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The Hydrolysis of Y^{3+}, La^{3+}, Gd^{3+}, and Er^{3+} Ions in an Aqueous Solution Containing 3 M (Li)ClO_4 as an Ionic Medium

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The hydrolysis equilibria of Y^{3+}, La^{3+}, Gd^{3+}, and Er^{3+} ions have been studied at 25 °C in 3 M (Li)ClO_4 by measuring the hydrogen-ion concentration with a glass electrode. All the test solutions containing hydrolyzed species prepared by the addition of alkali were acidified by means of constant-current coulometry. The data, which indicate a slight hydrolysis of the relevant ions, can be explained by assuming the formation of the following complexes: $Y(OH)_2^+$, $\log \beta_{2,1} = -17.0 \pm 0.1$; $Y_2(OH)_2^{4+}$, $\log \beta_{2,2} = -14.04 \pm 0.01$; $LaOH^{2+}$, $\log \beta_{1,1} = -10.04 \pm 0.01$; $GdOH^{2+}$, $\log \beta_{1,1} = -8.20 \pm 0.01$; $Er(OH)_2^+$, $\log \beta_{2,1} = -17.4 \pm 0.1$; $Er_2(OH)_2^{4+}$, $\log \beta_{2,2} = -13.72 \pm 0.01$.

So far, very few quantitative investigations have been made of the hydrolysis of rare-earth ions.[1)]

In 1946 Moeller[2)] measured the acidity of a series of rare-earth sulfate solutions at 25 °C by the use of a glass electrode and found that only a small part of the rare-earth ions were transformed to hydrolysis species of $LnOH^{2+}$ before precipitation started.

Wheelwright, Spedding, and Schwarzenbach[3)] titrated a 0.01 M $LaCl_3$ solution with NaOH using a glass electrode and reported the formation of $LaOH^{2+}$ with $\log \beta_{1,1} = -8.4$ (at 20 °C).

Tobias and Garrett[4)] studied the hydrolysis equilibria of Nd^{3+} and Pr^{3+} ions at 25 °C and found that a very small part of the metal ions could be present as hydrolysis products in solution. They found $NdOH^{2+}$ and $PrOH^{2+}$ to have the same stability constant of $\log \beta_{1,1} = -8.5$.

In 1961 Biedermann and Ciavatta[5)] investigated the hydrolysis of the La^{3+} ion by measuring the concentration of the hydrogen ion with a glass electrode. They explained the results in the $\log h$ range from -6.5 to -8.1 by assuming the formation of $LaOH^{2+}$, La_2OH^{5+}, and $La_5(OH)_9^{6+}$ (or $La_6(OH)_{10}^{8+}$), the corresponding stability constants being $\log \beta_{1,1} = -10.1$, $\log \beta_{1,2} = -9.9_5$, and $\log \beta_{9,5} = -71.4_5$ (or $\log \beta_{10,6} = -78.7_5$) (at 25 °C).

Biedermann and Newman[6)] investigated the hydrolytic reaction of the Ce^{3+} ion and reported that only the $Ce_3(OH)_5^{4+}$ species with $\log \beta_{5,3} = -35.7_5$ was formed.

In 1964 Biedermann and Ciavatta[7)] studied the hydrolysis equilibria of the Y^{3+} ion by the application of constant-current coulometry. Their data, which indicated that, at most 3% of the Y^{3+} ions were transformed to the hydrolysis species, without the formation of any precipitate, were explained by assuming the formation of a dimer, $Y_2(OH)_2^{4+}$, with $\log \beta_{2,2} = -14.30$ as the main species. As minor species they found the YOH^{2+} and $Y_3(OH)_5^{4+}$, the stability constants of which were $\beta_{1,1} = -9.1$ and $\log \beta_{5,3} = -33.8$.

From the previous investigations described above, it has been found that the hydrolytic reactions of rare-earth ions become measurable at $\log h \leq -5$, and that not more than a small percentage of the metal ions can be transformed to hydrolysis products without the formation of a precipitate.

In the present work, therefore, we made an effort to keep contamination with protolytic impurities to a minimum when preparing test solutions containing hydrolyzed species, and employed the "back titration" method with a constant current coulometer, which had been found to be suitable for the study of a slightly buffered solution.[7),8)]

The present study will deal with the hydrolytic reactions of Y^{3+}, La^{3+}, Gd^{3+}, and Er^{3+} ions in 3 M (Li)ClO_4.

Symbols

h	concentration of the free hydrogen ion.
H	analytical excess of hydrogen ions $= [ClO_4^-] - 3B - [Li^+]$.
B	total concentration of metal ions.
b	concentration of the free metal ion.
z	average number of hydrogen ions set free per metal ion.
p	number of OH groups bound to hydrolyzed species.
q	number of metal present in hydrolyzed species.
$\beta_{p,q}$	equilibrium constant of the following reaction: $q Ln^{3+} + p H_2O = Ln_q(OH)_p^{(3q-p)+} + pH^+$
(p, q)	Complex, $Ln_q(OH)_p^{(3q-p)+}$
E	emf (mV).
Ln^{3+}	rare-earth ion.

Experimental

Reagents and Analysis. The lanthanum perchlorate solution was prepared from lanthanum oxide of a 99.99%

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* Present address: NGK Insulators Co., Mizuho, Nagoya.

1) a) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes", The Chemical Society, London (1964). b) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes, Supplement No. 1", The Chemical Society, London (1971).

2) T. Moeller, *J. Phys. Chem.*, **50**, 242 (1946).

3) E. J. Wheelwright, F. H. Spedding, and G. Schwarzenbach, *J. Amer. Chem. Soc.*, **75**, 4196 (1953).

4) R. S. Tobias and A. B. Garrett, *ibid.*, **80**, 3532 (1958).

5) G. Biedermann and L. Ciavatta, *Acta Chem. Scand.*, **15**, 1347 (1961).

6) G. Biedermann and L. Newman, *Arkiv Kemi*, **22**, 303 (1964).

7) G. Biedermann and L. Ciavatta, *ibid.*, **22**, 352 (1964).

8) G. Biedermann and L. Ciavatta, *Acta Chem. Scand.*, **16**, 2221 (1962).

purity supplied by the Shin-estu Chemical Co. The oxide, which had been ignited at around 900 °C, was dissolved in a slight excess of hot perchloric acid, and the lanthanum perchlorate was recrystallized twice from water. In the stock solution thus prepared, no chloride, sulfate, or ferric ions could be detected. The La(III) content of the stock solution was determined by the precipitation of the La^{3+} ion as the oxalate and by ignition to the oxide. The total perchlorate concentration in the stock solution was determined by neutralization after passing a definite amount of the solution through a column of the cation exchange resin, Dowex 50W-12, of the H^+ form.

The other rare-earth perchlorate solutions were prepared and analyzed by the same procedures as those used for the $La(ClO_4)_3$ solution.

The lithium perchlorate was prepared by the method described by Biedermann and Ciavatta.[5)]

Apparatus. The titration cell consisted of two Wilhelm-type half-cells[9)] for emf measurements and for constant-current coulometry.

Glass electrodes of the Beckman type No. 40498 were employed.

The pH meter used was a Radiometer PHM-4C pH-meter (Copenhagen).

A Coulometric Analyzer (Leeds & Northrup Co., Philadelphia) was used as the constant-current power source.

Preparation of Test Solutions. The hydrolyzed test solutions of rare-earth ions were prepared by the following two methods. (1) For the system of the Y^{3+} ion, a slightly acidic yttrium perchlorate solution was electrolyzed to reduce the H^+ ions by constant-current coulometry to the point where the value of Z was around 0.015; this was found to be the highest value to be reached without precipitation. For the electrolysis, the same circuit as Ciavatta's[10)] was used. In the test solution thus prepared, no colloidal precipitate could be detected nephelometrically.

(2) For the systems of La^{3+}, Gd^{3+}, and Er^{3+} ions, the test solutions were prepared as follows.

We started with a slightly acidic rare-earth perchlorate solution ($\log h \leqq -3$) which had been freed from CO_2 by passing purified nitrogen gas through. The solution was electrolyzed to reduce H^+ ions by using a d.c. power supply until precipitates appeared. Equilibration was made at 25 °C by stirring the mixture for about two days with a Teflon-covered bar; then, the precipitates were removed through G4 glass filters. These procedures were carried out under an atmosphere of nitrogen gas. In each case, the filtered solution was carefully examined for turbidity, but no suspended particle could be detected. No indication of slow precipitation was found in an aliquot of the filtered solution which was occasionally tested for turbidity over half a year's time.

Emf Measurements. The general composition of a test solution can be written as:

B M Ln^{3+}, H M H^+, $(3-3B-H)$ M Li^+, 3 M ClO_4^-, where H, the analytical hydrogen ion concentration is often negative.

The test solution was titrated by means of constant-current coulometry, a coulometric circuit similar to Ciavatta's[10)] being used.

The potentiometric measurements were made by the use of this cell:

$$\text{GE} \mid \text{test solution} \mid \text{Ref} \qquad \text{(A)}$$

where GE denotes a glass electrode, and Ref, the reference half-cell |3 M $LiClO_4$| 2.99 M $LiClO_4$+0.01 M $AgClO_4$| AgClAg. The emf of the cell(A) at 25 °C can be described as;

$$E = E_0 + 59.15 \log h \qquad (1)$$

where E_0 is a constant into which the term of the activity coefficient of the hydrogen ion and that of the liquid-junction potential are incorporated.

All the emf measurements were performed at 25.00±0.01 °C in a parrafin oil thermostat in a room thermostated at 25±1 °C.

Results and Discussion

The values of $Z(\log h)_B$ for each metal ion, which form the basis of the following calculations, are graphically shown in Fig. 1.

The experimental data were treated by graphical methods to determine the compositions of the hydrolysis species and the corresponding approximate stability constants; then, computer calculations were made to find the most probable values of the stability constants.

If the formation of a series of reaction products with the general composition of $Ln_q(OH)_p{}^{(3q-p)+}$ is assumed, the concentration of the hydrogen ion set free by hydrolysis, BZ, is given by the general form:

$$BZ = \sum_p\sum_q p\beta_{p,q}[Ln^{3+}]^q[H^+]^{-p} = \sum_p\sum_q p\beta_{p,q}b^q h^{-p} \qquad (2)$$

Since the maximal value of Z never exceeds 0.02 in the solutions studied, we may simplify, without introducing any appreciable error, the preliminary calculations by using this approximation:

$$[Ln^{3+}] = b \simeq B \qquad (3)$$

By substituting this relation into Eq. (2) and by rearranging, we obtain:

$$Zh = \sum_p pK_p h^{-(p-1)} \qquad (4)$$

where:

$$K_p = \sum_q \beta_{p,q} B^{q-1} \qquad (5)$$

Primary information on the compositions of the hydrolysis species and the corresponding stability constants was obtained by the use of Eqs. (4) and (5).

For the system of the Y^{3+} ion, the plots of Zh against h^{-1} gave a set of straight lines with various slopes and with a zero intercept. This indicates that p is equal to 2. In order to determine the values of q, the values of the ($K_2 = 2\sum_q \beta_{2,q}B^{q-1}$) slope were plotted against B. The plot closely approximated a straight line; this establishes that q is equal to 1 and 2 at $p=2$. Thus, the hydrolysis species formed are $Y(OH)_2{}^+$ and $Y_2(OH)_2{}^{4+}$. Their stability constants were estimated from the intercept and slope of the straight line according to Eq. (5).

For the system of the La^{3+} ion, the plots of Zh *vs.* h^{-1} showed a horizontal line independent of B; this indicates that p and q are equal to 1. The hydrolysis species formed is $LaOH^{2+}$. The stability constant was estimated from the intercept.

For the system of the Gd^{3+} ion, the plots of Zh *vs.* h^{-1} gave the same results as that for the system of the La^{3+} ion: p and q are equal to 1. The hydrolysis

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9) W. Forsling, S. Hietanen, and L. G. Sillén, *ibid.*, **6**, 901 (1952).

10) L. Ciavatta, *Arkiv Kemi*, **20**, 417 (1962).

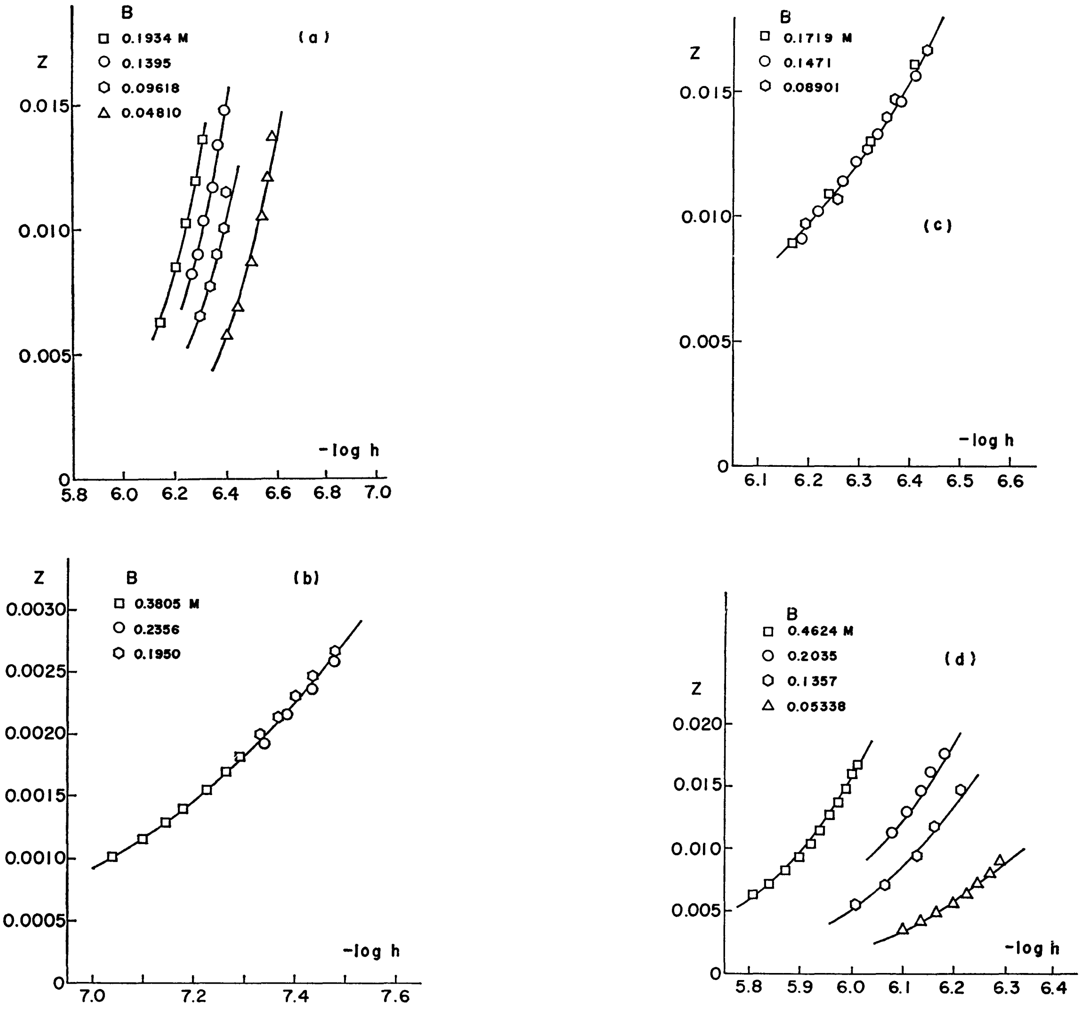

Fig. 1. Average number, Z, of OH bound per a) Y(III), b) La(III), c) Gd(III), and d) Er(III), as a function of log h. The drawn curves were calculated with the stability constants listed in Table 1.

species formed is $GdOH^{2+}$.

For the system of the Er^{3+} ion, the plots of Zh *vs.* h^{-1} were used to determine the values of p. The plots gave a set of straight lines with various slopes and with a zero intercept; this indicates that p is equal to 2. Then, in order to determine the values of q, the values of the $(K_2=2\sum_q \beta_{2,q}B^{q-1})$ slope were plotted against B. The plot gave a straight line, indicating that q is equal to 1 and 2 at $p=2$. The hydrolysis species formed are $Er(OH)_2^+$ and $Er_2(OH)_2^{4+}$. Their stability constants were estimated from the intercept and slope of the straight line according to Eq. (5).

The most probable values of their stability constants were determined by computer calculations. Generalized least-squares methods undertaken with the aid of an electronic computer (HITAC 5020) were used in order to make the error square sum $U=\sum(Z-Z_{\mathrm{calcd}})^2$ a minimum for the set of the stability constants. Z_{calcd} denotes the $Z_{\mathrm{calcd}}=\sum\sum p\beta_{p,q}b^q h^{-p}/B$ value for a particular set of stability constants.

Since the hydrolysis schemes predicted by the graphical analysis gave a satisfactory agreement between the experimental and calculated Z values, no further attempt was made to search for species other than those found by the graphical methods.

Table 1. The stability constants for the hydrolysis species of the rare-earth ions in 3M (Li)ClO_4[a]

	Y^{3+}	La^{3+}	Gd^{3+}	Er^{3+}
$-\log\beta_{1,1}$	——	10.04 ±0.01	8.20 ±0.01	——
$-\log\beta_{2,1}$	16.8 ±0.1	——	——	17.2 ±0.1
$-\log\beta_{2,2}$	14.04±0.01	——	——	13.72±0.01

a) The uncertainties of the constants were estimated as 3σ.

The most probable values for the stability constants of the hydrolyzed species of Y^{3+}, La^{3+}, Gd^{3+}, and Er^{3+} ions thus calculated are listed in Table 1.

The present results for the Y^{3+} and La^{3+} ions were compared with those obtained by Biedermann and Ciavatta[5,7] in the same ionic medium (3 M (Li)ClO_4). For the system of the Y^{3+} ion, the values for $\beta_{p,q}$ they obtained were $\log\beta_{1,1}=-9.1\pm0.1$, $\log\beta_{2,2}=-14.30\pm0.05$, and $\log\beta_{5,3}=-33.8\pm0.1$. For the (2,2) species, the stability constant we obtained was a little larger than that they obtained. We found neither the (1,1) nor the (5,3) species they detected. Instead, we found the (2,1) species. For the system of the La^{3+} ion, the values for $\beta_{p,q}$ they obtained were log $\beta_{1,1}=-10.0\pm 0.1$, $\beta_{1,2}=-9.9_5\pm 0.1$, and log $\beta_{9,5}=-71.4_5\pm 0.1$ (or log $\beta_{10,6}=-78.7_5\pm 0.1$). The stability constants for the (1,1) species obtained by us was the same as that obtained by Biedermann and Ciavatta. None of the (1,2) and (9,5) (or (10.6)) complexes they found were detected in the present work.

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