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Equilibrium Studies in Self-medium; Application to the Hydrolysis of Th^{4+}

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It is suggested that added information on polynuclear complexes, A_pB_q, between the reagents, A and B, may be obtained by working with an ionic medium where one of the reagents, say B, forms the major part of the ions of one charge. This is termed the "self-medium method", as distinguished from the "inert medium method", *e. g.* with $NaClO_4$, in current use. The self-medium method favors complexes A_pB_q with low values for p/q so that information may be obtained about such complexes with a greater certainty than from work with inert media.

The self-medium method has been applied to the hydrolysis of Th^{4+}. The data indicate the two reactions $2Th^{4+} + 2H_2O \rightleftharpoons Th_2(OH)_2^{6+} + 2H^+$ (equil. const. β_{22}) and $2Th^{4+} + H_2O \rightleftharpoons Th_2OH^{7+} + H^+$ (β_{12}). In the medium 0.5 Th, 2.2 (Na)Cl, $\log \beta_{22} = -5.02 \pm 0.04$, $\log \beta_{12} = -2.8 \pm 0.2$. In 0.7 Th, 3.0 (Na)Cl, $\log \beta_{22} = -5.09 \pm 0.04$, $\log \beta_{12} = -2.9 \pm 0.2$. Temperature 25°C.

Symbols

A, B = reactants, here OH^- ($-H^+$) and Th^{4+}; a = concentration of free A, here $a = h^{-1}$, eqn. (17); b = concentration of free B; B = total concentration of B; E = electromotive force of cell (16); E_0 = constant in eqn (18); $f = 2u^2 + 2ku$, eqn (12); $F(h) = BZ + \Delta$, eqn (19); $F'(h)$, theoretical expression for $F(h)$; $h = [H^+]$; H = analytical excess of H^+, often negative; j = constant in term for liquid junction potential, eqn (18); k = parameter defined by eqn (11); p, q = coefficients in formula of complex A_pB_q; K'_p = equilibrium constant for formation of the "A_p group" of complexes, eqn (4); P, Q = coefficients in formula of single complex; u = normalized variable, corresponding to a, eqns (7) or (11); Z = average number of A (here OH^-) bound per B (here Th^{4+}); β_{pq} = equilibrium constant for formation of A_pB_q, eqn (1); Δ = analytical error in H, eqn (19).

In the equations, equilibrium constants, and figures, the unit M (Mole/liter) is used throughout. However, in some of the tables, and in the text, the more convenient unit mM, mmole/liter, is sometimes used.

The inert medium method

In accurate work on complicated equilibria where charged species appear, say, equilibria between a metal ion, B, and a ligand, A, it has been increasingly common, since the work of Leden [1], to add to the solvent an "inert medium", *i.e.* an excess of ions like Na^+ and ClO_4^-, which are supposed not to take part in the reactions. In the studies of the hydrolysis of cations [2] and anions [3] in this laboratory, an inert medium has practically always been used, usually 3 M $(Na)ClO_4$ for cations, and 3 M $Na(ClO_4)$ for anions.

It is assumed that the activity factors keep constant when an inert medium is used; they are conventionally set = 1. Biedermann and Sillén [4] have given some experimental evidence for this assumption, and also for the assumption that the liquid junction potential is a (linear) function of $[H^+]$ only, at least as the method is applied in this laboratory. Forthcoming papers by Biedermann [5] will make use of a large amount of experimental evidence to indicate the range of applicability of the method, and the deviations obtained when the concentrations of the reactants, A and B, cease to be negligible in comparison with those of the medium ions.

The great advantage of the inert medium method is that the calculations are much simpler and much more reliable than if the variation of the activity factors must be considered. Emf measurements give the concentrations of free ions directly, and concentrations may be used in the law of mass action. One may indeed say that only by using the inert medium method has it been possible to draw reliable conclusions on the formulas of the species formed in many complicated systems with several products, especially in those where polynuclear species appear.

The available range in B, the total concentration of B, is limited by the decreasing experimental accuracy for low values of B, and by the deviations of the activity factors at high values of B. Using 3 M $(Na)ClO_4$ as inert medium, it has been thought advisable not to go much beyond 0.1 or 0.2 M in B for polyvalent cations.

Self-medium method

We would suggest that additional information on the species formed may be obtained by what we are going to term the "self-medium" method, which implies that the ionic medium is made to consist chiefly of the ion B to be studied, with an "inert" counter ion. In the present paper on Th^{4+} hydrolysis, 0.5 M $ThCl_4$, or 0.7 M $ThCl_4$ has been used as the main constituent; for anion hydrolysis one might think of, say, 2 M Na_2CrO_4 (or $Na_2Cr_2O_7$), 4 M $NaAs(OH)_4$ *etc.* In order not to change the ionic medium, and the activity factors, too much, one must keep the added amount of the ligand A, and thus Z, fairly low.

To make possible the necessary variations in Z, one must in general either change the concentration of the counter ion slightly, or add a small amount of an inert ion of the same sign of charge as B. Both ways have been used in the present work; the second seems preferable.

Let us assume that the two reactants, A and B, form a number of complexes, A_pB_q with the formation constants β_{pq}. For each set (p, q) we have

$$[A_pB_q] = \beta_{pq}a^pb^q \tag{1}$$

From the definitions, it follows for B (the total concentration of B) and BZ (moles of A bound to B per liter):

$$B = [B] + \sum_p\sum_q q[A_pB_q] = b + \sum_p\sum_q q\beta_{pq}a^pb^q \tag{2}$$

$$BZ = \sum_p\sum_q p[A_pB_q] = \sum_p\sum_q p\beta_{pq}a^pb^q \tag{3}$$

If Z is kept at such low values that practically $b \approx B$, we have

$$BZ = \sum_p pK'_pa^p; \quad K'_p = \sum_q \beta_{pq}B^q \tag{4}$$

From data $Z(\log a)$, measured in self-medium, it would be possible to compute the constants, K'_p in (4), for instance using curve-fitting (Sillén [6]). One might formally describe K'_p as the equilibrium constant for the association reaction, $pA \rightleftharpoons A_p$, in the medium in question. We may conventionally write A_p for the whole set of complexes A_pB_q, with varying q but the same p, since self-medium data will give practically no direct information on q. Even in those cases where a small correction for B—b is necessary, the accuracy does not allow a decision on the value for q.

Information on species

It might be held as a disadvantage that the information on the formulas of the species which is obtained with the self-medium method is thus still more restricted than that with the inert medium method, which is again more restricted than that obtained from dilute solutions. On the other hand, even the "restricted" information might have been unobtainable by the other methods.

To take an example, from equilibrium studies in *dilute* borate *solutions* one may conclude that there is a mononuclear species containing one B atom and having the charge —1; from the equilibrium data alone it is, however, not possible to decide between formulas with varying amounts of the solvent, H_2O: BO_2^-, $H_2BO_3^-$, $B(OH)_4^-$. Only the last formula is, by the way, supported by structural work.

From equilibrium studies in an *inert ionic medium* such as $Na^+ClO_4^-$, one may in addition deduce the formulas and equilibrium constants of polynuclear complexes: $B_3O_3(OH)_4^-$, and $B_3O_3(OH)_5^{2-}$, or $B_4O_5(OH)_4^{2-}$, information which could not have been obtained from studies in dilute solutions (Ingri *et al.*[3]).

On the other hand, it is not possible to discern between species that differ by containing various amounts of water, and of the medium ions: "$[B_3O_3(OH)_4^-]$" is thus really $= \Sigma[B_3O_3(OH)_4(H_2O)_x(Na)_y\,(ClO_4)_z^{y-1-z}]$.

In this special case, there may have been no strong reason to suppose that the medium ions would play any important role; it has been tested [7] that the formulas of the species are the same, and the equilibrium constants are not much effected on changing to a different inert medium, like Li^+Br^-, or Na^+Br^-.

In other cases, this consideration may be more serious. For instance, by equilibrium studies in the medium $NH_4^+NO_3^-$, it would not be possible to distinguish between $Hg(NH_3)_2^{2+}$, $HgNH_2^+$, $Hg(OH)_2$, and other species that could briefly be written as "HgH_{-2}" (Sillén [8]). In such a case it is very important to make equilibrium studies in several different media, or to add structural evidence.

With the *self-medium* method, the information obtained would seem still more restricted since it would not be possible to distinguish between species with different numbers, q, of the reagent B; on the other hand, one might hope in this way to obtain information not available in other ways.

In the example of the borate equilibria, one might choose $Na^+B(OH)_4^-$ as self-medium (reagents $A = H^+$, $B = B(OH)_4^-$), and would then group together species such as $AB = B(OH)_3$ and $AB_3 = B_3O_3(OH)_5^{2-}$ in the A_1-group, and species like $A_2B_3 = B_3O_3(OH)_4^-$ and $A_2B_4 = B_4O_5(OH)_4^{2-}$ in the A_2-group. (Note that the present choice of A and B differs from that in Ref.[3]).

Similarly, in the present study on the hydrolysis of Th^{4+} with mainly $ThCl_4$ as self-medium, there is evidence for a species with a deficit of two protons, for which the formula $Th_2(OH)_2^{6+}$ seems plausible. Really, however, it would not be possible to distinguish between formulas with varying amounts of solvent and medium ions:

$$"[Th_2(OH)_2^{6+}]" = \Sigma\Sigma\Sigma[Th_qH_{-2}(H_2O)_xCl_y^{(4q-2-y)}]$$

One might thus, slightly more correctly, refer to this species as "H_{-2}" or "$(OH)_2$".

In the cases that have hitherto been studied, this limitation in the self-medium method has not proved very serious. In general the numbers of ligands have come out low, 1 or 2, and it has been possible to deduce the most important value for q fairly reliably by comparing the equlibrium constant obtained in the self-medium with data from inert media. Structural considerations may also give some guidance.

Which species are favored?

One might ask which types of complexes are favored by measurements in self-medium as compared with measurements in an inert medium with lower values of B. It is plausible to suggest that the accuracy of the experiments with different values of B will be comparable at identical values of BZ.

Suppose that there are only two complexes with the sets $(p'q')$ and $(p''q'')$, and concentrations $c' = \beta' a^{p'} B^{q'}$, $c'' = \beta'' a^{p''} B^{q''}$, since $b \approx B$ (1). If $BZ = p'c' + p''c''$ (3) is kept constant, one may easily deduce

$$\left(\frac{\partial \ln(c'/c'')}{\partial \ln B}\right)_{BZ} = \frac{(p'c' + p''c'')}{(p'p'c' + p''p''c'')}\,(q'p'' - q''p') \tag{5}$$

In the expression to the right in (5), the fraction is certainly positive, provided BZ is positive, so the sign of the derivative is determined by $(q'p''-q''p')$. If all coefficients p and q are positive (we omit the case where one of p' and p'' is negative), c'/c'' will increase with B, provided $q'/p' > q''/p''$. In general, increasing B (*e.g.* using the self-medium method) will favor complexes with high values for q/p. So it might be hoped that the self-medium method would give more certain evidence for some complexes with high ratios q/p than can be obtained using an inert medium.

Some arguments might be given for comparing, instead, points of equal Z. For instance, in self-media of different B, the uncertainty from the activity factors may set a limit at roughly the same Z. If $\ln(c'/c'')$ is differentiated with respect to $\ln B$ at constant Z, the third term to the right in (5) becomes $((q'-1)p''-(q''-1)p')$. Hence, complexes with high values for $(q-1)/p$ are favored, which will in general work in the same direction.

Sometimes, the limit of the experimental range will be set by the precipitation of a solid, say A_NB(s), at low Z before the uncertainty from the activity factors becomes serious. A_NB(s) may, of course, also contain solvent and inert ions, but these are left out as usual. For any complex we would have at the point of precipitation, and thus at equilibrium with A_NB(s)

$$[A_pB_q] = \text{constant} \cdot b^{q-pN^{-1}} \approx \text{constant} \cdot B^{q-pN^{-1}}$$

Increase in B would then give a wider concentration range to be studied, and thus more information for any single complex with $p/q < N$. Of two complexes, the one with the higher value for $(Nq-p)$ will be favored.

The equilibrium constants in a self-medium may be expected to differ somewhat from those in an inert medium of the same concentration of inert counter ion. However, our experience hitherto has shown that the differences are only of the order of 0.1 in the logarithm of the formation constant.

Correcting for decrease in *b*

In the present work it was desirable to extend the measurements up to Z-values of around 0.10. Here, the difference between the total concentration, B, and the free concentration, b, is no longer negligible and a correction must be made.

Single complex. If the whole effect measured is due to a single complex, A_PB_Q, then from (2) and (3)

$$B = b + Q\beta_{PQ}a^Pb^Q \; ; \; BZ = P\beta_{PQ}a^Pb^Q \tag{6}$$

Eliminating $b = B(1-ZQP^{-1})$, we find

$$Z(1-ZQP^{-1})^{-Q} = a^P P \beta_{PQ} B^{Q-1} = u^P \tag{7}$$

Here, u is a normalized variable corresponding to a. We may use eqn (7) to calculate a normalized curve $Z(\log u)$ and move it along the experimental data, $Z(\log a)$. If a fit is obtained for a certain set (P, Q), one may obtain β_{PQ} from the constant difference

$$\log u - \log a = P^{-1}(\log P + \log \beta_{PQ} + (Q-1) \log B) \tag{8}$$

In actual fact the shape of the curve $Z(\log u)$ is mainly determined by P. Any reasonable value of Q will only cause a minor change, in the upper part of the Z range, in comparison with the curve obtained from $Z = u^P$. This is what eqn (7) reduces to if one puts $Q = 0$ that is neglects the difference between b and B.

Two complexes. If two complexes must be considered, the experimental data $Z(\log a)$ must be compared with a family of curves $Z(\log u)_k$, where k is a parameter containing the formation constants for the two complexes. The procedure will be illustrated for the combination of two complexes AB_2 and A_2B_2, which will be useful in this paper, and in a following one on the hydrolysis of UO_2^{2+}.

From (2) and (3) we have

$$B = b + 2\beta_{12}ab^2 + 2\beta_{22}a^2b^2 \tag{9}$$

$$BZ = \beta_{12}ab^2 + 2\beta_{22}a^2b^2 \tag{10}$$

We shall define the normalized variable u (corresponding to a), the parameter k, and the useful abbreviation f:

$$u^2 = 2\beta_{22}a^2B \; ; \; ku = 2\beta_{12}aB \tag{11}$$

$$f = 2u^2 + 2ku \tag{12}$$

Eliminating b, we obtain finally from (9 to 12)

$$Z = \frac{f - ku}{1+f+\sqrt{1+2f}} = (f - ku)f^{-2}(1+f-\sqrt{1+2f}) \tag{13}$$

Using eqn (13) one may calculate a family of curve $Z(\log u)_k$, for a number of values of k, and compare them with the experimental curve $Z(\log a)$. If a fit is obtained for a certain value of k, one may notice the difference of coordinates $(\log u - \log a)$ and obtain the equilibrium constants from:

$$\log \beta_{22} = 2(\log u - \log a) - \log 2B \tag{14}$$

$$\log \beta_{12} = \log k + (\log u - \log a) - \log 2B \tag{15}$$

which are easily deduced from (11).

HYDROLYSIS OF Th^{4+} IN $ThCl_4$ SELF-MEDIUM

Composition of solutions

It was decided to use Cl^- as the inert anion, which has some advantages since practically the same solution can then be used in the reference electrode.

Our first work on the hydrolysis of thorium (Hietanen[9]) was made in 1 M (Na)ClO_4 medium, like the work of Kraus and Holmberg[10]. In the meantime, studies with 3 M (Na)Cl as inert ionic medium have been performed, which will shortly be published[11].

The total concentration, *B*, of Th was chosen as 0.5 or 0.7 M, and kept constant in each series. The analytical hydrogen excess, *H*, was varied either by varying $[Cl^-]$ or by adding Na^+, at constant $[Cl^-]$. The solutions studied had the following compositions:

Medium	*B*	*H*	$[Na^+]$	$[Cl^-]$
0.5 Th(Cl)	0.5	*H*	—	$2 + H$
0.5 Th, 2.2 (Na)Cl	0.5	*H*	$0.2 - H$	2.2
0.7 Th, 3.0 (Na)Cl	0.7	*H*	$0.2 - H$	3.0

The solutions were mixed, as usual in this laboratory, by a titration procedure, starting with around 40 ml of a certain solution S, and adding from a buret increasing amounts of another solution T. The value of *B* was the same in both solutions S and T. Usually, one of them had a positive value for *H* (H^+ excess), and the other a negative value. The compositions of S and T used are given in Table 1.

In our titrations with 0.5 Th(Cl), S was 0.5 M $ThCl_4$ with a certain excess of HCl, whereas T was partly hydrolysed thorium chloride with 0.5 M Th but a deficiency in Cl^-. With the others, the solution with negative *H* could be obtained simply by mixing $ThCl_4$, NaCl(HCl), and NaOH($NaHCO_3$) solutions in calculated amounts.

Reagents

Thorium chloride, p.a. (from Lindsay Chemical Company, West Chicago, Illinois) contained a small amount of Fe, which was removed by extraction with *iso*propyl ether from 6 M HCl solution. The HCl was removed by evaporation under a heating lamp; in general, this resulted in solutions that were partly hydrolyzed, thus had less than 4 Cl per Th, which was rather convenient for our studies.

In the first experiments, the thorium chloride solutions were prepared by evaporating thorium nitrate (puriss, Kebo) repeatedly with concentrated HCl, extracting the iron, and then evaporating again.

The solutions were analysed for Th by precipitating with oxine, igniting the precipitate, and weighing as ThO_2. The total amount of Cl^- was determined by passing the solution through a H^+ saturated ion exchanger (Wofatite KPS-200) and titrating the eluate with standard NaOH. These data gave the analytical H^+ excess of the solution, $H = [Cl^-] - 4\ [Th]_{total}$.

The sodium chloride (Merck p. a., or Baker p. a.) contained a small amount of alkaline impurity, probably carbonate, which was neutralized with HCl. For instance, 3 M NaCl needed an addition of 0.02 mM HCl.

Hydrochloric acid (p.a.) was standardized against solid $KHCO_3$, and standard NaOH. *Sodium hydrogen carbonate* (Merck p.a.) was analysed against HCl. A 50 % *sodium hydr-*

oxide solution was prepared in a polythene bottle from commercial p. a. material. The clear solution was pipetted out and diluted with de-aerated water, and the dilute solution standardized against hydrazine sulfate, and against HCl; the determinations with the two methods agreed within less than 0.1 %.

Apparatus

The reference half-cell was

$$\text{RE}|| = \text{Ag, AgCl}|B \text{ M ThCl}_4\text{, equilibrated with AgCl}|B \text{ M ThCl}_4$$

with $B = 0.5$ or 0.7 M, as in the solution to be studied.

The Ag, AgCl electrodes were prepared according to Brown [12]. The $ThCl_4$ solution in the reference electrode was equilibrated with AgCl, either by shaking with solid AgCl in a thermostated room, or by passing it twice through a tube, filled with AgCl. The solubility of AgCl in these solutions is of the order of a few mM. If the reference electrode solution is not saturated with AgCl, the AgCl may be dissolved off the solid electrode; in any case the half-cell will finally give a steady potential. The equilibration was more carefully done with 0.7 M Th, which may account for the smaller variation of E_0 (Table 1).

The hydrogen ion concentration, h, was measured in a cell

$$\text{—Pt,H}_2\text{(1 atm)|equilibrium solution||RE+} \tag{16}$$

The lightly platinized Pt electrodes were prepared approximately as described by Bates [13]. The electrode vessel was of the usual "Wilhelm" type [14], and the emfs were measured by means of a Vernier potentiometer. Our experiments were carried out in a thermostated room at 25°C, and with the cell immer-

Table 1. Survey of titrations. All concentrations, including B and H, are given in the unit mM.

		S			T				
Symbol	B	Na^+	H	Cl^-	Na^+	H	Cl^-	H-range	Corr mV
□	500	—	200	2 200	—	−145.3	1 854.7	200→ −38	0.3
◩	500	—	200	2 200	—	−145.3	1 854.7	200→ −42	—
+	500	—	201.2	2 201.2	—	−473.1	1 527	201→ −91	0.5
○	500	—	200	2 200	345.3	−145.3	2 200	200→ −42	—
◇	500	345.3	−145.3	2 200	—	200	2 200	−145→ 135	+0.5
□	500	—	210.2	2 210.2	392.2	−192.2	2 200	205→ 9	−0.2 *
△	500	641.5	−441.5	2 200	—	210.2	2 210.2	−197→ − 8	−1.3
●	700	—	200	3 000	400	−200	3 000	200→ 0	—
◒	700	400	−200	3 000	—	200	3 000	−172→ 0	—
◒	700	—	200	3 000	400	−200	3 000	200→ 0	—
◓	700	400	−200	3 000	—	200	3 000	−200→ 0	—
◐	700	350	−150	3 000	—	200	3 000	−150→ 87	—
◑	700	—	200	3 000	350	−150	3 000	200→ 13	−1.5

* Correction in H: −5 mM.

sed in a paraffin oil thermostat at 25.0°C. As usual with the hydrogen electrode, one often had to wait 15—20 min after each addition of T from the buret to get a constant E. There was no indication of slowness in the Th^{4+} equilibria, and titrations with increasing and decreasing Z gave the same results.

Calculations

As in the other studies of cation hydrolysis equilibria [15], we shall find it convenient to write the hydrolysed complexes as $A_pB_q = Th_q(OH)_p^{(4q-p)+}$, to count formally a proton deficiency, $-H^+$, as the ligand A, and to set

$$a = h^{-1} \tag{17}$$

The primary experimental data were E, measured emf in the cell (16), (corrected for the barometric pressure, and the vapor pressure of water), and H, the analytical excess of H^+; in many of our solutions, H was negative. If the data from different experiments with the same medium were plotted in a diagram $E(H)$, these were seen to be small shifts. Now, the following equations should hold for E of cell (16), and H:

$$E = E_0 - 59.15 \log h + jh \tag{18}$$

$$H = h - BZ - \Delta = h - F(h) \tag{19}$$

In eqn (18), E_0 can be assumed to be a constant, when short periods like one or two days are considered. However, E_0 is known to vary slightly between different reference electrodes, and also to change slightly over longer periods for one and the same reference electrode. The term jh stands for the liquid junction potential [4]; j is a constant which may be assumed to be the same in all experiments with the same medium.

In eqn (19), Δ is the possible error in the analytically determined H, which is the difference between two large numbers. BZ is a function of h, which is defined by eqns (2 and 3), or, under more special assumptions, by (4), by (6), or by (9 and 10), remembering that $a = h^{-1}$ (17). It is convenient, in the discussion, to treat the sum $BZ + \Delta$ as a single function, $F(h)$.

The fact that the curves $E(H)$ for different titrations do not coincide exactly might be ascribed to small differences in E_0, or to small differences in Δ. In the former case, there would be parallel shifts along the E-axis, in the second along the H-axis.

In order to decide whether a certain curve I can be made to coincide with another curve II, one may take a set of points from curve I, make each of these points in turn coincide with the origin of a transparent coordinate paper, and then draw on the paper the segment of curve II that falls in the nearest quadrant. If the curves I and II can be made to coincide, the segments should intersect in one point, which is the vector head of the necessary displacement.

Such plots were made, taking arbitrarily one titration as the standard for each medium. In all cases but one, the vector of displacement proved to be parallel with the E-axis: the curves could be made to coincide by a shift in

Table 2. Medium 0.5 Th(Cl). Experimental data H and E (corrected) for three titrations. Every other point given, log h calculated from E with $E_0 + 3 \cdot 59.15 = 384.1$ mV and $j = 22$ mV M^{-1}; Z from $h - H = BZ$.

H	E	log h	Z	H	E	log h	Z
symbol ■				symbol ◪ contd			
0.2000	252.2	−0.692	0.006	−0.0158	312.5	−1.788	0.064
0.1916	253.1	−0.711	0.006	−0.0374	321.0	−1.933	0.098
0.1616	256.8	−0.784	0.006	symbol +			
0.1308	261.4	−0.875	0.005	0.2012	252.1	−0.689	0.007
0.0847	270.6	−1.047	0.010	0.1591	257.2	−0.792	0.005
0.0518	280.3	−1.225	0.016	0.1399	260.0	−0.846	0.005
0.0271	290.5	−1.406	0.024	0.1307	261.0	−0.868	0.010
0.0024	303.4	−1.629	0.042	0.1132	264.6	−0.936	0.005
−0.0223	315.4	−1.837	0.074	0.0888	269.6	−1.031	0.009
−0.0377	321.4	−1.940	0.098	0.0592	277.7	−1.178	0.014
symbol ◪				0.0456	282.6	−1.266	0.017
0.2000	252.1	−0.689	0.009	0.0326	287.8	−1.358	0.022
0.1953	252.7	−0.701	0.002	0.0203	293.7	−1.462	0.028
0.1759	254.9	−0.752	0.003	0.0085	299.9	−1.568	0.037
0.1308	261.5	−0.877	0.004	−0.0134	310.9	−1.759	0.061
0.0849	270.6	−1.047	0.009	−0.0333	319.1	−1.899	0.092
0.0520	280.1	−1.220	0.016	−0.0517	325.0	−2.001	0.123
0.0274	290.3	−1.402	0.024	−0.0685	329.4	−2.075	0.153
0.0027	303.2	−1.627	0.042	−0.0914	334.7	−2.165	0.196

Table 3. Medium 0.5 Th, 2.2 (Na)Cl. Experimental data H and E (corrected) for four titrations; log h calculated from E with $E_0 + 3 \cdot 59.15 = 380.5$ mV, $j = 39$ mV M^{-1}; Z from $BZ = h - H$.

H	E	log h	Z	H	E	log h	Z
symbol ○				symbol □			
0.2000	251.9	−0.694	0.004	0.2052	251.5	−0.684	0.004
0.1916	252.8	−0.717	0.000	0.2002	252.0	−0.697	0.001
0.1485	257.7	−0.826	0.001	0.1771	254.3	−0.750	0.002
0.1202	261.8	−0.912	0.004	0.1453	258.0	−0.833	0.003
0.0847	268.4	−1.046	0.011	0.1183	261.9	−0.916	0.006
0.0518	277.6	−1.222	0.016	0.0955	266.0	−0.998	0.010
0.0271	287.5	−1.401	0.025	0.0709	271.9	−1.113	0.012
0.0024	300.1	−1.624	0.043	0.0502	278.1	−1.230	0.017
−0.0161	309.2	−1.783	0.065	0.0293	286.5	−1.382	0.024
−0.0305	315.1	−1.884	0.087	0.0092	296.7	−1.563	0.036
symbol ◈				symbol △			
−0.1453	340.6	−2.320	0.300	−0.1167	335.9	−2.241	0.245
−0.1325	338.6	−2.187	0.275	−0.1012	333.2	−2.195	0.215
−0.0896	330.9	−2.156	0.193	−0.0807	329.0	−2.123	0.176
−0.0641	325.5	−2.063	0.145	−0.0626	324.9	−2.053	0.143
−0.0363	317.3	−1.921	0.096	−0.0518	322.0	−2.003	0.123
−0.0088	306.0	−1.727	0.055	−0.0281	314.6	−1.876	0.083
0.0204	290.7	−1.458	0.029	−0.0084	306.1	−1.729	0.054
0.0397	282.0	−1.301	0.021				
0.0653	273.4	−1.145	0.013				
0.0838	268.6	−1.051	0.010				
0.1089	263.3	−0.946	0.009				
0.1251	261.2	−0.900	0.000				

Table 4. Medium 0.7 Th, 3.0 (Na)Cl. Experimental data H and E (corrected), points fo rsix titrations; log h calculated from E with $E_0 + 3 \cdot 59.15 = 359.7$ mV, $j = 22$ mV M^{-1}, Z from $BZ = h - H$.

H	E	log h	Z	H	E	log h	Z
symbol ●				symbol ◓			
0.2000	227.9	−0.697	0.001	−0.2000	317.8	−2.290	0.293
0.1628	232.0	−0.780	0.004	−0.1721	314.3	−2.231	0.254
0.1200	238.6	−0.907	0.006	−0.1404	310.1	−2.160	0.210
0.0909	244.1	−1.010	0.010	−0.1137	305.9	−2.087	0.174
0.0462	255.9	−1.223	0.020	−0.0909	301.7	−2.016	0.143
0.0133	269.6	−1.465	0.030	−0.0667	296.4	−1.925	0.112
				−0.0286	286.7	−1.757	0.066
symbol ◒				0.0000	275.4	−1.565	0.039
−0.1721	313.9	−2.224	0.254	symbol ◐			
−0.1333	308.5	−2.133	0.201	−0.1500	311.0	−2.175	0.225
−0.0909	301.5	−2.013	0.143	−0.1224	307.0	−2.107	0.186
−0.0712	297.2	−1.949	0.118	−0.1062	304.5	−2.063	0.164
−0.0462	291.5	−1.842	0.087	−0.0722	298.0	−1.954	0.119
−0.0133	280.3	−1.649	0.051	−0.0227	283.9	−1.712	0.060
0.0000	274.6	−1.551	0.040				
symbol ◒				0.0085	271.1	−1.490	0.034
0.2000	227.4	−0.689	0.007	0.0465	255.8	−1.222	0.019
0.1809	229.9	−0.738	0.003	0.0770	246.7	−1.059	0.015
0.1404	234.8	−0.834	0.009	0.0867	245.2	−1.029	0.010
0.1200	238.6	−0.907	0.006	symbol ◑			
0.0909	243.9	−1.007	0.011	0.2000	227.7	−0.694	0.003
0.0462	256.0	−1.225	0.019	0.1641	232.1	−0.782	0.002
0.0133	269.3	−1.460	0.031	0.1222	238.1	−0.899	0.006
0.0000	275.3	−1.563	0.039				
				0.0727	248.0	−1.083	0.014
				0.0385	258.7	−1.276	0.021
				0.0133	268.5	−1.446	0.032

E (last column in Table 1). In one case, however (marked in Table 1), a displacement of 5 mM along the H-axis was also necessary. This corresponds to an error of 0.25 % in the analysis for acid or thorium, or in the mixing of the solutions, and was a warning that unexpected errors of this order of magnitude might occur.

After these small shifts, the data obtained with each of the self-media fell on a smooth curve $E(H)$. These three sets of data were then treated separately by successive approximations, based on eqns (18) and (19). The data are given in Tables 2, 3, and 4, for every other experimental point; the Figures give every point. Points with very high Z values (> 0.25) have been left out.

For an ion which begins to hydrolyse at lower acidities than Th^{4+}, it might have been possible to determine Δ straight-forwardly by a Gran plot [16], and then E_0 and j directly from the region where $h \approx H$ by plotting $E + 59.15 \log H$ as a function of H. In the present work, the strong hydrolysis of Th^{4+} caused both plots to be curved, and so the somewhat more laborious method of successive approximations had to be used.

The aim was to find a theoretical function $F'(h)$, and two constants E_0 and j such that a) if h' is calculated from H with F' and (19), a plot of

($E + 59.15 \log h'$) *versus* h' according to (18) will give a linear plot with the constants E_0 and j, and b) if h is calculated from E, with E_0, j, and (18), then the $F(h)$ calculated from (19), $F(h) = H - h$, will give good agreement with $F'(h)$.

The linear part of the plot ($E + 59.15 \log H$) *versus* H at high acidities was used to obtain the first approximate values E_{01} and j_1. Using these constants and eqn (18), an auxiliary function $j_1h(E)$ was calculated. It was then possible from the various E-values and (18) to calculate a first set of approximate values h_1. Inserting these into (19), a first approximate function $F_1(h_1) = h_1 - H$ was calculated. This function was plotted as F_1 ($\log h_1$) and compared with various theoretical curves, and from the best fit a first theoretical function $F'_1(h)$ was chosen. The function $h'_1(H)$, defined by $h'_1 - F'_1(h'_1) = H$, was calculated for each experimental point. From a plot of ($E + 59.15 \log h'_1$) *versus* $\log h'_1$ and eqn (18), improved approximations E_{02} and j_2 were obtained.

As before, with the auxiliary function $j_2h(E)$, a new approximation h_2 was calculated from $-59.15 \log h_2 = E - E_{02} - j_2h_2$; h_2 was in turn used for calculating $F_2(h_2) = h_2 - H$. If the F_2 calculated from the data agreed well with the theoretical F'_1 used in the calculations, an acceptable solution had been found. Otherwise, another theoretical function F'_2, a better approximation to F_2, would have been adopted and a new cycle of approximations made.

In applying this procedure to the present data for thorium hydrolysis, it was first assumed that there was no analytical error, thus $\Delta = 0$. The data covered a range up to $Z \sim 0.25$. Because of the increasing uncertainty of activity factors, little attention was however paid to data with $Z > 0.1$.

The first approximation curves, F_1 ($\log h_1$), were first compared with the theoretical curves, $F' = BZ$ *versus* $\log h$, calculated for the single complexes A_1, A_2, or A_3, using (7) with $Q = 0$, and $P = 1$, 2, and 3. Between $Z = 0.05$ and 0.10, there was fair agreement with the A_2 curve. At lower values for Z, there were deviations and the shape approached that of the curve for the complex A_1. This would indicate that, under the present experimental conditions, the most important complexes formed are those containing 1 or 2 OH-groups, and that neither can be neglected.

In correcting for the change in b, it was assumed that in both cases the binuclear complexes predominated, thus $Th_2(OH)_2^{6+}$, and Th_2OH^{7+} — of course, possibly with extra H_2O and Cl^- attached. This assumption will be justified by arguments given in the discussion below.

A comparison with theoretical curves $F' = BZ$ *versus* $\log u$ calculated from (7) with $Q = 2$ and $P = 1$ or 2 gave the same result as before; the curves are intermediate between those for complexes with 1 and 2 A.

Next, theoretical curves were tried assuming two complexes, AB_2 and A_2B_2 (*viz.* Th_2OH^{7+} and $Th_2(OH)_2^{6+}$). Using (13), families of curves $F' = BZ$ ($\log u)_k$ were calculated for a series of values of k. Successive approximations (two steps sufficed) gave the values for the parameters, and hence β_{22} and β_{12} given in Table 5, for the three sets of data ("assumption $\Delta = 0$").

The values for $Z(= F/B)$ and h, given in Tables 2—4, were calculated with E_0 and j from Table 5. The corresponding plots of Z *versus* $\log h$, compared with the theoretical curve, and of ($E + 59.15 \log h$) *versus* h, are given in Figs 1 and 6 for 0.5 Th(Cl); in Figs 2, 4 and 7 for 0.5 Th, 2.2 (Na)Cl; and in

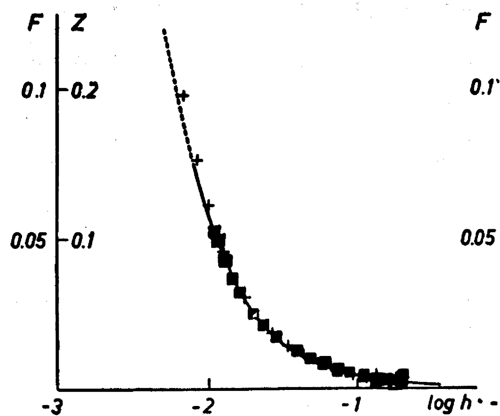

Fig. 1. Hydrolysis of Th^{4+}, medium 0.5 Th(Cl). $F = BZ$ *versus* log h. Points: calculated from experimental data $E(H)$, using E_0 and j from Table 5. Curve: calculated F', assuming $\Delta = 0$ and values for β_{22} and β_{12} in Table 5.

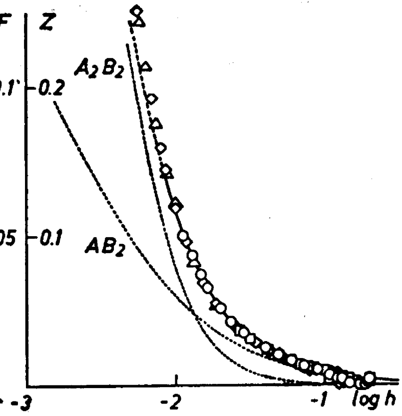

Fig. 2. Hydrolysis of Th^{4+}, medium 0.5 Th, 2.2 (Na)Cl. Experimental points and fulldrawn curve obtained as in Fig. 1. Dotted curves calculated assuming only one of the complexes present and with the same formation constant as in the full-drawn curve. See also Fig. 4.

Figs 3, and 5 for 0.7 Th, 3.0 (Na)Cl. In Figs 2, and 4 for comparison, are given also two (dotted) curves which have been calculated neglecting either AB_2 or A_2B_2, to indicate the contribution of each.

The occurrence of a single experiment with a deviation in H of 5 mM (0.01 in Z) was, however, a warning that systematic errors might exist in the analytical

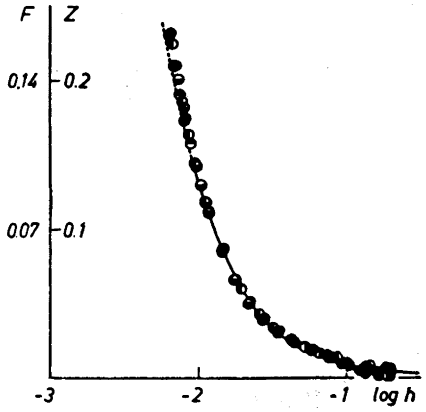

Fig. 3. Hydrolysis of Th^{4+}, medium 0.7 Th, 3.0 (Na)Cl. Experimental points and curve obtained as in Fig. 1. See also Fig. 5.

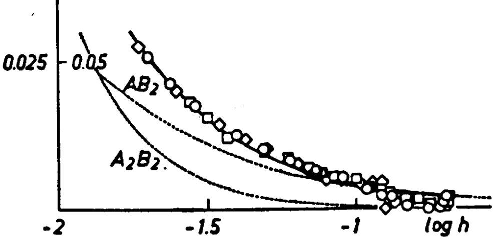

Fig. 4. Medium 0.5 Th, 2.2 (Na)Cl. Part of Fig. 2 on a larger scale.

Table 5. Equilibrium constants *etc*, obtained by successive approximations from the experimental data $E(H)$. Emfs in mV, concentrations in M.

Assumption	Quantity	0.5 Th(Cl)	0.5 Th,2.2(Na)Cl	0.7 Th,3.0(Na)Cl
$\Delta = 0$	$\log k$	-0.3	-0.3	-0.3
	$\log u - \log a$	-2.52	-2.51	-2.47
	$\log \beta_{22}$	-5.04	-5.02	-5.09
	$\log \beta_{12}$	-2.82	-2.81	-2.92
	j	22	39	22
	$E_0 + 3 \cdot 59.15$	384.1	380.5	359.7
$\beta_{12} = 0$	Δ	0.009	0.009	0.011
	$\log u - \log a$	-2.42	-2.43	-2.475
	$\log \beta_{22}$	-4.84	-4.86	-4.95
	j	24	38	25
	$E_0 + 3 \cdot 59.15$	384.7	381.3	360.0

Estimated uncertainty, approximately ± 0.2 in $\log k$ and $\log \beta_{12}$, ± 0.02 in $\log u - \log a$, ± 0.04 in $\log \beta_{22}$, under the assumption given.

H. Now, with a large enough correction, Δ, it might be possible to fit the data to the curves for the single complex $Th_2(OH)_2^{6+} = A_2B_2$. To test, how certain the evidence for AB_2 is, another series of successive approximations was made, where it was assumed that only the complex A_2B_2 existed, thus $\beta_{12} = 0$, and an attempt was made to get a good fit by adjusting Δ and β_{22}.

The values for Δ and $\log \beta_{22}$ thus obtained are also given in Table 5, "assumption $\beta_{12} = 0$". The corresponding best plots for 0.5 Th, 2.2 (Na)Cl are given in Figs 8 and 9. The plot for E_0 is seen to be less linear than that obtained assuming $\Delta = 0$ (Fig 7). The E_0 plot is at any rate very sensitive to small changes in F'. However, assuming $\beta_{12} = 0$, it seemed inevitable to get two bends in the plot, whatever changes were made in F'.

Moreover, a large analytical error must be assumed to make $\beta_{12} = 0$: a value for Δ of 9 mM would correspond to an error of around 0.45 % in the analysis for Th (weighing ThO_2) or Cl^- (really a H^+ titration). Analytical errors of this order of magnitude do not seem likely, and even if β_{12} may be

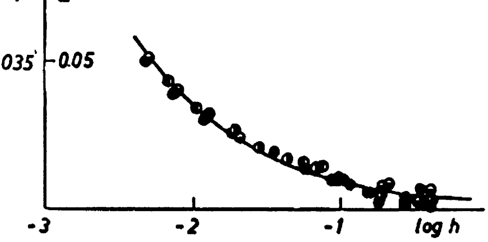

Fig. 5. Medium 0.7 Th, 3.0 (Na)Cl. Part of Fig. 3 on a larger scale.

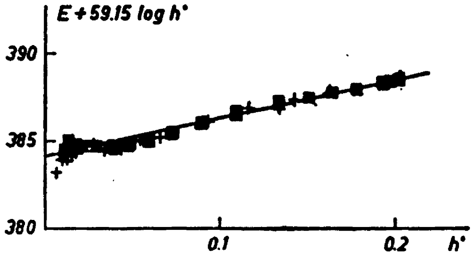

Fig. 6. Medium 0.5 Th(Cl). Abscissa: h', M, calculated from H and F' using (19) and values for β_{12} and β_{22} in Table 5. Ordinate: $E + 59.15$ ($\log h' + 3$) mV. Straight line: given by values of j and E_0 in Table 5, $\Delta = 0$.

Added in proof: In Figs. 6, 7, and 9, the ordinate is mislabeled: ($\log h' + 3$) was really used.

slightly in error, we think there is good evidence for the existence of the complex Th_2OH^{7+}, and for an equilibrium constant of the order of magnitude given.

We would thus prefer the values for $\Delta = 0$ and propose the following set of equilibrium constants:

Medium	$\log \beta_{12}$	$\log \beta_{22}$
0.5 Th, 2.2 (Na)Cl	-2.8 ± 0.2	-5.02 ± 0.04
0.7 Th, 3.0 (Na)Cl	-2.9 ± 0.2	-5.09 ± 0.04

With the medium 0.5 Th(Cl), practically the same equilibrium constants were obtained as with 0.5 Th, 2.2 (Na)Cl. The equilibrium constants thus do not seem to be very sensitive to small changes in the ionic medium. However, the constants for 0.5 Th(Cl) are left out since it seems preferable to leave the anion medium unchanged when the reactions studied are between cations;

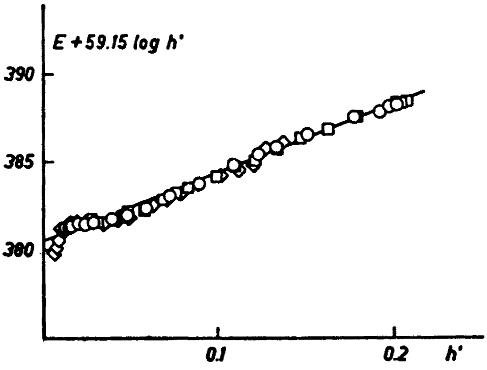

Fig. 7. Medium 0.5 Th, 2.2 (Na)Cl. $E + 59.15$ ($\log h' + 3$) mV *versus* h', M, calculated as in Fig. 6.

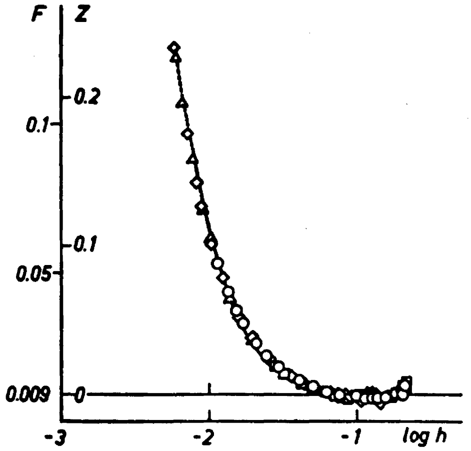

Fig. 8. Medium 0.5 Th, 2.2 (Na)Cl. Best fit assuming $\beta_{12} = 0$. $F = BZ + \Delta$ *versus* log h. Points: calculated from $E(H)$ with E_0 and j from Table 5. Curve: F' calculated with values for Δ and β_{22} from Table 5.

it has been found [4] that activity factors of cations are much more influenced by changes in the anion medium than by changes in the cation medium.

The agreement between the experimental $F(h)$ and the theoretical $F'(h)$ in Figs 1, 2 (4), and 3 (5) is very satisfactory up to beyond $Z = 0.10$. At higher values of Z, a considerable part of the ionic medium has been exchanged, and deviations are observed, especially in Fig 1, where the anionic medium changes.

The differences in E_0 and j in Table 5 are natural, considering the differences in the media.

DISCUSSION

The hydrolysis of Th^{4+} has been studied in inert medium, especially in Stockholm and Oakridge. Using 1(Na)ClO$_4$, Hietanen [9] found evidence for complexes $Th((OH)_3Th)_n^{(4+n)+}$, with log $\beta_{3n,n+1} \approx -7.50\ n$: according to Rossotti, Rossotti and Sillén [17], the data are still better described with log $\beta_{3n,n+1} = 0.06 - 7.53\ n$.

Using 1(NaClO$_4$) medium and a glass electrode, Kraus and Holmberg [10], who studied particularly the region of low Z, claimed evidence for mononuclear $ThOH^{3+}$, $Th(OH)_2^{2+}$ and dinuclear $Th_2(OH)_2^{6+}$, with the formation constants log $\beta_{11} = -4.3$, log $\beta_{21} = -7.7$, and log $\beta_{22} = -4.7$. Using measurements with 0.5 M NaClO$_4$ medium, Pan and Hseu [18] calculated, for infinite dilution, log $\beta_{11} = -3.89$ and log $\beta_{21} = -8.09$ (only mononuclear constants).

Literature data, presumably those of Hietanen, have later on been recalculated by Lefevbre [19], who has decided on a different set of complexes, with log $\beta_{21} = -7.42$, log $\beta_{22} = -4.56$, log $\beta_{12,5} = -29.5$; he also claims evidence for $Th_7(OH)_x$, with $x = 18$ to 21.

Later work in this laboratory using 3 M (Na)Cl medium [11] and studying lower concentrations, has given evidence for, in addition to the complexes

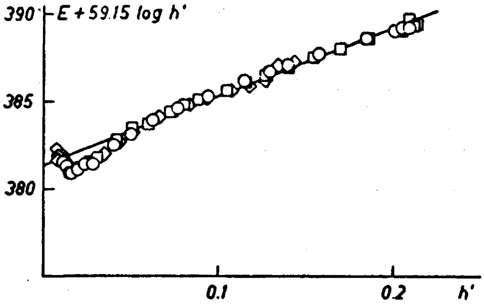

Fig. 9. Medium 0.5 Th, 2.2 (Na)Cl. Best fit assuming $\beta_{12} = 0$. $E + 59.15 (\log h' + 3)$ *versus* h', calculated as in Fig. 6.

$Th_{n+1}(OH)_{3n}^{(4+n)+}$, the complex $Th_2(OH)_2^{6+}$ with the equilibrium constant $\log \beta_{22} \approx -4.7$.

We may now ask whether the formulas assigned to our complexes, $Th_2(OH)_2^{6+}$ and Th_2OH^{7+}, are plausible or not. As mentioned, a change in the number of Th-atoms would only mean a small correction in the F' curves so, strictly speaking, the only information obtainable from the data is that there are one or more complexes with 2 OH, and one or more with 1 OH; the equilibrium constants interpreted as β_{12} and β_{22} are really the over-all constants K_1' and K_2' of eqn (4).

The value for log β_{22} obtained is in good agreement with those obtained from work in inert media of comparable anionic composition [10,11]. This, in itself, would favor the assumption of 2 Th in the complex.

The idea that any of these complexes are mononuclear can, we think, easily be ruled out. If the constants interpreted here as $\log \beta_{12} \approx -2.9$ and $\log \beta_{22} \approx -5.0$ had really been the mononuclear log β_{11} and log β_{21}, they would have been much higher than the values deduced by earlier workers [10,18]. Moreover, if there had existed mononuclear complexes with formation constants of this order of magnitude, hydrolysis would have started at much higher h than observed in earlier experiments [9,10,11], and the "mononuclear wall" would have been pratically the only Z curve obtained.

On the other hand, a formulation with three or more Th-atoms sharing 2 or 1 OH^- would seem rather awkward geometrically, and would moreover give compositions still farther removed from the $Th_{n+1}(OH)_{3n}^{(4+n)+}$ concluded for higher degrees of hydrolysis.

So it seems to us that the formulas $Th_2(OH)_2^{6+}$ and Th_2OH^{7+}, of course probably with some H_2O and Cl^- attached, are the only plausible ones.

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