Studies on the Hydrolysis of Metal Ions

58. The Hydrolysis of Cerium(IV) in 3 M (Na)NO₃ Medium

PIER ROBERTO DANESI*

Department of Inorganic Chemistry, Royal Institute of Technology (KTH), Stockholm 70, Sweden

The hydrolysis of Ce(IV) ions was studied at 25°C in the medium, 3 M (Na)NO₃. $[H^+] = h$ was measured with a glass electrode and $[Ce^{4+}] = b$ with a gold redox electrode.

The $[Ce(IV)]_{tot}$ was varied from 10 mM to 100 mM. There was evidence of slow reactions. The data were treated with the computer program LETAGROP with independent adjustment of analytical errors. By writing the reactions as: $qCe^{4+} + pH_2O \rightleftharpoons Ce_q(OH)_p^{(4q-p)+} + pH^+$ and the equilibrium constants as $\beta_{p,q}$, the "best" combination of complexes and equilibrium constants was found to be $Ce_2(OH)_3^{5+}$, $\beta_{3,2} = (5.1 \pm 0.3) \times 10^{-2}$, $Ce_2(OH)_4^{4+}$, $\beta_{4,2} = (2.3 \pm 0.3) \times 10^{-3}$; $Ce_6(OH)_{12}^{12+}$, $\beta_{12,6} = (1.36 \pm 0.06) \times 10^{-2}$.

Even if the narrow Ce(IV) concentration range studied limits the conclusions on the existing species, it seems certain that larger complexes than dimers must be formed.

Although it is universally recognized that aqueous cerium(IV) solutions hydrolyze strongly when the hydrogen ion concentration is lowered, not very much is known about the nature of the species formed. Noyes and Garner[1] studied the oxidation potential of the cerium(III,IV) couple in nitric acid, using a hydrogen electrode as a reference. They stated that in the nitric acid concentration range 2.00—0.500 M no hydrolysis of Ce(IV) occurred when the metal concentration was varied between 0.026 and 0.087 M. Later Sherill, King and Spooner[2] made a similar study in perchloric acid, and explained their data with the *a priori* assumption that only mononuclear hydrolysis products were formed.

It seems that not until 1948 was the presence of polynuclear complexes in aqueous cerium(IV) solutions suggested. Heidt and Smith,[3] studying the photochemical reduction of ceric ions in perchlorate medium, proposed the species $CeOH^{3+}$, $Ce(OH)_2^{2+}$, $Ce_2(OH)_2^{6+}$, $Ce_2(OH)_3^{5+}$ and other polymers of unspecified formula. They calculated $2CeOH^{3+} \rightleftharpoons Ce_2(OH)_2^{6+}$, $\log K = 1.70$ and $CeOH^{3+} + Ce(OH)_2^{2+} \rightleftharpoons Ce_2(OH)_3^{5+}$, $\log K = 2.00$.

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* Permanent address: Laboratori di Chimica, Centro Studi Nucleari, Casaccia C.N.E.N., Rome, Italy.

Similarly, Kraus, Holmberg and Nelson [4] reported that in cerium(IV) perchlorate solutions they had found, from spectrophotometric and glass electrode measurements, an average hydroxyl number of 2.35 at pH = 2 and that polynuclear complexes were forming slowly in the solutions. Subsequently a number of papers appeared [5-15] in which, although the formation of polynuclear complexes was recognized, equilibrium constants were calculated considering only the formation of the two species $CeOH^{3+}$ and $Ce_2(OH)_2^{6+}$.

Hardwick and Robertson [5] have reported $Ce^{4+} + H_2O \rightleftharpoons CeOH^{3+} + H^+$, $\log K_1 = 0.72$ and $2CeOH^{3+} \rightleftharpoons Ce_2(OH)_2^{6+}$, $\log K = 1.22$ in 2 M $NaClO_4$ at 25°C, obtained spectrophotometrically.

King and Padow [8] studied, again spectrophotometrically, the Ce(IV) hydrolysis and found that it was possible to explain their data by assuming the formation of either only monomeric and dimeric or only monomeric and trimeric hydrolytic products. They reported $\log K_1 \geq 0.48$ in $0.85-2.57$ M perchloric acid.

According to Duke and Parchen [9] (reaction kinetics), even in $5-6$ M perchloric acid there was evidence of monomeric and polymeric hydrolysis products. Similarly, Blaustein and Gryder [10] (extraction and emf measurements), and Dorfman and Gryder [15] (reaction kinetics) stated that dimers are present in 5.5 M HNO_3 solutions and also found evidence of mixed complexes between Ce(III) and Ce(IV).

On the other hand Baker, Newton and Kahar,[13] by studying the reaction kinetics between U(IV) and Ce(IV) in perchlorate medium at an ionic strength of 2 found that the predominating species was $CeOH^{3+}$ in the $[H^+]$ range $2.00-0.30$ M, ($\log K_1 = 1.15$ at 15°C).

If we consider that, simply on the basis of its ionic radius and charge, cerium(IV) should hydrolyze even more than thorium(IV) and uranium(IV),* it seems very likely that in a complete picture of the Ce(IV) hydrolysis complex polynuclear products have to play an important role.

The majority of the studies published up to now have been carried out in perchlorate medium because the tendency of the perchlorate anion to form complexes is especially weak and Ce(IV) is particularly strongly hydrolyzed as evidenced by its very high oxidation potential. However, one might fear a tendency to decompose to Ce(III) and O_2.

Moreover, preliminary studies started in this laboratory by Hietanen,[17] have seemed to indicate (see also Ref. 4) that the Ce(IV) hydrolysis equilibria are very slow in perchlorate medium.

It was thought, therefore, that a study of the cerium(IV) hydrolysis in another medium might be worth trying. Bearing in mind the strong oxidizing power of cerium(IV) ions, which makes them very reactive with many inorganic and organic anions, and since we wanted to avoid too strongly complexing bulk electrolytes, such as, for instance, the sulfates, we subsequently have chosen the nitrate medium.

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* Their crystal ionic radii are [16] $Ce^{4+} = 0.94$ Å, $Th^{4+} = 1.02$ Å and $U^{4+} = 0.97$ Å.

SYMBOLS

B = total concentration of Ce(IV); b = concentration of free cerium(IV) ions in solution; b' = concentration of cerium(III) ions in solution; h = [H$^+$], equilibrium concentration of hydrogen ions; H = analytical excess of hydrogen ions; p = number of OH groups bound to the hydrolyzed species; q = number of metal ions present in the hydrolyzed species; $r = B/b'$; $\beta_{p,q}$ = equilibrium constant of reaction: $q\text{Ce}^{4+} + p\text{H}_2\text{O} \rightleftarrows \text{Ce}_q(\text{OH})_p^{(4q-p)+} + p\text{H}^+$; $\eta = \log (B/b)$.

EXPERIMENTAL

The hydrolysis of Ce^{4+} was studied by means of emf measurements at 25°C in the medium 3 M (Na)NO$_3$. The reactions were followed by measuring h and b by means of glass and gold redox electrodes.

Materials and analysis. NaNO$_3$ Merck *pro analysi*, recrystallized twice from water, was used for preparing a stock solution, the concentration of which was determined both by passing an aliquot through a cation exchanger resin in the hydrogen form and by evaporating a known volume to dryness and constant weight.

Ce(III) nitrate, supplied by Lindsay Chemical Company, of 99 % purity was used without further purification. A stock solution of Ce(III) nitrate was prepared by dissolving the salt in water and then adding a certain amount of HNO$_3$ Merck *pro analysi*. A stock solution of Ce(IV) was prepared by anodic oxidation (Pt anode) of the previously mentioned solution.

The total cerium concentration was determined by oxidizing the Ce(III) to Ce(IV) with ammonium peroxidisulfate using silver nitrate as a catalyst,[18] and then titrating with an Fe(II) solution detecting the equivalence point potentiometrically. The Ce(IV) was determined analogously without oxidation. The total cerium concentration was also determined gravimetrically by precipitating the cerium hydroxide and igniting it to CeO$_2$ which was then weighed. The free HNO$_3$ content in the Ce(IV) stock was determined by adding a concentrated KBr solution (twice the number of moles stoichiometrically required) which reduced Ce(IV) to Ce(III), extracting the bromine with water-saturated CS$_2$, and then titrating the aqueous phase with a standardized NaOH solution using methyl red as indicator. The HNO$_3$ content in the Ce(III) stock solution was similarly determined by titrating with NaOH using methyl red as indicator. The Ce(IV) stock solution was stored in the dark. The Ce(IV) content was checked every three weeks and it was found to keep constant within ± 0.3 % (the experimental scatter) over a period of four months.

NaOH solutions were prepared by diluting a 50 % solution using the usual precautions in order to eliminate the CO$_2$. Their concentration was determined against standardized HNO$_3$. HNO$_3$ Merck *pro analysi* was used without further purification. Tl$_2$CO$_3$ Merck *pro analysi*, recrystallized twice from water, was used for standardizing the HNO$_3$ solutions.

A Beckman glass electrode of type 40498 was used. Ag,AgCl electrodes were prepared according to Brown.[19] AgNO$_3$ Merck *pro analysi*, recrystallized twice from water and then dried, was directly weighed for preparing a silver nitrate solution of known concentration.

Bright Pt and Au electrodes were used as redox electrodes. Although they both gave the same emf's, Au electrodes reached a constant emf value in a much shorter time and were therefore employed in the majority of the measurements.

The emf, E, was measured with a Radiometer PHM4 potentiometer calibrated against a Cambridge Vernier potentiometer.

Preliminary experiments. Some preliminary experiments were carried out in order to find out if the equilibria in the solutions were sufficiently fast to enable us to study the hydrolysis reactions by a titration technique.

A solution having the composition:

$B = 0.0100$ M, $b' = 0.00478$ M, $H = 0.200$ M, (Na)NO$_3$ = 3.000 M

was placed, half an hour after its preparation from stock solutions, in a titrating flask in which a glass and a gold electrode were dipped and the potential of these two electrodes was measured using as a reference a silver-silver ion electrode. A continuous drift of the potential was noticed for both the glass and the gold electrodes, which stopped only after about two days. Several other solutions were then tried in which B and H were varied. From these experiments it was established that to obtain a constant value (to $\pm$ 0.5 mV) for the emf of the cell, it was necessary to wait about $10-12$ h for the more acidic solutions ($h \approx 500$ mM), and about three — four days for the less acidic ones ($h \approx 100$ mM), the total drift between the initial and the final E values being sometimes several tens of millivolts. The time necessary for attaining this steady potential value was increased by decreasing B. When acid was added to an already hydrolyzed solution this time was always longer and sometimes constancy in E was not reached even after a week.

It was also established that the Ce(IV) hydrolysis becomes perceptible at pH values between 0 and 1, depending on the total metal concentration. It would have been desirable to vary B over a broad range but, for reasons to be stated, it proved advisable to keep B within the limits of 10 and 100 mM. For $B < 10$ mM great difficulties were encountered in the measurements since the emf values were very unstable. Moreover, reduction to Ce(III) could not be neglected. For example, a solution having initially the following composition

$B = 0.00500$ M, $b' = 0.00334$ M, $H \approx 0.50$ M, (Na)NO_3 = 3.000 M
was found, after standing for three days, to have changed to
$B = 0.00363$ M, $b' = 0.00471$ M, $H \approx 0.50$ M, (Na)NO_3 = 3.000 M.

METHOD OF INVESTIGATION

It was, therefore, decided to prepare a certain number of solutions (generally ten) in which B and b' as well as [NO_3^-] = 3.00 M, were kept constant while H was varied from 1.00 M downward. These solutions were stored in a thermostated room at 25 $\pm$ 0.5°C in cylindrical bottles. A reference silver-silver ion electrode, a glass electrode, a gold electrode and in certain cases a bright platinum electrode were dipped into the solutions at the time of measurement (Fig. 1 and 2). The solutions were measured four or five days after their preparation. Then H was further reduced or again increased (back titration), always keeping B, b' and the NO_3^- concentration constant. The new solutions were then measured according to the same procedure. The lowest acidity reached was $h \approx 0.100$ M since at lower values the emf of the cell was too unstable to be measured with any accuracy.

At the end of each series of measurements B was determined again in order to ascertain that no reduction to Ce(III) had occurred. The cells used for measuring h and b can be schematized as follows:

−GE/test solution/2.990 M $NaNO_3$, 0.010 M $AgNO_3$/AgCl,Ag + (A)
−Ag,AgCl/2.990 M $NaNO_3$, 0.010 M $AgNO_3$/test solution/Pt + (B).
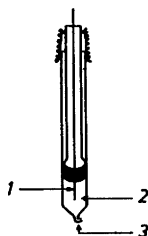
GE represents a glass electrode.

Fig. 1. Reference electrode. 1) Pt wire coated with Ag and AgCl. 2) $AgNO_3$ 0.010 M, $NaNO_3$ 2.990 M solution. 3) Hook-shaped capillary.
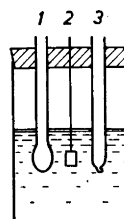

Fig. 2. 1) Glass electrode. 2) Gold electrode. 3) Reference electrode.

All test solutions were of composition:
B M Ce(IV), b' M Ce(III), H M H$^+$, $(3 - 4B - 3b' - H)$ M Na$^+$, 3 M NO$_3^-$.
The emf of the cells (A) and (B) at 25°C are given by the expressions:

$$E = E_0 + Jh + 59.15 \log h \tag{1}$$
$$E' = E_0' - Jh + 59.15 \log b/b' \tag{2}$$

The values E_0, E_0' and J were determined by plotting the quantities $E - 59.15 \log$ H and $E' - 59.15 \log B/b'$ against H for strongly acidic solutions. These plots gave straight lines in the region 500 mM $\leq H \leq$ 1.00 M with slope and intercepts independent of B and r (ratio between B and b') when $B <$ 100 mM, thus indicating that no appreciable hydrolysis occurred in that acidity range. The difference $E_0' + 59.15 \log 0.01 =$ $(e^0(\text{Ce}^{4+}/\text{Ce}^{3+}) - {}_0e \ (\text{Ag}^+/\text{Ag}))$, $i.e.$ E_0' corrected to unit silver concentration, was found to be equal to $(+ 803.1 \pm 0.5)$ mV for $B =$ 0.010, 0.020, and 0.050 M, whereas for $B =$ 0.100 M its value was $(+ 800.7 \pm 0.5)$ mV.

E_0 also proved to be constant within $\pm$ 0.5 mV for $B <$ 0.100 M. However, its value was checked by means of an acid base-titration, in absence of cerium, before each series of measurements was started. The two values were always found to agree within $\pm$ 0.5 mV. For $B =$ 0.100 M a lower E_0 value (of about three mV) was obtained. J was found to be equal to $- 22$ mV/M H$^+$ for $B =$ 0.010, 0.020, and 0.050, and -10 mV/M H$^+$ for $B =$ 0.100 M.

Since Ce(III) hydrolyzes very little,[20] b and η could be directly calculated from (2). (In a 1 M Ce(III) perchlorate solution of pH $=$ 6 less than 0.01 % of Ce is hydrolyzed which can be safely extended to nitrate solutions.) Log h was calculated from (1).

RESULTS AND ANALYSIS OF DATA

It will be assumed that the main Ce(IV) species at the highest acidities studied is unhydrolyzed Ce^{4+} or rather one or more hydrolyzed nitrate complexes, which cannot be distinguished from Ce^{4+} by measurements in a nitrate medium. This assumption is also supported by many other authors. However, the present data, taken alone, would also be compatible with, say, CeOH^{3+} as the least hydrolyzed species.
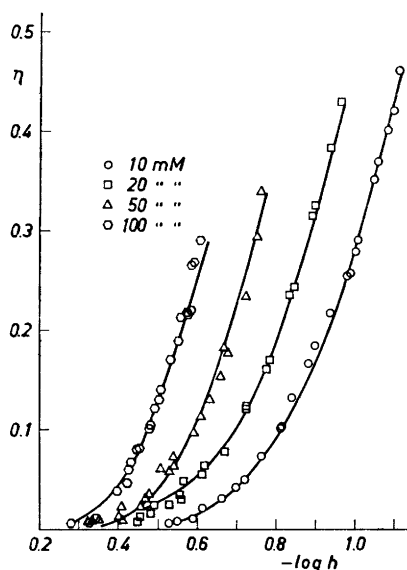

Fig. 3. Data $\eta(\log h)_\text{B}$. The solid lines were calculated assuming $\log \beta_{3,2} = -1.68$, $\log \beta_{4,2} = -2.29$, and $\log \beta_{12,6} = -1.98$ and the "group constants" $(\delta\eta)$ $K_1 = -0.014$, $K_2 = -0.003$, $K_3 = -0.027$, and $K_4 = -0.023$.

Since the hydrolysis of Ce(IV) occurs in so highly acidic solutions, the difference $h - H$ was always too small to allow any accurate calculations of $Z = (h - H)/B$. In Table 1 and in Fig. 3 the experimental results are summarized as $\eta(-\log h)$ data.

Table 1. Experimental data in the form: $-\log h$, $\eta \times 10^3$ and 10^3 ($\eta_{calc} - \eta_{exp}$). In calculating η_{calc} we used $\log \beta_{3,2} = -1.68 \pm 0.24$, $\log \beta_{4,2} = -2.29 \pm 0.14$, $\log \beta_{12,6} = -1.98 \pm 0.11$ and the following "group constants" $(\delta\eta)$: $K_1 = -0.014$, $K_2 = -0.003$, $K_3 = -0.027$, $K_4 = -0.023$.

$\triangle$ points obtained from a back titration, $+$ points for which an apparent decrease in B was noticed.

1) $B = 0.0100$ M; $r = 2.09$; 0.529,5, -1; 0.553, 8,0; 0.592,10,3; 0.615,20, -2;
0.664,30,0; 0.699,41,0; 0.723,49,1; 0.764,73, -4; $\triangle$0.813,101, -4;
0.815,102, -4; $\triangle$0.842,133, -15; 0.886,167, -13; $\triangle$0.901,185, -16; 0.940,218, -8;
0.983,256,6; 0.989,257,13; $\triangle$1.004,279,12; 1.011,291,10; $+$1.051,352,7;
$+\triangle$1.060,371,2; $+\triangle$1.085,413,0; $+$1.099,426,13; $+$1.114,462, -1; $r = 1.66$.
0.610,9; 0.670,37; 0.744,63; 0.775,86.

2) $B = 0.0200$ M; $r = 2.09$; 0.448,7,9; $\triangle$0.455,12,6; 0.483,16,7; $\triangle$0.493,24,0;
0.529,25,7; 0.556,34,4; $\triangle$0.558,29,10; 0.568,49, -5; $\triangle$0.612,55,1; 0.617, -5;
$\triangle$0.671,78,1; $\triangle$0.723,122, -6; 0.725,120, -3; 0.776,161,0; 0.784,170, -1;
0.832,236, -13; 0.847,243, -1; 0.892,315, -11; 0.899,326, -11; $+$0.941,384, -4;
$+$0.965,431, -12; $r = 1.66$; 0.433,15; 0.764,132; 0.799,180; $r = 0.20$; 0.524,27;
0.582,43; 0.639,63; 0.703,99; 0.818,203;

3) $B = 0.050$ M; $r = 1.66$; $\triangle$0.326,9, -14; 0.338,9, -11; 0.348,9, -11;
$\triangle$0.402,12, -4; 0.411,22, -11; 0.415,17,4; $\triangle$0.461,22,2; 0.468,31, -3;
0.478,26,5; $\triangle$0.507,61, -17; 0.531,58, -1; $\triangle$0.539,73, -11; 0.543,63, -11;
0.592,97,3; 0.610,113,3; $\triangle$0.632,130,9; 0.659,154,17; $\triangle$0.671,183,3;
0.680,177,20; 0.724,235,24; $+$0.752,284,8; $+$0.762,340, -21;
0.533,59; 0.600,110.

4) $B = 0.100$ M; $r = 1.66$; 0.282,5,1; 0.328,7,11; 0.346,10,13; 0.399,37,8;
$\triangle$0.426,46,15; 0.428,61,1; 0.435,66,1; $\triangle$0.451,80,0; 0.456,81,2; $\triangle$0.482,102,4;
0.484,105,4; $\triangle$0.495,122, -2; 0.506,130,1; 0.510,140, -4; 0.536,171, -3;
0.556,189,3; $\triangle$0.560,213, -14; 0.573,218, -1; $\triangle$0.577,216,6; $+\triangle$0.583,221,10;
$+$0.585,240, -5; $+$0.595,267, -17; $+$0.609,271, -4.

After the emf measurements were completed a number of solutions were taken at random and analyzed for Ce(IV). If Fe(II) was added to the solutions without previous treatment, an apparent decrease in titer of Ce(IV) was noticed for the less acidic points ($H \approx 100$ mM).

However, if before the analysis the samples were boiled for a few minutes with concentrated nitric acid, the initial B values were found. A blank test using only Ce(III) gave negative response. A visual sign of this apparent decrease in Ce(IV) titer was the lightening of the yellow colour of the solutions.

The following Ce(IV) concentrations have been studied: 0.0100, 0.0200, 0.0500, and 0.100 M.

In Fig. 3 the points are seen to fall on different curves for different B values thus indicating the formation of polynuclear complexes of general formula $Ce_q(OH)_p^{(4q-p)+}$. Moreover, the fact that at different r and same B the points fall on the same curves indicates that one may neglect mixed complexes containing both Ce(III) and Ce(IV).

In order to obtain some preliminary information about the most probable values of p and q our experimental points were compared with a group of normalized curves, $\log y$ vs. $\log \alpha$ where $y = B/b$ and $\alpha^p = \beta_{q,p} \, qb^q h^{-p}$, calculated for combinations between $q = 1, 2, 4, 6$, and $p = 1, 2, 3, 4, 6, 12$. From this comparison it was seen that it was not possible to fit all our experimental points with only one pair of p and q values (at least for the p and q values chosen by us), thus indicating that more than one species must be important in the region covered by our experimental data. However, all the points at $B = 0.100$ M, and some of the points at the other B values, fell on the normalized curves calculated with $p = 12$ and $q = 6$.

TREATMENT BY LETAGROP

The experimental data have been then treated by means of LETA-GROP,[21-24] a computer program designed to find the minimum for a function of a number of unknown constants. We have tried to find the equilibrium constants that minimized the error square sum $U = \sum (\eta_{exp} - \eta_{calc})^2$.

Several combinations between 27 different complexes, whose possible formula had been suggested either by the previous comparison with normalized curves or by the existing literature on the subject, were tried. During these calculations the combination of the three complexes ($p = 3$, $q = 2$), ($p = 4$, $q = 2$), and ($p = 12$, $q = 6$) emerged as the one giving rise to the lowest error square sum value. Then, by using the "species selector"[23] all the rejected complexes were once more passed through the computer having as initial set the three previously mentioned species and trying to add one complex after the other. None of the complexes was found to decrease the error square sum appreciably thus leaving the initial set invaried.

Table 2 lists these rejected complexes and estimated maximum values for their equilibrium constants. For all of them the "best" value was found to

Table 2. Estimated maximum values $\log (\beta + 3\sigma)$, for $\log \beta$ of "rejected" complexes.

p	q	$\log \beta_{max}$	p	q	$\log \beta_{max}$
1	1	-1.96	10	5	0.25
2	1	-1.47	12	5	-5^a
3	1	-4^a	14	5	-13
4	1	-5^a	6	6	-3
1	2	-1^a	10	6	-1.08
2	2	-2.30	11	6	-1.45
4	3	-2.15	14	6	-11
6	4	-1.45	15	6	-12
8	4	-3	11	7	-1.60
9	4	-10	12	7	-1.08
10	4	-7.46	13	7	-1.55
12	4	-14	12	8	-0.05

[a] for these constants $\beta + 3\sigma(\beta)$ came out negative:

$$\beta_{3,1} \pm \sigma(\beta_{3,1}) = (-5.9 \pm 1.6) \times 10^{-4}$$
$$\beta_{4,1} \pm \sigma(\beta_{4,1}) = (-4.9 \pm 0.8) \times 10^{-5}$$
$$\beta_{1,2} \pm \sigma(\beta_{1,2}) = (-2.4 \pm 0.5) \times 10^{-1}$$
$$\beta_{12,5} \pm \sigma(\beta_{12,5}) = (-7.6 \pm 1.8) \times 10^{-5}$$
$$\beta_{14,5} \pm \sigma(\beta_{14,5}) = (-3.9 \pm 0.9) \times 10^{-7}$$

be less than its standard deviation, $\beta < \sigma(\beta)$, and log β_{max} represents the maximum value (log $\beta_{max} = \log(\beta + 3\sigma(\beta))$). Again the present data do not give any support to the existence of the corresponding species.

It was then tried to further lower U by taking into account possible systematic errors on η. We have therefore assumed that in each series there was a constant error on η, $\delta\eta$, which could be due, for instance, to an error in the calculation of E_0''s in (2). These systematic errors, $\delta\eta$, were treated by LETA-GROP as unknown "group constants". The "best" values for these "group constants", found by LETAGROP, were of an order of magnitude comparable with that of our experimental errors, and they reduced U to about one third of its starting value.

It appears, therefore, that the scheme involving the formation of the three complexes $Ce_2(OH)_3^{5+}$, $Ce_2(OH)_4^{4+}$, and $Ce_6(OH)_{12}^{12+}$ with the equilibrium constants reported in Table 1, gives the "best" fit to our experimental data. The solid lines of Fig. 3 have been calculated according to this set of values.

In Fig 4 the Z vs. log h curves are reported.

These curves have been calculated by assuming the hydrolysis products and equilibrium constants of Table 1. Again, if the starting species were to be $CeOH^{3+}$, all Z values should be increased by 1.

DISCUSSION

In thorium chloride [25] and thorium perchlorate solutions [26],[27] groups containing six Th atoms have been indicated in addition to some monomeric, dimeric, and tetrameric species. Similarly, in the Ce(IV) case, besides dimeric species, a complex containing six cerium atoms is again required to explain the data, which may indicate a common tendency for these 4-valent elements to form hexanuclear groups in their solutions. The group $Ce_6O_4(OH)_4^{12+}$ has been also found in the crystal structure of a basic cerium(IV) sulfate and its isomorphous uranium(IV) salt,[28] where the atoms are arranged in the form of an octahedron of six cerium and a cube of eight O (4 OH and 4 O). It seems likely then that the same type of octahedra of cerium atoms joined to a cube of oxygen atoms, (by emf work two OH and one O are indistinguishable), are able to exist in both solutions and crystal salts. The fact that a relation could
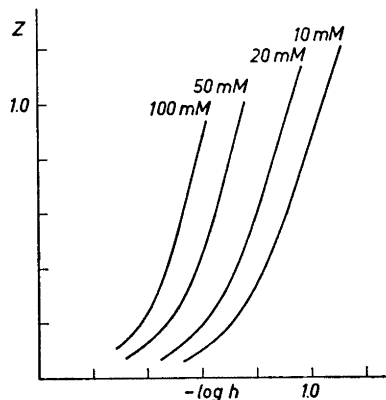

Fig. 4. $Z(\log h)_B$ curves calculated by assuming log $\beta_{3,2} = -1.68$, log $\beta_{4,2} = -2.29$, and log $\beta_{12,6} = -1.98$.

exist between the products of hydrolysis and the structure of basic salts of some 4-valent ions had already been pointed out by Lundgren [29] and our results seem to agree with this hypothesis.

However, for the reasons stated earlier, we were able to study only a limited B range. This limits to some extent the conclusions which we can draw on the formulas of the hydrolytic species. Other complexes could still exist in appreciable amounts outside the concentration range studied by us. Perhaps, even a different set of hydrolysis products might satisfy the experimental results better over a much broader B range. Because of the experimental uncertainty in the $\eta(\log h)$ curves, especially pronounced for the lowest η values studied, the existence of monomeric species could not be inferred from our data, although their existence might be detected by more accurate or different experimental techniques.

From the present work it seems, however, that the existence of dimeric species is quite well established, and that species containing more than two cerium atoms are formed as the hydrolysis proceeds. From the present investigation the $Ce_6(OH)_{12}{}^{6+}$ complex would be suggested.

REFERENCES

1. Noyes, A. A. and Garner, C. S. *J. Am. Chem. Soc.* **58** (1936) 1256.
2. Sherrill, M. S., King, C. B. and Spooner, R. C. *J. Am. Chem. Soc.* **65** (1943) 170.
3. Heidt, L. J. and Smith, M. E. *J. Am. Chem. Soc.* **70** (1948) 2476.
4. Kraus, K. A., Holmberg, R. W. and Nelson, F. *114th Meeting Am. Chem. Soc.*, Sept. 1948 Ab. 4—0.
5. Hardwick, T. J. and Robertson, E. *Can. J. Chem.* **29** (1951) 818.
6. Duke, F. R. and Bremer, R. F. *J. Am. Chem. Soc.* **73** (1951) 5179.
7. Gryder, J. W. and Dodson, R. W. *J. Am. Chem. Soc.* **73** (1951) 2860.
8. King, E. L. and Padow, M. L. *J. Am. Chem. Soc.* **74** (1952) 1966.
9. Duke, F. R. and Parchen, F. R. *J. Am. Chem. Soc.* **78** (1956) 1540.
10. Blaustein, B. D. and Gryder, J. W. *J. Am. Chem. Soc.* **79** (1957) 540.
11. Wadsworth, E., Duke, F. R. and Goetz, C. A. *Anal. Chem.* **29** (1957) 1824.
12. Tuazon, L. O. *Iowa State Univ., Ames, Dissertation Abstr.* **20** (1959) 904.
13. Baker, F. B., Newton, T. W. and Kahar, M. *J. Phys. Chem.* **64** (1960) 109.
14. Conley, H. L. *U. S. At. Energy Comm.* UCRL-9332, 46 p. (1960).
15. Dorfman, M. K. and Gryder, J. W. *Inorg. Chem.* **1** (1962) 799.
16. *Handbook of chemistry and physics*, 45th Ed., The Chemical Rubber Co. 1964—65.
17. Hietanen, S. *Personal communication.*
18. Willard, H. H. and Young, P. J. *Am. Chem. Soc.* **50** (1928) 1322.
19. Brown, A. S. *J. Am. Chem. Soc.* **56** (1934) 646.
20. Biedermann, G. and Newman, L. *Arkiv Kemi* **22** (1964) 303.
21. Sillén, L. G. *Acta Chem. Scand.* **13** (1959) 533.
22. Ingri, N. and Sillén, L. G. *Acta Chem. Scand.* **16** (1962) 173.
23. Sillén, L. G. *Acta Chem. Scand.* **18** (1964) 1085.
24. Ingri, N. and Sillén, L. G. *Arkiv Kemi* **23** (1964) 97.
25. Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* **18** (1964) 1018.
26. Hietanen, S. *Unpublished results.*
27. Baes, C. F., Meyer, N. J. and Robertson, C. E. *Inorg. Chem.* **4** (1965) 518.
28. Lundgren, G. *Arkiv Kemi* **10** (1956) 183.
29. Lundgren, G. *Svensk Kem. Tidskr.* **71** (1959) 200.