorium concentration was held below 10^{-5} mol-dm^{-3} (typically 10^{-7} mol-dm^{-3}) to avoid polynuclear complexation and the formation of colloids at circumneutral pH.[26] High-purity NaOH[19] was added to the AKUFVE by automatic burettes to obtain the desired pH. Acetylacetone decomposition was investigated using spectrophotometry and was found to be negligible in the pH range of the experiments conducted in this study. The measured solvent extraction data for 15°C are given in the Appendix; full details are available on request.

3. COMPUTATIONAL PROCEDURE

3.1. Potentiometic Measurements: Hydrolysis Constants (First and Second Series)

The complexation and hydrolysis reactions, Eqs. (1 and 2), examined in the present study are described by the stability constants β_{mnr} as given in Eqs. (3 and 4)

$$m \, \text{Th}^{4+} + n \, \text{Aa}^- \leftrightarrow \text{Th}_m\text{Aa}_n^{(4m-n)+} \tag{1}$$

$$m \, \text{Th}^{4+} + r \, \text{H}_2\text{O} \leftrightarrow \text{Th}_m(\text{OH})_r^{(4m-r)+} + r \, \text{H}^+ \tag{2}$$

$$\beta_{mn0} = \frac{[\text{Th}_m\text{Aa}_n^{(4m-n)+}]}{[\text{Th}^{4+}]^m[\text{Aa}^-]^n} \tag{3}$$

$$\beta_{m0r} = \frac{[\text{Th}_m(\text{OH})^{(4m-r)+}][\text{H}^+]^r}{[\text{Th}^{4+}]^m} \tag{4}$$

where Aa$^-$ denotes the acetylacetonate ion. Each species will be represented by either its formula or as the (m,n,r) triplet.

The potentiometric data were analyzed using the computer program MINIQUAD.[12-14] MINIQUAD separately and independently minimizes both $\{[\text{H}]_{\text{T(calc)}} - [\text{H}]_{\text{T(obs.)}}\}^2$ and $\{[\text{M}]_{\text{T(calc)}} - [\text{M}]_{\text{T(obs)}}\}^2$ as defined by the mass balance equations and experimental observations. It is an updated version of the original program[27,28] containing the following additional features:

1. Numerical refinement of the analytical proton excess at the beginning of a titration, allowing a titration to begin at any pH value, irrespective of the extent of reaction.

2. Optional numerical refinement of the relation between pH values and hydrogen ion concentrations using Eq. (5)

$$[H^+] = \frac{10^{-pH}}{\lambda} \qquad (5)$$

where λ is a correction to the observed pH values and includes the proton activity coefficient and other contributions (assumed constant) such as the liquid-junction potential, asymmetry potential, and calibration errors. The use of Eq. (5) in the numerical refinement procedure negates the need for Gran titrations.

3. Optional numerical refinement of negative formation constants.

4. Two automated model (as opposed to species) selection procedures in addition to the "manual" method described by Gans et al.[28]

The bulk of the data was analyzed using previously stated model selection criteria[12] (see Results and Discussion): namely, (a) the computational standard deviations of all species in the model are $\leq 10\%$; and (b) R [the normalized agreement factor[29]] is less than 0.002.

3.2. Potentiometric Measurements: Acetylacetonate and Hydrolysis Constants (Second Series)

The method used for the evaluation of the potentiometric titrations was introduced by Bjerrum in the 1940s.[30] In his method, Bjerrum used the average ligand number, as defined in Eq. (6)

$$\bar{n} = \frac{[L^-]_{bound}}{[M]_{tot}} \qquad (6)$$

which, when expressed as a function of the ligand concentration, is called the formation function.

In the case of a ligand releasing one proton in the complexation reaction, and assuming that the deprotonation of the ligand is negligible compared to other contributions of protons, the derivation of the formation function is given by Eq. (7)

$$[H^+]_m = [H^+]_0 - [OH^-]_{tit} + [ML^{z-1}] + 2[ML_2^{z-2}] + \ldots \qquad (7)$$

where $[H^+]_m$ is the total concentration of protons, $[H^+]_0$ is the initial proton concentration, $[OH^-]_{tit}$ is the concentration of base added, and z is the charge of the metal ion M. Equation (7) can be rewritten in terms of the stability constants described in Eqs. (3 and 4), namely

$$[H^+]_m = [H^+]_0 - [OH^-]_{tit} + \beta_1[M^{z+}][L^-] + 2\beta_2[M^{z+}][L^-]^2 + \ldots \qquad (8)$$

A mass balance for the total metal concentration, if no polynuclear complexes are formed, yields

$$[M^{z+}] = \frac{[M]_{tot}}{\sum\limits_{j=0}^{n} \beta_j [L^-]^j} \tag{9}$$

Combining Eqs. (8 and 9) yields the following expressions for the average ligand number

$$\overline{n} = \frac{\sum\limits_{j=1}^{n} i\beta_i [L^-]^i}{\sum\limits_{j=0}^{n} \beta_j [L^-]^j} \tag{10}$$

or

$$\overline{n} = \frac{[H^+]_m - ([H^+]_0 - [OH^-]_{tit})}{[M]_{tot}} \tag{11}$$

Thus, it is possible to obtain $(\overline{n}, [L^-])$ pairs, thereby allowing a subsequent least-squares fitting procedure to be used to determine the stability constants.

For the hydroxide constant determination, the quotient given in Eq. (12) was used.

$$\frac{\overline{n}}{1-\overline{n}} = \beta_1 [OH^-] \tag{12}$$

This equation was derived with the assumption that only the first hydrolysis complex was present in the pH range examined in the first series of hydrolysis experiments. The fitting was thus reduced to just a linear curve fit. The assumption was tested by examination of the average ligand number and by evaluating the titration curves with the method used to evaluate the second series of hydrolysis titration curves.

3.3. Solvent Extraction Measurements

The distribution of thorium D_{Th} between an aqueous solution and a toluene phase containing acetylacetone may be expressed as

$$D_{Th} = \frac{\lambda_4 \beta_{140} [Aa^-]}{1 + \sum\limits_{n=1}^{4} \beta_{1n0} [Aa^-]^n + \sum\limits_{p=1}^{4} \beta_{10p} [H^+]^p} \tag{13}$$

where λ_4 is the distribution of the $ThAa_4$ complex between the organic and

aqueous phase, assuming that it is the only extractable thorium complex in the system, and that polynuclear complexes can be neglected in comparison with the HAa complexes. The concentration of acetylacetonate in the aqueous phase may be calculated using

$$[Aa^-] = \frac{K_a[HAa]_{tot}}{[H^+](1 + k_d + K_a[H^+])} \tag{14}$$

where $[HAa]_{tot}$ is the original concentration of acetylacetone in the organic phase, K_a is the dissociation constant for HAa, and k_d is the distribution constant for HAa between the organic and aqueous phases. The concentration of protons $[H^+]$ in Eq. (14), for $NaClO_4$ at an ionic strength of 1.0, is calculated from the measured pH using Eq. (15), as was shown by Fanghänel et al.[31]

$$-\log[H^+] = pH + \log \lambda \tag{15}$$

where $\log \lambda$ is 0.23. Indeed, this is in good agreement ($0.26 < \log \lambda < 0.31$) with the relation between $[H^+]$ and pH found in the present study for the first series of potentiometric measurements (see Section 4.1).

3.4. Uncertainty Analysis

The uncertainty in the solvent extraction data was obtained using the chi-squared method.[32] In this method, it is assumed that the deviation from the curve fitted to the data is, at each point, normally distributed according to Eq. (16)

$$N = \frac{x - y}{ky} \tag{16}$$

where x is the experimentally obtained value, y is the calculated value, and k is a weight factor. If Eq. (16) is calculated for each sample point, squared, and the results added together, it expresses a sum of squared normal distributions, which is chi-square distributed. This sum may equal unity if divided by its degrees of freedom ν, since the expected value for a chi-square distribution is equal to the degrees of freedom (Eq. 17).

$$U = \frac{1}{\nu} \sum_i \frac{(x_i - y_i)^2}{k^2 y_i^2} \tag{17}$$

The variance is twice the expected value. Thus, the variance in the fitted parameters can be obtained by changing the parameters until U reaches twice its original value. The standard deviation is, therefore, the square root of the variance. If a 95% confidence interval is desired, the standard deviation is multiplied by 1.96. Although this method is obviously not completely strin-

gent, it is a good approach for assigning confidence intervals when the largest uncertainty lies in the fitting of parameters and when the fitting algorithm does not allow for a more elaborate calculation.[32]

In the case where the stability constants were measured potentiometrically, and a number of estimates were made [*i.e.*, (1,0,1) and (4,0,8)], the uncertainty was determined from the statistical standard deviation of the various estimates. Alternatively, for those stability constants measured potentiometrically where only a single estimate was made, the uncertainty was calculated using Eq. (18)[33]

$$\sigma_{\overline{X}} = \sqrt{s_X^2 + \sum_j s_j^2} \tag{18}$$

where $\overline{X}$ is the selected stability constant, $\sigma_{\overline{X}}$ is its estimated uncertainty, s_X is the standard deviation, as calculated by MINIQUAD (see below), and s_j is the estimation of systematic errors incurred in the measurement of the stability constants (*e.g.*, pH, Th concentration, titrant concentration, temperature, ionic strength). Each s_j must be related to $\overline{X}$ and be expressed in the same units.[33] The estimated uncertainty, which is significantly larger than the standard deviation, is a measure of the reliability and reproducibility of the stability constant whereas the standard deviation is a measure of the precision of the experiment only.[33]

4. RESULTS AND DISCUSSION

4.1. Potentiometric Measurements: Hydrolysis Constants (First Series)

A summary of the titrations used in the numerical analysis, for the three temperatures, is given in Table I. Two sets of potentiometric measurements were conducted at 25°C. For the data from all temperatures, only a single model could be found using MINIQUAD, which met the acceptance criteria: (a) the computational standard deviations of all species in the model are no greater than 10%; and (b) R [the normalized agreement factor[29]] is less than 0.002. This model contained the species $Th(OH)_2^{2+}$, $Th4(OH)_8^{8+}$, and $Th_6(OH)_{15}^{9+}$. The numerical analysis results are given in Table II, together with the results of Baes *et al.*,[6] which were obtained from measurements in the same ionic medium.

In Eq. (5), the value of λ was found to be 2.048, 1.818, 1.981, and 1.963 for the 15 and 35°C data and the two sets of data at 25°C, respectively. The values at 25°C are in good agreement with the value 1.970 found by Khoe *et al.*,[15] also in 1.0 mol-dm^{-3} NaClO$_4$, indicating, as expected, that

Table I.   Summary of Titrations of Thorium(IV) in 1.0 mol-dm^{-3} NaClO$_4$

°C	Total initial Th(IV) concentration (μmol-dm^{-3})	pH range	Number of points
15	104	3.605–4.192	57
	50.1	3.514–4.015	45
	19.6	3.401–4.172	49
	9.57	3.407–4.193	44
25	98.9	3.552–4.279	61
	49.2	3.552–3.831	31
	19.4	3.453–4.201	48
	9.25	3.404–4.224	47
25	123	3.643–4.468	57
	61.5	3.626–3.905	33
	23.7	3.762–4.611	33
	11.6	3.591–4.153	73
35	103	3.232–3.972	97
	48.9	3.302–3.989	78
	19.1	3.403–4.021	49
	10.4	3.508–4.028	32

the magnitude of λ is dependent on ionic strength. The data from the present study indicate that the value of λ is also temperature dependent.

Additional titration data were needed to determine the first monomeric hydrolysis constant [for formation of Th(OH)$^{3+}$]. This data was in the pH range 3.0–3.3 for all temperatures. Numerical analysis using MINIQUAD was also performed on these data, and enabled the stability constant of the (1,0,1) species to be determined at all temperatures. The calculated constants are listed in Table III. The numerical refinement of these data, however, did not meet the accepted model criteria listed above. Nevertheless, there is good agreement between the constants determined from these refinements and those determined from our other measurements (see below).

4.2. Potentiometric Measurements: Acetylacetonate and Hydrolysis Constants (Second Series)

To determine the first monomeric hydrolysis constant, three or four titrations were performed at each temperature. Generally, each titration was conducted from pH 1.8 to 3.1 and the stability constant of Th(OH)$^{3+}$ was estimated by using Eq. (12). The use of this equation assumes that Th(OH)$^{3+}$ is the only species that forms over the pH range examined. The calculated stability constants for the (1,0,1) species are listed for each temperature in Table IV.

Table II. Results of Potentiometric Measurements of Hydrolysis of Thorium(IV) in 1.0 mol-dm^{-3} NaClO$_4$

°C	Total TH(IV) concentration (mmol-dm^{-3})	Species	$-\log \beta_{m0r}$	SD	SD of β_{m0r} (relative %)
15	0.00957–0.104	(1,2)	8.78	0.02	4.51
		(4,8)	20.55	0.01	2.74
		(6,15)	41.44	0.03	7.81
25	0.00925–0.989	(1,2)	8.55	0.02	5.19
		(4,8)	19.18	0.01	2.84
		(6,15)	39.01	0.04	8.87
25	0.0116–0.123	(1,2)	8.54	0.02	5.25
		(4,8)	18.95	0.01	3.19
		(6,15)	40.07	0.04	9.59
35	0.0104–0.103	(1,2)	8.36	0.04	8.56
		(4,8)	17.86	0.01	2.03
		(6,15)	36.58	0.04	9.75
0[a]	1.58–20.6	(1,1)	4.32	0.02	4.6
		(1,2)	8.48	0.03	6.9
		(2,2)	5.60	0.02	4.6
		(4,8)	22.79	0.02	4.6
		(6,15)	43.84	0.02	4.6
25[a]	0.25–15.0	(1,1)	4.15	0.04	9.2
		(1,2)	7.70	0.03	6.9
		(2,2)	4.61	0.02	4.6
		(4,8)	19.01	0.02	4.6
		(6,15)	36.76	0.02	4.6
95[a]	2.15–20.0	(1,1)	2.29	0.02	4.6
		(1,2)	4.50	0.01	2.3
		(2,2)	2.55	0.03	6.9
		(4,8)	10.49	0.03	6.9
		(6,15)	20.63	0.02	4.6

[a] Results from Baes *et al.* (Ref. 6).

Table III. Estimated Values of Stability Constant of Th(OH)$^{3+}$ from the First Series of Potentiometric Measurements

°C	$-\log \beta_{101}$	SD	SD of β_{101}[a]
15	3.34	0.05	11.1
25	3.35	0.06	12.8
35	3.19	0.07	15.8

[a] Relative %.

Table IV. Estimated Values of Hydrolysis Constants from the Second Series of Potentiometric Measurements

°C	Titration number	Species	-log β_{m0r}
	Using Eq. (14)		
15	1	(1,0,1)	3.66
	2		3.61
	3		3.59
25	1	(1,0,1)	3.28
	2		3.19
	3		3.24
35	1	(1,0,1)	3.08
	2		3.04
	3		3.22
	Using MINIQUAD		
15	1	(1,0,1)	3.71
	1	(4,0,8)	20.00
	2	(1,0,1)	3.64
	2	(4,0,8)	20.07
	3	(1,0,1)	3.80
25	1	(1,0,1)	3.42
	1	(4,0,8)	19.22
	2	(1,0,1)	3.25
	2	(4,0,8)	19.01
	3	(1,0,1)	3.59
	3	(4,0,8)	19.05
	4	(1,0,1)	3.35
35	1	(1,0,1)	3.29
	1	(4,0,8)	17.96
	2	(1,0,1)	3.27
	2	(4,0,8)	18.06
	3	(1,0,1)	3.13

These data were also analyzed using MINIQUAD. The calculated constants from these numerical refinements are also listed in Table IV. The results obtained using MINIQUAD indicate that the (1,0,1) species is not the only one to form in the pH range studied. The polymeric (4,0,8) species also formed under some conditions; however, it is a relatively minor species and, hence, the estimate of the stability constant of the (1,0,1) species, determined using Eq. (12), is believed to be reasonable. As can be seen from the data given in the table, there is good agreement between the stability constants calculated by the two methods.

Potentiometric measurements were also carried out to determine the stability constant of $Th(Aa)^{3+}$. Although the titration curves obtained using this technique could be used to determine the stability constants of both the

(1,1,0) and (1,2,0) species, only the stability constant of $Th(Aa)^{3+}$ was used because of to the greater precision in the stability constant of $Th(Aa)_2^{2+}$ obtained by solvent extraction. The calculated stability constant of $Th(Aa)^{3+}$ is given in Table V.

4.3. Solvent Extraction Measurements

A typical extraction curve for the thorium–acetylacetone–water system is given in Fig. 1. As shown in the figure, the plot may be divided somewhere on the plateau. To the left of the division, hydrolysis is negligible, and thus, the distribution function is simplified, allowing the stability constants of $Th(Aa)_2^{2+}$, $Th(Aa)_3^+$, and $Th(Aa)_4$ to be determined. The calculated stability constants of these species are given in Table V. Subsequently, all the data were used to determine the stability constants of $Th(OH)_3^+$ and $Th(OH)_4$. The calculated stability constants of these hydrolysis species are also given in Table V.

There is, however, a drawback in using solvent extraction for this particular system. The points at the far left of Fig. 1 have the lowest distribution ratio detectable in the system. Therefore, the concentration of the acetylacetonate ion in the water phase does not reach sufficiently low levels to allow the free thorium concentration to dominate the concentrations of thorium–acetylacetonate complexes. As a result, the first term (unity) in the denomina-
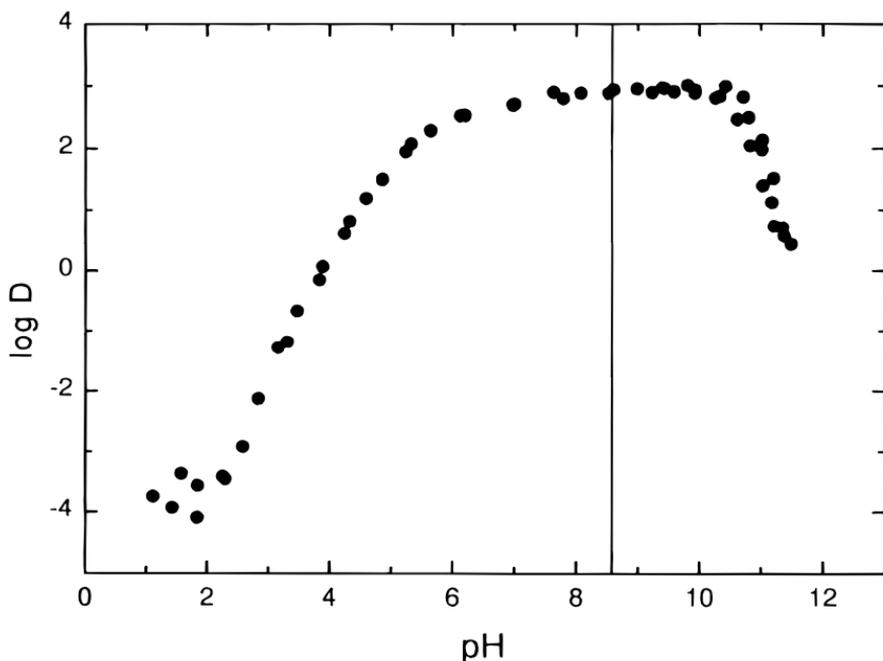

Fig. 1. Extraction curve for the thorium–acetylacetone–water system.

Table V. Estimated Stability Constants for Thorium(IV) Hydrolysis and Acetylacetone Species in 1.0 mol-dm^{-3} NaClO$_4$

°C	Species	$-\log \beta_{m0r}$	Uncertainty
		Hydrolysis	
15	(1,0,1)	3.6	0.1
	(1,0,2)	8.8	0.1
	(1,0,3)	14.9	2.8
	(1,0,4)	22.0	0.4
	(4,0,8)	20.2	0.3
	(6,0,15)	41.4	0.2
25	(1,0,1)	3.3	0.1
	(1,0,2)	8.6	0.1
	(1,0,3)	14.2[a]	—
	(1,0,4)	19.4	0.5
	(4,0,8)	19.1	0.1
	(6,0,15)	39.5	0.2
35	(1,0,1)	3.2	0.1
	(1,0,2)	8.4	0.1
	(1,0,3)	12.7	3.5
	(1,0,4)	17.8	0.4
	(4,0,8)	18.0	0.1
	(6,0,15)	36.6	0.2
		Acetylacetone	
15	(1,1,0)	9.4	0.1
	(1,2,0)	16.5	0.3
	(1,3,0)	22.2	0.5
	(1,4,0)	26.7	0.4
25	(1,1,0)	9.0	0.2
	(1,2,0)	16.7	0.6
	(1,3,0)	22.8	0.6
	(1,4,0)	27.4	0.2
35	(1,1,0)	8.8	0.1
	(1,2,0)	17.1	0.5
	(1,3,0)	23.5	0.5
	(1,4,0)	27.9	0.4

[a] Estimated from the other monomeric stability constants at 25°C and the stability constants of (1,0,3) at 15 and 35°C.

tor of Eq. (13) may be omitted. It is now possible to divide the stability constants by an arbitrary constant and, as such, the task of obtaining the stability constants has an infinite number of solutions.[34] However, the ratio between two successive constants is always the same, so if it is possible to obtain a value for the stability constant for the first complex, the remaining values can also be determined. In this work, the first stability constant was determined by potentiometric titrations, as described above.

4.4. Combined Data

The calculated stability constants (with uncertainties) for the hydrolysis of thorium(IV) are listed in Table V. The uncertainties for the (1,0,1) and (4,0,8) species were the standard deviations determined from the set of the stability constants calculated for each of these species. Conversely, only a single determination was made of the stability constants of the (1,0,2) and (6,0,15) species. The uncertainty for these species was determined using Eq. (18). The selected stability constants for the thorium(IV)-acetylacetone complexes are also given in Table V.

Uncertainties were also determined using Eq. (18) for the calculated stability constants of $Th(OH)^{3+}$ given in Table III. The values calculated were 0.09, 0.11 and 0.13 for 15, 25, and 35°C, respectively. These values compare favorably with the estimated uncertainties given for $Th(OH)^{3+}$ in Table V (calculated from the standard deviation of the various estimates), namely 0.14, 0.13, and 0.09, indicating that all the systematic errors in the potentiometric experiments have been taken into account.

The measurements made by Baes *et al.*[6] and Kraus and Holmberg[7] were carried out in the same medium (1.0 mol-dm^{-3} NaClO$_4$) as those of the present study. The results of the two earlier studies, as calculated by Baes *et al.*,[6] are presented in Table II. In comparing the results of these studies with those of the present study (Table V), some areas of agreement can be highlighted, but there are other areas of disagreement. Both studies were able to detect the species $Th(OH)^{3+}$, $Th(OH)_2^{2+}$, $Th_4(OH)_8^{8+}$, and $Th_6(OH)_{15}^{9+}$. The present study, however, did not detect the $Th_2(OH)_2^{6+}$ species, possibly because of the reduced thorium concentrations used (see Table II). Similarly, the studies of Baes *et al.*[6] and Kraus and Holmberg[7] were not able to detect the $Th(OH)_3^+$ or $Th(OH)_4$ species because of the occurrence of precipitation reactions at higher pH. The use of the solvent extraction technique can largely eliminate precipitation reactions, enabling the stability constants of the (1,0,3) and (1,0,4) species to be determined.

As is illustrated in Fig. 2a, where estimated stability constants are plotted against the reciprocal of absolute temperature, there is excellent agreement between the stability constants of $Th_4(OH)_8^{8+}$ determined in the present study with those determined by Baes *et al.*[6] Furthermore, Fig. 2a also shows that there is good agreement between the measured stability constants of $Th_6(OH)_{15}^{9+}$ from the two studies. Figure 3a indicates that $Th_6(OH)_{15}^{9+}$ is the dominant species at the higher thorium concentrations and moderate pH values used in the present study; at lower pH, $Th(OH)^{3+}$ dominates whereas at higher pH the most important species is $Th(OH)_4$ (see Fig. 3a). Figure 3a, however, also indicates that $Th_4(OH)_8^{8+}$ is an important species at these higher thorium concentrations.
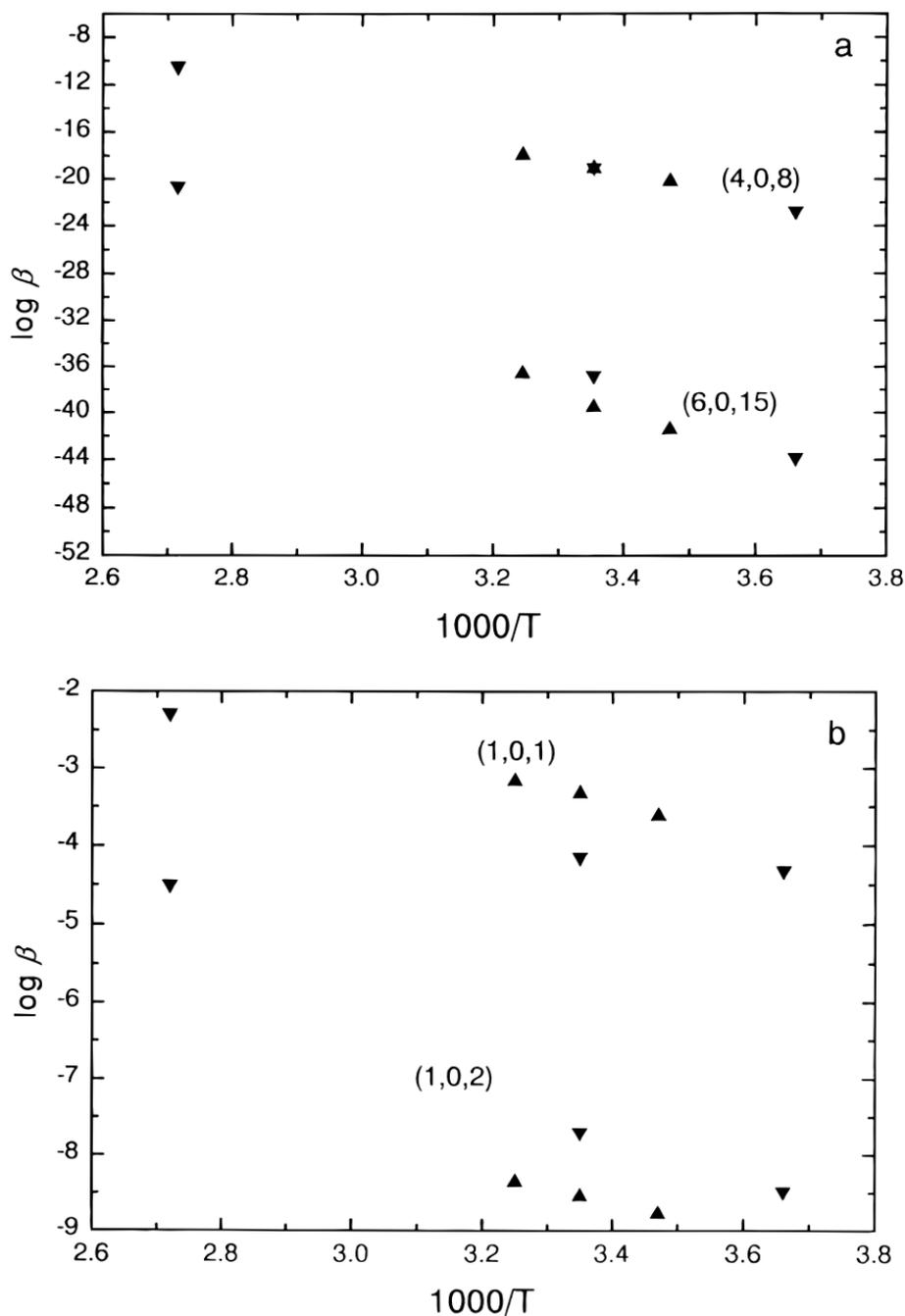
Fig. 2. Stability constants (log β) of thorium hydrolysis species plotted as a function of reciprocal absolute temperature comparing the results of the present study (▲) with those from Baes et al.[6] (▼): (a) $Th_4(OH)_8^{8+}$ and $Th_6(OH)_{15}^{9+}$; and (b) $Th(OH)^{3+}$ and $Th(OH)_2^{2+}$.
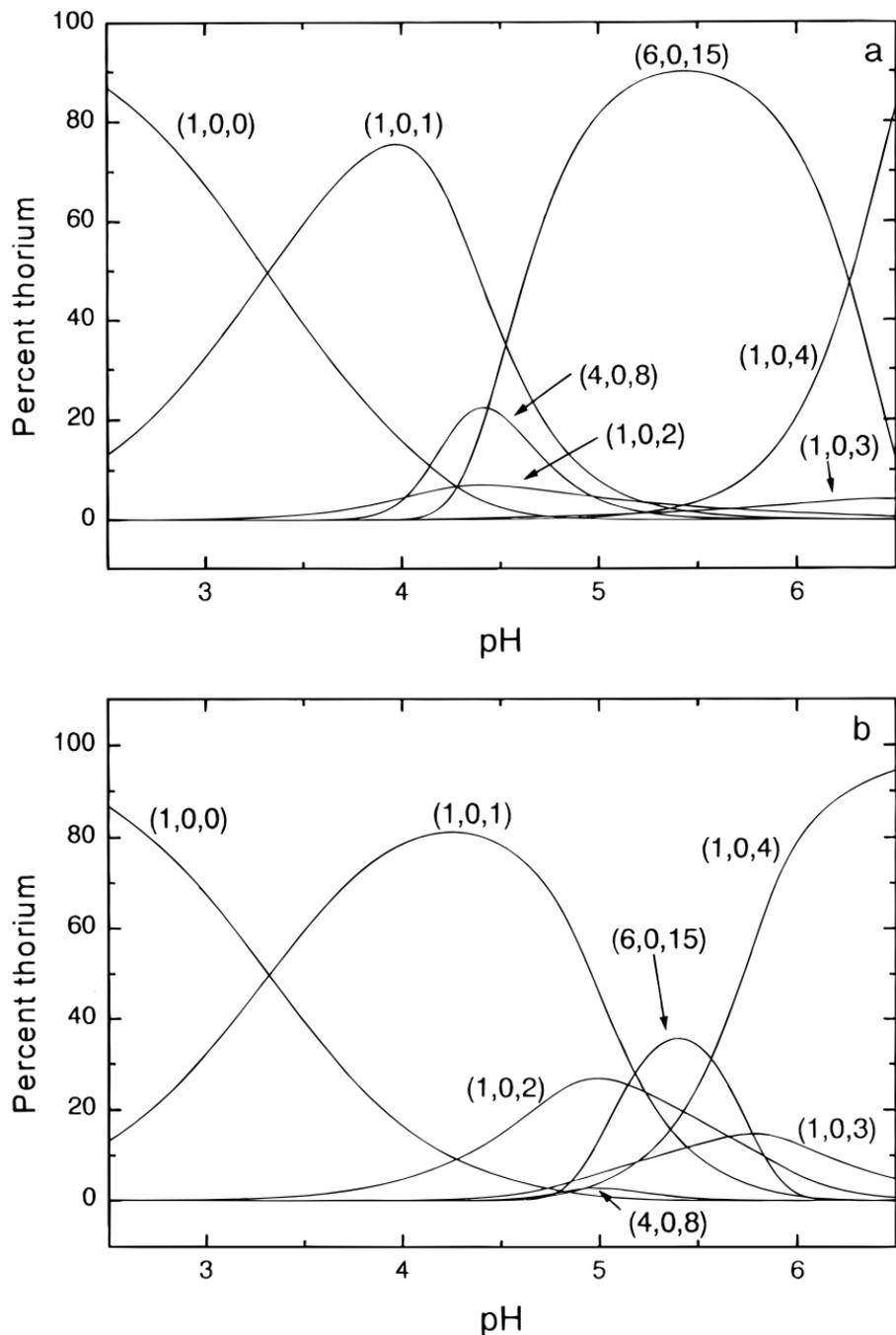
Fig. 3. Percentage distribution of thorium(IV) in various hydrolytic species at 25°C and in 1.0 mol-dm^{-3} NaClO$_4$ at a total thorium concentration of (a) 0.12 mmol-dm^{-3} and (b) 0.01 mmol-dm^{-3}.

In contrast to the results for the polymeric species, there is relatively poor agreement between the calculated constants of $Th(OH)^{3+}$ and $Th(OH)_2^{2+}$ determined by Baes *et al.*[6] and the present study, as is shown in Fig. 2b. The stability constants calculated by Baes *et al.*[6] for the (1,0,1) and (1,0,2) species are questionable since the stepwise constants (*e.g.*, log $K_1 = -4.15$ and log $K_2 = -3.55$ at 25°C) indicate that the formation of $Th(OH)_2^{2+}$ from $Th(OH)^{3+}$ has greater stability than the formation of $Th(OH)^{3+}$ from Th^{4+} at all three experimental temperatures. It is usual for the converse to occur, that is, the formation of $Th(OH)_2^{2+}$ from $Th(OH)^{3+}$ is weaker than the formation of $Th(OH)^{3+}$ from Th^{4+}, as is indicated by the stability constants found in the present study (*i.e.*, log $K_1 = -3.3$ and log $K_2 = -5.3$ at 25°C). In addition, the calculated stability constant for $Th(OH)^{3+}$ at 25°C from the present study (log $\beta_{110} = -3.3$) is in reasonable agreement with that measured previously by Brown *et al.*[10] (*i.e.*, log $\beta_{110} = -2.98$) in 0.10 mol-dm^{-3} KNO$_3$ at the same temperature, taking into account the differences in ionic strength and medium used in the two studies. At the lower thorium concentrations used in the present study (Fig. 3b), the monomeric species $Th(OH)^{3+}$ and $Th(OH)_2^{2+}$ dominate at lower pH, whereas $Th(OH)_3^{+}$ and $Th(OH)_4$ dominate at high pH. However, Fig. 3b also indicates that in a narrow range of pH the polymeric species $Th_6(OH)_{15}^{9+}$ will dominate the speciation, even at this low thorium concentration (0.01 mmol-dm^{-3}).

Very few determinations of the stability constants of $Th(OH)_3^{+}$ and $Th(OH)_4$ have been made. From the solubility measurements of ThO_2 in 0.1 mol-dm^{-3} NaClO$_4$ at 17°C carried out by Nabivanets and Kudritskaya,[35] and using only the data below a thorium concentration of 10^{-5} mol dm^{-3} and above pH 4.5, Baes and Mesmer[36] calculated a stability constant of -17.4 (log β) for $Th(OH)_4$ and an upper limit of -12.7 for the stability constant of $Th(OH)_3^{+}$ When the present data are corrected to 17°C (see below), the calculated constants of $Th(OH)_3^{+}$ and $Th(OH)_4$ are in reasonable agreement with those determined by Baes and Mesmer,[36] particularly when the differences in ionic strength are considered.

The calculated stability constants of thorium(IV)–acetylacetone complexes from this study (Table V) at 25°C are in reasonable agreement with those measured previously by Rydberg[37–39] when differences in ionic strength are considered. These latter data, in conjunction with the present data, were used to calculate stability constants for thorium(IV)–acetylacetone complexes at zero ionic strength. Using the specific ion interaction theory,[33] the logarithm of the stability constant at zero ionic strength and 25°C was calculated to be 8.3, 16.1, 22.5, and 27.6 for $Th(Aa)^{3+}$, $Th(Aa)_2^{2+}$, $Th(Aa)_3^{+}$, and $Th(Aa)_4$, respectively. These latter values are in reasonable agreement with stability constants calculated by Izatt *et al.*[40] at 30°C and zero ionic strength (*i.e.*, 8.8, 16.2, 22.5, and 26.7, respectively).

4.5. Enthalpy and Entropy of Reaction

The enthalpy and entropy change of a reaction, such as that given by Eq. (2), can be determined from Eq. (19), if the temperature dependence of $\Delta H°$ and $\Delta S°$ is negligible,

$$\log \beta = \frac{-\Delta H°}{\ln 10 \cdot R}\left[\frac{1}{T}\right] + \frac{\Delta S°}{\ln 10 \cdot R} \qquad (19)$$

where T is the absolute temperature, β is the stability constant for the reaction, R is the molar gas constant, and $\Delta H°$ and $\Delta S°$ are the enthalpy and entropy changes for the reaction. Thus, both the enthalpy and entropy of reaction can be determined from the stability constants using Eq. (19), assuming that the temperature dependence of $\Delta H°$ and $\Delta S°$ is negligible, by plotting log β against (1/T) for each species. Such plots are given in Fig. 4. The linearity of the plots indicate that $\Delta H°$ and $\Delta S°$ do, indeed, have negligible temperature dependence within the temperature interval investigated in the present study, particularly when the uncertainty in the estimated stability constants is taken into account (see Fig. 4). The calculated enthalpies and entropies of reaction for each species are given in Table VI. Also given in Table VI, are the calculated entropies and entropies of reaction for the thorium–acetylacetone complexes.

The entropy and enthalpy data calculated by Baes et al.[6] are also given in Table VI for comparative purposes. As was found in the present study, Baes et al.[6] found that the stability constant of each of the thorium species was a linear function of the reciprocal of absolute temperature. However, although the magnitude of the various values are similar between the two studies, the absolute values are somewhat different. These differences may arise from the narrow temperature range studied in the present work compared to that studied by Baes et al.[6] and differences resulting from the thorium concentrations employed (see above). Nevertheless, there is reasonable agreement between the overall results of Baes et al.[6] and those of the present work.

5. CONCLUSIONS

The stability constants of thorium(IV) hydrolysis species have been measured at 15, 25, and 35°C (in 1.0 mol-dm^{-3} NaClO$_4$ using both potentiometry and solvent extraction. In the pH range 2.0–4.5, the potentiometric measurements indicated the presence of the monomeric species Th(OH)$^{3+}$ and Th(OH)$_2^{2+}$, in addition to the polymeric species Th$_4$(OH)$_8^{8+}$ and Th$_6$(OH)$_{15}^{9+}$. Baes et al.[6] had also found evidence for all these species in the same ionic medium. The polymeric species were found to be important, although the total thorium concentration was limited to 0.01–0.1 mmol-dm^{-3}.
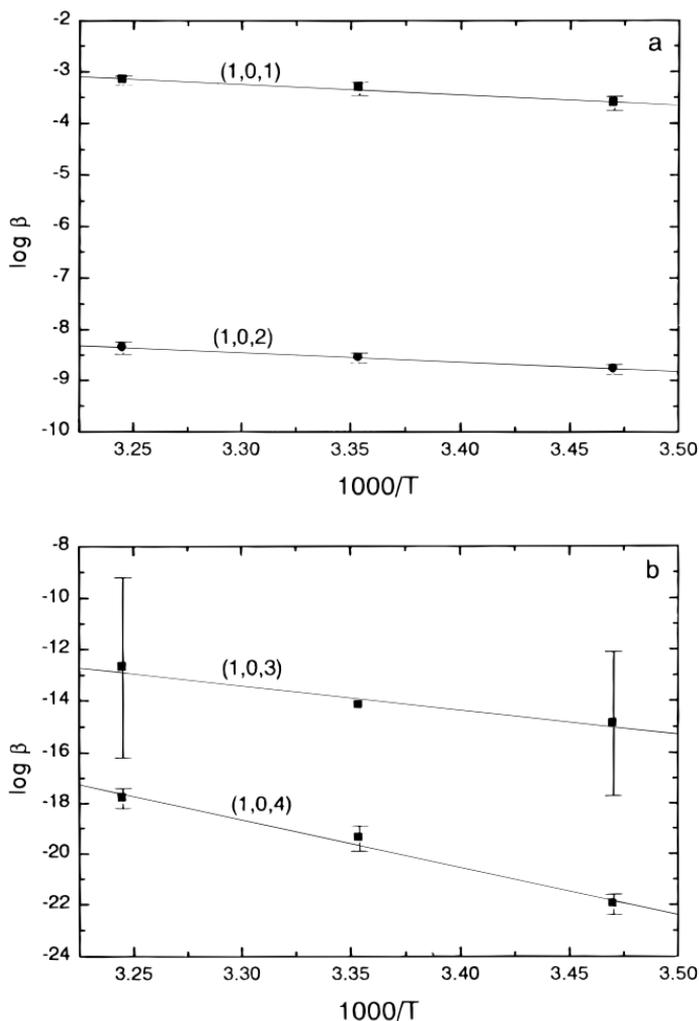
Fig. 4. Plots of the stability constants (log β) of thorium hydrolysis species against reciprocal absolute temperature: (a) $Th(OH)^{3+}$ and $Th(OH)_2^{2+}$; (b) $Th(OH)_3^+$ and $Th(OH)_4$; and (c) $Th_4(OH)_8^{8+}$ and $Th_6(OH)_{15}^{9+}$.

At higher pH, the solvent extraction measurements indicated the presence of the monomeric species $Th(OH)_3^+$ and $Th(OH)_4$, although the stability constant determined for the former species is relatively uncertain. The solvent extraction measurements required the use of acetylacetone. As such, the stability constants of thorium–acetylacetonate species were also measured using both techniques. All logarithms of the stability constants were found to be linear functions of the reciprocal temperature (in kelvin) indicating that $\Delta H°$ and $\Delta S°$ of reaction are both independent of temperature over the range examined in the study.
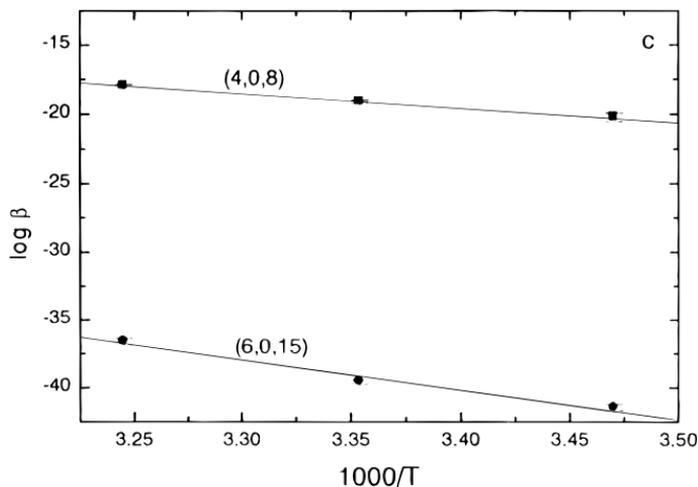
Fig. 4. Continued.

Table VI.   Enthalpy and Entropy of Thorium(IV) Hydrolysis and Acetylacetone Species Formation in 1.0 mol-dm^{-3} NaClO$_4$

Species	ΔH^o (kJ-mol^{-1})	ΔS^o (J-mol^{-1}-deg^{-1})
	This study	
ThOH^{3+}	38±6	60±20
Th(OH)$_2^{2+}$	36±1	−44±4
Th(OH)$_3^+$	190±40	(3±1)×10^2
Th(OH)$_4$	360±40	(8±1)×10^2
Th$_4$(OH)$_8^{8+}$	191±3	280±10
Th$_6$(OH)$_{15}^{9+}$	410±60	(6±2)×10^2
Th(Aa)$^{3+}$	−60±10	−10±40
Th(Aa)$_2^{2+}$	50±10	490±40
Th(Aa)$_3^+$	110±7	810±30
Th(Aa)$_4$	102±8	860±30
	From Baes *et al.* (Ref 16)[a]	
ThOH^{3+}	24.7	3.8
Th(OH)$_2^{2+}$	58.1	46.0
Th$_4$(OH)$_8^{8+}$	241.3	445.8
Th$_6$(OH)$_{15}^{9+}$	453.7	818.4

[a] For 25°C.

APPENDIX

Table AI. Potentiometric Data Acquired at 15°C (Summarized in Table I)

Vol. added (cm³)	pH	Vol. added (cm³)	pH	Vol. added (cm³)	pH	Vol. added (cm³)	pH
$[Th^{4+}] = 0.000104$ mol-dm^{-3}; $[OH^-] = 0.102$ mol-dm^{-3} (titrant); initial volume $= 58.075$ cm³							
0.000	3.605	0.375	3.726	0.750	3.844	1.125	4.004
0.025	3.613	0.400	3.734	0.775	3.850	1.150	4.016
0.050	3.623	0.425	3.742	0.800	3.861	1.175	4.031
0.075	3.632	0.450	3.749	0.825	3.871	1.200	4.046
0.100	3.641	0.475	3.757	0.850	3.879	1.225	4.061
0.125	3.649	0.500	3.764	0.875	3.889	1.250	4.077
0.150	3.657	0.525	3.771	0.900	3.900	1.275	4.094
0.175	3.665	0.550	3.779	0.925	3.909	1.300	4.112
0.200	3.673	0.575	3.787	0.950	3.919	1.325	4.131
0.225	3.681	0.600	3.794	0.975	3.931	1.350	4.150
0.250	3.689	0.625	3.801	1.000	3.942	1.375	4.172
0.275	3.696	0.650	3.810	1.025	3.954	1.400	4.192
0.300	3.705	0.675	3.818	1.050	3.966		
0.325	3.712	0.700	3.827	1.075	3.978		
0.350	3.720	0.725	3.836	1.100	3.991		
$[Th^{4+}] = 0.0000501$ mol-dm^{-3}; $[OH^-] = 0.102$ mol-dm^{-3} (titrant); initial volume $= 53.380$ cm³							
0.00	3.514	0.24	3.644	0.48	3.784	0.72	3.914
0.02	3.525	0.26	3.656	0.50	3.796	0.74	3.925
0.04	3.535	0.28	3.669	0.52	3.807	0.76	3.938
0.06	3.545	0.30	3.680	0.54	3.817	0.78	3.950
0.08	3.555	0.32	3.692	0.56	3.829	0.80	3.962
0.10	3.565	0.34	3.703	0.58	3.838	0.82	3.974
0.12	3.576	0.36	3.714	0.60	3.849	0.84	3.987
0.14	3.587	0.38	3.726	0.62	3.860	0.86	4.000
0.16	3.598	0.40	3.738	0.64	3.871	0.88	4.015
0.18	3.609	0.42	3.750	0.66	3.881		
0.20	3.621	0.44	3.762	0.68	3.892		
0.22	3.632	0.46	3.773	0.70	3.903		
$[Th^{4+}] = 0.0000196$ mol-dm^{-3}; $[OH^-] = 0.102$ mol-dm^{-3} (titrant); initial volume $= 52.440$ cm³							
0.00	3.401	0.26	3.530	0.52	3.704	0.78	3.951
0.02	3.409	0.28	3.541	0.54	3.720	0.80	3.974

Table AI.   Continued.

Vol. added (cm^3)	pH	Vol. added (cm^3)	pH	Vol. added (cm^3)	pH	Vol. added (cm^3)	pH
0.04	3.419	0.30	3.553	0.56	3.737	0.82	3.996
0.06	3.428	0.32	3.565	0.58	3.754	0.84	4.018
0.08	3.437	0.34	3.577	0.60	3.772	0.86	4.041
0.10	3.447	0.36	3.591	0.62	3.790	0.88	4.065
0.12	3.456	0.38	3.603	0.64	3.809	0.90	4.090
0.14	3.466	0.40	3.617	0.66	3.827	0.92	4.115
0.16	3.476	0.42	3.630	0.68	3.847	0.94	4.143
0.18	3.487	0.44	3.644	0.70	3.868	0.96	4.172
0.20	3.497	0.46	3.659	0.72	3.888		
0.22	3.507	0.48	3.673	0.74	3.908		
0.24	3.518	0.50	3.689	0.76	3.930		

$[Th^{4+}] = 0.00000957$ mol-dm^{-3}; $[OH^-] = 0.102$ mol-dm^{-3} (titrant); initial volume $= 51.600$ cm^3

Vol. added (cm^3)	pH	Vol. added (cm^3)	pH	Vol. added (cm^3)	pH	Vol. added (cm^3)	pH
0.00	3.407	0.22	3.520	0.44	3.667	0.66	3.879
0.02	3.416	0.24	3.531	0.46	3.683	0.68	3.904
0.04	3.425	0.26	3.543	0.48	3.699	0.70	3.930
0.06	3.435	0.28	3.555	0.50	3.716	0.72	3.957
0.08	3.445	0.30	3.568	0.52	3.734	0.74	3.986
0.10	3.455	0.32	3.581	0.54	3.752	0.76	4.016
0.12	3.465	0.34	3.594	0.56	3.772	0.78	4.047
0.14	3.475	0.36	3.608	0.58	3.791	0.80	4.081
0.16	3.486	0.38	3.622	0.60	3.812	0.82	4.116
0.18	3.497	0.40	3.637	0.62	3.834	0.84	4.154
0.20	3.508	0.42	3.651	0.64	3.856	0.86	4.193

Table AII.   Solvent Extraction Data Acquired at 15°C

$-\log [H^+]$	$\log D$	$-\log [H^+]$	$\log D$	$-\log [H^+]$	$\log D$	$-\log [H^+]$	$\log D$
		$[Th^{4+}] = 10^{-7}$ mol-dm^{-3}; $\log K_a = -9.11$, Eq. (14); $\lambda_4 = 280$, Eq. (13)					
3.317	−3.225	4.977	0.672	7.147	2.286	9.865	2.090
3.616	−2.116	5.424	1.279	7.195	2.385	10.064	2.389
3.698	−1.626	5.427	1.383	7.515	2.420	10.586	2.217
3.986	−1.220	5.836	1.811	7.839	2.352	11.371	1.714
4.184	−0.741	5.936	1.791	8.128	2.333	11.446	0.891
4.227	−0.513	6.391	2.171	8.559	2.409	11.555	1.062
4.622	0.092	6.498	2.159	8.572	2.293	11.596	0.253
4.759	0.356	6.727	2.315	9.049	2.293	11.673	0.080
4.972	0.705	6.917	2.307	9.252	2.390	11.729	−0.120

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