Linear Free-energy Relationships in the Hydrolysis of Metal Ions. The Effect of the Ionic Medium

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The effect of a lithium, sodium, and potassium chloride medium on the hydrolysis of thorium(IV) has been studied by a potentiometric and calorimetric method. The data obtained show that the extent of hydrolysis of thorium, the stability constants of its hydrolytic complexes, and the associated thermodynamic parameters are affected by the ionic medium. Correlations between the free energies of the hydrolytic processes and the properties of the medium are considered by the linear free-energy approach. The uranyl and nickel hydrolysis data imply generality of the proposed relationship.

In previous work,[1,2] the effect of the ionic medium on the hydrolysis of thorium(IV) ions was observed. For its consideration the relationship (1) was suggested,[2] where $K_{M(w)}$ and $K_{M(m)}$ denote equilibrium constants of the metal-ion hydrolysis in pure water and in an ionic medium respectively. The empirical constant, $F_{(m)}$, the medium factor, is characteristic of the medium, concerning interactions of its ions with water molecules, whereas n is determined by reaction of the metal ions with anions of the medium. An improved expression for the medium factor, (2), has been established, correlating the extent of hydrolysis with the properties of the medium (the hydration energy, E_h, concentration, c, and charge, z, of the ions). Expression (2) is thermodynamically more correct than equation (1) and gives a better correlation between the extent of hydrolysis and the properties of 1 : 1, 2 : 1, and 1 : 2 electrolyte media.[3] The subscripts (c) and (a) denote cations and anions of the medium respectively. (Experiments which should yield information on parameters of constant n are underway, therefore, in this work constant n will not be considered.)

$$\log K_{M(w)} - \log K_{M(m)} = n\,F_{(m)} \qquad (1)$$

$$F_{(m)} = c_{(a)}E_{h(a)}z_{(a)} + c_{(c)}E_{h(c)}z_{(c)}^{-1} \qquad (2)$$

Equation (1) is similar to the linear free-energy relationship originally suggested by Hammett.[4] Therefore, in this work, the effect of the ionic medium is considered by a linear free-energy approach. Assuming that the free-energy changes of the metal-ion hydrolysis in various media are linear, one can obtain the parameters of the medium which should give a linear dependence of the free-energy quantities on the medium factor. The advantage of this approach is that neither deviation of some data from linearity [due to non-completeness of expression (2)] nor difficulties in separation of the parameters which determine complex formation of the metal ions with anions of the medium rather than OH^- ions should affect the result.

Since it is difficult to obtain reliable values for the equilibrium constants of the hydrolytic reaction, due to the effect of the medium, stability constants for the particular complexes, β_{pq}, or the experimental values of the hydroxide number could be used. The hydroxide number (the average number of OH^- ions bonded per metal ion) is a function of the total concentration of metal ions and pH, therefore, considering the effect of the medium, the hydroxide number of a specific concentration of metal ions, at specific pH, and at constant temperature should be used.

If the hydrolytic processes follow the linear free-energy changes and if the medium factor includes the most important parameters of the ionic medium, the representation of the hydroxide numbers ($Z_{M(m)}$) of a specific concentration of metal ions and at a specific pH as a function, (3), should lead to a straight line. This linearity supports a correlation between the extent of metal-ion hydrolysis and the medium factor, while its absence would indicate that $F_{(m)}$ does not include some important parameters of the medium (for instance, dielectric constant), or that c, E_h, and z are not expressed correctly in (2).

$$\log Z_{M(m)} = f[F_{(m)}] \qquad (3)$$

In order to check the validity of equation (1) for the chloride media, as well as to correlate the energy changes of the system with the medium factor, hydrolysis of thorium(IV) ions in various chloride media [3.0 mol dm^{-3} (Li)Cl, 3.0 mol dm^{-3} (K)Cl, 0.5—3.0 mol dm^{-3} (Na)Cl] has been studied by potentiometric and calorimetric methods.†

EXPERIMENTAL

Reagents and Analysis.—All chemicals were of reagent grade. In addition, thorium, lithium, sodium, and potassium salts were purified by double recrystallization, while hydrochloric acid and sodium hydroxide were used without further purification.

Thorium chloride stock solution was prepared from thorium nitrate by double precipitation of thorium with ammonium hydroxide and dissolving the precipitate in hydrochloric acid. The solution was evaporated and the solid heated for several hours at 500 °C and dissolved in hydrochloric acid. The thorium content was determined

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† Designation of the medium is in accordance with ref. 5.

by precipitation with ammonia and oxalic acid. Both precipitates were converted into ThO_2 (at 1 000 °C) and gave the same results within $\pm 0.2\%$. The concentration of the initial acid was determined potentiometrically by coulometric alkalification of the solution. The equivalence point was determined by a Gran plot.[6]

Sodium, potassium, and lithium stock solutions were prepared by dissolution of the corresponding salts. Their concentrations were determined by evaporating a known volume at 350 °C.

Hydrochloric acid solution was standardized by coulometric titration and against standardized sodium hydroxide. Both methods gave the same results within $\pm 0.2\%$.

Nitrogen gas for stirring and providing an inert atmosphere was purified in the course of titration.[1]

Apparatus and Procedure.—The e.m.f. measurements were carried out as potentiometric forward titrations using coulometric alkalification of the solutions. After reaching a certain value of the hydroxide number of thorium, the equilibrium solutions were transferred into the calorimetric vessel, where calorimetric measurements were carried out as back titrations with a standardized solution of hydrochloric acid.

To follow the change in the heat of dehydrolysis of thorium in various media under the same conditions, all potentiometric titrations were carried out with the same total concentration of thorium (10 mmol dm^{-3}), and up to the same concentration as the free hydrogen ions ($-\log h = 3.00$). Using the more precise coulometric method, instead of burettes, the changes in initial volume and composition of solution due to replacement of H^+ with Na^+, K^+, and Li^+ were avoided.

During the e.m.f. measurements the Wilhelm bridge and titration vessel were inserted in a paraffin oil thermostat at 25.00 ± 0.05 °C, which was placed in a room thermostatted to 25.0 ± 0.5 °C.

The cell was : glass electrode/thorium solution, HCl, ionic medium/Ag, AgCl/ionic medium saturated with AgCl. During the titrations a platinum mesh was inserted in the equilibrium solution as the coulometric cathode and the connecting tube to another Wilhelm bridge with ionic medium and a silver foil electrode as anode.

The concentration of free H^+ (denoted by h) at each point is calculated by Nernst's formula, (4), where E is the

$$E = E_0 + E_j + 59.16 \log h \qquad (4)$$

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 described.[1]

The e.m.f. was measured with a digital voltmeter, type DM-2022 S, Dynamco Ltd. The current source for coulometric titrations was a Metrohm–Herisau coulometer E-211. The calorimetric measurements were carried out in a LKB reaction calorimeter of the constant-temperature environment type, equipped with a thermostatted burette and a cooling device.

RESULTS AND DISCUSSION

Potentiometric Measurements.—The e.m.f. data for the hydrolysis of thorium(IV) ions obtained in various chloride media are presented in Figures 1 and 2, as $Z_{Th} = f(-\log h)$. The hydroxide number of thorium, Z_{Th}, was calculated from the analytical excess of hydrogen ions,* H, the measured concentration of the free hydrogen ions, h, and the total concentration of thorium(IV) ions, B, according to the expression: $Z_{Th} = (h - H)/B$. Figures 1 and 2 show that the hydroxide number of thorium, at the same equilibrium concentration of the hydrogen ions, has different values both at the same concentration of the various chloride media [3.0 mol dm^{-3} (K)Cl, 3.0 mol dm^{-3} (Na)Cl, 3.0 mol dm^{-3} (Li)Cl] and at various concentrations of the same medium [0.5—3.0 mol dm^{-3} (Na)Cl].

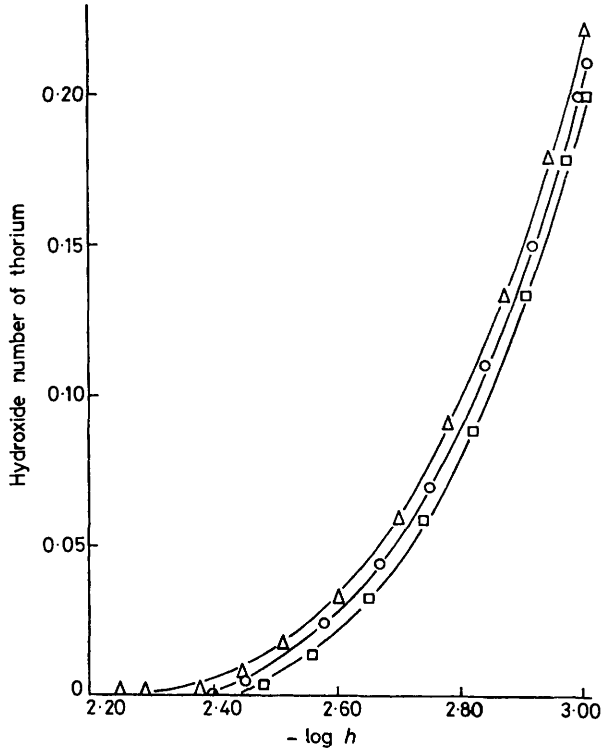

FIGURE 1 Hydrolysis of 10 mmol dm^{-3} thorium(IV) in various chloride media: (K)Cl (△); (Na)Cl (○); (Li)Cl (□), all 3 mol dm^{-3}. Points are experimental data, while the full curves have been calculated by the set constants given in Table 1

The representation of the data in the form of the function given by equation (3) for a specific pH shows that the hydroxide number of thorium decreases linearly with increasing medium factor, irrespective of whether its values are a result of different hydration energies of the cations or different concentrations of the medium (Figure 3). A similar dependence was obtained in nitrate media.[2] The extrapolation of the straight lines, one for nitrate [2] and the other for a chloride medium, gives the same values for $\log Z_{M(m)}$ at zero value of the medium factor, *i.e.* for pure water, $\log Z_{M(w)}$. This observation should be checked with additional experiments, since it implies a negligible effect of the anions of thorium salts on their hydrolysis in pure water.

Since the experimental values for the hydroxide

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* In the course of the titration, H decreases and become negative in hydrolyzed solution.

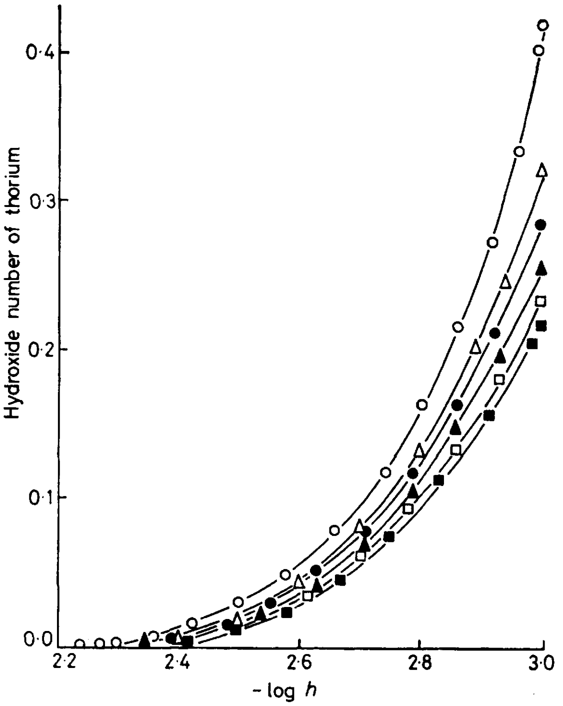

FIGURE 2 Hydrolysis of 10 mmol dm^{-3} thorium(IV) in various concentrations of sodium chloride medium: 0.5 (○); 1.0 (△); 1.5 (●); 2.0 (▲); 2.5 (□); 3.0 mol dm^{-3} (■). Points are experimental data, while curves have been calculated by the set constants given in Table 1

number of thorium, as primary data, indicated the effect of the medium, it was interesting to see whether the medium influenced the composition of the hydrolytic complexes and their stability constants.

Supposing that the thorium(IV) ion, on interaction with water molecules, forms one or more hydrolytic complexes of general formula $[Th_q(OH)_p]^{(4q-p)+}$, formation constants β_{pq} for each species (p,q) can be defined as the equilibrium constant of reaction (5). In equation (5) the hydration of the individual ions and complex formation of thorium with chloride ions is omitted. The

$$p\, H_2O + q\, Th^{4+} \rightleftharpoons [Th_q(OH)_p]^{(4q-p)+} + p\, H^+ \quad (5)$$

latter case is justified by maintaining a constant concentration of chloride ions in the course of the titration.

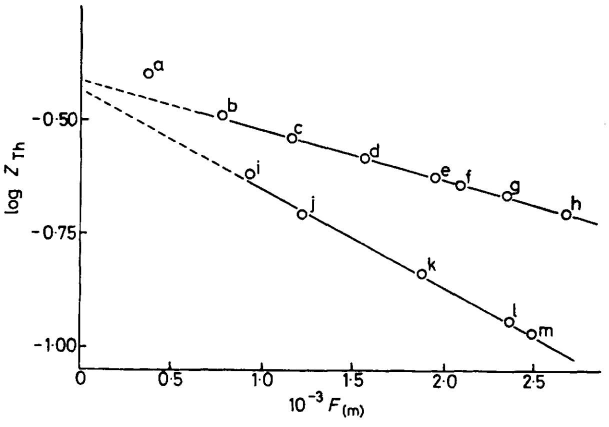

FIGURE 3 Dependence of the hydroxide number of 10 mmol dm^{-3} thorium(IV) (at pH 3) on the medium factor. Points a—h from this work, i—m from ref. 2. Points a—e and g in (Na)Cl; 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 mol dm^{-3} respectively. Point f: 3.0 mol dm^{-3} (K)Cl; point h: 3.0 mol dm^{-3} (Li)Cl. Points i and k in (K)NO$_3$, 1.5 and 3.0 mol dm^{-3} respectively. Points j and m in (Li)NO$_3$, 1.5 and 3.0 mol dm^{-3} respectively. Point l in (Mg)NO$_3$, 3.0 mol dm^{-3}

The composition of the complexes and their stability constants have been determined by minimization of the error square sum $U = \Sigma(Z_{calc.} - Z_{exp.})^2$ using the generalized least-squares program Letagrop[7] and the procedure described in previous work.[1]

Table 1 gives the set of accepted complexes which gave the 'lowest' minimum in U, together with their β_{pq} values and standard deviations, as log $(\beta \pm 3\sigma)$.

TABLE 1

Stability constants, log $(\beta_{pq} \pm 3\sigma)$, of the hydrolytic complexes of thorium in various chloride media and the corresponding values of the medium factor, $F_{(m)}$

Medium[a]	$10^{-3}F_{(m)}$[b]	log $(\beta_{2,2} \pm 3\sigma)$	log $(\beta_{3,2} \pm 3\sigma)$
3.0 (Li)Cl	2.68	−5.23 ± 0.15	−8.28 ± 0.12
3.0 (Na)Cl	2.35	−5.08 ± 0.20	−8.23 ± 0.18
3.0 (K)Cl	2.09	−5.04 ± 0.11	−8.16 ± 0.17
2.5 (Na)Cl	1.96	−5.06 ± 0.12	−8.12 ± 0.15
2.0 (Na)Cl	1.56	−5.02 ± 0.16	−8.11 ± 0.12
1.5 (Na)Cl	1.17	−4.95 ± 0.15	−8.01 ± 0.10
1.0 (Na)Cl	0.77	−4.88 ± 0.03	−7.93 ± 0.13
0.5 (Na)Cl	0.38	−4.90 ± 0.16	−7.72 ± 0.05

[a] Values are concentrations of solutions in mol dm^{-3}. [b] $F_{(m)}$ is calculated according to equation (2); c in mol dm^{-3}, E_h in kJ mol^{-1} (D. W. Smith, *J. Chem. Educ.*, 1977, **54**, 541), z an integer.

The results indicate the existence of complexes $[Th_2(OH)_2]^{6+}$ and $[Th_2(OH)_3]^{5+}$ in all media, but with different values of stability constant. Since the same complexes are found in various concentrations of potassium, lithium, magnesium, calcium, strontium, and barium chloride media,[3] it seems that the nature and concentration of the chloride media influence only the stability constants of the hydrolytic complexes. However, in sodium, lithium, potassium, and magnesium nitrate media,[1,3] besides the complex $[Th_2(OH)_2]^{6+}$, complexes $[Th_3(OH)_5]^{7+}$ and $[Th_6(OH)_{15}]^{9+}$ are also found indicating the anion effect of the medium on the composition of hydrolytic complexes. This effect is more pronounced due to the different complex formation of thorium with chloride and nitrate ions, as competitive ions to OH$^-$ ions. This is supported by the different slopes of the curves obtained for chloride and nitrate media (Figure 3).

Graphical representation of the values of stability constants of the obtained complexes (Table 1) in the form of function (3) gives a linear dependence on the medium factor indicating correlation between the free-energy quantities and properties of the ionic medium.

The linear dependence of the free-energy quantities of the uranyl[3] and nickel[8] ion hydrolysis on the medium factor implies generality of relationship (1). Successful application of relationship (1) to the literature data concerning complex formation of lead with chloride ion, iron with cyanide ion, and dissociation of acetic acid and water in various media[3] indicates the possibility of using the medium factor for consideration of the effect of the medium on other reactions in aqueous solution.

Calorimetric Measurements.—The calorimetric data, presented as the dependence of the heat of hydrolysis on the hydroxide number of thorium (Figures 4 and 5), show that the measured heat for the same changes in Z (for instance $\Delta Z = 0.2 - 0.1$) decreases with increasing concentration of the medium or the hydration energy of the cations of the medium. From these data, the changes in the heat for constant differences of the hydroxide number of thorium, $\Delta Q(\Delta Z$ constant), or the relative hydrolysis enthalpy, ΔH_r, were calculated and represented as the function $\Delta H_r = f[F_{(m)}]$ (Figure 6). The linearity obtained is in good agreement with the above consideration, indicating that the medium factor represents the properties of the ionic medium satisfactorily.

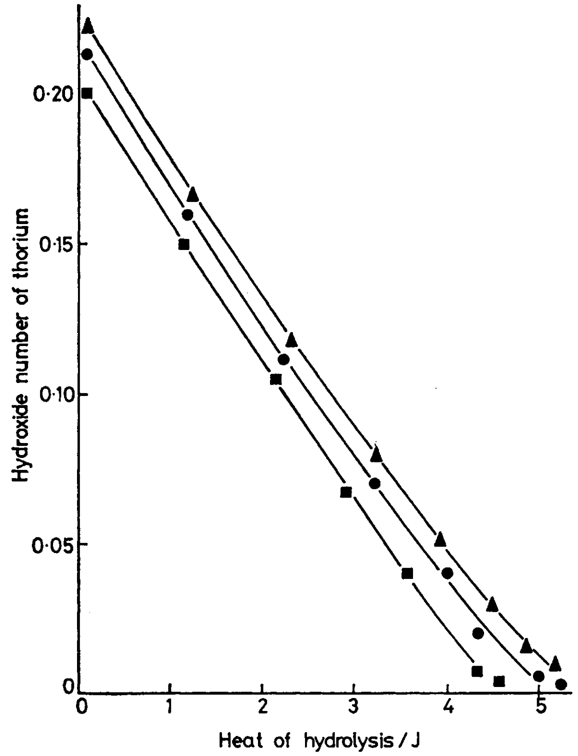

FIGURE 4 Dependence of the heat of hydrolysis of 10 mmol dm^{-3} thorium(IV) on its hydroxide number obtained in various chloride media: (K)Cl (▲); (Na)Cl(●); (Li)Cl(■), all 3 mol dm^{-3}

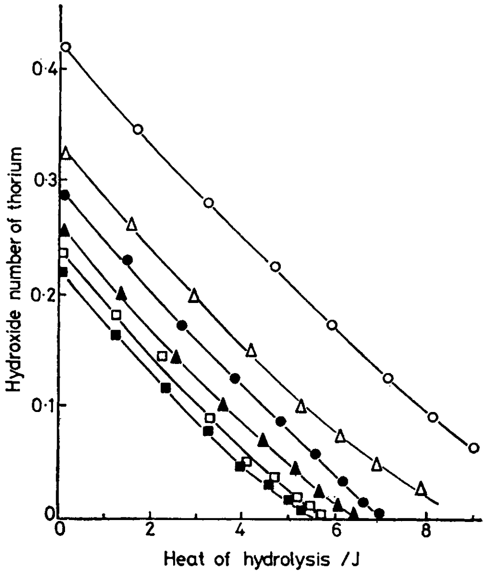

FIGURE 5 Dependence of the heat of hydrolysis of 10 mmol dm^{-3} thorium(IV) on its hydroxide number obtained in various concentrations of sodium chloride medium: 0.5 (○); 1.0 (△); 1.5 (●); 2.0 (▲); 2.5 (□); 3.0 mol dm^{-3} (■)

In order to obtain more information on the effect of the ionic medium on the hydrolytic processes of thorium it is useful to split up the free-energy change, (6), into the

$$\Delta G_{pq(m)} = -RT \ln \beta_{pq(m)} \qquad (6)$$

enthalpy change $\Delta H_{pq(m)}$ and the entropy change $\Delta S_{pq(m)}$ according to relation (7). The enthalpy change $\Delta H_{pq(m)}$

$$\Delta G_{pq(m)} = \Delta H_{pq(m)} - T\Delta S_{pq(m)} \qquad (7)$$

of reaction (5), as the relative molar enthalpy of the complex $[\mathrm{Th}_q(\mathrm{OH})_p]^{(4q-p)+}$ using the calorimeter version of the Letagrop program,[9] has been calculated. The $\Delta H_{pq(m)}$ values are given in Table 2. From these data and the corresponding stability constants, $\beta_{pq(m)}$, the free-energy [equation (6)] and the entropy [equation (7)] changes are calculated and are also given in Table 2. The data show that the thermodynamic parameters are also affected by the ionic medium. At low values of the medium factor, enthalpies of (2,2) and (3,2) complexes are similar and comparable with the value of $\Delta H_{(2,2)}$ (61.9 kJ mol^{-1}) obtained in 1 mol dm^{-3} (Na)ClO$_4$ medium,[10] while the large differences in enthalpies of these complexes, at high values of $F_{(m)}$, might be a consequence of some structural changes caused by the presence of a high concentration of the medium ions. The entropy data also indicate that the system proceeds from a state of lesser to a state of greater randomness. At low values of the medium factor, entropies of (2,2) and (3,2) com-

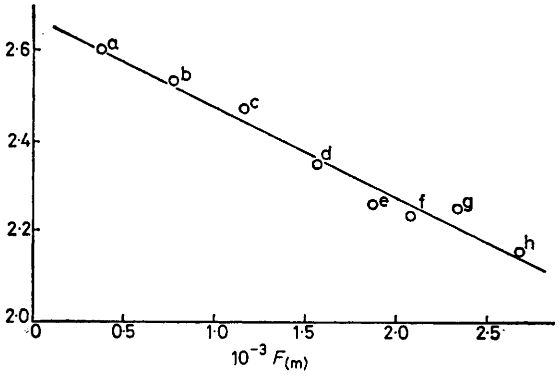

FIGURE 6 Dependence of the relative hydrolysis enthalpy of thorium(IV) on the medium factor. Points a—e and g in (Na)Cl; 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 mol dm^{-3}. Point f in (K)Cl, 3.0 mol dm^{-3}; point h in (Li)Cl, 3.0 mol dm^{-3}

plexes are comparable, indicating a similar degree of randomness, while at high values of $F_{(m)}$, the large differences in entropies of these complexes indicate different abilities of the complexes to orient water molecules beyond the innermost layer. Concerning the direction of changes of thermodynamic quantities, Table 2 shows that the values of $\Delta G_{(2,2)(m)}$, $\Delta H_{(2,2)(m)}$, and $\Delta S_{(2,2)(m)}$ increase linearly with increasing medium factor, while the values of $\Delta H_{(3,2)(m)}$ and $\Delta S_{(3,2)(m)}$ are changed (linearly) in the opposite direction. As both complexes are formed in the same media, the change of the enthalpy in the opposite direction might indicate competition between these two complexes. Calculation of the concentration and distribution of these complexes by the Haltafall program [11] is in agreement with this supposition. Thus, the data show 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. This is also in agreement with changes in the water activity. Namely, at lower values of the medium factor, the activity of water is higher, and thorium is more likely to interact with water molecules. The result of these interactions might be either a higher concentration of a certain hydrolytic species or formation of a complex with a higher number of OH^- ions per thorium ion. It seems that in the case of formation of two complexes the effect of the ionic medium is reflected through the competition between complexes, while in the case of a single complex the effect is reflected only through changes in its concentration.

TABLE 2

Thermodynamic parameters $\Delta G_{pq(m)}$, $\Delta H_{pq(m)}$, and $\Delta S_{pq(m)}$ for the hydrolytic reactions of thorium(IV) ions in various chloride media

Medium *	$\Delta G_{(2,2)(m)}$ /kJ mol^{-1}	$\Delta H_{(2,2)(m)}$ /kJ mol^{-1}	$\Delta S_{(2,2)(m)}$ /J K^{-1} mol^{-1}	$\Delta G_{(3,2)(m)}$ /kJ mol^{-1}	$\Delta H_{(3,2)(m)}$ /kJ mol^{-1}	$\Delta S_{(3,2)(m)}$ /J K^{-1} mol^{-1}
3.0 (Li)Cl	29.8	133.6	348.3	47.2	23.1	−80.9
3.0 (Na)Cl	28.9	119.0	302.3	46.9	21.2	−86.2
3.0 (K)Cl	28.7	101.9	245.6	46.5	38.1	−28.2
2.5 (Na)Cl	28.8	110.3	273.5	46.3	33.3	−43.6
2.0 (Na)Cl	28.6	109.8	272.5	46.2	45.3	−3.0
1.5 (Na)Cl	28.2	98.3	235.2	45.7	60.1	48.3
1.0 (Na)Cl	27.8	87.0	198.7	45.2	76.8	106.0
0.5 (Na)Cl	27.9	86.7	197.3	44.4	90.7	155.4

* Values are concentrations in mol dm^{-3}.

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