A Physico-chemical Study on the Hydrolysis of Thorium Nitrate

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It has been known that all tetrapositive ions exhibit strong tendencies toward polymerization accompanied by hydrolysis. The hydrolysis and polymerization of zirconium in perchloric acid solution has been investigated by Connick and his coworkers[1,2] and it has been shown that in 2 M perchloric acid at 25°C the average zirconium species at low zirconium concentration has a charge somewhere between +3 and +4, corresponding to a mixture of Zr^{+4} and $ZrOH^{+3}$ or possibly ZrO^{2+}. It has also been known that thorium salts produce acidic solution and that gelatinous thorium hydroxide is precipitated from an old aqueous solution of thorium nitrate. Qualitatively, however, thorium salts exhibit a less marked tendency to hydrolyze in aqueous solution than zirconium, and little quantitative investigation has been found in previous literatures[*][3]. The purpose of the present work is to study the hydrolysis of thorium nitrate in a very dilute solution and in the presence of sodium perchlorate which has been used for maintaining the solution at constant ionic strength by means of the pH measurement with glass electrode. The assumption is that in the presence of sodium perchlorate, there is no complicating effect such as polymerization and colloid formation except in the case of hydrolytic behavior. For purposes of calculation, the data are treated as though the activity coefficients of all ion species are equal to unity in a very dilute solution, or remain constant at constant ionic strength. The equilibrium constants of thorium ion species are calculated stoichiometrically from the data of hydronium ion concentration observed and the total concentration of thorium nitrate.

Experimental

A) **Materials.**—Conductivity water with a specific conductivity of 1.6 to 2.4×10^{-6} mho was used throughout this experiment.

Thorium nitrate of C. P. grade was purified by the hydrogen peroxide method[4] and then by the hexamine method[5]. The washed hydroxide was digested in sufficient nitric acid, and evaporated to dryness after each of repeated additions of water to remove the excess of acid. The hydrate of thorium nitrate was obtained by recrystallization. The stock solution of thorium nitrate was prepared directly by dissolving the salt in conductivity water free from carbon dioxide. The concentration of the stock solution was checked by the gravimetric method before use.

B) **Procedure and Apparatus.**—Solutions with the initial concentration of 10^{-2} mol. of thorium nitrate were made to be 0.05, 0.1, 0.3 and 0.5 M with respect to sodium perchlorate, respectively. Each solution was diluted successively with an equal volume of the sodium perchlorate solution of the specified concentration, so that the concentration of thorium nitrate was diluted to one half while the solution was kept practically at constant ionic strength.

The change in pH during the dilution was followed with a vacuum tube potentiometer, constructed in our laboratory as shown in one of the previous papers[6]. The glass electrode made by Beckman Instrument Inc., in U.S.A., and a vacuum tube, UX-54 A, made by Matsuda Co. in Japan were used in the potentiometer circuit.

The glass electrode was frequently calibrated against a series of pH buffer solutions. The pH measurement was carried out in an oil thermostat controlled at 25°±0.1°C. Approximately ten-minute intervals were allowed for the attainment of equilibrium in each measurement.

Result and Discussion

When thorium nitrate dissolves in a dilute solution and in the presence of sodium perchlorate which is used for maintaining the solution at constant ionic strength, it may be assumed that the pH value of the solution is governed by no complicating effect, but the hydrolytic behavior for which the following reactions involving thorium ion species may be supposed:

$$Th^{+4}+H_2O \rightleftarrows Th(OH)^{+3}+H^+,\ K_1 \qquad (1)$$

$$Th^{+4}+2H_2O \rightleftarrows Th(OH)_2^{+2}+2H^+,\ K_2 \qquad (2)$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$Th^{+4}+nH_2O \rightleftarrows Th(OH)_n^{4-n}+nH^+,\ K_n. \qquad (3)$$

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[*] There are some reports on this problem, e.g., K. A. Kraus and R. W. Holmberg, U.S. Atomic Energy Commission Report (1950), which are not available to us.

[1] Robert E. Connick and William H. McVey, *J. Am. Chem. Soc.*, **71**, 3182 (1949).

[2] Robert E. Connick and William H. Reas, ibid., 73, 1171 (1951).

[3] R. Schaal and J. Faucherre, *Bull. soc. chim. France*, **1947**, 927.

[4] Arthur C. Neish, *J. Am. Chem. Soc.*, **26**, 781, (1904).

[5] H. H. Willard and L. Gordon, *Anal. Chem.*, 26, 165 (1948).

[6] K. Pan and T. M. Hseu, This Bulletin, **26**, 126 (1953).

Then if the most possible type of reaction among them is the *n*-th type, the hydrolysis constant, K_n, may be given by the following equation:

$$K_n=\frac{a_X \cdot a_H}{a_{Th}}=\frac{f_X f_H{}^n}{f_{Th}}\cdot\frac{C_X\cdot C_H{}^n}{C_{Th}}, \tag{4}$$

where a_{Th}, a_X, a_H; f_{Th}, f_X, f_H and C_{Th}, C_X, C_H are the activities, activity coefficients and concentrations of ion species, Th^{+4}, $Th(OH)_n{}^{+4-n}$ and H^+, respectively.

Then if the degree of hydrolysis is small, as a first approximation, equation (4) may be expressed as follows:

$$K_n \fallingdotseq \frac{f_X\cdot f_H{}^n}{f_{Th}}\;\frac{C_H{}^{n+1}}{nC} \tag{5}$$

$$\fallingdotseq K_f\frac{a_H{}^{n+1}}{nC}, \tag{6}$$

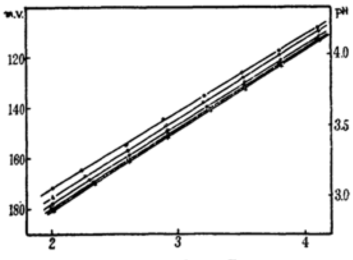
where C is the total concentration of the salt and $K_f=\dfrac{f_X}{f_{Th}\cdot f_H}$ is a constant at a constant ionic strength, consequently,

$$\mathrm{pH}=\frac{1}{n+1}[pK_n-pK_f-\log n]-\frac{1}{n+1}\log C \tag{7}$$

$$=K-\frac{1}{n+1}\log C, \tag{8}$$

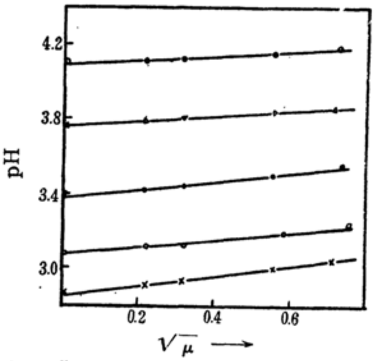
that is to say, a linear relation may be held between pH and $-\log C$, and the differential quotient of pH with respect to $-\log C$ is $\dfrac{1}{n+1}$.

As shown in Fig. 1, the curves plotting pH vs. $-\log C$ from 0.01 to 0.0001 M of thorium nitrate in sodium perchlorate solution as well as in pure water run parallel with each other and the slope is nearly equal to 1/2, that is, $n=1$, one may pressume that the existence of the ion, $Th(OH)^{+3}$ is highly probable. The linear relationship between the square root of ionic strength and pH at each concentration is indicated in Fig. 2.



×: in pure water
○: in 0.05M $NaClO_4$ soln.
●: in 0.1M $NaClO_4$ soln.
△: in 0.3M $NaClO_4$ soln.
○: in 0.5M $NaClO_4$ soln.

Fig. 1.



○: C 7.8×10^{-5}　△: $C=3.125\times10^{-4}$
●: 1.25×10^{-3}　□: 5.00×10^{-3}
×: 1.00×10^{-2}

Fig. 2.

In fact, since the hydrogen ion concentration in thorium nitrate solution is not so low as to be negligible against the total concentration of the salt, the above calculation is nothing but an approximate estimation. It suggests, however, that the average thorium ion species at this concentration range has a charge between +4 and +3 or even possibly +2, corresponding to a mixture of Th^{+4}, $Th(OH)^{+3}$ and $Th(OH)_2{}^{+2}$ or possibly ThO^{+2}.

For the purposes of calculating the equilibrium constants the data are treated as though the activity coefficients of all species in solution remain strictly constant at constant ionic strength and the general equilibrium constant is stoichiometrically expressed as

$$K_n=\frac{[Th(OH)_n{}^{4-n}]\ [H^+]^n}{[Th^{+4}]}. \tag{9}$$

Thus by expressing the total concentration of thorium and hydronium ion in a solution as a function of the equilibrium constants of all ion species as shown by the following stoichiometric relations,

$$[Th]_t=[Th^{+4}]+[Th(OH)^{+3}]+[Th(OH)_2{}^{+2}]\cdots\cdots$$

$$=[Th^{+4}]\left\{1+\frac{K_1}{[H^+]}+\frac{K_2}{[H^+]^2}\cdots\cdots\right\}$$

$$=[Th^{+4}]\left\{1+\sum_n\frac{K_n}{[H^+]^n}\right\} \tag{10}$$

and

$$[H^+]=[Th(OH)^{+3}+2[Th(OH)_2{}^{+2}]$$

$$+3[Th(OH)_3{}^{+1}]\cdots\cdots=[Th^{+4}]\left\{\frac{K_1}{(H^+)}+\right.$$

$$\left.\frac{K_2}{[H^+]^2}+\cdots\cdots\right\}=[Th^{+4}]\sum_n n\frac{K_n}{[H^+]^n}. \tag{11}$$

The stoichiometric ratio, r, of the hydronium ion concentration and the total concentration of thorium in the solution is expressed as follows:

$$r=\frac{[H^+]}{[Th]_t}=\frac{\sum n\ K_n/[H^+]^n}{1+\sum K_n/[H^+]^n}, \qquad (12)$$

where $[Th]_t$ is the total concentration of thorium.

An attempt has been made to apply the experimental data to equation (12) for calculating the equilibrium constants of four ion species of $Th(OH)_n^{4-n}$, where n takes all the values of 1. 2, 3 and 4, using the least square method, but two negative values are obtained for two of the four constants which indicates the inadequacy of the application.

On the other hand, by assuming the existence of the ion species of Th^{+4}, $Th(OH)^{+3}$ and $Th(OH)_2^{+2}$ in the same solution of the specified condition as suggested by the above approximate estimation, and applying the same data to equation (12) to calculate the equilibrium constants, reasonable values of K_1 and K_2 for reactions (1) and (2) are obtained by the same method, as shown in Table I. Experimental values of r are plotted against $\frac{1}{[H^+]}$ at varying ionic strengths in Fig. 3.

TABLE I

CONCENTRATION EQUILIBRIUM CONSTANTS AT VARYING IONIC STRENGTHS AT 25°C

Ionic strength (In $NaClO_4$ solutions)	$K_1(\times 10^4)$	$K_2(\times 10^9)$
0.5 M	0.55	5.2
0.3 M	0.76	6.5
0.1 M	1.0	7.3
0.05 M	1.2	7.7
0	1.3	8.2
In pure water	1.7	8.2

The dissociation constants expressed as concentration equilibrium constants are strictly valid, however, only for solutions at constant ionic strength. The limiting values of K_1 and K_2 obtained by plotting K_1 and K_2 against $\sqrt{\mu}$ in Fig. 4, and extrapolating to zero ionic strength are 1.3×10^{-4} and 8.2×10^{-9}, respectively.

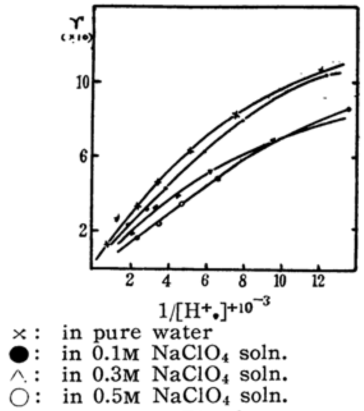


Fig. 3.

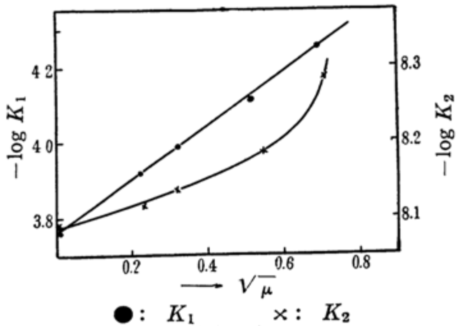


Fig. 4.

Summary

1) The dilution effect on the pH change in a dilute solution and in the presence of sodium perchlorate was followed by a glass electrode.

2) A linear relationship is held between pH and $-\log C$. The curves plotting pH vs. $-\log C$ run parallel with each other at varying ionic strengths, and the slope is nearly equal to 1/2 by which the most possible existence of $Th(OH)^{+3}$ is pressumed.

3) The equilibrium constants for ion species, $ThOH^{+3}$ and $Th(OH)_2^{+2}$, are calculated stoichiometrically from the data of hydronium ion concentration observed and the total concentration of thorium nitrate.

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