

Studies on the Hydrolysis of Metal Ions

39. The Hydrolysis of Pb^{2+} in $\text{Mg}(\text{ClO}_4)_2$ and $\text{Ba}(\text{ClO}_4)_2$ Medium

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The hydrolysis of Pb^{2+} in 1.5 M $\text{Mg}(\text{ClO}_4)_2$ or $\text{Ba}(\text{ClO}_4)_2$ has been studied by emf methods. In both media the hydrolysis products $\text{Pb}_2\text{OH}^{3+}$ and $\text{Pb}_4(\text{OH})_4^{4+}$ have been identified. These complexes have also been found in a previous investigation¹ with 3 M NaClO_4 as salt back-ground. From an analysis of the results at high concentrations of Pb^{2+} it is inferred that the self-medium method of Hietanen and Sillén² can yield reliable results in a region where as much as up to 10 % of the free metal ions have been changed to hydrolysis products.

The hydrolysis products of many metal ions have been identified in dilute solution by emf methods³. The measurements have been made with solutions containing a high salt back-ground, usually 3 M NaClO_4 . In such solutions the activity factors vary but little, which is a necessary condition for the successful identification of the complexes formed.

When a metal ion forms polynuclear hydrolysis products, the relative amounts of the species formed will depend both on the total concentration of the metal ion, B , and on the concentration of hydrogen ion, h . It is therefore possible that in concentrated solutions of the metal salt new complexes appear, whose concentrations at low B are so small that they cannot be identified.

The self-medium method proposed by Hietanen and Sillén² can be used to identify the hydrolysis products at high values of B . However, from such studies, reliable results can be expected only from measurements with small ranges in Z , since otherwise the variation in the composition of the solutions and hence in the activity factors, may become so large that it will interfere with the interpretation of the data.

Self-medium studies^{1,4} on Be^{2+} and Pb^{2+} in 3 M $(\text{Na})\text{ClO}_4$ medium have indicated that reliable results can be obtained if the investigation is confined to the Z range $0 < Z < 0.1$. The species identified were Be^{2+} , $\text{Be}_2\text{OH}^{3+}$ and $\text{Be}_3(\text{OH})_3^{3+}$, and Pb^{2+} , $\text{Pb}_2\text{OH}^{3+}$ and $\text{Pb}_4(\text{OH})_4^{4+}$. For higher values of Z , deviations occurred between the experimental data (Z , $\log h$) and those calculated on the assumption that the above-mentioned complexes were

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formed. Two possible explanations for this were suggested; the formation of other complexes, or the variation of activity factors.

The present investigation was undertaken in an effort to obtain more information on this point. If substantial changes are found in the shapes of the curves $Z(\log h)_B$ with different media it appears reasonable to ascribe the cause of the deviation to changes in the activity factors and not to new complexes. It should, however, be observed that we can not choose unequivocally between the two hypotheses. The Pb^{2+} ion was used in this study, since $\text{Pb}(\text{ClO}_4)_2$ solutions are easy to analyse for their analytical hydrogen ion excess, which is essential if accurate values of Z are to be obtained. As salt back-grounds $\text{Mg}(\text{ClO}_4)_2$ and $\text{Ba}(\text{ClO}_4)_2$ have been used.

SYMBOLS

B = total metal ion concentration; b = free metal ion concentration; H = analytical hydrogen ion excess (often negative); h = free hydrogen ion concentration; Z = average number of OH^- bound per metal ion ($= (h-H)/B$); $\beta_{p,q}$ = equilibrium constant of the reaction $pA + qB \rightleftharpoons A_pB_q$; $y(x)_v = y$ as a function of x at constant v .

Concentrations are expressed in moles/l (M) and equilibrium constants are given on the M-scale.

MATERIALS AND ANALYSES

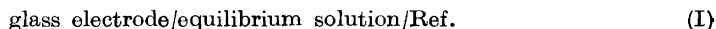
Magnesium and barium perchlorate were prepared by reacting MgCO_3 and $\text{Ba}(\text{OH})_2$ (Merck p.a.) with HClO_4 (Kebo p.a.). The products were twice recrystallized from water. The stock solutions of $\text{Mg}(\text{ClO}_4)_2$ and $\text{Ba}(\text{ClO}_4)_2$ were analysed by evaporating known quantities with H_2SO_4 and weighing the residues as MgSO_4 and BaSO_4 . The neutrality of these solutions was checked potentiometrically as described in Ref.⁵

The "basic" lead perchlorate stock solution was prepared from PbO (Baker p.a.), which had been repeatedly washed with distilled water, and perchloric acid. An excess of the oxide was used and the mixture of oxide and solution was allowed to stand for a couple of days in order to precipitate foreign metal ions. The solution was then filtered and traces of tetravalent lead removed by bubbling H_2 through the solution using platinum black as a catalyst. Finally the solution was filtered in a N_2 atmosphere and then stored and handled under the same gas. The Pb^{2+} concentration in this solution was found by precipitating lead as PbSO_4 and the analytical hydrogen ion excess, which is a negative quantity in this solution, was determined potentiometrically using Gran's⁶ method to obtain the equivalence point.

The "neutral" lead perchlorate solution was prepared from stoichiometric amounts of PbO and HClO_4 . It was analysed in the same way as the "basic" lead perchlorate solution.

EXPERIMENTAL

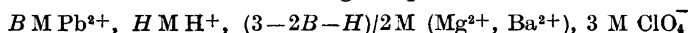
The experiments were carried out as potentiometric titrations, at 25.0°C, in an oil thermostat. The hydrogen ion concentration, h , was measured with a calibrated glass electrode and using the cell



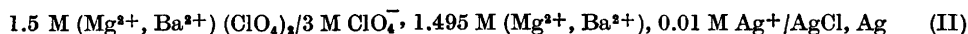
Assuming the activity factors to be constant the emf of cell (I) can be written

$$E = E^\circ - 59.15 \log h - E_j \quad (1)$$

The equilibrium solutions had the following composition



and the reference half-cell used was



In each experiment B and $[\text{ClO}_4^-] = 3 \text{ M}$ were kept constant and H was varied by the addition of a hydrolysed lead perchlorate solution or by the addition of HClO_4 . The emf of cell (I) was measured with a Radiometer valve potentiometer (PHM 4) to $\pm 0.2 \text{ mV}$.

Titration procedure. Two different titration procedures were used depending on the value of B . With $B = 0.05 \text{ M}$ and 0.1 M three solutions were used, each 3 M in ClO_4^- by addition of the ionic medium;

S_1 : The "starting" solution, containing $B \text{ M Pb}(\text{ClO}_4)_2$,

S_2 : The "basic" solution, containing $B \text{ M PbOHClO}_4$

S_3 : The "acid" solution, containing $B \text{ M Pb}(\text{ClO}_4)_2$ and $H \text{ M HClO}_4$

Solution S_2 , $V \text{ ml}$, was gradually added from a buret to a known volume, $V_0 \text{ ml}$, of the "starting" solution, S_1 , and the emf of cell(I) was measured after each addition ("basic titration"). When the desired volume of S_2 had been added, then solution S_3 was introduced in order to give values of H between 0.005 and 0.025 M ("acid titration").

The values of E measured in the acid titration were used to determine the analytical hydrogen ion concentration (H_b) in the basic lead solution, S_2 , by Gran's method⁶. \bar{H} was then calculated from the analytical data for each point in the acid titration and E° determined from a plot of $E' = E + 59.15 \log H$ versus \bar{H} . The straight line ($E + 59.15 \log H$) (H) was extrapolated to $H = 0$ to give E° (Ref.⁷).

With E° known from the acid titration $\log h$, H and Z in the basic titration can be calculated from

$$\log h = (E^\circ - E) / 59.15 \quad (2)$$

$$H = H_b V / (V_0 + V) \quad (3)$$

$$Z = (h - H) / B \quad (4)$$

At the higher Pb^{2+} concentrations, $B \geq 0.25 \text{ M}$, only two solutions were used. To the starting solution, $V_0 \text{ ml}$, containing $B \text{ M Pb}(\text{ClO}_4)_2$ and a known amount of HClO_4 (ca. 0.025 M), $V \text{ ml}$ of basic lead solution, S_2 , were added from a buret. The first few points in the acid solution were used to determine the analytical hydrogen ion excess in S_2 and E° . Two basic solutions were employed. One solution had a $\text{OH}^- / \text{ClO}_4^-$ ratio equal to 1 and the other had a lower $\text{OH}^- / \text{ClO}_4^-$ ratio so that accurate results could be obtained at low Z . In these titrations $\log h$ was found from eqn. (2) and H from

$$H = H_b(V - V_e) / (V_0 + V) \quad (5)$$

where V_e denotes the equivalence point from the Gran extrapolation. Z was calculated from eqn. (4).

All solutions were carefully protected against CO_2 and were mixed and handled under a N_2 atmosphere. If severe precautions were not taken and CO_2 came into contact with the solution this resulted in the precipitation of lead hydroxide carbonates.

RESULTS AND CALCULATIONS

The experimental data, Z and $\log h$, are presented in Fig. 1 and Table 1. With $\text{Ba}(\text{ClO}_4)_2$ as medium the following values of B were used; $B = 0.05, 0.1, 0.25, 0.5, 1,$ and 1.45 M . With $\text{Mg}(\text{ClO}_4)_2$ titrations with $B = 0.05, 0.5, 1,$ and 1.45 M were made. Two titrations with NaClO_4 as medium were performed also and they agreed within 0.3 mV with previously published titrations¹, where NaOH was used as the base, and are therefore not included in Table 1.

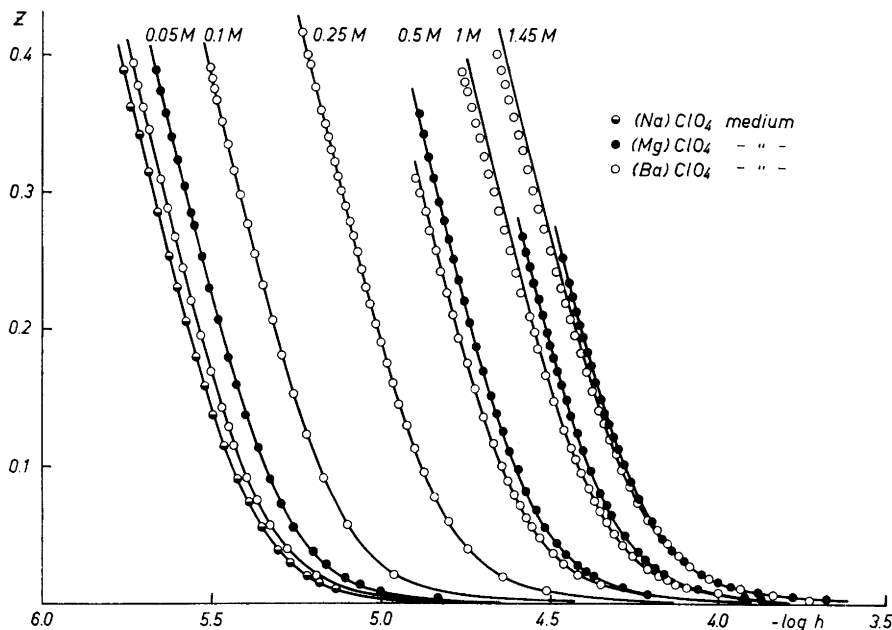


Fig. 1. Z , average number of OH^- bound per Pb(II) atom as a function of $\log h$. Drawn curves have been calculated with the equilibrium constants given in the text.

From the data we observe that for $B \leq 0.25$ M the curves are parallel and considering the data with $\text{Ba}(\text{ClO}_4)_2$ medium only, $t = (\Delta \log B / \Delta \log h)_Z$ is found to be a constant $= 1.33 \pm 0.02$.

From the data with $B \geq 0.5$ M it is found that the shifts between the curves $Z(\log h)_B$ for the different media tend to diminish as B increases. This is particularly obvious with $B = 1.45$ M for $Z < 0.05$. In this range the curves coincide. This is of course due to the fact the compositions of the solutions tend to become the same, namely $\text{Pb}(\text{ClO}_4)_2$, as B increases and Z decreases. As Z increases the curves $Z(\log h)_B$ in the three media become separate and the values of $l = |(\Delta Z / \Delta \log h)_B|$ for a given value of Z , always follow the order $l(\text{in NaClO}_4) < l(\text{in Ba}(\text{ClO}_4)_2) < l(\text{in Mg}(\text{ClO}_4)_2)$.

IDENTIFICATION OF THE COMPLEXES FORMED AT $B \leq 0.25$ M.

As stated above the value of $(\Delta \log B / \Delta \log h)_Z = 1.33 \pm 0.02$ for $B \leq 0.25$ M in 1.5 M $\text{Ba}(\text{ClO}_4)_2$ medium. The composition of the complexes formed can then, according to Sillén⁸, be written $\text{Pb}(\text{Pb}(\text{OH})_{4/3})_n^{(2+2n/3)+}$. Conceivable values of n are obtained from the relation $n = 3m$ with $m = 1, 2, 3 \dots$. With $n = 3$, which means that the complex $\text{Pb}_4(\text{OH})_4^{4+}$ is formed, an excellent fit was found between the experimental curves $Z(\log h)_B$ and the "normalized" curve for the formation of $\text{Pb}_4(\text{OH})_4^{4+}$. The formation of $\text{Pb}_4(\text{OH})_4^{4+}$ was

Table 1. Corresponding values of $-\log h$ and Z .Ba(ClO₄)₂ medium

$B = 0.05$ M. $-\log h, Z$; 5.166, 0.015; 5.193, 0.019; 5.243, 0.029; 5.279, 0.038; 5.330, 0.056; 5.368, 0.074; 5.397, 0.091; 5.438, 0.115; 5.470, 0.142; 5.505, 0.168; 5.532, 0.195; 5.560, 0.220; 5.585, 0.244; 5.607, 0.267; 5.627, 0.288; 5.649, 0.308; 5.668, 0.327; 5.685, 0.345; 5.701, 0.362; 5.717, 0.378; 5.729, 0.394.

$B = 0.1$ M. $-\log h, Z$; 4.959, 0.019; 5.101, 0.056; 5.171, 0.090; 5.220, 0.122; 5.260, 0.152; 5.293, 0.180; 5.321, 0.206; 5.348, 0.231; 5.370, 0.254; 5.392, 0.275; 5.414, 0.296; 5.433, 0.315; 5.451, 0.334; 5.468, 0.351; 5.484, 0.367; 5.490, 0.375; 5.497, 0.383; 5.506, 0.391.

$B = 0.25$ M. $-\log h, Z$; 4.638, 0.018; 4.743, 0.038; 4.843, 0.077; 4.902, 0.112; 4.948, 0.145; 4.985, 0.175; 5.017, 0.204; 5.032, 0.217; 5.047, 0.230; 5.069, 0.255; 5.093, 0.278; 5.118, 0.300; 5.137, 0.321; 5.155, 0.340; 5.174, 0.359; 5.191, 0.376; 5.206, 0.393; 5.218, 0.405; 5.230, 0.416.

$B = 0.5$ M. $-\log h, Z$; 4.178, 0.004; 4.347, 0.013; 4.459, 0.028; 4.516, 0.042; 4.554, 0.055; 4.582, 0.067; 4.604, 0.078; 4.623, 0.088; 4.642, 0.099; 4.670, 0.115; 4.699, 0.135; 4.726, 0.155; 4.748, 0.174; 4.772, 0.192; 4.790, 0.209; 4.809, 0.225; 4.826, 0.241; 4.841, 0.256; 4.858, 0.271; 4.871, 0.285; 4.887, 0.298; 4.900, 0.310.

$B = 1$ M. $-\log h, Z$; 3.967, 0.005; 4.089, 0.012; 4.150, 0.017; 4.197, 0.023; 4.229, 0.029; 4.254, 0.034; 4.275, 0.040; 4.307, 0.049; 4.332, 0.058; 4.351, 0.067; 4.369, 0.075; 4.385, 0.083; 4.407, 0.094; 4.423, 0.104; 4.437, 0.113; 4.461, 0.125; 4.491, 0.146; 4.513, 0.165; 4.540, 0.184; 4.550, 0.196; 4.565, 0.208; 4.589, 0.225; 4.604, 0.241; 4.638, 0.271; 4.668, 0.299; 4.697, 0.325; 4.723, 0.349; 4.746, 0.372; 4.763, 0.386.

$B = 1.45$ M. $-\log h, Z$; 3.898, 0.008; 3.999, 0.015; 4.053, 0.022; 4.107, 0.031; 4.143, 0.040; 4.172, 0.048; 4.202, 0.056; 4.221, 0.064; 4.239, 0.071; 4.260, 0.080; 4.292, 0.096; 4.325, 0.117; 4.359, 0.141; 4.393, 0.168; 4.427, 0.194; 4.456, 0.218; 4.483, 0.241; 4.520, 0.272; 4.552, 0.301; 4.582, 0.329; 4.609, 0.354; 4.636, 0.377; 4.660, 0.399; 4.674, 0.413.

Mg(ClO₄)₂ medium

$B = 0.05$ M. $-\log h, Z$; 4.831, 0.004; 4.990, 0.009; 5.061, 0.014; 5.103, 0.018; 5.159, 0.028; 5.201, 0.037; 5.259, 0.055; 5.297, 0.073; 5.328, 0.089; 5.365, 0.113; 5.399, 0.136; 5.428, 0.158; 5.453, 0.179; 5.480, 0.205; 5.507, 0.229; 5.527, 0.252; 5.549, 0.274; 5.560, 0.284; 5.578, 0.304; 5.600, 0.323; 5.617, 0.340; 5.634, 0.357; 5.649, 0.373; 5.663, 0.388.

$B = 0.5$ M. $-\log h, Z$; 3.987, 0.002; 4.207, 0.006; 4.283, 0.010; 4.332, 0.015; 4.369, 0.019; 4.393, 0.023; 4.452, 0.035; 4.481, 0.043; 4.542, 0.067; 4.596, 0.096; 4.640, 0.124; 4.677, 0.150; 4.719, 0.186; 4.756, 0.219; 4.787, 0.250; 4.816, 0.278; 4.846, 0.309; 4.875, 0.341.

$B = 1$ M. $-\log h, Z$; 3.727, 0.002; 3.920, 0.005; 4.004, 0.008; 4.094, 0.013; 4.160, 0.021; 4.216, 0.031; 4.268, 0.045; 4.352, 0.080; 4.403, 0.110; 4.439, 0.135; 4.469, 0.158; 4.493, 0.178; 4.520, 0.204; 4.537, 0.221; 4.562, 0.245; 4.584, 0.266.

$B = 1.45$ M. $-\log h, Z$; 3.276, 0.001; 3.600, 0.002; 3.737, 0.004; 3.839, 0.006; 3.935, 0.010; 4.008, 0.016; 4.067, 0.023; 4.100, 0.030; 4.131, 0.038; 4.167, 0.049; 4.195, 0.059; 4.236, 0.075; 4.281, 0.100; 4.314, 0.120; 4.339, 0.138; 4.366, 0.160; 4.391, 0.182; 4.413, 0.202; 4.435, 0.223; 4.466, 0.251.

confirmed by the "integration method" derived by Sillén⁹. This method gave invariant values of \bar{p} and $\bar{q} = 4$. \bar{p} and \bar{q} are the average values of p and q of the complexes $\text{Pb}_q(\text{OH})_p^{(2q-p)+}$ formed. The formation of $\text{Pb}_4(\text{OH})_4^{4+}$ in 1.5 M Ba(ClO₄)₂ is thus well established. The same complex has also been found in 3 M NaClO₄ medium. In 1.5 M Mg(ClO₄)₂ it is also likely that the same complex is formed to judge from the good agreement between the experi-

mental $Z(\log h)$ curve for $B = 0.05$ M and the normalized curve. This conclusion is confirmed by the results from the titrations with $B \geq 0.5$ M in this medium.

With $B = 0.05$ M, measurements have been made with all the three media and we observe three $Z(\log h)$ curves which are parallel along the $\log h$ axis. The shifts between the curves can be understood, if the activity factors stay constant in each medium but are different from one medium to another.

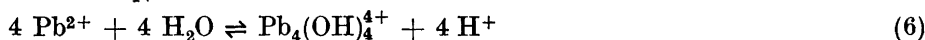
IDENTIFICATION OF THE COMPLEXES FORMED AT $B \geq 0.5$ M

Whereas for $B \leq 0.25$ M the formation of the complex $\text{Pb}_4(\text{OH})_4^{4+}$ can explain the experimental data, additional complexes must be present for $B \geq 0.5$ M at low values of Z . This is indicated by the fact that $(\Delta \log B / \Delta \log h)_Z$ at low Z is no longer 1.33 but tends to diminish with increasing B and that the curves $Z(\log h)_B$ fall off to zero less rapidly than required for " $-(\text{OH})_4$ " complexes.

The values of p and q of the complexes formed at low Z , $\text{Pb}_q(\text{OH})_p^{(2q-p)+}$, can be estimated from the relations $p = -(\Delta \log Z / \Delta \log h)_B$ and $q = (\Delta \log Z / \Delta \log B)_h + 1$, as described in Ref.¹ When the present data for $0 < Z < 0.01$ were treated as described there, they yielded $p = 1$ and $q = 2$. The new complex formed at low Z would then be $\text{Pb}_2\text{OH}^{3+}$. The "integration method" was next applied to all the data and an example of the results is shown in Fig. 2. From this graph we may conclude that the main complexes formed are $\text{Pb}_2\text{OH}^{3+}$ and $\text{Pb}_4(\text{OH})_4^{4+}$. It is thus established that in NaClO_4 , $\text{Mg}(\text{ClO}_4)_2$ and $\text{Ba}(\text{ClO}_4)_2$ medium the main hydrolysis products are the same.

DETERMINATION OF THE EQUILIBRIUM CONSTANTS

From the data with $B \leq 0.25$ M only the equilibrium constant for the formation of $\text{Pb}_4(\text{OH})_4^{4+}$



$$\beta_{4,4} = [\text{Pb}_4(\text{OH})_4^{4+}] h^4 / b^4 \quad (6a)$$

can be determined, since the concentration of $\text{Pb}_2\text{OH}^{3+}$ is so small. The determination of $\beta_{4,4}$ has been made by graphical methods using a "normalized" curve, which can be derived from the two basic equations

$$B = b + 4[\text{Pb}_4(\text{OH})_4^{4+}] \quad (7)$$

$$BZ = h - H = 4[\text{Pb}_4(\text{OH})_4^{4+}] \quad (8)$$

If b is eliminated we obtain

$$X = \log h - 0.25 \log (4\beta_{4,4}B^3) = \log (1-Z) - 0.25 \log Z \quad (9)$$

In position of best fit between the normalized curve $Z(X)$ and the experimental curve $Z(\log h)_B$ the difference between the coordinates on the X - and $\log h$ -axes = $-0.25 \log (4\beta_{4,4}B^3)$ which is used to find $\beta_{4,4}$. The values of $\log \beta_{4,4}$ so obtained are given below.

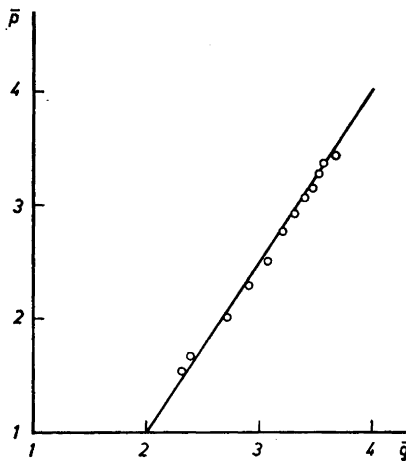


Fig. 2. \bar{p} versus \bar{q} for $B = 1$ M. The straight line passes through (2,1) and (4,4).

$\text{Ba}(\text{ClO}_4)_2$: $\log \beta_{4,4} = -19.16 \pm 0.05$ ($B = 0.05, 0.1$ and 0.25 M)

$\text{Mg}(\text{ClO}_4)_2$: $\log \beta_{4,4} = -18.90 \pm 0.05$ ($B = 0.05$ M)

For $B \geq 0.5$ M the complexes $\text{Pb}_2\text{OH}^{3+}$ and $\text{Pb}_4(\text{OH})_4^{4+}$ have definitely been identified. The determination of the equilibrium constants $\beta_{1,2}$ and $\beta_{4,4}$ was therefore started on the assumption that only these two complexes were formed. The agreement between the calculated and experimental $Z(\log h)_B$ curves will then show if this hypothesis is correct or has to be modified.

A first set of values of $\beta_{1,2}$ and $\beta_{4,4}$ (necessary for further calculations with electronic computer programs) was obtained as follows

$$BZ = \beta_{1,2}b^2h^{-1} + 4\beta_{4,4}b^4h^{-4} \quad (10)$$

In this expression b is approximated with

$$b = B(1-2Z) \text{ for } Z < 0.01 \text{ and } b = B(1-Z) \text{ for } Z > 0.01 \quad (11a), (11b)$$

Inserting these values for b in eqn. (10) and rearranging we obtain for $Z < 0.01$

$$Zh/(1-2Z)^2 = B\beta_{1,2} + 4\beta_{4,4}B^3(1-2Z)^2h^{-3} \quad (12a)$$

and for $Z > 0.01$

$$Zh/(1-Z)^2 = B\beta_{1,2} + 4\beta_{4,4}B^3(1-Z)^2h^{-3} \quad (12b)$$

The plots of eqn. (12a), (12b) for the data with $\text{Mg}(\text{ClO}_4)_2$ medium were straight lines as required by the hypothesis. With $\text{Ba}(\text{ClO}_4)_2$ medium, however, the lines were curved for $Z > (0.1-0.2)$, the actual value of Z being somewhat dependent on the value of B .

The equilibrium constants found from the plots were used as first approximations in the final adjustment of the constants. This adjustment was done by means of the computer program LETAGROP¹⁰. The best set of constants found with this program is that, which makes $\Sigma(Z_{\text{exp}} - Z_{\text{calc}})^2$ a minimum. The following values of the equilibrium constants were obtained for the Z

ranges given in the table. The limits of error given in the $\log \beta$ are three times the standard deviation.

B	$\text{Mg}(\text{ClO}_4)_2$	Z	$\text{Ba}(\text{ClO}_4)_2$	Z
0.5 M	$\log \beta_{1,2} = -6.49 \pm 0.09$	<0.3	-6.30 ± 0.2	<0.26
	$\log \beta_{4,4} = -18.949 \pm 0.003$		-19.12 ± 0.02	
1 M	$\log \beta_{1,2} = -6.57 \pm 0.09$	<0.25	-6.39 ± 0.06	<0.12
	$\log \beta_{4,4} = -18.978 \pm 0.003$		-19.11 ± 0.01	
1.45 M	$\log \beta_{1,2} = -6.45 \pm 0.06$	<0.25	-6.24 ± 0.06	<0.12
	$\log \beta_{4,4} = -19.045 \pm 0.003$		-19.12 ± 0.02	

DISCUSSION

With $B = 1.45$ M the two media are almost identical and we should therefore expect the β also to be the same. The fact that two different sets of β are obtained arises from the principle used in selecting the best values of β , namely to find the values of β which reproduce the experimental Z values over as broad a Z range as possible with the restriction that $|Z_{\text{exp}} - Z_{\text{calc}}|$ should not exceed 0.002 systematically in any part of the range. The standard deviation in Z is less than 0.001 for the data in the table. If the calculations on the $\text{Ba}(\text{ClO}_4)_2$ data are restricted to the range $Z < 0.05$, values of β are obtained which are closer to the β values with $\text{Mg}(\text{ClO}_4)_2$ medium. The same is true of the older data with NaClO_4 medium for $B = 1.49$ M. We should like here to correct the values given in Ref.¹ for $B = 1.49$ M. Calculations with the program LETAGROP give the new values $\log \beta_{1,2} = -6.30 \pm 0.09$ and $\log \beta_{4,4} = -19.19 \pm 0.02$ ($Z < 0.1$). The values of the equilibrium constants must, however, be regarded as a kind of "average" values in the Z range used in the calculations.

With the $\text{Mg}(\text{ClO}_4)_2$ data there is very good agreement between the calculated and experimental data whereas the deviation found with $\text{Ba}(\text{ClO}_4)_2$ would call for additional complexes for the higher values of Z . Let us assume that the activity factors stay constant in a titration and limit the discussion to the titrations with $B = 1.45$ M. The values of the β would then be nearly the same. The differences between the $Z(\log h)$ curves with NaClO_4 and $\text{Ba}(\text{ClO}_4)_2$ and that with $\text{Mg}(\text{ClO}_4)_2$ suggest that the amount of the unknown species with $\text{Ba}(\text{ClO}_4)_2$ would be ca. 10 % and with NaClO_4 ca. 20 % of the total amount of lead hydrolysed. Since there is no evidence of these unknown species in $\text{Mg}(\text{ClO}_4)_2$ one would estimate that the equilibrium constants of the unknown species would be less by a factor of 10 in $\text{Mg}(\text{ClO}_4)_2$ as compared with the other two media. This, however, seems very unlikely from the approximate constancy of the values of the $\beta_{4,4}$ and $\beta_{1,2}$.

The deviations are the larger the larger is the value of B . This would require that the unknown complexes have a ratio $\text{OH}^-/\text{Pb}(\text{II}) < 1$ (Ref.²). Conceivable complexes of this type, e.g. $\text{Pb}_4(\text{OH})_3^{5+}$, have values of t smaller than the

experimental value 1.33. The relative positions of the $Z(\log h)_B$ curves along the $\log h$ axis do not therefore support the hypothesis that additional complexes are formed.

Since the assumption of constant activity factors leads to a contradiction with the experimental results we may conclude that the deviations are due to variations of the activity factors, which at $Z \approx 0.1$ have become so large as to interfere with the interpretation of the data. If mixed complexes between the cation of the medium and Pb^{2+} and OH^- are formed these complexes will, of course, interfere with the interpretation of the data in the self-medium range. It is, however, unlikely that such complexes are formed since $\beta_{4,4}$ is found to be virtually constant despite changes in the medium and in addition the tendency for Ba^{2+} and Mg^{2+} to associate with OH^- is very weak^{11,12}.

The inference on the self-medium method which can be drawn from this work would then be that reliable conclusions can be drawn only from the range where $Z \lesssim 0.05$ with $B > 1$ M. Of course the limit set can claim no general validity but may vary greatly from one system to another as shown by the combination $\text{Pb}(\text{ClO}_4)_2 + \text{Mg}(\text{ClO}_4)_2$, where good results are obtained at least up to $Z = 0.25$.

If "finger-prints" of the complexes could be obtained the question whether new complexes are formed or not could be settled. Unfortunately this does not seem possible at present. The Raman spectra of dilute solutions are not sufficiently intense and good infrared spectra are difficult to obtain because of the strong absorption of the water itself.

The same question again arises when attempts are made to determine the structure of complexes in solution by means of X-ray diffraction. Such studies are made with concentrated solutions and the interpretation of the X-ray data is probably best made by correlating such data with a knowledge of the composition of the complexes, as inferred from emf work.

Acknowledgements. We wish to thank Professor Lars Gunnar Sillén for his continual interest in our work and Dr. Derek Lewis for having corrected the English of this paper. This work has been supported by *Statens Tekniska Forskningsråd (Swedish Technical Research Council)* and by a fellowship granted to one of us (L.P.) by *Svenska Institutet för Kulturellt Utbyte med Utlandet (Swedish Institute for Cultural Relations)*.

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Received November 28, 1961.