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Hydrolysis of the Thorium(IV) Ion in Magnesium, Calcium, Strontium and Barium Chloride Media

Terezija M. Šuranji and Nikola B. Milić*

Faculty of Science, The University, 21000 Novi Sad, and *Faculty of Science, Svetozar Marković University, 34000 Kragujevac, Yugoslavia

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The hydrolysis of the thorium(IV) ion in various concentrations of magnesium, calcium, strontium and barium chloride media was studied by the emf method at 25 °C. The data show that the extent of thorium hydrolysis decreases with increasing concentration and hydration energy of the medium ions. The contribution of the concentration of the medium ions to the total medium effect is higher than the contribution of their energy of hydration. The stability constants of the hydrolytic complexes $\text{Th}_2(\text{OH})_2^{6+}$ and $\text{Th}_2(\text{OH})_3^{5+}$ also differ slightly from one concentration of medium to another. The obtained data are in agreement with the linear free energy relationship proposed for metal ion hydrolysis.

INTRODUCTION

Studies on the hydrolysis of thorium in various ionic media¹⁻⁴ indicate the effect of the medium on the extent of hydrolysis on the composition of the hydrolytic complexes and their stability constants. In previous work^{2,3} it was observed that the medium effect depends on the concentration, c , hydration energy, E_h , and charge, z , of the ions of the medium. Correlating these parameters and the extent of hydrolysis, the medium factor, $F_{(m)}$

$$F_{(m)} = c_{(a)} E_{h(a)} z_{(a)} + c_{(c)} E_{h(c)} z_{(c)}^{-1} \quad (1)$$

and the linear free energy relationship

$$\log K_{M(w)} - \log K_{M(m)} = n F_{(m)} \quad (2)$$

have been established. In equation (1) the subscripts (c) and (a) denote cations and anions of the medium, while $K_{M(w)}$ and $K_{M(m)}$ in equation (2) denote equilibrium constants of metal-ion hydrolysis in pure water and in an ionic medium, respectively. The medium factor, $F_{(m)}$, is characteristic of the medium concerning the interactions of medium ions with water molecules, whereas constant n is determined by the reaction of the metal ions with anions of the medium. The relationship (2) gives some possibility of predicting the extent of hydrolysis and the stability constants of the predominant complexes of a given metal ion. However, it is more important that this kind of

* Author to whom correspondence should be addressed.

quantitative examination should lead to an evaluation of the contribution of each parameter of the medium to the total medium effect and consequently to a better understanding of the complicated interactions in water solutions.

In order to get some information on the particular contribution of concentration and hydration energy of divalent cations to the total medium effect, in this work hydrolysis of the thorium(IV) ion has been studied in various concentrations of magnesium, calcium, strontium and barium chloride media.

EXPERIMENTAL

Reagents and Analysis.

All chemicals were of reagent grade. In addition, thorium, magnesium, calcium, strontium and barium salts were purified by double recrystallization.

Thorium chloride stock solution was prepared from $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ by the oxalate procedure⁵. To prevent initial hydrolysis of the thorium(IV) ion in the stock solution a small amount of hydrochloric acid was added. Its free concentration was determined potentiometrically using a Gran plot⁶. The thorium content was determined by precipitation with oxalic acid and ammonia. The precipitates were ignited at 1000 °C and weighed as ThO_2 . Both methods gave the same results to within $\pm 0.11\%$.

Magnesium content in stock solution was determined by transforming magnesium chloride into sulfate⁷ and heating the residue at 700 °C, by complex formation with EDTA at pH = 10 in the presence of Eriochrome black T as indicator⁸, and by precipitation in form of crystalline⁷ MgNH_4PO_4 which was heated at 950 °C. These three methods gave the same results to within $\pm 0.20\%$.

Calcium content in stock solutions was determined by complex formation with EDTA at pH = 12–13 in the presence of Murexid as the indicator⁹, and by transforming calcium chloride into fluoride⁷ which was heated at 700 °C. Both methods gave the same results to within $\pm 0.38\%$.

Strontium stock solution was prepared from strontium nitrate, $\text{Sr}(\text{NO}_3)_2$, which was transformed to strontium oxide by heating at 820 °C. This was then dissolved in hydrochloric acid, the solution filtered (Jena glass filter G-4) and recrystallized three times. Strontium content was determined by transforming strontium chloride into sulfate⁷ at 600 °C and by precipitation as the oxalate⁷ which was dried at room temperature and weighed as the monohydrate, $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. Both methods gave the same results to within $\pm 0.18\%$.

Barium content in stock solutions was determined by precipitation in the form of sulfate¹⁰ which was heated at 900 °C and by evaporating a known volume of barium chloride at 330 °C (ref. 7). Both methods gave the same results to within $\pm 0.30\%$.

Standardization of hydrochloric acid solutions was achieved by coulometric titration and against standardized sodium hydroxide. Both methods gave the same results to within $\pm 0.23\%$.

Nitrogen gas for stirring and providing an inert atmosphere was purified by passing through 10% NaOH and 10% H_2SO_4 and saturated with water vapour by bubbling through water and the corresponding ionic medium.

Apparatus and Procedure

The emf measurements were carried out as potentiometric titrations with coulometric alkalification. During measurements the titration vessel and Wilhelm bridges (one for the potentiometric part, and the other for the coulometric part of the system) were inserted in a paraffin oil thermostat at 25.0 ± 0.2 °C. The cell was: — glass electrode/thorium solution, HCl, ionic medium/RE +, where RE = Ag, AgCl/ionic medium saturated with AgCl. For coulometric generation of OH^- ions a platinum foil was inserted into the equilibrium solution to act as the coulometric cathode, which was connected through the bridge to a silver wire anode. At the anode (separated from the equilibrium solution) Ag^+ ions were produced according to the following reaction:

while the cathode reaction was



so that OH^- ions were produced.

The coulometric method, as compared to burettes, besides being more precise, also avoids the changes in the initial volume and composition of solution.

The concentration of free H^+ ions (denoted by h) at each point is calculated by Nernst's formula

$$E = E_0 + E_j + 59.16 \log h. \quad (3)$$

In equation (3) 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. Determination of E_0 and E_j has already been described¹¹.

The emf was measured with a Beckman Digital pH meter, Model 4500. The current source for coulometric titrations was a Metrohm-Herisau coulostat, Model E-524.

RESULTS AND DISCUSSION

The emf data of the hydrolysis of 10 mM Th^{4+} in 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 M $(\text{Mg})\text{Cl}$, $(\text{Ca})\text{Cl}$, $(\text{Sr})\text{Cl}$ and $(\text{Ba})\text{Cl}$ media are represented in Figures 1—4, as a graph of the hydroxide number of thorium versus the concentration of free hydrogen ions, h . The hydroxide number of thorium, Z_{Th} , (the average number of OH^- ions bonded per thorium) was calculated from the analytical excess of hydrogen ions, H , the measured concentration of the free hydrogen ion, h , and the total concentration of the thorium(IV) ions, B , according to the expression $Z_{\text{Th}} = (h - H)/B$. The data obtained show that the hydroxide number of thorium, at a given pH, in all four media decreases with increasing

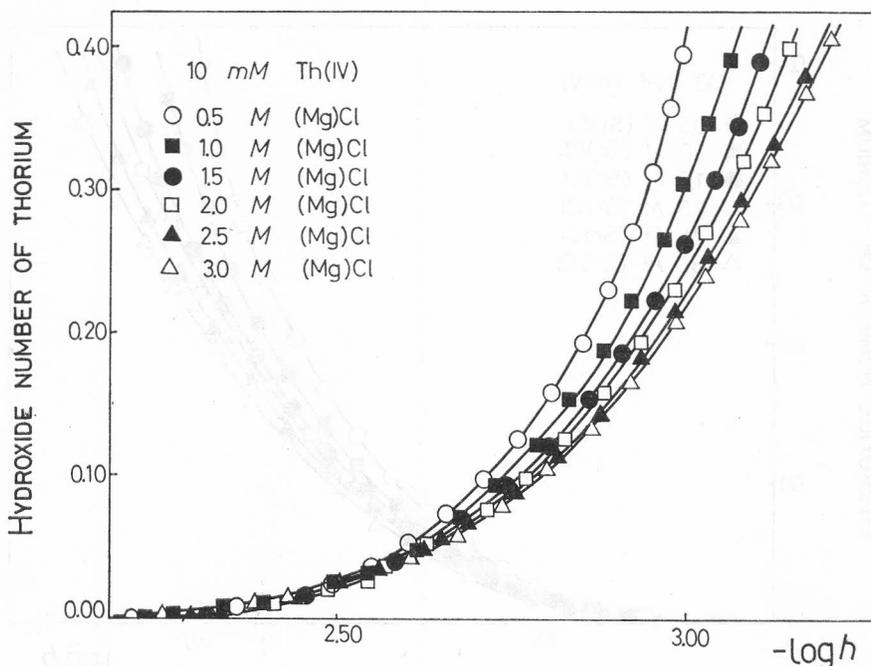


Figure 1. Hydrolysis of 10 mM Th^{4+} in various concentrations of magnesium chloride medium

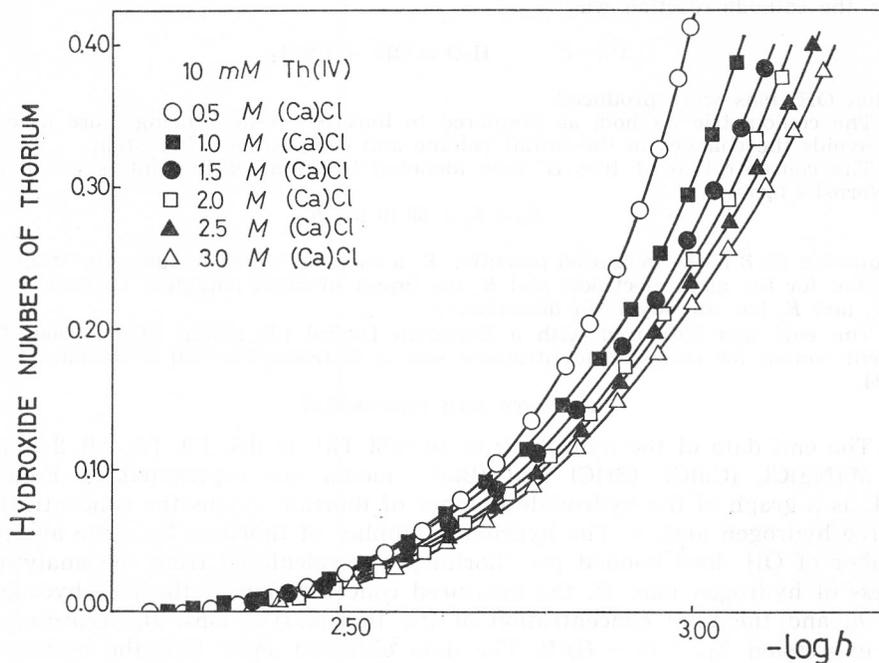


Figure 2. Hydrolysis of 10 mM Th^{4+} in various concentrations of calcium chloride medium

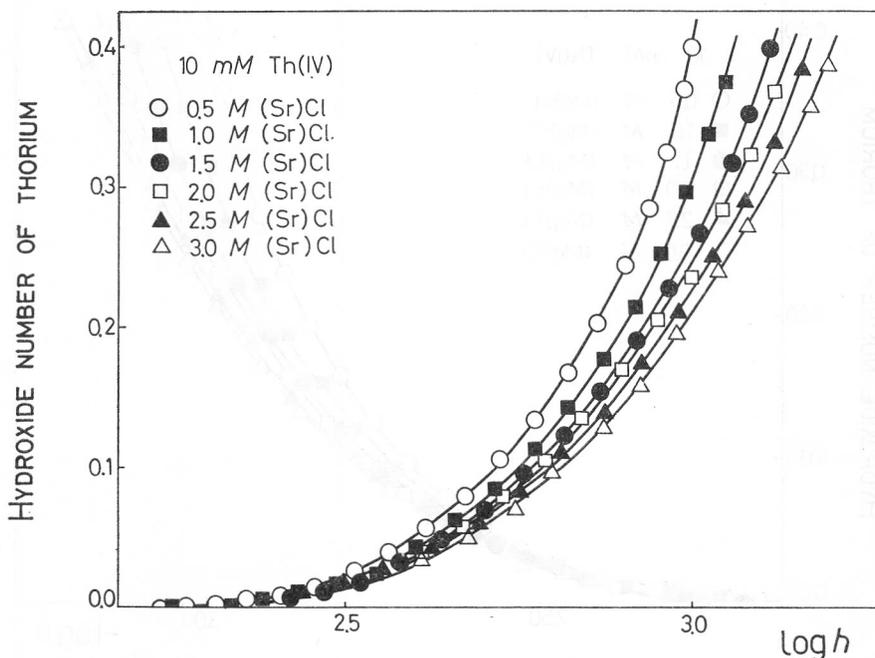


Figure 3. Hydrolysis of 10 mM Th^{4+} in various concentrations strontium chloride medium

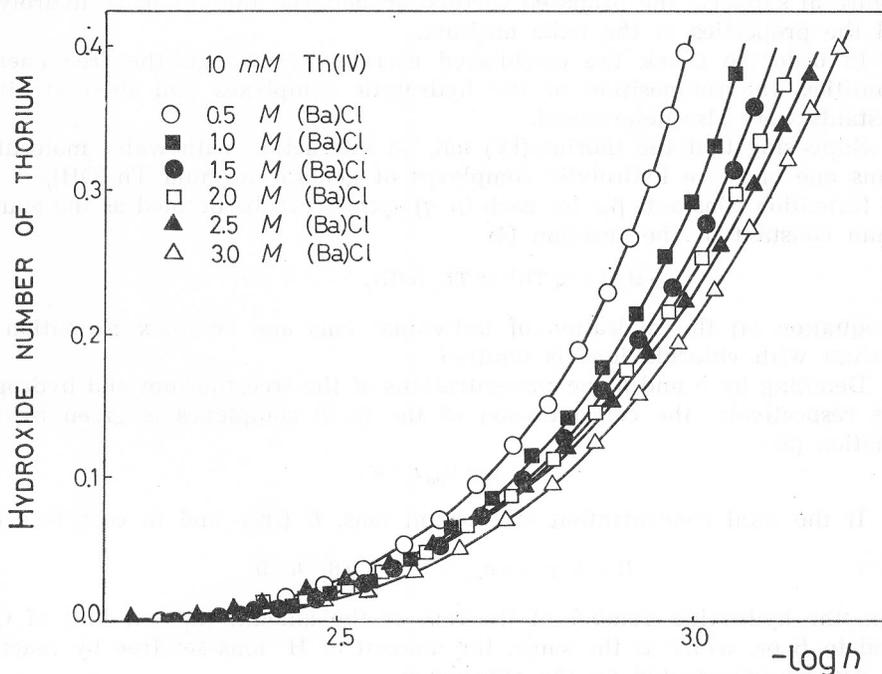


Figure 4. Hydrolysis of 10 mM Th^{4+} in various concentrations of barium chloride medium

concentration of medium ions. Representation of the values of the hydroxide number on the graph of the hydration energy of magnesium, calcium, strontium, and barium¹² indicates that the extent of hydrolysis decreases slightly with increasing the hydration energy of the cations of the medium. However, this decrease is lower than in the case of the univalent cations⁴, perhaps due to a smaller difference in their energy of hydration. Comparison of the decrease in extent of hydrolysis obtained by increasing the concentration of medium cations, or by a similar increase in their hydration energies, indicates that the concentration contributes more to the medium effect than does hydration energy. This is in agreement with the data obtained in lithium, sodium and potassium chloride media⁴.

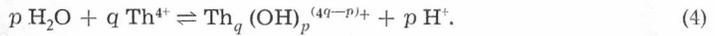
Although the hydroxide number is not exactly proportional to equilibrium constants, K , or to stability constants*, β_{pq} , (equation (7)), it can be used in a consideration of the medium effect by the linear free energy approach. Therefore, the data obtained in various concentrations of magnesium, calcium, strontium and barium chloride media are represented in Figure 5, as function $\log Z_{M(m)} = f(F_{(m)})$. The linear dependence of the hydroxide number of thorium on the medium factor indicates the possibility of predicting the extent of hydrolysis of a given metal ion in the similar ionic media. Good agreement with data obtained in lithium, sodium and potassium chloride media^{3,4}

* The hydroxide number approaches proportionality with β_{pq} , only if one species predominates or if the Z_M values are chosen in the pH range where only the main complex exists.

(Figure 5) supports the proposed correlation between the extent of hydrolysis and the properties of the ionic medium.

In order to check the established correlation through the free energy quantities, the composition of the hydrolytic complexes and their stability constants were also determined.

Supposing that the thorium(IV) ion, on interaction with water molecules, forms one or more hydrolytic complexes of general formula $\text{Th}_q(\text{OH})_p^{(4q-p)+}$ the formation constants β_{pq} for each (p, q) species can be defined as the equilibrium constant of the reaction (4)



In equation (4) the hydration of individual ions and complex formation of thorium with chloride ions is omitted.

Denoting by b and h the concentrations of the free thorium and hydrogen ions respectively, the concentration of the (p, q) complexes is given by the equation (5)

$$c_{pq} = \beta_{pq} h^{-p} b^q \quad (5)$$

If the total concentration of thorium ions, B (free and in complexes) is

$$B = b + \sum q c_{pq} = b + \sum q \beta_{pq} h^{-p} b^q \quad (6)$$

then, the hydroxide number of thorium or the amount (in mol/dm³) of OH⁻ bond to B or, which is the same, the amount of H⁺ ions set free by reaction (4), can be represented by the expression

$$Z = \sum p c_{pq} / B = (\sum p \beta_{pq} h^{-p} b^q) / (b + \sum q \beta_{pq} h^{-p} b^q) \quad (7)$$

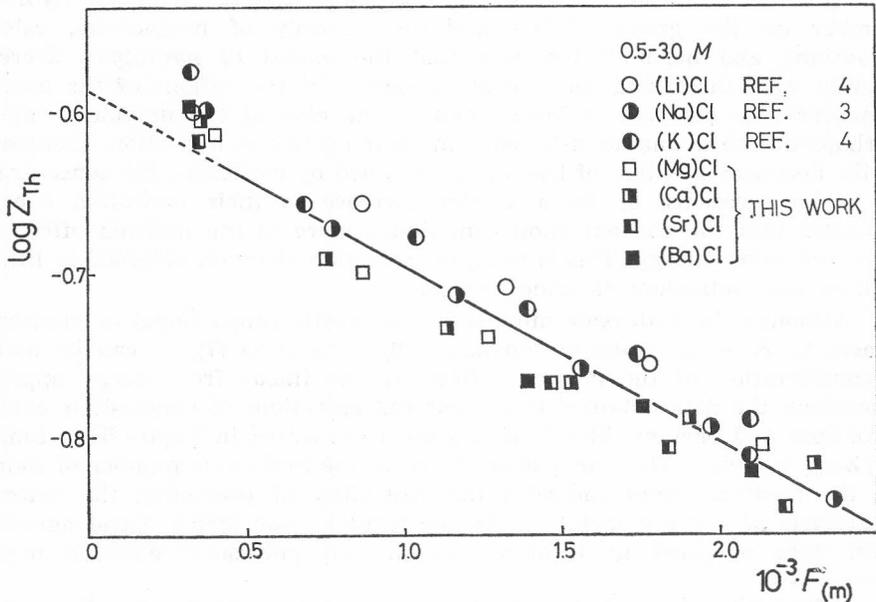


Figure 5. Dependence of the logarithmic values of the hydroxide number of thorium (obtained in various chloride media at pH = 2.9) on the medium factor

The composition of the hydrolytic complexes and their stability constants can be determined by minimization of the error square sum

$$U = \sum (Z_{\text{cal}} - Z_{\text{exp}})^2 \quad (8)$$

using the generalized least-squares program Letagrop¹³. In equation (8) Z_{cal} denotes the hydroxide number of thorium calculated from equation (7), while Z_{exp} denotes the experimental values of the hydroxide number obtained from the analytical data and measured concentration h . For various values of (p, q) of the complexes the computer searches for the set of equilibrium constants β_{pq} which will give the lowest values of the squares sum given by equation (8).

The data obtained indicate formation of the polynuclear complexes $\text{Th}_2(\text{OH})_2^{6+}$ and $\text{Th}_2(\text{OH})_3^{5+}$ with stability constants $(\log \beta_{pq} \pm 3\sigma)$ given in Table I. Formation of the same complexes in all concentrations of these four media, as well as in media of monovalent cations^{3,4}, indicates that in chloride media a pronounced effect is only observed on the values of the stability constants. Table I shows that values of the stability constant of complex (2,2) increase slightly with increasing medium factor, while values of the stability constant of complex (3,2) are changed in the opposite direction, indicating

TABLE I

Stability Constants, $\log (\beta_{pq} \pm 3\sigma)$, of the Hydrolytic Complexes of the Thorium(IV) Ion in Magnesium, Calcium, Strontium, and Barium Chloride Media and the Corresponding Values of the Medium Factor, $F_{(m)}$

Medium	$F_{(m)} \cdot 10^{-3}$	$\log (\beta_{2,2} \pm 3\sigma)$	$\log (\beta_{3,2} \pm 3\sigma)$
0.5 M (Mg)Cl	0.41	—	-7.62 ± 0.01
1.0 M (Mg)Cl	0.88	-5.12 ± 0.13	-7.91 ± 0.05
1.5 M (Mg)Cl	1.27	-5.01 ± 0.07	-8.09 ± 0.04
2.0 M (Mg)Cl	1.70	-4.93 ± 0.06	-8.29 ± 0.07
2.5 M (Mg)Cl	2.13	-4.90 ± 0.05	-8.47 ± 0.09
3.0 M (Mg)Cl	2.56	-4.90 ± 0.05	-8.56 ± 0.09
0.5 M (Ca)Cl	0.37	—	-7.59 ± 0.01
1.0 M (Ca)Cl	0.75	-4.96 ± 0.06	-7.97 ± 0.05
1.5 M (Ca)Cl	1.14	-4.95 ± 0.06	-8.13 ± 0.05
2.0 M (Ca)Cl	1.52	-4.97 ± 0.06	-8.23 ± 0.05
2.5 M (Ca)Cl	1.91	-4.92 ± 0.05	-8.37 ± 0.07
3.0 M (Ca)Cl	2.29	-4.92 ± 0.05	-8.53 ± 0.11
0.5 M (Sr)Cl	0.36	-5.53 (max -5.24)	-7.66 ± 0.03
1.0 M (Sr)Cl	0.73	-5.29 ± 0.19	-7.95 ± 0.04
1.5 M (Sr)Cl	1.10	-5.06 ± 0.10	-8.09 ± 0.05
2.0 M (Sr)Cl	1.47	-4.95 ± 0.07	-8.25 ± 0.08
2.5 M (Sr)Cl	1.84	-4.93 ± 0.05	-8.41 ± 0.06
3.0 M (Sr)Cl	2.21	-4.97 ± 0.05	-8.52 ± 0.07
0.5 M (Ba)Cl	0.34	-5.56 (max -5.21)	-7.62 ± 0.04
1.0 M (Ba)Cl	0.69	-5.12 ± 0.15	-7.92 ± 0.05
1.5 M (Ba)Cl	1.05	-5.02 ± 0.10	-8.10 ± 0.07
2.0 M (Ba)Cl	1.40	-4.91 ± 0.04	-8.29 ± 0.05
2.5 M (Ba)Cl	1.75	-4.90 ± 0.04	-8.39 ± 0.07
3.0 M (Ba)Cl	2.11	-4.96 ± 0.04	-8.50 ± 0.07

competition between these two complexes. Linear dependence of these and previous^{3,4} values of stability constants of both complexes on the medium factor confirms a correlation between the free energy changes and the medium factor (Figure 6).

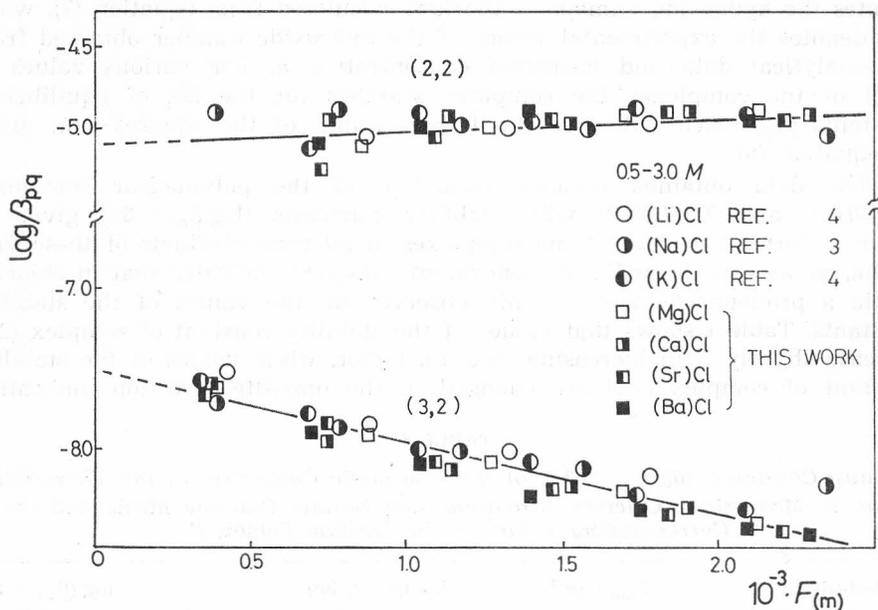


Figure 6. Dependence of the logarithmic values of the stability constants of the thorium complexes (formed in various chloride media) on the medium factor

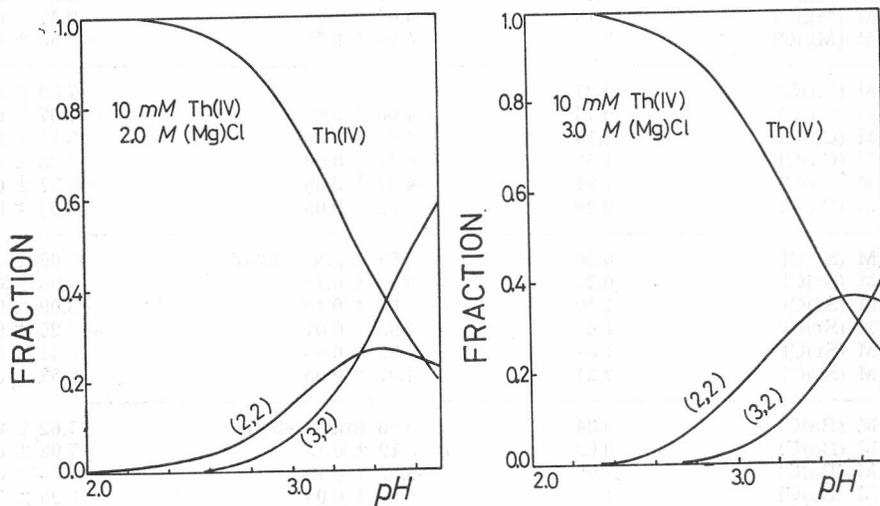


Figure 7. Distribution of the hydrolytic complexes of thorium formed in 2.0, and 3.0 M (Mg)Cl media

The fact that complex $\text{Th}_2(\text{OH})_2^{6+}$ is formed in chloride^{1,3,4}, nitrate^{1,2,14} and perchlorate² media indicates that dinuclear oxobridging structure¹⁵ is favoured. Concerning the different number of OH^- ligands ($p = 2$ and 3), one can suppose that two OH^- ions are in the bridge, while additional ligands substitute anions of the medium or water molecules present in the hydrolytic complex.

Determination of the distribution of complexes (2,2) and (3,2) using the Haltafall program¹⁶ shows that the concentration of the complex (2,2) increases with increasing medium factor, while the concentration of the complex (3,2) decreases under the same conditions. As an illustration, in Figure 7 distribution of the complexes (2,2) and (3,2) in 2.0 and 3.0 M (Mg)Cl media only is given. The distribution obtained is in agreement with changes in the water activity calculated from the osmotic coefficients of magnesium, calcium, strontium and barium chloride. Namely, at lower values of the medium factor the water activity is higher and consequently the concentration of the complex with a higher number of OH^- ligands increases. The activity coefficient of thorium is also changed in the presence of different concentrations of the studied salts. However, it is difficult to calculate these changes due to the limitation of the specific ionic interaction theory to the dilute solutions. This is valid particularly for polyvalent electrolytes, because the contribution of the parameter z^2 to the calculated values of the activity coefficient is unreliably high. In the case of thorium chloride ($z = 4$, $z = 1$) this contribution is extremely high.

REFERENCES

1. C. F. Baes and R. E. Mesmer, *The Hydrolysis of Cations*, New York, Wiley-Interscience Publ., 1976.
2. N. B. Milić, *J. Chem. Soc. Dalton Trans.* (1973) 229.
3. N. B. Milić, *J. Chem. Soc. Dalton Trans.* (1981) 1445.
4. T. M. Šuranji and N. B. Milić, *Bull. Soc. Chim. Beograd* **46** (1981) 657.
5. F. P. Treadwell, *Kvalitativna hemijska analiza*, Beograd, Naučna knjiga, 1949, p. 450.
6. G. Gran, *Analyst* **77** (1952) 661.
7. L. Erdey, *Gravimetric Analysis*, Oxford, Pergamon Press, 1965.
8. I. Sajó, *Kompleksometrija*, Budimpešta, Műszaki kiadó, 1973, p. 213.
9. R. Prshibil, *Kompleksony v himicheskom analize*, Moskva, Izd. inostr. lit. 1960, p. 338.
10. A. H. Heyn and E. Schupak, *Anal. Chem.* **26** (1954) 1243.
11. N. B. Milić, Ž. D. Bugarčić, and M. V. Vasić, *Bull. Soc. Chim. Beograd* **45** (1980) 349.
12. D. W. Smith, *J. Chem. Ed.* **54** (1977) 541.
13. P. Brauner, L. G. Sillén, and R. Whiteker, *Arkiv Kemi* **31** (1968) 365.
14. N. B. Milić and T. M. Šuranji, *Canad. J. Chem.* (in press).
15. G. Johansson, *Acta Chem. Scand.* **22** (1968) 389.
16. N. Ingri, W. Kakolowicz, L. G. Sillén, and B. Warnqvist, *Talanta* **14** (1967) 1261.

SAŽETAK**Hidroliza torijum(IV)-jona u magnezijum, kalcijum, stroncijum i barijum hloridnim sredinama**

Terezija M. Šuranji i Nikola B. Milić

Izučavana je hidroliza torijum(IV)-jona u različitim koncentracijama magnezijum, kalcijum, stroncijum i barijum hloridnih sredina metodom potenciometrijsko-kolumetrijskih titracija na 25 °C. Dobijeni rezultati pokazuju da obim hidrolize torijuma opada sa porastom koncentracije jonske sredine, kao i sa porastom energije hidratacije katjona hloridne sredine. Pri tome je doprinos koncentracije ukupnom efektu sredine znatno veći od doprinosa energije hidratacije njenih katjona. Vrednosti konstanti kompleksa $\text{Th}_2(\text{OH})_2^{6+}$ i $\text{Th}_2(\text{OH})_3^{5+}$, takođe, se razlikuju idući od jedne sredine ka drugoj. Razmatranje rezultata efekta sredine pristupom linearnih promena slobodne energije ukazuje na njihovu dobru saglasnost sa pravilom ustanovljenim za reakcije hidrolize jona metala.