

## Studies on the Hydrolysis of Metal Ions

### 61. Hydrolysis of the Thorium(IV) Ion in Lithium, Potassium, and Magnesium Nitrate Media

NIKOLA B. MILIĆ

*Department of Inorganic Chemistry, Royal Institute of Technology (KTH), Stockholm 70, Sweden and Boris Kidrič Institute of Nuclear Sciences, Vinča—Beograd, Yugoslavia*

The hydrolysis equilibria of  $\text{Th}^{4+}$  in the media 3 M  $(\text{Li})\text{NO}_3$ , 3 M  $(\text{K})\text{NO}_3$ , and 3 M  $(\text{Mg})\text{NO}_3$  has been studied at 25°C by emf titrations using a glass electrode in a concentration range for Th between 0.100 M and 0.001 M. Tables 1, 2, and 3, as well as Figs. 1, 2, and 3 give the data in the form  $Z(\log h)_B$ . A large number of combinations of hydrolysis products  $\text{Th}_q(\text{OH})_p$  were tried using the generalized least squares program LETAGROP.

The "best" sets of complexes and their equilibrium constants ( $\beta_{pq}$ ) are given in Table 4. The main species (2,2) is the same in all three media, but some of the secondary species found are different.

Earlier investigations on the hydrolysis of thorium ion are collected in *Stability Constants*<sup>1</sup> and several papers.<sup>2-4</sup>

In order to get some information about the influence of cations in nitrate media on the hydrolysis equilibria of thorium, a study has been made in 3 M  $(\text{Li})\text{NO}_3$ , 3 M  $(\text{K})\text{NO}_3$ , and 3 M  $(\text{Mg})\text{NO}_3$ , (*i.e.* 1.5 M  $\text{Mg}(\text{NO}_3)_2$ ). The experimental method was emf titrations using a glass electrode.

#### EXPERIMENTAL

##### Reagents and analysis

*Thorium nitrate* stock solutions were prepared from recrystallized  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ , Merck, *p.a.*, and by addition of a small amount of nitric acid to prevent initial hydrolysis.

The thorium content was determined by precipitating with oxide and oxalate, igniting the precipitate (950–1000°C), and weighing as  $\text{ThO}_2$ . Both methods gave the same results within  $\pm 0.2\%$ .

Initial acid concentration in stock solutions of thorium, as well as in solutions used in the titrations, were determined by potentiometric and coulometric titrations using the Gran plot.<sup>5,6</sup> The coulometric titrations were carried out by acidification of the solutions. Agreement between the two methods was within  $\pm 0.3\%$ .

*Potassium and magnesium nitrate* stock solutions were prepared from recrystallized  $\text{KNO}_3$  and  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , both Merck, *p.a.*

*Lithium nitrate* was prepared from nitric acid, Merck, *p.a.* and lithium carbonate, Mallinckrodt, *p.a.* Concentrated  $\text{HNO}_3$  was stirred mechanically in a beaker, and  $\text{Li}_2\text{CO}_3$  added spoonwise until a small excess had been added. Then a small excess of  $\text{HNO}_3$  was added, the solution was boiled and neutralized with  $\text{LiOH}$  to  $\text{pH} \sim 8$  (phenolphthalein indicator). The solution was kept standing for three days. During this time impurities (as Fe, Al, Si *etc.*) precipitated out. A Whatman-ashless tablet was added, and the solution was filtered through a G-4 Jena glass filter. The solution was acidified and the lithium nitrate was recrystallized twice.

The potassium, magnesium, and lithium content in stock solutions was determined by passing the solutions through a  $\text{H}^+$ -saturated cation exchanger (Dowex 50-X4) and titrating the  $\text{H}^+$  ions released with standardized  $\text{NaOH}$ . The reproducibility was within  $\pm 0.3\%$ .

*Potassium hydrogen carbonate* solutions were prepared from twice recrystallized  $\text{KHCO}_3$  Merck, *p.a.*, and their concentration was checked against standardized  $\text{HNO}_3$ .

*Sodium and lithium hydroxide* were prepared in polythene bottles as a 50% (20% for lithium hydroxide) solution from solid  $\text{NaOH}$ , Merck, *p.a.*, and  $\text{LiOH}$ , Mallinckrodt, *p.a.* After a few days  $\text{Na}_2\text{CO}_3$  (or  $\text{Li}_2\text{CO}_3$ ) was removed by filtering through a G-4 Jena glass filter. The solution was diluted with boiled water and standardized against potassium acid phthalate, Merck, *p.a.*, which had been dried at  $120^\circ\text{C}$  to constant weight.

*Nitric acid* was made by dilution of  $\text{HNO}_3$ , Merck, *p.a.*, and standardized against  $\text{NaOH}$ .

The distilled water was always boiled to expel  $\text{CO}_2$ .

$\text{N}_2$  gas for stirring was purified by passing through 10%  $\text{NaOH}$  and 10%  $\text{H}_2\text{SO}_4$  and saturated with  $\text{H}_2\text{O}$  vapor by bubbling through water and ionic medium.

## Apparatus and procedure

All emf measurements were carried out as potentiometric titrations with a glass electrode (Beckman, 40498) and an  $\text{Ag,AgCl}$  electrode as a reference electrode (RE). During measurements the "Wilhelm" bridge<sup>7</sup> and the titration vessel were inserted in a paraffin oil thermostat at  $25 \pm 0.05^\circ\text{C}$ , which was placed in a room thermostated to  $25 \pm 0.5^\circ\text{C}$ .

$\text{Ag, AgCl}$  electrodes were prepared according to Brown.<sup>8</sup>

The cell was:

– glass electrode | thorium solution | RE +

where RE =  $\text{Ag, AgCl} | 3.0/n \text{ M Me}^{n+}, 0.01 \text{ M Ag}^+, 3.0 \text{ M NO}_3^-$ ;  $\text{Me}^{n+}$  stands for  $\text{K}^+, \text{Li}^+$ , and  $\text{Mg}^{2+}$ .

Titration were carried out by adding to the initial solution of thorium, either  $\text{KHCO}_3$  solution (for  $\text{KNO}_3$  and  $\text{Mg}(\text{NO}_3)_2$  medium) or  $\text{LiOH}$  solution (for  $\text{LiNO}_3$  medium) in portions from one buret, as well as a thorium solution, from another buret. In this way the total thorium concentration ( $B$ ) and the total concentration of nitrate ion (3 M) were kept constant, while the analytical  $\text{H}^+$  excess,  $H$ , was decreased, so that it became negative during the course of the titration. The solution had the general composition:

$B \text{ M Th}^{4+}, H \text{ M H}^+ (3.0 - H - 4 B) \text{ M K}^+ \text{ (or Li}^+), 3 \text{ M NO}_3^-$ , or

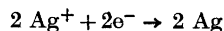
$B \text{ M Th}^{4+}, H \text{ M H}^+ (1.5 - H - 4 B) \text{ M Mg}^{2+}, 3 \text{ M NO}_3^-$

The emf ( $E$ ) was measured after each new addition of the solutions from burets, until the potential was constant to within  $\pm 0.02$  mV when using a digital voltmeter, or  $\pm 0.1$  mV when using a Metrohm instrument.

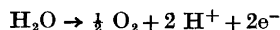
To avoid precipitation due to local excess of  $\text{OH}^-$ , as well as to reach equilibrium faster, the solutions were stirred by bubbling  $\text{N}_2$ .

In some experiments (1.5 mM Th in  $\text{KNO}_3$ , 5 mM and 2.5 mM Th in  $\text{Mg}(\text{NO}_3)_2$ ), after having reached a certain value of  $Z$  ( $\sim 0.5$ ) ( $Z$  is the average number of  $\text{OH}^-$  bound per Th in solution) the direction was changed by adding  $\text{HNO}_3$  instead of  $\text{KHCO}_3$ , to a solution with negative value of  $H$ . In several cases (10 and 2.5 mM Th in  $\text{LiNO}_3$ , 3.0 mM Th in  $\text{KNO}_3$ , and 1.3 mM Th in  $\text{Mg}(\text{NO}_3)_2$ ), these back titrations were carried out by a coulometric method.<sup>9</sup> A Pt-net was inserted in the equilibrium solution as the coulometric

anode which was connected with another "Wilhelm" bridge to the cathode (a Pt-foil). At the cathode (separated from the equilibrium solution)  $\text{Ag}^+$  ions were deposited on the Pt-foil according to the following reaction:



while the anode reaction was



so that  $\text{H}^+$  was produced.

When the back titration was started with a value  $Z > 0.5$  a small hysteresis effect was observed. For this reason data with  $Z > 0.5$  have not been used in the calculations.

The concentration of free  $\text{H}^+$  ( $h$ ) in each point is calculated by Nernst's formula:

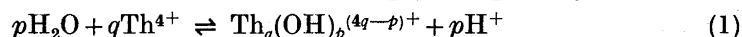
$$E = E_0 + E_j + 59.16 \log h$$

where  $E$  is the measured potential,  $E_0$  a constant which includes the standard potential for the glass electrode and  $E_j$  the liquid junction potential which is an approximately linear function of  $h$ , i.e.  $E_j = j h$ .<sup>10</sup> In order to determine  $E_0$  and  $j$ , a Gran plot was first made to get a better value of  $H$ , which was then used to plot  $E - 59.16 \log h$  versus  $h$  (or  $H$ ), which gave  $E_0$  (limiting value) and  $j$  (from slope).  $E_0$  was determined for each titration directly from the part of the titration where no hydrolysis occurred, while  $j$  was determined in solutions not containing thorium. The influence of thorium on  $j$  is assumed to be negligible.

Emf was measured with a Digital Voltmeter type DM-2022 S, Dynamco, LTD, except, for titrations in which thorium concentrations were higher than 10 mM in  $\text{KNO}_3$  medium where a Metrohm Herisau Compensator E-388, was used. The current source for coulometric titrations was a Metrohm Herisau Coulometer, E-211.

#### NOTATION

To be consistent with other papers in this series we shall denote by  $\beta_{pq}$  the equilibrium constant for the formation of the  $(p,q)$  complex, by the reaction



$$c_{pq} = \beta_{pq} h^{-p} b^q \quad (2)$$

where:  $p$  = number of  $\text{OH}^-$  groups in the  $(p,q)$  complex;  $q$  = number of Th atoms in the  $(p,q)$  complex;  $b$  = concentration of free thorium  $\text{Th}^{4+}$  in solution;  $h$  = equilibrium concentration of hydrogen ions;  $c_{pq}$  = concentration of the complex. In the text the following additional symbols will be used:  $B$  = total concentration of Th(IV);  $H$  = analytical excess of hydrogen ions in the solution which became negative in hydrolysed solutions;  $Z = (h - H)B^{-1}$  = average number of  $\text{OH}^-$  bound per thorium in the solution.

#### THE DATA

The experimental data are collected in Tables 1, 2, and 3, and are represented graphically in Figs. 1, 2, and 3, as  $Z = f(-\log h)_B$ . The total concentrations of thorium ( $B$ ) were the following: 2.5, 5, 10, 20, 40, 79, and 121 mM Th in  $\text{LiNO}_3$ , 1.5, 3.0, 6, 10, 20, 40, 63, and 126 mM Th in  $\text{KNO}_3$  and 1.3, 2.5, 5, 10, 20, 40, 79, and 121 mM Th in  $\text{Mg}(\text{NO}_3)_2$  medium. Each curve in  $\text{KNO}_3$  and  $\text{Mg}(\text{NO}_3)_2$  corresponds to at least two titrations, while in  $\text{LiNO}_3$  curves for 121, 79, 20, and 5 mM Th correspond only to one titration.

Table 1. Hydrolysis of thorium ion in 3 M (Li)NO<sub>3</sub>. The experimental data ( $Z$ ,  $-\log h$ )<sub>B</sub> are given and for the points used in the LETAGROP calculations also  $1000(Z_{\text{calc}} - Z_{\text{exp}})$  using the "best" set of equilibrium constants and  $\delta Z$ .

$B = 121$  mM. 1.888, 0.011, 0; 2.090, 0.023, +2; 2.250, 0.047, -2; 2.362, 0.077, +2; 2.441, 0.106, 0; 2.507, 0.134, +1; 2.557, 0.160, +1; 2.597, 0.184, 0, 2.633, 0.207, 0; 2.665, 0.227, 0; 2.716, 0.264, 0; 2.737, 0.280; 0; 2.783, 0.316, 0; 2.828, 0.352, +1; 2.889, 0.403, +4;  
 2.016, 0.004; 2.203, 0.027; 2.335, 0.053; 2.430, 0.084; 2.501, 0.113; 2.556, 0.140; 2.602, 0.165; 2.641, 0.188; 2.673, 0.210; 2.716, 0.239; 2.786, 0.292; 2.823, 0.322;  
 $B = 79$  mM. 1.786, 0.012, -8; 1.905, 0.010, -3; 2.030, 0.013, 0; 2.155, 0.020, +2; 2.351, 0.049, +2; 2.479, 0.084, +2; 2.564, 0.117, +1; 2.670, 0.172, 0; 2.708, 0.195, 0; 2.785, 0.248, -1; 2.814, 0.268, 0; 2.851, 0.296, 0; 2.900, 0.336, +1; 2.932, 0.364, +2; 2.118, 0.015; 2.288, 0.030; 2.446, 0.070; 2.548, 0.102; 2.647, 0.146; 2.774, 0.230; 2.902, 0.330;  
 $B = 40$  mM. 2.054, 0.007, -7; 2.286, 0.018, +2; 2.508, 0.048, +4; 2.777, 0.150, 0; 2.861, 0.200, -2; 2.929, 0.247, -2; 2.986, 0.290, -2; 3.034, 0.329, -1; 3.077, 0.366, 0; 3.114, 0.399, +2; 3.148, 0.430, +4; 3.162, 0.445, +4;  
 2.733, 0.120; 2.830, 0.180; 2.900, 0.230; 2.980, 0.279; 3.045, 0.340; 3.061, 0.347; 3.100, 0.381; 3.140, 0.413; 2.200, 0.010; 2.305, 0.015; 2.357, 0.020; 2.405, 0.030; 2.430, 0.036; 2.500, 0.044; 2.571, 0.058; 2.600, 0.071; 2.640, 0.083; 2.670, 0.094; 2.700, 0.112; 2.750, 0.135; 2.801, 0.160;  
 $B = 20$  mM. 2.285, 0.013, -2; 2.533, 0.028, +3; 2.738, 0.072, +1; 2.877, 0.125, 0; 2.973, 0.177, -1; 3.042, 0.222, -2; 3.096, 0.262, -2; 3.140, 0.297, -2; 3.177, 0.327, 0; 3.233, 0.377, +2; 3.273, 0.418, +2;  
 2.613, 0.032; 2.784, 0.090; 2.898, 0.130; 2.980, 0.178; 3.042, 0.210; 3.089, 0.246; 3.177, 0.320;  
 $B = 10$  mM. 2.640, 0.010, 0; 2.746, 0.039, +2; 2.847, 0.060, +2; 2.938, 0.088, +1; 3.016, 0.121, -1; 3.083, 0.156, -2; 3.143, 0.191, -2; 3.196, 0.226, -1; 3.241, 0.261, -1; 3.283, 0.294, 0; 3.320, 0.327, +1; 3.354, 0.358, +3; 3.383, 0.388, +2; 3.406, 0.418, -2;  
 Back titration by coulometer: 2.670, 0.012; 2.700, 0.018; 2.750, 0.032; 2.800, 0.049; 2.901, 0.076; 3.001, 0.107; 3.050, 0.141; 3.140, 0.177; 3.170, 0.193; 3.200, 0.232; 3.210, 0.236; 3.230, 0.245; 3.260, 0.265; 3.280, 0.285; 3.310, 0.306; 3.330, 0.326; 3.340, 0.348; 3.402, 0.391;  
 $B = 5$  mM. 2.782, 0.020, 0; 2.873, 0.036, 0; 3.028, 0.071, 0; 3.142, 0.112, -2; 3.223, 0.153, -4; 3.286, 0.189, -2; 3.343, 0.228, -1; 3.421, 0.287, +3; 3.464, 0.327, +5; 3.510, 0.373, +6; 3.529, 0.396, +4;  
 2.942, 0.040; 3.173, 0.126; 3.243, 0.170; 3.372, 0.260; 3.433, 0.310;  
 $B = 2.5$  mM. 2.891, 0.012, +8; 3.034, 0.031, +7; 3.174, 0.066, +3; 3.298, 0.114, 0; 3.401, 0.170, -2; 3.484, 0.228, -3; 3.550, 0.284, -3; 3.603, 0.337, -3; 3.639, 0.387, -14; 3.095, 0.036; 3.228, 0.090; 3.341, 0.140; 3.434, 0.180; 3.508, 0.230; 3.567, 0.300; 3.614, 0.340;  
 Back titration by coulometer: 3.147, 0.062; 3.221, 0.080; 3.277, 0.100; 3.332, 0.130; 3.385, 0.160; 3.436, 0.180; 3.486, 0.220; 3.532, 0.252; 3.562, 0.280; 3.598, 0.330; 3.622, 0.342;

The points are experimental data and the full drawn curves are calculated with the "best" set of constants given in Table 4.

#### TREATMENT OF DATA

It is obvious from the titration curves (Figs. 1, 2, and 3) that polynuclear complexes are formed. The average composition ( $\bar{p}, \bar{q}$ ) was calculated with the general integration method,<sup>11</sup> using the computer program MESA<sup>12</sup>. For these calculations the only assumption needed is that the law of mass action is valid in its simple stoichiometric form. For these calculations one titration for each  $B$  was used. The results are represented in Figs. 4, 5, and 6, as  $\bar{q}$  versus ( $2\bar{q} - \bar{p}$ ). In such a diagram each possible complex corresponds to one point,

Table 2. Hydrolysis of thorium ion in 3 M (K)NO<sub>3</sub>. The experimental data ( $Z$ ,  $-\log h$ )<sub>B</sub> are given and for the points used in the LETAGROP calculations also 1000( $Z_{\text{calc}} - Z_{\text{exp}}$ ) using the "best" set of equilibrium constants and  $\delta Z$ .

$B=126$  mM. 1.436, 0.003, -2; 1.522, 0.008, -5; 1.637, 0.006, -2; 1.764, 0.010, -3; 1.931, 0.014, 0; 2.101, 0.030, 0; 2.238, 0.056, -1; 2.355, 0.086, +2; 2.436, 0.119, +1; 2.507, 0.152, +3; 2.621, 0.216, +9; 2.697, 0.277, +5; 2.873, 0.434, 0; 2.422, 0.010; 2.549, 0.164; 2.748, 0.313; 2.922, 0.480; 2.397, 0.088; 2.510, 0.143; 2.662, 0.247; 2.802, 0.361;

$B=63$  mM. 1.495, 0.001, +1; 1.569, 0.003, -1; 1.667, 0.001, +1; 1.909, 0.001, +5; 2.416, 0.064, -2; 2.728, 0.005, +2; 2.900, 0.342, -7; 3.022, 0.468, -13; 2.564, 0.092; 2.799, 0.235; 2.955, 0.368; 3.058, 0.488; 3.115, 0.597; 2.505, 0.069; 2.657, 0.139; 2.860, 0.280; 2.995, 0.409;

$B=40$  mM. 1.549, 0.001, +1; 1.614, 0.004, -2; 1.695, 0.002, 0; 1.787, 0.003, 0; 1.903, 0.001, +2; 2.046, 0.005, +3; 2.212, 0.021, -3; 2.429, 0.045, 0; 2.602, 0.095, -4; 2.852, 0.222, +4; 3.119, 0.486, +1; 2.545, 0.064; 2.762, 0.155; 2.951, 0.290; 3.162, 0.549; 2.444, 0.042; 2.654, 0.109; 3.092, 0.438; 3.178, 0.596; 2.724, 0.137; 2.841, 0.201; 2.912, 0.262; 2.976, 0.314; 3.039, 0.366;

$B=20$  mM. 1.548, 0.000, 0; 1.592, 0.000, 0; 1.637, 0.003, -2; 1.687, 0.002, +3; 1.734, 0.001, 0; 1.687, 0.002, +3; 1.734, 0.001, 0; 1.787, 0.001, +1; 1.844, 0.002, +3; 1.902, 0.001, +2; 1.963, 0.004, -1; 2.034, 0.002, +1; 2.109, 0.006, 0; 2.197, 0.007, +1; 2.292, 0.013, -1; 2.399, 0.023, -2; 2.516, 0.037, -3; 2.633, 0.060, -3; 2.736, 0.091, -3; 2.825, 0.127, -1; 2.903, 0.165, +2; 2.966, 0.205, +3; 3.023, 0.244, +6; 3.069, 0.283, +5; 3.108, 0.322, +2; 3.172, 0.396, -1; 3.213, 0.466, -10; 2.108, 0.005; 2.195, 0.006; 2.346, 0.014; 2.512, 0.037; 2.684, 0.073; 2.860, 0.144; 2.992, 0.222; 3.142, 0.357; 3.230, 0.497; 2.457, 0.027; 2.578, 0.045; 2.784, 0.106; 2.934, 0.183; 3.088, 0.300; 3.196, 0.429;

$B=10$  mM. 1.609, 0.012, -12; 1.638, 0.001, +1; 1.665, 0.001, +2; 1.693, 0.002, -1; 1.722, 0.001, 0; 1.783, 0.001, -1; 1.816, 0.001, -1; 1.848, 0.001, +1; 1.884, 0.001, +1; 1.919, 0.001, +2; 1.959, 0.001, +1; 1.999, 0.001, +1; 2.042, 0.001, +2; 2.089, 0.001, +2; 2.137, 0.004, 0; 2.196, 0.001, +4; 2.254, 0.004, +1; 2.322, 0.006, +1; 2.395, 0.012, -2; 2.476, 0.021, -6; 2.581, 0.025, -1; 2.683, 0.044, +6; 2.801, 0.065, -2; 2.908, 0.100, 0; 2.999, 0.143, -1; 3.082, 0.191, +2; 3.149, 0.243, +1; 3.210, 0.295, +3; 3.259, 0.349, +3; 3.290, 0.404, -7; 3.315, 0.458, -14; 2.400, 0.003; 2.479, 0.014; 2.577, 0.023; 2.687, 0.037; 2.796, 0.063; 2.904, 0.097; 2.992, 0.141; 3.079, 0.188; 3.149, 0.239; 3.208, 0.291; 3.252, 0.346; 3.287, 0.400; 3.314, 0.454; 3.370, 0.612;

$B=6.1$  mM. 2.005, 0.001, +1; 2.057, 0.001, 0; 2.111, 0.003, -1; 2.171, 0.001, +2; 2.231, 0.005, -2; 2.298, 0.006, -2; 2.372, 0.006, 0; 2.450, 0.011, -2; 2.541, 0.014, -2; 2.641, 0.023, -3; 2.756, 0.036, -3; 2.875, 0.061, -6; 2.996, 0.097, -3; 3.105, 0.144, +1; 3.194, 0.200, +3; 3.270, 0.258, +7; 3.327, 0.319, +7; 3.395, 0.441, +8; 2.500, 0.004; 2.599, 0.008; 2.706, 0.020; 2.826, 0.040; 2.946, 0.071; 3.059, 0.116; 3.159, 0.168; 3.242, 0.226; 3.304, 0.287; 3.369, 0.379; 3.429, 0.527;

$B=3.0$  mM. 2.274, 0.001, +2; 2.344, 0.006, -3; 2.427, 0.004, 0; 2.520, 0.009, -3; 2.638, 0.006, +3; 2.774, 0.024, -5; 2.957, 0.046, -3; 3.169, 0.110, 0; 3.355, 0.227, 0; 3.472, 0.381, 0; 3.529, 0.547, +4; 2.851, 0.036; 2.894, 0.045; 2.998, 0.060; 3.048, 0.075; 3.106, 0.089; 3.206, 0.136; 3.258, 0.162; 3.304, 0.192; 3.389, 0.258; 3.423, 0.296; 3.447, 0.336; 3.488, 0.417; 3.520, 0.455; 3.551, 0.624;

Back titration by coulometer: 3.573, 0.583; 3.562, 0.544; 3.545, 0.486; 3.526, 0.429; 3.502, 0.373; 3.426, 0.257; 3.343, 0.185; 3.281, 0.146; 3.215, 0.113; 3.140, 0.083; 3.073, 0.061; 3.008, 0.044; 2.947, 0.032; 2.809, 0.011; 2.719, 0.026; 2.642, 0.019; 2.578, 0.015;

$B=1.5$  mM. 2.472, 0.002, 0; 2.522, 0.012, -9; 2.582, 0.003, 0; 2.646, 0.008, -3; 2.723, 0.004, +3; 2.808, 0.012, 0; 2.912, 0.019, -1; 3.039, 0.034, -1; 3.183, 0.080, -15; 3.356, 0.149, -10; 3.518, 0.265, +7; 3.597, 0.434, +1; 2.650, 0.015; 2.687, 0.011; 2.767, 0.017; 2.857, 0.033; 2.979, 0.033; 3.119, 0.060; 3.285, 0.114; 3.453, 0.214; 3.565, 0.365; 3.624, 0.543;

Back titration by buret: 3.629, 0.541; 3.577, 0.386; 3.484, 0.257; 3.222, 0.105; 3.098, 0.076; 2.996, 0.058; 2.912, 0.045; 2.842, 0.030; 2.633, 0.018; 2.570, 0.013; 2.512, 0.006;

Table 3. Hydrolysis of thorium ion in 3 M (Mg)NO<sub>3</sub>. The experimental data ( $Z, -\log h$ )<sub>B</sub> are given and for the points used in the LETAGROP calculation also 1000( $Z_{\text{calc}} - Z_{\text{exp}}$ ) using the "best" set of equilibrium constants and  $\delta Z$ .

$B = 121$  mM. 1.772, 0.006, 0; 1.928, 0.011, 0; 2.084, 0.023, 0; 2.218, 0.041, 0; 2.320, 0.062, 0; 2.454, 0.105, 0; 2.572, 0.161, 0; 2.684, 0.230, 0; 2.797, 0.315, -1; 2.861, 0.369, 0; 2.909, 0.410, +1;  
 2.247, 0.036; 2.424, 0.081; 2.527, 0.123; 2.650, 0.190; 2.752, 0.260; 2.821, 0.313; 2.900, 0.381; 2.931, 0.408; 2.976, 0.449;  
 $B = 79$  mM. 1.695, 0.003, 0; 1.757, 0.004, -1; 1.824, 0.006, 0; 1.897, 0.008, -1; 1.977, 0.010, 0; 2.063, 0.014, 0; 2.151, 0.020, 0; 2.235, 0.030, 0; 2.315, 0.041, 0; 2.384, 0.055, 0; 2.445, 0.070, +1; 2.579, 0.117, +2; 2.717, 0.190, +1; 2.811, 0.253, +1; 2.935, 0.352, +2; 3.017, 0.426, +4;  
 1.815, 0.001; 2.046, 0.009; 2.309, 0.033; 2.492, 0.078; 2.609, 0.127; 2.694, 0.173; 2.760, 0.216; 2.861, 0.290; 2.980, 0.392; 3.043, 0.449; 3.114, 0.521; 3.161, 0.577; 3.188, 0.611;  
 $B = 40$  mM. 1.464, 0.001, 0; 1.521, 0.001, 0; 1.580, 0.001, +1; 1.642, 0.001, 0; 1.711, 0.001, +1; 1.786, 0.001, +1; 1.870, 0.002, +1; 1.967, 0.003, +2; 2.079, 0.006, +1; 2.282, 0.018, 0; 2.358, 0.025, 0; 2.507, 0.048, +1; 2.630, 0.081, 0; 2.726, 0.118, -1; 2.804, 0.157, -2; 2.870, 0.197, -2; 2.979, 0.272, -2; 3.063, 0.343, -3; 3.221, 0.499, -1;  
 1.897, 0.001; 2.063, 0.004; 2.197, 0.010; 2.275, 0.015; 2.510, 0.047; 2.646, 0.081; 2.743, 0.122; 2.822, 0.164; 2.891, 0.205; 2.974, 0.266; 3.067, 0.342; 3.143, 0.413; 3.207, 0.478; 3.257, 0.539; 3.292, 0.596;  
 $B = 20$  mM. 1.442, 0.001, 0; 1.495, 0.001, +1; 1.550, 0.001, 0; 1.609, 0.001, 0; 1.671, 0.002, -1; 1.739, 0.002, -1.816, 0.001, 0; 1.900, 0.002, 0; 1.998, 0.004, -1; 2.117, 0.005, 0; 2.267, 0.008, +1; 2.457, 0.021, 0; 2.673, 0.054, +1; 2.857, 0.113, 0; 2.922, 0.145, -1; 2.993, 0.185, -1; 3.101, 0.259, -1; 3.189, 0.334, -1; 3.266, 0.406, +1; 3.328, 0.477, +2; 2.751, 0.076; 2.914, 0.141; 3.042, 0.214; 3.137, 0.289; 3.224, 0.362; 3.293, 0.434; 3.348, 0.503;  
 $B = 10$  mM. 1.954, 0.002, -1; 2.069, 0.003, -1; 2.207, 0.004, 0; 2.384, 0.007, +1; 2.627, 0.023, +1; 2.775, 0.044, +1; 2.847, 0.061, -1; 2.985, 0.106, -1; 3.101, 0.161, 0; 3.196, 0.221, 0; 3.427, 0.437, +3;  
 2.625, 0.010; 2.918, 0.068; 3.042, 0.119; 3.146, 0.178; 3.236, 0.238; 3.309, 0.301; 3.373, 0.363; 3.461, 0.484; 3.505, 0.600;  
 $B = 5.0$  mM. 1.837, 0.001, 0; 1.945, 0.006, -5; 2.073, 0.004, -3; 2.231, 0.005, -3; 2.451, 0.004, +1; 2.815, 0.026, +2; 3.078, 0.082, +1; 3.202, 0.135, +1; 3.311, 0.198, +1; 3.404, 0.268, +3; 3.481, 0.342, +5; 3.576, 0.497, -4;  
 2.897, 0.020; 3.011, 0.049; 3.146, 0.092; 3.255, 0.153; 3.359, 0.219; 3.536, 0.406; 3.619, 0.640; 3.303, 0.187; 3.571, 0.485;  
 Back titration by buret: 3.571, 0.485; 3.535, 0.418; 3.489, 0.354; 3.432, 0.295; 3.365, 0.239; 3.293, 0.189; 3.215, 0.144; 3.133, 0.105; 3.046, 0.075; 2.959, 0.043; 2.875, 0.029;  
 $B = 2.5$  mM. 1.863, 0.004, -3; 1.979, 0.008, -7; 2.119, 0.005, -4; 2.299, 0.005, -3; 2.569, 0.008, -3; 2.670, 0.004, +3; 2.794, 0.006, +7; 2.947, 0.024, +2; 3.151, 0.058, +4; 3.368, 0.143, +2; 3.549, 0.276, 0; 3.663, 0.436, 0; 3.696, 0.521, +2;  
 3.028, 0.048; 3.252, 0.098; 3.452, 0.209; 3.613, 0.355; 3.657, 0.437;  
 Back titration by buret: 3.657, 0.437; 3.574, 0.314; 3.449, 0.210; 3.307, 0.129; 3.154, 0.077; 3.020, 0.046;  
 $B = 1.3$  mM. 1.962, 0.003, -3; 2.042, 0.001, +1; 2.130, 0.001, +1; 2.226, 0.001, 0; 2.340, 0.001, 0; 2.479, 0.005, -3; 2.565, 0.003, 0; 2.666, 0.008, -4; 2.796, 0.001, +5; 2.964, 0.011, +3; 3.072, 0.023, 0; 3.208, 0.042, 0; 3.370, 0.084, -2; 3.540, 0.165, -4; 3.682, 0.287, -10;  
 3.129, 0.025; 3.291, 0.059; 3.440, 0.114; 3.603, 0.212; 3.728, 0.346; 3.764, 0.424; 3.802, 0.590; 3.193, 0.037; 3.307, 0.068; 3.435, 0.108; 3.553, 0.170; 3.655, 0.247; 3.730, 0.338;  
 Back titration by coulometer: 3.658, 0.243; 3.540, 0.164; 3.426, 0.110; 3.315, 0.074; 3.215, 0.050;

at the corner of a square. If the solution contains only two complexes, the average composition of the complexes in the solution would correspond to points on the line connecting the points for the two complexes; and correspondingly for mixtures of more than two complexes.<sup>13</sup> The points distributed

Table 4. Equilibrium constants,  $\log(\beta_{pq} \pm 3\sigma)$  for  $\text{Th}^{4+}$  hydrolysis in 3 M (Li, K, Mg) $\text{NO}_3$ .

Medium	Complex	$\log \beta_{pq} \pm 3\sigma$
3 M (Li) $\text{NO}_3$	2,2	$-5.14 \pm 0.01$
	5,3	$-14.23 \pm 0.06$
	[3,3]	max = $-7.73$ ]*
3 M (K) $\text{NO}_3$	2,2	$-5.10 \pm 0.03$
	3,2	$-8.98 \pm 0.08$
	[2,1]	$-9.67$ , max = $-8.90$ ]*
	15,6	$-40.95 \pm 0.07$
3 M (Mg) $\text{NO}_3$	2,2	$-5.17 \pm 0.01$
	5,3	$-14.29 \pm 0.07$
	15,6	$-43.20 \pm 0.08$

\* The most uncertain values are put within parentheses.

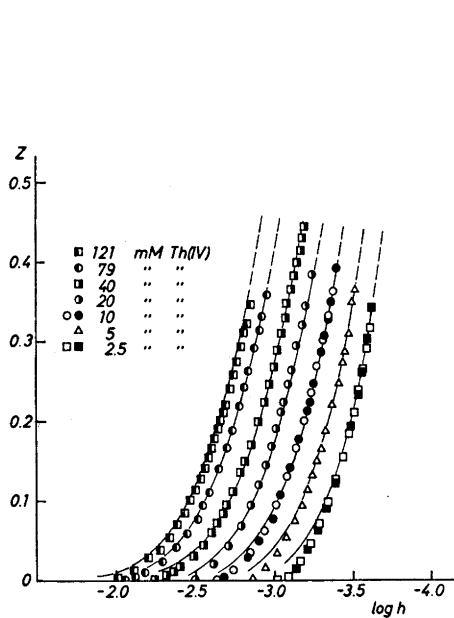


Fig. 1. Hydrolysis of thorium ion in 3 M (Li) $\text{NO}_3$  medium.  $Z$ , as a function of  $\log h$  for various total concentrations,  $B$ , of Th. The black symbols for  $B = 10$  and  $2.5$  mM refer to back titrations. Points are experimental data, while the full-drawn curves have been calculated by the set of constants given in Table 4.

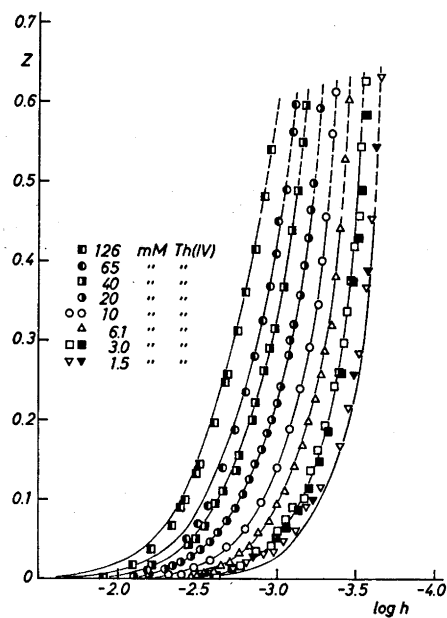


Fig. 2. Hydrolysis of thorium ion in 3 M (K) $\text{NO}_3$  medium.  $Z$  as a function of  $\log h$  for various total concentrations,  $B$ , of Th. The black symbols for  $B = 3.0$  and  $1.5$  mM refer to back titrations. Points are experimental data, while the full-drawn curves have been calculated by the set of constants given in Table 4.

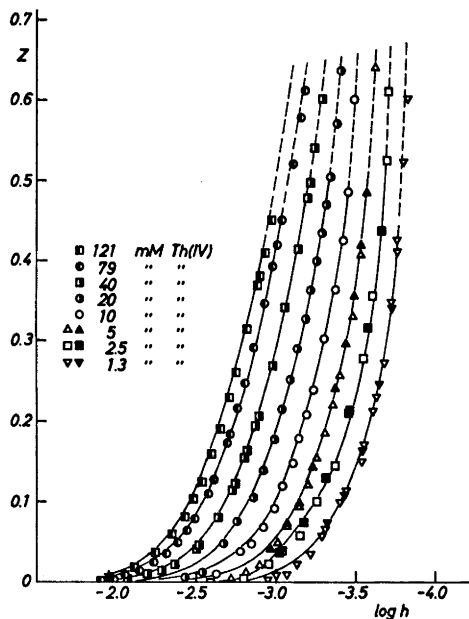


Fig. 3. Hydrolysis of thorium ion in 3 M (Mg)NO<sub>3</sub> medium.  $Z$  as a function of  $\log h$  for various total concentrations,  $B$ , of Th. The black symbols for  $B=5$ , 2.5, and 1.3 mM refer to back titrations. Points are experimental data, while the full-drawn curves have been calculated by the set of constants given in Table 4.

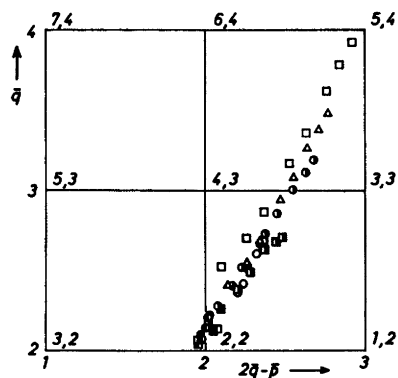


Fig. 4. Hydrolysis of thorium ion in 3 M (Li)NO<sub>3</sub> medium. Average composition of complexes as  $\bar{q}$  versus  $(2\bar{q} - \bar{p})$ , calculated by the MESAK program.

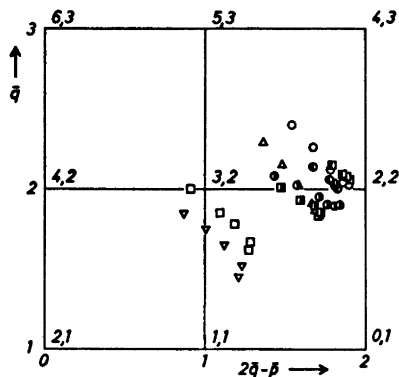


Fig. 5. Hydrolysis of thorium ion in 3 M (K)NO<sub>3</sub> medium. Average composition of complexes as  $\bar{q}$  versus  $(2\bar{q} - \bar{p})$ , calculated by the MESAK program.

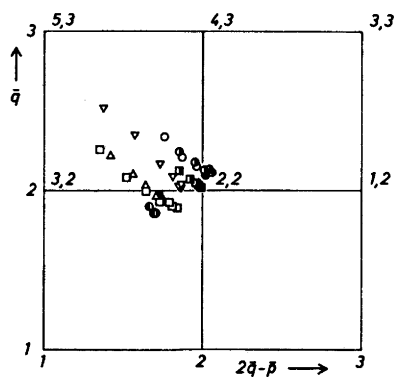


Fig. 6. Hydrolysis of thorium ion in 3 M (Mg)NO<sub>3</sub> medium. Average composition of complexes as  $\bar{q}$  versus  $(2\bar{q} - \bar{p})$ , calculated by the MESAK program.



around and near corner (2,2) in Figs. 4, 5, and 6 give evidence about complexes (2,2) in all three media, (3,2) and (5,3) in  $\text{KNO}_3$ , (5,3) in  $\text{Mg}(\text{NO}_3)_2$ , and (3,3), (4,3), and (5,4) in  $\text{LiNO}_3$  medium.

To get further information about the complexes formed and their equilibrium constants the computer program LETAGROP<sup>14-18</sup> was used. Complexes indicated by the MESAK program were first tried, and after that various other combinations of complexes were tried to find a set of equilibrium constants  $\beta_{pq}$  that would give the lowest value in the error square sum  $U = (Z_{\text{calc}} - Z_{\text{exp}})^2$ . Figs. 7a, 7b, and 7c show the  $(p,q)$  values tried.

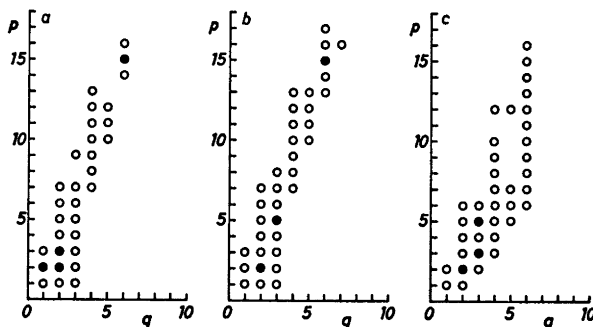


Fig. 7. Hydrolysis of thorium ion in 3 M (K)NO<sub>3</sub> (a), 3 M (Mg)NO<sub>3</sub> (b) and 3 M (Li)NO<sub>3</sub> (c) medium.  $(p,q)$  values tried in the LETAGROP calculations using the "species selector".

To get a rapid investigation of all possible complexes a "species selector"<sup>16</sup> was used. This part of the LETAGROP program gives the opportunity that besides the probable main complexes and their equilibrium constants one can introduce new complexes in turn one after another. The  $\beta_{pq}$  of a new complex is varied alone at first to get a better value than the starting estimate, and then varied together with the old constants.

It was reasonable to assume that the data might contain small systematic errors, such as a small error in  $E_0$ ,  $H$ , and even  $B$  and  $j$ . In order to take this into account a final refining calculation, employing the KOKS part of the LETAGROP program, was used. The resulting values for the quantities mentioned were small, indicating small errors. All complexes assumed to be present were retained during this procedure. The change in the goodness of fit is seen in Fig. 8, where  $(Z_{\text{calc}} - Z_{\text{exp}}) \times 10^3$  is plotted against  $-\log h$  for all titrations.

Table 4 shows the sets of accepted complexes which gave the "lowest" minimum in  $U$ , together with their  $\beta_{pq}$  and standard deviations, as  $\log(\beta + 3\sigma)$ . The complexes were rejected if the quotient  $\beta_{pq}/\sigma$  was smaller than the values given by "sigfak" (in our case 1.5).

#### DISCUSSION

Table 4 shows that only the (2,2) complex was found in all three cation-nitrate media, while other complexes were found only in one or two media.

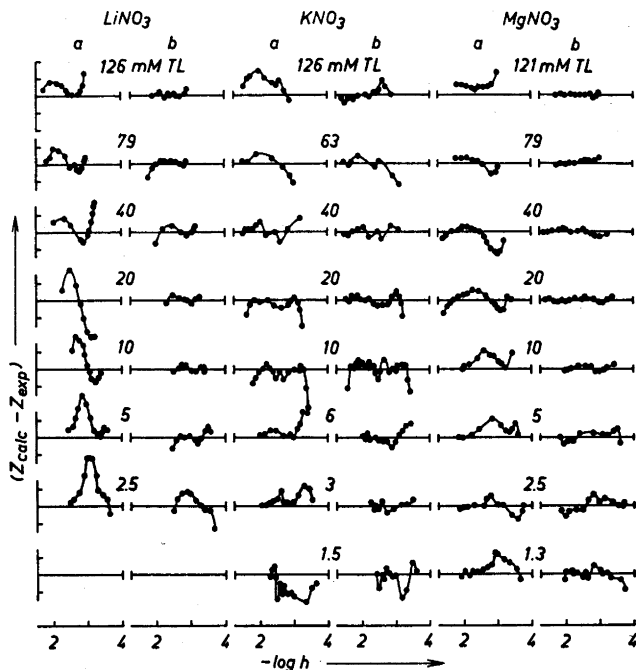


Fig. 8. Hydrolysis of thorium ion in 3 M (Li)NO<sub>3</sub>, 3 M (K)NO<sub>3</sub>, and 3 M (Mg)NO<sub>3</sub> medium.  $(Z_{\text{exp}} - Z_{\text{calc}}) \times 10^3$  versus  $-\log h$  for the different  $B$  values assuming complexes which gave the "best" values for the  $\beta_{p,q}$ : (a) using experimental data of analysis - LiNO<sub>3</sub>:  $\log \beta_{2,2} = -5.26$ ;  $\log \beta_{5,3} = -14.20$ ;  $\log \beta_{3,3} = -8.05$ ; KNO<sub>3</sub>:  $\log \beta_{2,2} = -5.14$ ;  $\log \beta_{3,3} = -8.94$ ,  $\log \beta_{15,6} = -41.06$ ,  $\log \beta_{2,1} = -8.80$ ; Mg(NO<sub>3</sub>)<sub>2</sub>:  $\log \beta_{2,2} = -5.21$ ,  $\log \beta_{5,3} = -14.24$ ,  $\log \beta_{15,6} = -43.27$ ; and (b) varying of all the constants,  $H$  and  $E_0$  (KOKS part of LETAGROP) - LiNO<sub>3</sub>:  $\log \beta_{2,2} = -5.14$ ,  $\log \beta_{5,3} = -14.23$ ,  $\log \beta_{3,3} = \text{max} = -7.73$ ; KNO<sub>3</sub>:  $\log \beta_{2,2} = -5.10$ ,  $\log \beta_{3,2} = -8.98$ ,  $\log \beta_{15,6} = -40.95$ ,  $\log \beta_{2,1} = -9.67$ ; Mg(NO<sub>3</sub>)<sub>2</sub>:  $\log \beta_{2,2} = -5.17$ ,  $\log \beta_{5,3} = -14.29$ ,  $\log \beta_{15,6} = -43.20$ .

For instance, complex (15,6) was found in K and Mg medium, while in Li medium this complex was rejected. Complex (5,3) was found in Mg and Li medium, while it was rejected in K medium. Complexes (3,2) and (2,1) found in K medium were rejected in both Mg and Li media. Since in the MESAK diagram for LiNO<sub>3</sub> (Fig. 4) the points are distributed in direction of relatively high value of  $q$  compared with  $p$ , the following complexes (5,4), (4,3), (3,3), (4,4), (6,4), (3,4), and (2,3) were tried, besides many others, but only (3,3) was accepted. Of the rejected complexes only (4,3) had a rather high value of the ratio  $\beta_{4,3}/\sigma$ , equal to 1.1. Since in our calculations "sigfak" had the value 1.5, this complex was rejected. There was some doubt about the nonexistence of the hexamer (15,6) in Li medium; therefore many other complexes of hexamer-type, were tried (Fig. 7c) but all were rejected.

Using the program HALTAFALL<sup>19</sup> (Figs. 9, 10, and 11) the (2,2) complex was found to be the main species, while all others are secondary. The data

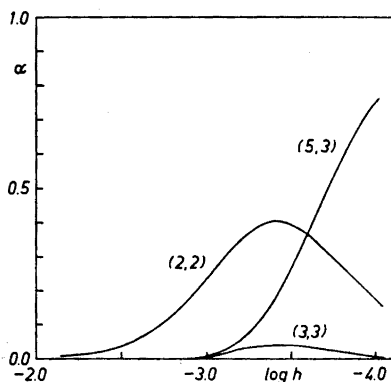


Fig. 9. Distribution of hydrolytic complexes of thorium in 3 M (Li)NO<sub>3</sub> medium, calculated by the HALTAFALL program using the "best" set complexes and their equilibrium constants given in Table 4.  $B = 40.0$  mM.

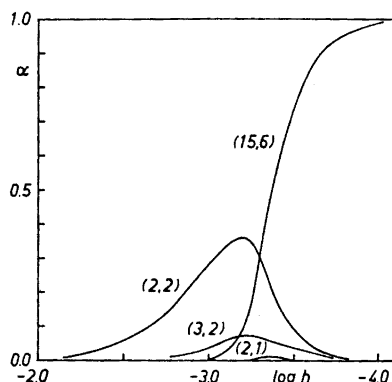


Fig. 10. Distribution of hydrolytic complexes of thorium in 3 M (K)NO<sub>3</sub> medium, calculated by the HALTAFALL program using the "best" set complexes and their equilibrium constants given in Table 4.  $B = 40.0$  mM.

obtained indicate that the medium cations have the strongest influence on the complex formation of the secondary species of thorium.

It is interesting to note the difference in composition of the secondary species in the various media. Similar results have been obtained in several other cases.<sup>2-4,20,21</sup> It is, of course, very difficult to evaluate all factors that influence the hydrolysis reaction. First of all the hydration of the ionic medium cation is different, magnesium is much more strongly hydrated than potassium, *etc.* This will have some influence on the hydration of Th<sup>4+</sup>. One should also be aware of the possibility of the formation complexes between Th and NO<sub>3</sub><sup>-</sup> which will vary somewhat from one medium to another. It is found that the hydrolysis of thorium decreases in the following order KNO<sub>3</sub> > LiNO<sub>3</sub> > Mg(NO<sub>3</sub>)<sub>2</sub> which is in agreement with the decreasing forma-

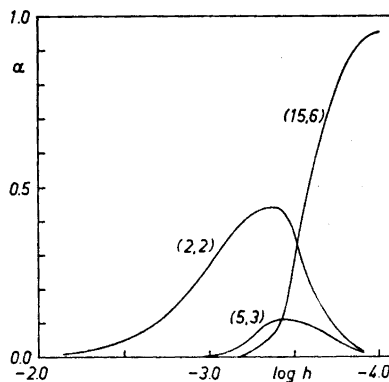


Fig. 11. Distribution of hydrolytic complexes of thorium in 3 M (Mg)NO<sub>3</sub> medium, calculated by the HALTAFALL program using the "best" set complexes and their equilibrium constants given in Table 4.  $B = 40.0$  mM.

tion of nitrate complexes of these cations.<sup>22-24</sup> This might be fortuitous. Anyway, it is clear that the medium cation is not negligible. It is also clear that we have not enough information to make even qualitative predictions as to what complexes are formed or how changes in hydration will affect the hydrolysis process. It is also difficult to judge whether some secondary species really exist or are due to other effects, *viz.* activity coefficient variations, experimental errors, *etc.*

*Acknowledgements.* I wish to express my gratitude to the late Professor Lars Gunnar Sillén for his interest and advice in connection with the present work. I should like to thank Dr. Sirkka Hietanen for her advice in the initial stage of this work, Dr. George Biedermann for helpful suggestions in connection with coulometric titrations, and Dr. Erik Högfeldt for his interest in the later stage of this work. I am greatly indebted to Dr. Björn Warnqvist for his advice concerning computer calculations, and Dr. Josef Havel and Dr. Diego Ferri for valuable discussions and their advice during computer calculations. Dr Peter Staples revised the English of the text.

This work has been supported by grants (scholarship) from the *Research Council, Boris Kidrič Institute of Nuclear Sciences, Beograd* (Yugoslavia) and in part by the *Swedish Natural Science Research Council (NFR)*.

#### REFERENCES

1. *Stability Constants*, (compilers: L. G. Sillén and A. E. Martell) *Chem. Soc. Spec. Publ.* 1964, No. 17.
2. Hietanen, S. *Acta Chem. Scand.* 8 (1954) 1626.
3. Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* 22 (1968) 265.
4. Danesi, P. R., Magini, M., Margherita, S. and D'Alessandrò, G. *Energie Nucl.* 15 (1968) 335.
5. Gran, G. *Analyst.* 77 (1952) 661.
6. Rossotti, F. J. C. and Rossotti, H. J. *Chem. Educ.* 42 (1965) 375.
7. Forsling, W., Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* 6 (1952) 901.
8. Brown, A. S. *J. Am. Chem. Soc.* 56 (1934) 646.
9. Biedermann, G. and Ciavatta, L. *Arkiv Kemi* 22 (1964) 253.
10. Biedermann, G. and Sillén, L. G. *Arkiv Kemi* 5 (1953) 425.
11. Sillén, L. G. *Acta Chem. Scand.* 15 (1961) 1981.
12. Sillén, L. G. and Warnqvist, B. *Unpublished*.
13. Dunsmore, H. S., Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* 17 (1963) 2644.
14. Ingri, N. and Sillén, L. G. *Arkiv Kemi* 23 (1965) 97.
15. Sillén, L. G. and Warnqvist, B. *Arkiv Kemi* 31 (1969) 315.
16. Sillén, L. G. and Warnqvist, B. *Arkiv Kemi* 31 (1969) 341.
17. Arnek, R., Sillén, L. G. and Wahlberg, O. *Arkiv Kemi* 31 (1969) 353.
18. Brauner, P., Sillén, L. G. and Whiteker, R. *Arkiv Kemi* 31 (1969) 365.
19. Ingri, N., Kakolowicz, W., Sillén, L. G. and Warnqvist, B. *Talanta.* 14 (1967) 1261.
20. Hietanen, S., Row, B. R. L. and Sillén, L. G. *Acta Chem. Scand.* 17 (1963) 2735.
21. Schedin, U. and Frydman, M. *Acta Chem. Scand.* 22 (1968) 115.
22. Banks, W. H., Righellato, E. C. and Davies, C. W. *Trans. Faraday Soc.* 27 (1931) 621.
23. Von Halban, H. and Eisenbrand, J. *Z. physik. Chem. (Leipzig)* 132 (1928) 401.
24. Robinson, R. A., Wilson, J. M. and Ayling, H. S. *J. Am. Chem. Soc.* 64 (1942) 1469.

Received December 7, 1970.