The Hydrolysis of Metal Ions. Part 5.[1] Thorium(IV)

Paul L. Brown and John Ellis
University of Wollongong, PO Box 1144, Wollongong, N.S.W. 2500, Australia
Ronald N. Sylva *
Australian Atomic Energy Commission Research Establishment, Lucas Heights Research Laboratories, N.S.W. 2232, Australia

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The hydrolysis of thorium(IV) in 0.10 mol dm^{-3} potassium nitrate has been investigated by potentiometric titration at 25 °C. Numerical analysis by our version of MINIQUAD has indicated that the only acceptable model involves the species $[Th(OH)]^{3+}$, $[Th_4(OH)_{12}]^{4+}$, and $[Th_6(OH)_{15}]^{9+}$, for which the overall formation constants, expressed as $-\log \beta_{pq}$, are 2.98 (0.007), 30.55 (0.03), and 34.41 (0.03), the estimated standard deviations being given in parentheses.

The hydrolysis of thorium(IV) has been investigated for more than 20 years.[2-8] The hydrolytic behaviour has been shown to be extremely complex because of the presence of extensive polymerisation reactions which occur in a narrow pH range (about 0.5 units) before the onset of additional, slow hydrolytic and/or precipitation reactions. Indeed, none of these studies has obtained a definitive result. Accordingly, we investigated the system (0.10 mol dm^{-3} KNO_3, at 25.0 °C) and herein present the results.

Experimental

Reagents.—Unless otherwise stated, all reagents were Merck Suprapur grade. The source of thorium was thorium(IV) nitrate 5-hydrate (Merck G.R.); the base used was potassium hydrogencarbonate (Fluka-Garantie reagent). Thorium analysis of the stock solution was carried out spectrophotometrically using 3,6-bis(*o*-arsonophenylazo)-4,5-dihydroxynapthalene-2,7-disulphonic acid (Arsenazo III).[9]

Procedure.—The previously described procedure [1] was used. In the expression $[H^+] = 10^{-pH}/\lambda$ the value of λ was found by numerical analysis to be 0.768 (for the 'best' model). All titrations were carried out in a solvent of 0.10 mol dm^{-3} KNO_3 at 25.0 ± 0.1 °C. A summary of the titrations is given in Table 1; full details are available on request.

Results

The stoicheiometric equilibrium constants for the formation of the hydrolysis products by the (hypothetical) reactions (1) are defined by (2), in accord with the previously adopted convention.[1,10-12] Each species is represented by either a (*p*,*q*) pair or its formula.

$$pTh^{4+} + qH_2O \rightleftharpoons [Th_p(OH)_q]^{(4p-q)+} + qH^+ \quad (1)$$

$$\beta_{pq} = [Th_p(OH)_q{}^{(4p-q)+}][H^+]^q/[Th^{4+}]^p \quad (2)$$

Our version of MINIQUAD [13] is an augmented version of the original [14,15] and has, among other things, the following features: (*i*) numerical refinement of the analytical proton excess at the beginning of a titration, allowing a titration to be commenced at any pH value irrespective of the extent of reaction; (*ii*) optional numerical refinement of the relationship between pH values and hydrogen ion *concentrations* (see Experimental section and refs. 10—12); (*iii*) optional refinement of negative formation constants; and (*iv*) two automated *model* (as opposed to *species*) selection procedures in addition to the 'manual' method as given by Gans *et al.*[15]

Table 1. Summary of titrations of thorium(IV) at 25 °C and in 0.1 mol dm^{-3} KNO_3

Total initial thorium(IV) concentration (10^{-3} mol dm^{-3})	pH range	Number of points
1.960	3.138—3.501	111
0.980	3.355—3.794	96
0.490	3.530—3.911	121
0.196	3.406—4.033	148

A preliminary examination of the data, largely by trial and error, indicated the likely presence of the species (1,1), (4,12), and (6,15). This model, indeed, satisfies our acceptance criteria,[10-12] namely estimated standard deviations of β_{pq} values of less than 10% and an agreement factor *R* of less than 0.002 (see Table 2). This, of course, does not demonstrate the uniqueness of this model. Accordingly, further, very extensive calculations were carried out using a systematic approach. Noting the various claims made in the earlier literature [2-8,16] for a variety of species and models (the distinction between which is often confused), the following 'species list' was considered: (1,2), (2,1), (2,2), (2,3), (2,4), (3,3), (3,4), (3,5), (3,6), (4,4), (4,5), (4,6), (4,7), (4,8), (4,9), (4,10), (4,11), (5,10), (5,11), (5,12), (6,14), and (6,16). It was used in two ways, namely: (*a*) to the base model of (1,1), (4,12), and (6,15), each species was added singly, and in pairs (253 models); (*b*) to the base model (1,1) and (6,15) was added each species both singly and in pairs [with the inclusion of the (4,12) species 276 models; 23 models are common to calculations (*a*) and (*b*)].† This model selection procedure was carried out by means of the subroutine NEXSET which is a completely general method of selecting combinational subsets from a given set (*i.e.* species list) according to any requirements, as specified by the user. The initial estimates of the formation constants of the added species were obtained from the extended Sylva-Davidson equation.[12] In both computer runs, all unknown parameters (formation constants, λ, in the proton mass-balance equation, and the initial proton excess values) were allowed to refine simultaneously.

Since an examination of models rather than species was required, values of the formation constants were allowed to become, and remain, negative throughout the refinement. Obviously, a negative formation constant for a species is as

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† In group (*b*) calculations, seven models containing the (1,1), (1,2), and (6,15) species, together with a fourth species, failed to converge.

physically meaningless as a model which contains a negative constant. But it does not necessarily follow that such a species is non-existent; deficiencies in the model (species present and/or the estimated formation constants) may cause a negative value to be assumed at some stage in the refinement process. Both LETAGROP[17] and MINIQUAD[14,15] can eliminate such species from a model (formation constant set to zero). However, our experience with MINIQUAD has demonstrated that this elimination can be premature or inappropriate; thus, a given model cannot always be examined after numerical convergence if one (or more) species has been rejected because the model has been altered. In addition, before final convergence, the sign of a formation constant can change several times such that the convergent model contains positive constants only. The permitted use of negative constants also often allows greater latitude in the choice of initial estimates for the constants.

None of the models so obtained was satisfactory, largely because of the presence of negative constants or, in a minority of instances, because of failure to meet our acceptance criteria (see above). Thus, our data indicate that under the experimental conditions used the three species $[Th(OH)]^{3+}$, $[Th_4(OH)_{12}]^{4+}$, and $[Th_6(OH)_{15}]^{9+}$ are the only ones that exist in detectable concentrations. Extension of the calculations to include this model and all members of the species list, taken three at a time (1 540 models), seems to us to be unwarranted.

Earlier work,[3,5] together with the present results, demonstrates that the onset of further, slow polymerisation and/or precipitation reactions in the thorium(IV) system can be a serious problem because of non-equilibrium effects. Indeed, Baes *et al.*[5] observed localised precipitation on the addition of base (NaOH) to their test solutions, which often disappeared on stirring, and hysteresis effects have also been observed,[3,8] Efforts in the present work to eliminate such problems include: (*i*) the use of low ionic strength, low total (initial) metal ion concentrations, and low pH values; and (*ii*) the use of 0.01 mol dm^{-3} base as titrant in the form of potassium hydrogencarbonate.

The presence of hysteresis effects is readily demonstrated under certain conditions but we believed it was imperative to examine the data actually used in the analysis for possible interference from this source. Accordingly, (*a*) 20 and (*b*) 40 data points were removed from the high-pH region of each titration curve and the numerical analysis was repeated with the following results: (*a*) $-\log \beta_{1,1} = 3.00$ (0.01), $-\log \beta_{4,12} = 30.64$ (0.04), $-\log \beta_{6,15} = 34.42$ (0.03), $\lambda = 0.771$, $R = 0.0018$; (*b*) $-\log \beta_{1,1} = 3.02$ (0.02), $-\log \beta_{4,12} = 30.71$ (0.05), $-\log \beta_{6,15} = 34.46$ (0.03), $\lambda = 0.769$, $R = 0.0018$. Comparison of these results with those obtained from the full data set (Table 2) thus demonstrates that these slow reactions made no significant contribution over the time period of the experiments.

Discussion

The present results are compared with some previously reported investigations in Table 2. This comparison is of limited significance because, in addition to differences in ionic strength and medium, the work cited appears to have either poorly defined or undefined species or model acceptance criteria. We also find aspects of this earlier work disconcerting for the following reasons.

(*i*) The choice of high total thorium(IV) concentrations (up to 500 mmol dm^{-3}) would invoke significant compositional changes (and hence errors) throughout a titration.[16] Such high concentrations rarely serve any useful purpose, and do not facilitate easier detection of higher polymeric species, as has been demonstrated in systems such as copper(II),[10] uranium(VI),[11] and lead(II),[12] and in the present work.

(*ii*) The use of very high ionic strengths might be seen to offset the criticism of (*i*) above. This, however, is illusory since high ionic strengths militate against the attainment of high pH values in titrations because of the increased ease of precipitation reactions under such conditions.[16] This is well borne out in the work of Milić[8] where the *maximum* average OH/Th ratio ($\bar{n}$) obtained is about 0.6 (in 3.0 mol dm^{-3} lithium, potassium, and magnesium nitrate media: models 10, 12, and 14 in Table 2). In the present work, $\bar{n}$ values of up to about 2.5 have been obtained. Thus, despite the very high precision of the data of Milić,[8,16] any conclusions that can be drawn from this work are very uncertain.

(*iii*) It appears that a somewhat cavalier attitude has been adopted towards species and/or model selection in earlier work. Thus, for example, Hietanen and Sillén[3] propose a number of models in attempts to explain their data and, in the absence of stated or established acceptance criteria, no unequivocal choice could be made. Two of these models each contain nine species and common to both models is the species $[Th_3(OH)]^{11+}$; we consider such models to be unrealistic.

In the work of Baes *et al.*[5] numerical differences between many models is slight and the chosen model is based solely on a goodness-of-fit parameter [see (*iv*) below]. Also, in the work of Danesi *et al.*,[7] the criteria for model selection are not given.

(*iv*) In an attempt to rationalise some of the earlier work,[3,5,8] Baes and Mesmer[16] have carried out further analysis of the data. They arrive at the two schemes: $[Th_2(OH)_2]^{6+}$, $[Th_4(OH)_8]^{8+}$, and $[Th_6(OH)_{15}]^{9+}$ (in perchlorate and nitrate media); and $[Th_2(OH)_2]^{6+}$, $[Th_2(OH)_3]^{5+}$, and $[Th_6(OH)_{14}]^{10+}$ (in chloride media). The choice of these schemes is based solely on the goodness-of-fit parameter, $\sigma(\bar{n})$ (estimated standard deviation based on the hydroxide number, $\bar{n}$), when the present and earlier work[1,10-12] clearly shows that this parameter, *alone*, cannot provide even an approximately satisfactory criterion of acceptability.

(*v*) All previous work on the hydrolysis of thorium(IV) (and the majority of other metal ions) has relied, for data analysis, on either graphical methods or, more recently, on non-linear least-squares analysis by computer. Of the latter, the best-known programs are LETAGROP,[17] the ORNL program of Rush *et al.*,[18] and MINIQUAD.[14,15] The first two programs have been used, for comparative purposes, to analyse the thorium(IV) hydrolysis data of Baes *et al.*[5] The excellent agreement obtained[19] suggests that no significant differences exist between the programs. If, however, MINIQUAD is compared to these programs, a very significant difference becomes apparent. In LETAGROP and the ORNL program the numerical refinement is based on minimising the quantity $(\bar{n}_{obs.} - \bar{n}_{calc.})^2$, as defined in equations (3) and (4). Here

$$\bar{n}_{obs.} = ([H] - [H]_T)/[M_T] \quad (3)$$

$$\bar{n}_{calc.} = \sum_{pq} q\beta_{pq}[M]^p[H]^{-q}/([M] + \Sigma p\beta_{pq}[M]^p[H]^{-q}) \quad (4)$$

$[H]_T$ and $[M]_T$ are total proton and metal-ion concentrations, [H] and [M] are free proton and metal-ion concentrations, and the other symbols have their usual meaning. The MINIQUAD program, in contrast, separately and independently minimises *both* $\{[H]_{T(obs.)} - [H]_{T(calc.)}\}^2$ and $\{[M]_{T(obs.)} - [M]_{T(calc.)}\}^2$, as defined by the mass-balance equations and experimental observations. Thus, whereas LETAGROP and the ORNL program require only one numerical relationship to be obeyed, MINIQUAD requires two such relationships to be

Table 2. Survey of potentiometric investigations of the hydrolysis of thorium(IV)

Model number	Medium	Temperature (°C)	Total thorium(IV) concentration (10^{-3} mol dm^{-3})	Species	$-\log \beta_{pq}$	Standard deviation in β_{pq} (relative per cent)	Ref.
1 [a]	NaCl (3 mol dm^{-3})	25	0.10—100.0	(1,1)	5.14	16.9	3
				(2,2)	4.78	3.1	
				(2,3)	8.72	6.1	
				(2,5)	17.16	10.8	
				(3,1)	1.50	17.7	
				(3,3)	6.86	10.8	
				(6,14)	36.42	2.3	
2 [b]	NaCl (3 mol dm^{-3})	25	0.10—100.0	(1,1)	4.97	12.3	3
				(2,2)	4.76	3.1	
				(2,3)	8.94	15.4	
				(2,5)	16.99	8.4	
				(3,1)	1.36	13.8	
				(3,3)	6.83	10.0	
				(4,8)	21.11	16.9	
				(6,14)	36.58	7.7	
				(10,25)	63.35	16.1	
3	$NaClO_4$ (1 mol dm^{-3})	0	1.58—20.6	(1,1)	4.32	4.6	5
				(1,2)	8.48	6.9	
				(2,2)	5.60	4.6	
				(4,8)	22.79	4.6	
				(6,15)	43.84	4.6	
4 [c]	$NaClO_4$ (1 mol dm^{-3})	25	0.25—15.0	(1,1)	4.15	9.2	5, 6
				(1,2)	7.70	6.9	
				(2,2)	4.61	4.6	
				(4,8)	19.01	4.6	
				(6,15)	36.76	4.6	
5	$NaClO_4$ (1 mol dm^{-3})	95	2.15—20.0	(1,1)	2.29	4.6	5
				(2,2)	2.55	6.9	
				(4,8)	10.49	6.9	
				(6,15)	20.63	4.6	
6	$LiNO_3$ (3 mol dm^{-3})	25	2.5—121.0	(2,2)	5.14	0.8	8
				(3,5)	14.73	4.6	
				(3,3)	>7.73		
7	KNO_3 (3 mol dm^{-3})	25	3.0—126.0	(2,2)	5.10	2.3	8
				(2,3)	8.98	6.1	
				(1,2)	>9.67		
				(6,15)	40.95	5.4	
8	$Mg(NO_3)_2$ (1.5 mol dm^{-3})	25	1.31—121.0	(2,2)	5.17	0.8	8
				(3,5)	14.29	5.4	
				(6,15)	43.20	6.1	
9	$NaClO_4$ (4 mol dm^{-3})	25	54.2—500	(2,1)	2.72	6.8	
				(2,4)	10.49	1.0	
				(3,5)	12.42	3.4	
				(4,8)	19.2	8.5	
				(6,14)	36.2	9.7	
10	$NaNO_3$ (4 mol dm^{-3})	25	10.0—500	(2,2)	5.5	3.1	7
				(3,6)	17.92	5.0	
				(4,12)	37.2	4.9	
11 [d]	KNO_3 (0.10 mol dm^{-3})	25	0.196—1.96	(1,1)	2.98	1.7	This work
				(4,12)	30.55	8.0	
				(6,15)	34.41	6.2	

[a] Model IIIB of Hietanen and Sillén [3] for which $p \leqslant 6$, and systematic error in q/p ratio is refined. [b] Model IVB of Hietanen and Sillén;[3] as for model 1 with value of p unrestricted. [c] Recalculation of data of Kraus and Holmberg [6] by Baes *et al.*[5] [d] Present work: $R = 0.001\,805$. The total thorium(IV) concentration range involves the *initial* concentrations. Estimated standard deviations (log units) are: (1,1), 0.007; (4,12), 0.03; and (6,15), 0.03. Calculations using present data with models in Table 2 gave unsatisfactory results (negative constants, poor goodness-of-fit, or poor standard-deviation estimates).

obeyed independently and, as such, is inherently more powerful.

Attempts at accommodating the various models in Table 2 with the present data gave unsatisfactory results. This lack of compatibility makes any further comparisons of doubtful value.

The present work indicates that, for the concentration ranges studied, $[Th(OH)]^{3+}$ is the most important species at low pH values. At higher pH values the tetrameric (4,12) species becomes dominant. The (6,15) polymer is a relatively minor species even at high pH and metal-ion concentrations.

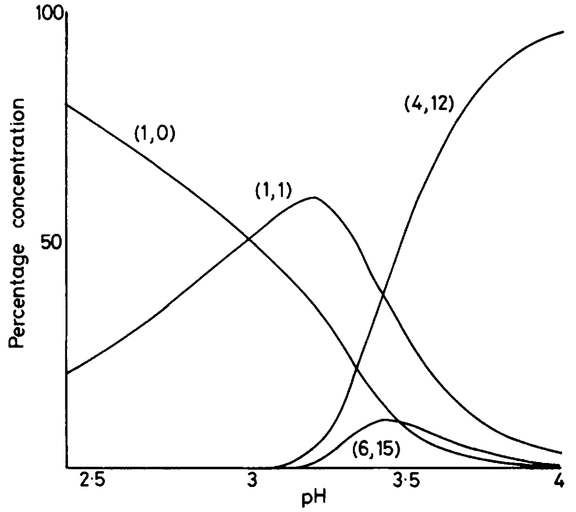

Figure. Percentage concentration of thorium(IV) hydrolysis products at total $[Th^{4+}] = 2 \times 10^{-3}$ mol dm^{-3} assuming $[H^+] = 10^{-pH}$ ($\lambda = 1$)

The Figure illustrates the species concentrations for a total metal-ion concentration of 2.0 × 10^{-3} mol dm^{-3} in the range pH 3—4.

Of the hydrolysis products of thorium(IV) previously documented,[2-8] the species $[Th_2(OH)_2]^{6+}$, and one or other of the hexamers, $[Th_6(OH)_{14}]^{10+}$ and $[Th_6(OH)_{15}]^{9+}$, have been postulated either singly or together in the presence of other species. The present work does not indicate any significant formation of a dimeric species; the reasons for this are not apparent but it has been suggested [16] that its formation may be inhibited at low ionic strength.

Danesi *et al.*[7] proposed the formation of the (4,12) species in 4.0 mol dm^{-3} nitrate medium (but not in 4.0 mol dm^{-3} perchlorate) in common with the present work. Further evidence for this species in the thorium(IV) system is not available. However, a recalculation of the data of Hietanen [20] by Baes and Mesmer [16] for the uranium(IV) system suggested the presence of the (1,1) and (6,15) species (q/p values of 1.0 and 2.5, respectively) together with an additional species having $q/p > 2.5$. Of all the species examined here, only three, namely (4,11), (4,12), and (6,16), meet this condition. Further work at our laboratories on the uranium(IV) and related systems might thus provide substantial evidence for the existence of tetramers of this stoicheiometry in metal(IV) systems.

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