Effect of the Ionic Medium on the Hydrolysis of Metal Ions: An Empirical Relation

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The effects of various ionic media on the hydrolysis of thorium(IV) ions is reflected in changes in the hydroxyl number. From a consideration of these effects, an empirical relation is established which shows the dependence of the hydroxyl number of a metal ion on the charges, concentrations, and energies of hydration of ions of the medium.

In a number of studies[1,2] on the hydrolysis of metal ions activity coefficients have been kept constant by using constant ionic strength or constant high concentration of the salt of the ionic medium. It was expected that the presence of the ions of the medium would not influence the hydrolysis of the metal ions. However, when the hydrolysis of uranium(VI),[3] thorium(IV),[4,5] and nickel(II)[6] ions was studied in various media, under the same conditions, different hydrolytic complexes were found (Tables 1 and 2) indicating that the influence of the ionic medium on hydrolysis is not negligible.

TABLE 1

Hydrolytic complexes of uranium(VI), $(UO_2)_q(OH)_p^{(2q-p)+}$, and their stability constants, log β_{pq}, in various media

Complex \ Medium	3M-(Na)Cl [a]	3M-(Mg)ClO$_4$ [b]	3M-(Ca)ClO$_4$ [b]	3M-(Na)ClO$_4$ [b]	3M-(K)NO$_3$ [b]	3M-(Mg)NO$_3$ [c]	5M-(Mg)NO$_3$ [c]
$(UO_2)_2(OH)^{3+}$		−3·81	−3·96		−4·1		
$(UO_2)_2(OH)_2^{2+}$	−6·64	−6·25	−6·20	−6·04	−5·96	−6·34	−6·52
$(UO_2)_3(OH)_4^{2+}$	−12·54	*ca.* −13·3	*ca.* −13·4	*ca.* −13·2	*ca.* −12·8		
$(UO_2)_3(OH)_5^{+}$	−18·57	−17·18	−16·91	−16·53	−16·21	−17·37	−17·76
$(UO_2)_4(OH)_6^{2+}$	−19·96	*ca.* −20·2				*ca.* −19·7	
$(UO_2)(OH)^{+}$				*ca.* −6·1		*ca.* −5·4	−5·53
$(UO_2)_4(OH)_7^{+}$	−24·9						

[a] Ref. 3*a*. [b] Refs. 3*b* and 3*c*. [c] Ref. 3*d*.

TABLE 2

Hydrolytic complexes of thorium(IV), $Th_q(OH)_p^{(4q-p)+}$, and their stability constants, log β_{pq}, in various media

Complex \ Medium	3M-(Li)NO$_3$ [a]	3M-(K)NO$_3$ [a]	3M-(Mg)NO$_3$ [a]	4M-(Na)NO$_3$ [b]	4M-(Na)ClO$_4$ [b]
$Th(OH)_2^{2+}$		*ca.* −9·67			
$Th_2(OH)^{7+}$					−2·72
$Th_2(OH)_2^{6+}$	−5·26	−5·10	−5·17	−5·5	
$Th_2(OH)_3^{5+}$		−8·98			
$Th_2(OH)_4^{4+}$					−10·49
$Th_3(OH)_3^{9+}$	*ca.* −8·0				
$Th_3(OH)_5^{7+}$	−14·20		−14·29		−12·42
$Th_3(OH)_6^{6+}$				−17·92	
$Th_4(OH)_8^{8+}$					−19·2
$Th_4(OH)_{12}^{4+}$				−37·2	
$Th_6(OH)_{14}^{10+}$					−36·2
$Th_6(OH)_{15}^{9+}$		−40·95	−43·20		

[a] Ref. 5. Ref. 4.

The changes observed in the composition of hydrolytic complexes of metal ions, going from one medium to another, could arise from a weakness in the method of determination used. Thus in computer analysis of hydrolytic processes some species sometimes occur only as the result of the 'best' fit of calculated and experimental data. In order to obtain more reliable information about the influence of the ionic medium on hydrolysis of metal ions, prior to confirmation of the different complexes formed, it was decided to compare only experimental values of the hydroxyl number of thorium(IV) ions in various media, under the same conditions. If the ionic medium were to influence the hydrolysis of thorium(IV), the value of its hydroxyl number should differ from one medium to another. Data used for comparison are from this and previous work.[5]

EXPERIMENTAL

The reagents, analytical methods, apparatus, and procedure have been described previously.[5]

RESULTS AND DISCUSSION

Data obtained for the hydrolysis of thorium(IV) ions in 1·5M-(K/Li)NO$_3$ media are given, together with those

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[1] 'Stability Constants of Metal-ion Complexes,' *Chem. Soc. Special Publ.*, No. 17, 1964; No. 25, 1971.

[2] L. G. Sillén, 'Proceedings of The Robert A. Welch Foundation Conferences on Chemical Research,' Houston, November 26—28, 1962, p. 187.

[3] (*a*) H. S. Dunsmore and L. G. Sillén, *Acta Chem. Scand.*, 1963, **17**, 2657; (*b*) H. S. Dunsmore, S. Hietanen, and L. G. Sillén, *ibid.*, p. 2644; (*c*) S. Hietanen, B. R. L. Row, and L. G. Sillén, *ibid.*, p. 2735; (*d*) U. Schedin and M. Frydman, *ibid.*, 1968, **22**, 115.

[4] P. R. Danesi, M. Magini, S. Margherita, and G. D'Alessandro, *Energia nucleare*, 1968, **15**, 335.

[5] N. B. Milić, *Acta Chem. Scand.*, 1971, **25**, 2487.

[6] K. A. Burkov, Ph.D. Thesis, University of Leningrad, 1966.

from previous work,[5] in Figure 1. The dependence of the hydroxyl number of thorium(IV) (Z_{Th}) on the hydrogen-ion concentration (pH) in various nitrate media (Figure 1) shows that the extent of hydrolysis of thorium(IV) ions in the media studied (*a*) decreases in the order 1·5M-KNO_3 $>$ 1·5M-$LiNO_3$ $>$ 3M-KNO_3 $>$ 1·5M-$Mg(NO_3)_2$ $>$ 3M-$LiNO_3$, (*b*) in the same medium, decreases with increasing concentration of the medium (1·5M-KNO_3 $>$ 3M-KNO_3,1·5M-$LiNO_3$ $>$ 3M-$LiNO_3$), and (*c*) at the same concentration of various media, decreases with increasing hydration energy of the cations of the medium [1·5M-KNO_3 $>$ 1·5M-$LiNO_3$ $>$ 1·5M-$Mg(NO_3)_2$].

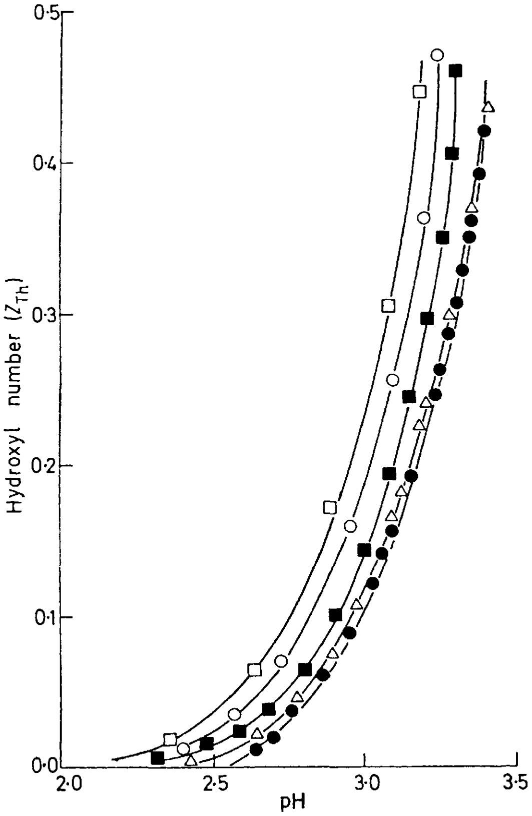

FIGURE 1 Hydrolysis of thorium(IV) (10 mM) in various nitrate media: (□), 1·5M-KNO_3; (○), 1·5M-$LiNO_3$; (■), 3M-KNO_3; (△), 1·5M-$Mg(NO_3)_2$; (●), 3M-$LiNO_3$

Consideration of these facts, together with the observation that the extent of hydrolysis of thorium(IV) ions decreases with decreasing water activity (Figure 2),[*] leads to the establishment of a relation between the hydroxyl number of thorium(IV) and some characteristics of the ionic medium.

Empirical Relation.—Since hydrolysis results from the interaction of metal ions with water molecules, the presence of foreign ions, having their own interaction with these molecules, should influence the process of hydrolysis. If the extent of hydrolysis of a metal ion in some ionic medium [represented by the hydroxyl number $Z_M(m)$] is assumed to be proportional to that in pure water [represented by the hydroxyl number $Z_M(w)$] [equation (1)], the problem is to interpret the

$$Z_M(m) = kZ_M(w) \qquad (1)$$

proportionality factor, *k*, in terms of such properties of the ionic medium as ionic charge, hydration energy, and concentration.

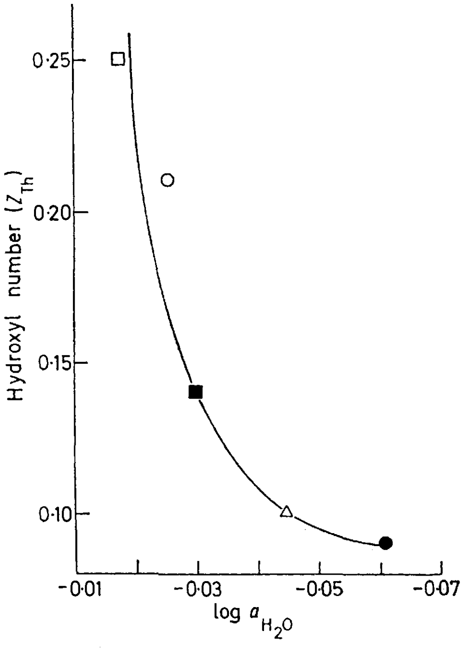

FIGURE 2 Dependence of the hydroxyl number of thorium(IV) ions (10 mM; pH 3) on water activity in (□), 1·5M-KNO_3; (○), 1·5M-$LiNO_3$; (■), 3M-KNO_3; (△), 1·5M-$Mg(NO_3)_2$; (●), 3M-$LiNO_3$

In solution, water molecules close to the metal ions are oriented by the electrostatic field of these ions. According to Samoilov,[8] who considered hydration of ions, the ions of the present nitrate media also change the orientation of these water molecules. Thus the presence of a cation of the ionic medium may cause the oriented water molecule to shift closer to the metal ion.[†] The resulting decrease in the distance between the metal ion and the water molecule enhances the interaction between them, and may finally result in 'splitting' of an H^+ ion from the water molecule and consequent formation of a hydrolytic complex. It follows that the extent of hydrolysis of metal ions should increase in the presence of cations of the medium. The same effect, but in the opposite direction, will appear

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[*] Water activity has been calculated using osmotic coefficients of the salts studied.[7]

[†] This shift may be suppressed by other interactions which occur concurrently in solution. Of these the most important are complex formation with negative ions, competition for water molecules between metal ions and cations of the medium, and dipole–dipole and short-range ion–ion interactions.

[7] R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' Butterworths, London 1968.

[8] T. A. Nosova and O. Ya. Samoilov, *Zhur. strukt. Khim.*, 1964, **5**, 363; O. Ya. Samoilov, *ibid.*, 1966, **7**, 15; M. N. Buslaeva, K. T. Dudnikova, and O. Ya. Samoilov, *ibid.*, 1969, **10**, 8.

in the presence of anions of the medium. The final influence of the ionic medium should therefore be a result of the difference between the effects of the cations and anions of the medium.

Hydration of cations and anions of the ionic medium may also influence hydrolysis, ions with higher energies of hydration causing the activity of water to decrease thus leading to decreasing hydrolysis. For the same reason, changes in the concentration of the ionic medium may also influence the hydrolysis of metal ions.

Considering these three effects one can conclude that the extent of hydrolysis of metal ions in an ionic medium decreases with increasing energy of hydration and concentration of ions of the medium and the charge on the anion of the medium, but increases with increasing charge on the cation of the medium. When the above dependences on the properties of the ionic medium are incorporated in the proportionality factor k it was found that equation takes the exponential form (2), where

$$Z_{\mathrm{M}}(\mathrm{m}) = Z_{\mathrm{M}}(\mathrm{w})e^{-F(\mathrm{m})} \qquad (2)$$

the exponent F(m) denoting ' the factor of the medium ' is given by equation (3). Here E_{h} is the hydration

$$F(\mathrm{m}) = c(\mathrm{c})E_{\mathrm{h}}(\mathrm{c})c(\mathrm{a})E_{\mathrm{h}}(\mathrm{a})z(\mathrm{a})/z(\mathrm{c}) \qquad (3)$$

energy (Table 3), z the charge, and c the concentration of ions of the medium (indices c and a denote the cation and anion respectively). Application of the logarithmic form of equation (2) to the present data and that of the

TABLE 3

Hydration energy of ions of the ionic medium

Ion	E_{h}/kcal mol^{-1}	Ion	E_{h}/kcal mol^{-1}
K^+	83·4 [a]	ClO_4^-	54 [b]
Na^+	103·6 [a]	NO_3^-	74 [b]
Li^+	129·7 [a]	Cl^-	80·3 [a]
Ba^{2+}	375·5 [a]	SO_4^{2-}	265 [b]
Ca^{2+}	394·5 [a]		
Mg^{2+}	473·3 [a]		

[a] Y. Markus and A. S. Kertes, ' Ion Exchange and Solvent Extraction of Metal Complexes,' Wiley–Interscience, New York, 1969, p. 13. [b] N. A. Izmailov, ' Electrokhimia rastvorov,' University of Harkov, 1959, p. 305.

$$\log Z_{\mathrm{M}}(\mathrm{m}) = \log Z_{\mathrm{M}}(\mathrm{w}) - 0{\cdot}4343F(\mathrm{m}) \qquad (4)$$

literature,[4,9,10] regarding the hydrolysis of thorium(IV) ions in various media, confirms the influence of the above properties of the ionic medium. Thus the data show a linear dependence of the hydroxyl number of thorium(IV) in various media, log Z_{Th}(m), on the factor of the medium, F(m) (Figure 3).

The available literature data, relating to hydrolysis of other metal ions [uranium(VI),[3,11,12] lead(II),[13,14] and nickel(II)[15,16]] in various media, also are in good agreement with equation (2) (Figures 4 and 5 *), indicating the possibility of general application of the relation established. However, there are some data, *e.g.* the hydrolyses of thorium(IV) in 3M-NaCl (Figure 3), uranium(VI) in 1·5M-Na$_2$SO$_4$ (Figure 4), and lead(II) in 1·5M-Mg(ClO$_4$)$_2$ (Figure 5), which show a great deviation. The spread of these points might be due to some experimental error in the available data, or as a consequence of some deficiency in the form of equation (2).

The relation established in this work shows that with decreasing F(m), *i.e.* the concentration of the medium in the case of only one medium, the value of the hydroxyl number of a metal ion approaches that which is characteristic in pure water. On the other hand, increasing the value of F(m) suppresses hydrolysis. If equation (2) holds, and only two values of the hydroxyl number of metal ions (at constant concentration of metal ion and pH) in one or two media are available, it

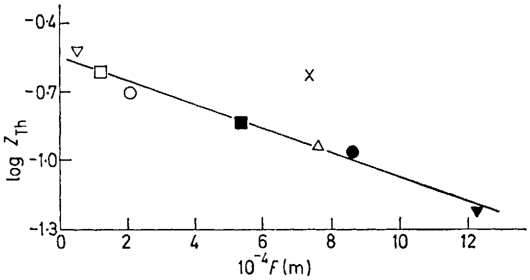

FIGURE 3 Dependence of the hydroxyl number of thorium(IV) ions (10 mM; pH 3) on the factor of the medium defined in equation (3). (▽), 1M-NaClO$_4$ (ref. 9); (□), 1·5M-KNO$_3$ (this work); (○), 1·5M-LiNO$_3$ (this work); (■), 3M-KNO$_3$ (ref. 5); (×), 3M-NaCl (ref. 10); (△), 1·5M-Mg(NO$_3$)$_2$ (ref. 5); (●), 3M-LiNO$_3$ (ref. 5); (▼), 4M-NaNO$_3$ (ref. 4)

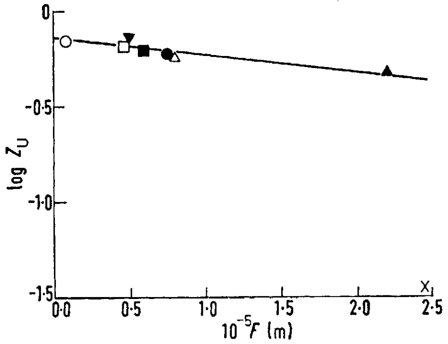

FIGURE 4 Dependence of the hydroxyl number of the uranium(VI) ion (20 mM; pH 4) on the factor of the medium. (○), 1M-NaCl (ref. 11; estimated value of Z); (□), 1·5M-Ca(ClO$_4$)$_2$ (ref. 3*c*); (▼), 3M-NaClO$_4$ (ref. 3*c*); (■), 1·5M-Mg(ClO$_4$)$_2$ (ref. 3*c*); (●), 3M-NaCl (ref. 3*a*); (△), 1·5M-Mg(NO$_3$)$_2$ (ref. 3*d*); (▲), 2·5M-Mg(NO$_3$)$_2$ (ref. 3*d*); (×), 1·5M-Na$_2$SO$_4$ (ref. 12)

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* Figure 5 shows that hydrolysis of Pb^{2+} and Ni^{2+} decreases on increasing F(m) as in equation (2), but does not definitely indicate a linear dependence.

[9] S. Hietanen, *Acta Chem. Scand.*, 1954, **8**, 1626.

[10] S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, 1968, **22**, 265.

[11] R. M. Rush, J. S. Johnson, and K. A. Kraus, U.S.A.E.C. Report ORNL-3278, 1963.

[12] A. Peterson, *Acta Chem. Scand.*, 1961, **15**, 101.

[13] A. Olin, *Acta Chem. Scand.*, 1960 **14**, 126.

[14] L. Pajdowski and A. Olin, *Acta Chem. Scand.*, 1962, **16**, 983.

[15] K. A. Burkov, L. S. Lilič, and L. G. Sillén, *Acta Chem. Scand.*, 1965, **19**, 14.

[16] K. A. Burkov and L. S. Lilič, *Vestnik Leningrad. Univ. (Fiz. Khim.)*, 1965, 103.

should be possible to predict the value of the hydroxyl number of the metal ion in the presence of any cations or anions, or for any concentration of different ionic media. Furthermore, the relation provides the possibility of estimating a value of the metal-ion hydroxyl number in any medium using the value for the same metal ion in pure water.

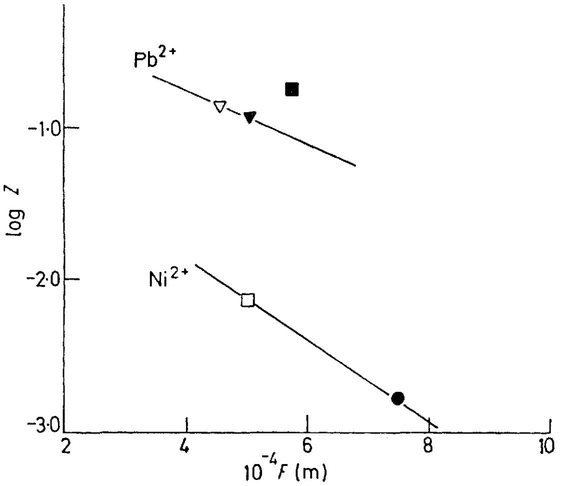

FIGURE 5 Dependence of the hydroxyl number of lead(II) (50 mM; pH 5·5) and nickel(II) (400 mM; pH 6·5) ions on the factor of the medium. (▼), 3M-NaClO$_4$ (ref. 13); (▽), 1·5M-Ba(ClO$_4$)$_2$ (ref. 14); (■), 1·5M-Mg(ClO$_4$)$_2$ (ref. 14); (□), 3M-NaClO$_4$ (ref. 15); (●), 3M-NaCl (ref. 16)

The equilibrium constant K or stability constants β_{pq} of complexes are more suitable quantities for characterising hydrolytic processes than the hydroxyl number Z which is extremely dependent on pH and the concentration of the metal ion. Therefore, it was interesting to consider the possibility of replacing the hydroxyl number Z in equation (2) by stability constants β_{pq} for the particular complexes [equation (5)]. It was found

$$\beta_{pq}(\mathrm{M,m}) = \beta_{pq}(\mathrm{M,w})e^{-F(\mathrm{m})} \qquad (5)$$

that the stability constants of the most hydrolysed complexes obey equation (5), *i.e.* decreasing linearly with increasing F(m) (Table 4). However, as there are no additional data confirming the existence of different hydrolytic complexes, it is better to use the hydroxyl number Z which is based directly on experimental data. In this way the possibility of a mistaken conclusion, arising from the appearance of some uncertain minor species, is avoided.

TABLE 4

Values of the stability constants, log β_{pq}, of the main hydrolytic complexes of uranium(VI) and thorium(IV) ions in various media

Medium	$10^{-4}F$(m)	log $\beta_{2,2}$	Ref.
	Uranium(VI)		
1·5M-Na$_2$SO$_4$	24·73	−8·17	12
2·5M-Mg(NO$_3$)$_2$	21·89	−6·52	3*d*
1·5M-Mg(NO$_3$)$_2$	7·87	−6·34	3*d*
3M-NaCl	7·48	−6·64?	3*a*
1·5M-Mg(ClO$_4$)$_2$	5·74	−6·25	3*b*
3M-NaClO$_4$	5·03	−6·04?	3*b*
1M-NaCl	0·83	−6·17	11
1M-KNO$_3$	0·61	−5·96	3*b*
	Thorium(IV)		
4M-NaNO$_3$	12·27	−5·50	4
3M-LiNO$_3$	8·63	−5·26	5
1·5M-Mg(NO$_3$)$_2$	7·87	−5·17	5
3M-NaCl	7·48	−4·70?	10
3M-KNO$_3$	5·55	−5·10	5
1M-NaClO$_4$	0·55	−4·61	9

The factor F(m) of the medium is defined in equation (3).

I wish to thank Professor Erik Högfeldt and Dr. Djordje Petković for valuable comments.

[2/1659 *Received*, 13*th July*, 1972]