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Studies on the Hydrolysis of Metal Ions

28. Application of the Self-medium Method to the Hydrolysis of Lead(II) perchlorate Solution

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The hydrolysis of Pb(II) has been studied at high Pb^{2+} concentrations, B, in order to enhance the relative amounts of species with a $OH^-/Pb(II)$ ratio < 1. The equilibrium solutions measured had the general composition

$$B \text{ M Pb(II)}, H \text{ M } H^+, (3-2B-H) \text{ M } Na^+, 3 \text{ M } ClO_4^-$$

and the hydrolysis was followed to $Z = 0.15$ for $B = 1.490$, 0.990 and 0.500 M. Z is the average number of OH^- groups bound to each Pb(II). If it is assumed that the activity factors stay constant at low Z, the data up to $Z = 0.10$ may be interpreted by the following reactions and equilibrium constants

$$4\,Pb^{2+} + 4H_2O \rightleftharpoons Pb_4(OH)_4^{4+} + 4H^+; \log \beta_{4,4} = -19.25\ (B = 0.50\text{ M}), -19.23\ (B = 0.99\text{ M}), -19.28\ (B = 1.49\text{ M}).$$

$$2Pb^{2+} + H_2O \rightleftharpoons Pb_2OH^{3+} + H^+; \log \beta_{1,2} = -6.45\ (B = 0.50\text{ M}), -6.45\ (B = 0.99\text{ M}), -6.34\ (B = 1.49\text{ M})$$

For higher values of Z deviations appear which may be due either to complexes other than Pb_2OH^{3+} and $Pb_4(OH)^{4+}$ or to variations in the activity factors.

In a previous study [1], where the hydrogen ion concentration and the concentration of Pb^{2+} in hydrolysed lead(II) perchlorate solutions were measured, evidence was presented for the formation of the species $Pb_4(OH)_4^{4+}$, $Pb_3(OH)_4^{2+}$, $Pb_6(OH)_8^{4+}$ and $PbOH^+$. At the highest Pb(II) concentrations then studied (0.080 M and 0.040 M) there were indications of complexes with a $OH^-/Pb(II)$ ratio < 1 at small degrees of hydrolysis. However the concentrations of these complexes were so small that their formulas could not be found. The self-medium method recently used by Hietanen and Sillén [2] in studies on the hydrolysis of Th^{4+} and UO_2^{2+} seemed to be useful for solving the present problem. The concentration of the unknown species could be expected to be favored by a high metal ion concentration.

When we are dealing with complicated equilibria in solution it is desirable to keep the activity factors constant so that concentrations can be used instead of activities in the law of mass action. Usually this is brought about by the addition of a large amount of a neutral salt. This method has been termed the inert medium method. However if only a minor part of the ions in for example a concentrated metal salt solution is converted to other species by complex formation one might hope that the ionic invironment would be but slightly changed and that therefore as a good approximation concentrations could be used instead of activities. Future experience with the method will show how far this approximation can be used. In the following we shall assume that the activity factors stay constant in the Z range studied here.

The more common symbols used are listed below for reference.

B	total concentration of Pb(II)
b	concentration of Pb^{2+}
H	analytical hydrogen ion concentration (often negative)
h	actual hydrogen ion concentration
Z	average number of OH^- groups bound per Pb(II) atom
$\beta_{p,q}$	equilibrium constant for the reaction $q\mathrm{Pb}^{2+} + p\mathrm{H_2O} \rightleftharpoons \mathrm{Pb}_q(\mathrm{OH})_p^{(2q-p)+} + p\mathrm{H}^+$

$y(x)_v$ y as a function of x at constant v

All concentrations are expressed in mole/l (M).

EXPERIMENTAL

Method and apparatus. In the present study we have made a minor alteration in the original method and decided to add $NaClO_4$ to our solutions so that they were always 3 M in ClO_4^-. At the highest total lead(II) concentration studied, 1.490 M, the compositions of the solutions corresponded to the self-medium idea but for the lower values of B the compositions of the solutions approached the inert medium method, but with the restriction that Z was allowed to reach a value of *ca* 0.1 only. The limit set for Z is quite arbitrary. The highest value of Z for which the approximation of constant activity factors may be used, is probably dependent on what species are formed. It may also be dependent on B.

The general composition of the solutions, S, investigated was

B M Pb(II), H M H^+, $(3-2B-H)$ M Na^+, 3 M ClO_4^-

The values of B used were 1.490, 0.990 and 0.500 M. B was kept constant in each run and H was varied by the addition of NaOH. The experiments were carried out as potentiometric titrations in an oil thermostat at 25.0°C. Log h was measured with a calibrated glass electrode using the cell

$$(-)\ \mathrm{ref}\ /\ \mathrm{S}\ /\ \mathrm{glass}\ (+)\quad (\mathrm{I});\ E = E^\circ + 59.15 \log h + E_j \qquad (1)$$

The reference half-cell used was

$$\mathrm{ref} = 3\ \mathrm{M}\ \mathrm{ClO_4^-},\ (3-2B)\ \mathrm{M}\ \mathrm{Na^+},\ B\ \mathrm{M}\ \mathrm{Pb(II)}\ /\ \mathrm{Pb-Hg}$$

The emf of cell (I) was registered on a Radiometer valve potentiometer (PHM4) to ± 0.2 mV.

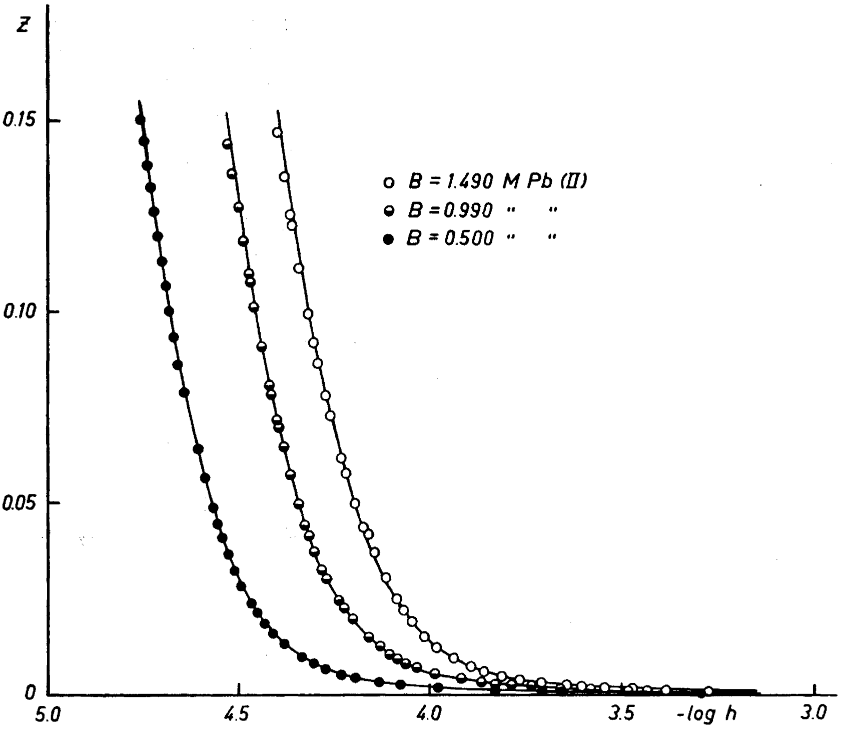

Fig. 1. Z, average number of OH^- bound per Pb(II) atom as a function of log h. Drawn curves have been calculated with the equilibrium constants given in the text.

Experimental details. The liquid junction potential, E_j, in cell (I) was determined in acid solution for $0.005 < h < 0.025$ M by replacing the glass electrode by a lead amalgam electrode. E_j was calculated from the emf's by the procedure described by Biedermann and Sillén[3]. The values thus found could be represented by $E_j = -(18 \pm 3)\ h$. The experimental accuracy did not allow us to determine the coefficient more accurately than this. For the calculations of our experimental quantities, E^0, log h and Z this uncertainty was without importance. The numerical value of the coefficient is reasonable considering the value -16.7 found with 3 M (Na)ClO$_4$.

The starting solution contained B M Pb(II) and *ca.* 0.025 M $HClO_4$ in 3 M (Na)ClO$_4$. Equal volumes of NaOH solution and a solution of $Pb(ClO_4)_2$ of concentration $2B$ in 6 M (Na)ClO$_4$ were added from two burets thus keeping $[Pb(II)] = B$ and $[ClO_4^-] = 3$ M during a run. The first few points for $H > 0.01$ M were used to determine E^0 and the analytical hydrogen ion concentration of the starting solution by a Gran extrapolation[4]. This provided us with a check, since this concentration was also known from the analysis of the stock solutions used to prepare the starting solution.

Two NaOH solutions of different strengths were employed in each titration. The first solution (*ca* 0.15 M) was used to determine E^0 and to study the hydrolysis for $Z < 0.02$. The second base solution (at least 0.75 M) was then introduced and Z followed to 0.15. We had to use such a strong base in order to limit the volume of solution to a reasonable amount. When the strong base was added a large amount of precipitate was formed. On shaking the precipitate immediately dissolved without leaving any residue. At least three titrations were made for each value of B.

Table 1. Corresponding values of $-\log h$ and Z.

○ B = 1.490 M. Run I. $-\log h, Z$ 2.736, 0.0002; 3.274, 0.0009; 3.600, 0.0022; 3.739, 0.0035; 3.808, 0.0048; 3.854, 0.0060; 3.888, 0.0072; 3.933, 0.0094; 3.977, 0.0122; 4.008, 0.0147; 4.050, 0.0194; 4.075, 0.0240; 4.112, 0.0300; 4.158, 0.0416; 4.217, 0.0577; 4.263, 0.0726; 4.290, 0.0864; 4.305, 0.0927; 4.315, 0.0993; 4.341, 0.1095; 4.341, 0.1113; 4.359, 0.1224; 4.364, 0.1254; 4.380. 0.1354; 4.400, 0.1472.

Run II. $-\log h, Z$ 3.382, 0.0012; 3.470, 0.0015; 3.539, 0.0018; 3.637, 0.0025; 3.678, 0.0029; 3.705, 0.0032; 3.771, 0.0042; 3.972, 0.0118; 3.996, 0.0139; 4.010, 0.0154; 4.028, 0.0168; 4.040, 0.0187; 4.057, 0.0204; 4.063, 0.0220; 4.075, 0.0238; 4.079, 0.0253; 4.112, 0.0305; 4.143, 0.0371; 4.172, 0.0435; 4.195, 0.0500; 4.227, 0.0615; 4.256, 0.0721; 4.271, 0.0780.

◒ B = 0.990 M. Run I. $-\log h, Z$ 3.431, 0.0010; 3.654, 0.0017; 3.783, 0.0024; 3.862, 0.0032; 3.915, 0.0039; 3.982, 0.0054; 4.026, 0.0067; 4.060, 0.0080; 4.082, 0.0093; 4.102, 0.0104; 4.126, 0.0126; 4.151, 0.0146; 4.219, 0.0225; 4.268, 0.0300; 4.298, 0.0372; 4.324, 0.0442; 4.364, 0.0573; 4.393, 0.0694; 4.418, 0.0807; 4.440, 0.0910; 4.459, 0.1009; 4.474, 0.1099; 4.488, 0.1183; 4.501, 0.1264.

Run II. $-\log h, Z$ 3.480, 0.0011; 3.578, 0.0014; 3.729, 0.0021; 3.825, 0.0028; 3.952, 0.0046; 3.982, 0.0054; 4.101, 0.0103; 4.156, 0.0151; 4.197, 0.0198; 4.234, 0.0244; 4.282, 0.0332; 4.314, 0.0416; 4.341, 0.0496; 4.363, 0.0572; 4.381, 0.0646; 4.398, 0.0715; 4.413, 0.0782; 4.440, 0.0905; 4.469, 0.1077; 4.496, 0.1273; 4.520, 0.1360; 4.532, 0.1440.

● B = 0.500 M. Run I. $-\log h, Z$ 3.292, 0.0002; 4.129, 0.0030; 4.270, 0.0065; 4.332, 0.0097; 4.380, 0.0128; 4.408, 0.0157; 4.430, 0.0184; 4.449, 0.0211; 4.464, 0.0235; 4.491, 0.0282; 4.510, 0.0324; 4.525, 0.0365; 4.542, 0.0406; 4.566, 0.0485; 4.589, 0.0563; 4.608, 0.0640; 4.642, 0.0788; 4.667, 0.0930; 4.691, 0.1066; 4.711, 0.1197; 4.730, 0.1323; 4.746, 0.1445.

Run II. $-\log h, Z$ 3.653, 0.0006; 3.705, 0.0007; 3.828, 0.0010; 3.977, 0.0016; 4.074, 0.0023; 4.190, 0.0041; 4.229, 0.0051; 4.302, 0.0081; 4.555, 0.0446; 4.659, 0.0859; 4.682, 0.0998; 4.701, 0.1132; 4.721, 0.1260; 4.740, 0.1383; 4.758, 0.1502.

The equilibria were rapidly established. Within 10 min after each addition of base the emf of the glass electrode showed a constant value.

The $NaClO_4$, $HClO_4$ and NaOH solutions used in the present investigation were prepared and analysed as described previously [1].

The $Pb(ClO_4)_2$ solution was prepared by dissolving PbO (Baker, p.a.) in $HClO_4$ (Kebo, p.a.). The following procedure was used. The oxide was first repeatedly washed with distilled water and then dissolved in acid using an excess of the oxide. This gave us a slightly alkaline solution which was left standing for a week in order to precipitate foreign metal ions as the hydroxides. After filtration the solution was analysed to determine the deficit of hydrogen ions, and a calculated amount of $HClO_4$ was added in order to give the solution the analytical composition $Pb(ClO_4)_2$. Upon addition of the acid the solution turned light brown from the presence of tetravalent lead. The PbO_2 was destroyed by adding platinum black and bubbling with H_2 gas for a few hours. The solution so prepared was optically blank (reference H_2O) for $\lambda > 2\,800$ Å. At $\lambda \simeq 2\,800$ Å Pb(II) started to absorb light as indicated by a very rapid increase in the optical density of the solution.

The analysis of the solution was done as described previously [1].

RESULTS AND CONCLUSIONS

The data are presented giving Z as a function of $\log h$ in Fig. 1 and Table 1. Z is the average number of OH^- groups bound per lead(II) atom.

The hydrolysis was followed till Z reached *ca* 0.15. Our basic assumption will be that the activity factors stay constant at low values of Z. However we do not know the value of Z above which this ceases to be true.

We shall start our attempt to interpret the data by comparing the experimental $Z(\log h)_B$ with theoretical curves calculated on the assumption that only one of the complexes $(PbOH^+)_n$ with $n = 1, 2, \ldots$ is formed. From such a comparison we get an idea of how many OH^- groups are present in the complexes formed. The choice of a ratio $OH^-/Pb(II) = 1$ in the complexes is quite arbitrary, but since the number of metal atoms in the complex is less important than the number of OH^- groups in fixing the shape of the $Z(\log h)_B$ curve, a not too large change in this ratio would not alter our conclusions.

The 0.500 M titration fits well the theoretical $Z(\log h)$ curve for $Pb_4(OH)_4^{4+}$ at high values of Z. At lower values of Z the experimental curve is less steep than the theoretical curve. Complexes with $n = 4$ are thus indicated at high Z. At low Z complexes with < 4 OH^- must also be present.

The 0.990 M titration for high values of Z showed agreement with the theoretical $Z(\log h)$ curve for $Pb_3(OH)_3^{3+}$. However if the theoretical and experimental curves were made to fit at high Z values, the experimental curve became steeper than the theoretical curve at intermediate values of Z; this is an impossible result. At low Z the reverse is true. The same statements hold for the 1.490 M titration. From these two titrations we may draw the conclusion that at low Z complexes with < 3 OH^- are formed. It would appear unlikely that both $Pb_3(OH)_3^{3+}$ and $Pb_4(OH)_4^{4+}$ are present simultaneously in comparable amounts. If such were the case the deviations from the theoretical $Z(\log h)_B$ curve for $Pb_4(OH)_4^{4+}$ would have been most pronounced for $B = 0.500$ M, since a lower value fo B favors the formation of $Pb_3(OH)_3^{3+}$ relative to $Pb_4(OH)_4^{4+}$. No evidence for $Pb_3(OH)_3^{3+}$ was found in the previous work with 3 M $(Na)ClO_4$ medium.

It would be very reasonable if $Pb_4(OH)_4^{4+}$ it the main complex formed at high Z. This complex has been shown in a previous work [1] to predominate for lower B values in the Z region now investigated. The position of the $Z(\log h)_B$ curves on the log h axis is also in agreement with the value of $\log \beta_{4,4} = -21.25$ found earlier.

Now we turn to the data for very low Z. Whereas at low Z practically no information can be obtained from a single $Z(\log h)_B$ curve about the number of metal atoms in a complex, we can group the complexes with regard to the number of OH^- groups they contain. Also we are allowed to put $b \simeq B$. Thus we get

$$Z = \Sigma\ \beta_{1,q}\, B^{q-1}h^{-1} + 2\ \Sigma\ \beta_{2,q}B^{q-1}h^{-2} + \ldots p\ \Sigma\ \beta_{p,q}B^{q-1}h^{-p} \qquad (2)$$

If complexes with a certain value of p predominate we find

$$(\partial \log Z/\partial \log h)_B = -p \qquad (3)$$

A plot of log Z *versus* log h should then yield a straight line and p is found from the slope of this line. The presence of complexes with different values of p would give a curved line.

Provided that the changes of the activity factors are not too large on going from one value of B to another, information on the value of q can be found from $(\partial \log Z/\partial \log B)_h$. For the case that complexes with one value only for q are present the difference quotient is equal to $(q-1)$.

Owing to the large value of the formation constant for $Pb_4(OH)_4^{4+}$, as estimated from the upper parts of the $Z(\log h)_B$ curves, the term for this complex in eqn. (2) is small only if $Z < 0.003$. Therefore it is necessary to substract the term for this complex in order to get a reasonably broad range in Z and $\log h$ from which to determine p.

The term for $Pb_4(OH)_4^{4+}$ was calculated with $b = B$ and assuming $\log \beta_{4,4} = -19.25$ which is the value found from the measurements with 3 M (Na)ClO$_4$. The choice is somewhat arbitrary but from the 0.500 M titration a value close to -19.25 was indicated by "curve fitting" against a normalized $Z(\log h)$ curve. The Z corrected for $[Pb_4(OH)_4^{4+}]$ will be denoted by Z_c. The calculations were performed only for $Z < 0.01$. The correction at this value of Z is *ca.* 0.005.

The $\log Z_c(\log h)_B$ plots did not deviate much from linearity, and the best straight lines were drawn through the points. The values of the slopes of these lines $(= -p)$ were, $B = 0.500$ M, $p = 1.1$; $B = 0.990$ M, $p = 1.0$; $B = 1.490$, $p = 1.1$. Since p must be a whole number we may conclude $p = 1$. The average value of $(\Delta \log Z_c/\Delta \log B)_h$ was 1.2. This would indicate $q = 2$.

From the above considerations it seems likely that the complex Pb_2OH^{3+} is formed at low Z. This complex has a ratio $OH^-/Pb(II) = 0.5$ whereas the ratio $OH^-/Pb(II) = 1$ in $Pb_4(OH)_4^{4+}$. The quotient $[Pb_2OH^{3+}]/[Pb_4(OH)_4^{4+}]$ would thus be expected to increase with B keeping Z constant. This is in agreement with the experimental results. The deviation of the experimental curves from the calculated $Z(\log h)_B$ curve for $Pb_4(OH)_4^{4+}$ is most pronounced for $B = 1.490$ M. Since the value of q is uncertain we shall briefly discuss other possibilities. For $q = 1$ we would have $PbOH^+$. This complex cannot predominate at low Z because the deviations from the theoretical curve should then be most pronounced for $B = 0.500$ M. From the value of $\log \beta_{1,1} = -7.9$ obtained with 3 M (Na)ClO$_4$ medium one would also expect the concentration of $PbOH^+$ to be very small. Values of $q > 2$ seem increasingly less likely from the geometry of the complexes. We will thus try to explain our data on the assumption that $Pb_4(OH)_4^{4+}$ and Pb_2OH^{3+} are the only important complexes formed.

Hietanen and Sillén [2] have outlined a method by which two equilibrium constants can be determined by fitting the experimental $Z(\log h)_B$ curves to a family of normalized curves. The shape of each normalized curve is determined by a parameter containing the two equilibrium constants. When the normalized curve has been found which fits the experimental curve best one equilibrium constant is found from the difference between the coordinates on the $\log h$ axes and the other from the parameter. This method has the advantage that it is based on a direct comparison of the experimental $Z(\log h)_B$ with the normalized curves. Therefore its is easier to judge if differences observed between the experimental and normalized curves are reasonable or not.

Now we shall derive the expression for our set of complexes Pb_2OH^{3+} and $Pb_4(OH)_4^{4+}$.

$$B = b + 2\beta_{1,2}b^2h^{-1} + 4\beta_{4,4}b^4h^{-4} \tag{4}$$

$$BZ = \beta_{1,2}b^2h^{-1} + 4\beta_{4,4}b^4h^{-4} \tag{5}$$

It will prove convenient to introduce

$$v = 4B\beta_{1,2}h^{-1} \text{ and } l = \beta_{4,4}/(4B\beta_{1,2}^4) \qquad (6),\ (7)$$

Eliminating b we find

$$Z = v^{-1}(\sqrt{1 + v(1-Z)} - 1)^2 + l(\sqrt{1 + v(1-Z)} - 1)^4 \tag{8}$$

We were not able to express Z as a function of v explicitly. The $Z(-\log v)_l$ curves had to be calculated by successive approximations for each value of l tested. These calculations proved to be very timeconsuming. Therefore it was decided to determine preliminary values of $\beta_{1,1}$ and $\beta_{4,4}$ first. It may be noted, as can be seen directly from eqn. (8), that $Z(\log [h(1-Z)^{-1}])_B$ curves can be normalized explicitly. However we preferred a direct comparison with the experimental $Z(\log h)_B$ data.

Determination of preliminary values of $\beta_{1,2}$ *and* $\beta_{4,4}$. If approximate values of the equlibrium constants are known we can calculate l from eqn. (7). Then we know beforehand for what values of l our family of normalized curves can be expected to fit the experimental curves thus reducing the number of $Z(-\log v)_l$ curves which need to be calculated.

We shall determine the preliminary values of $\beta_{1,2}$ and $\beta_{4,4}$ from a projection map described by Biedermann and Sillén [5] (See also Ref.[6]). The formulas derived in Ref. [5] were used for calculations on systems where a transition from mononuclear to polynuclear complexes takes place. However analogous formulas can be derived for the case in which one polynuclear complex changes to another complex which is also polynuclear. In the present study we have a transition from Pb_2OH^{3+} to $Pb_4(OH)_4^{4+}$.

$$Z = \frac{\beta_{1,2}bh^{-1} + 4\beta_{4,4}b^3h^{-4}}{1 + 2\beta_{1,2}bh^{-1} + 4\beta_{4,4}b^3h^{-4}} \tag{9}$$

The following substitutions are introduced

$$k^3 = 4\beta_{4,4};\quad u = kbh^{-4/3};\quad v = \beta_{1,2}bh^{-1} \qquad (10),\ (11),\ (12)$$

As the coordinates for the experimental data we shall use

$$x = \log B - \log h \tag{13}$$

$$y = \log B - 4/3 \log h \tag{14}$$

and as the corresponding coordinates for the projection map we shall use

$$X = x + \log \beta_{1,2} \tag{13a}$$

$$Y = y + \log k \tag{14a}$$

It is easily verified that

$$X = \log v + \log (1 + 2v + u^3) \tag{15}$$

$$Y = \log u + \log (1 + 2v + u^3) \tag{16}$$

$$Z = \frac{v + u^3}{1 + 2v + u^3} \tag{17}$$

Thus we can calculate $Y(X)_Z$ curves for different values of Z as the parameter. These curves are then fitted to the experimental $y(x)_Z$ curves and the equilibrium constants found from the differences between the coordinates on the axes. Cuts were made at $Z = 0.01$, 0.02, 0.03, 0.04 and 0.05. Since each $Z(\log h)_B$ curve has to be treated independently the $y(x)_Z$ curve degenerates to a single point. The method, in fact, is closely related to that given in Ref [7].

Final adjustment of $\beta_{1,2}$ and $\beta_{4,4}$. With l found from the values of $\beta_{1,2}$ and $\beta_{4,4}$ determined by means of the projection map, normalized curves were calculated. In addition curves were constructed also for values of l somewhat smaller and higher than those obtained from the preliminary $\beta_{1,2}$ and $\beta_{4,4}$.

It was not possible to find constants which could reproduce the data up to $Z = 0.15$ for the two highest values of B. The equilibrium constants given in the table account for the data to 0.001 Z unit or better in the Z range given in the fourth column.

B	$\log \beta_{1,2}$	$\log \beta_{4,4}$	Z
0.500 M	-6.45 ± 0.1	-19.25 ± 0.1	<0.15
0.990 M	-6.45 ± 0.1	-19.23 ± 0.1	<0.12
1.490 M	-6.34 ± 0.1	-19.28 ± 0.1	<0.10

We do not know the reason for the bad agreement at high Z for the two largest values of B. Beside experimental errors as an explanation it may be suggested either that complexes other than Pb_2OH^{3+} and $Pb_4(OH)_4^{4+}$ are also present or that the change in the ionic medium is too large for the activity factors to remain constant. The change of the ionic medium is larger the larger B is and one would expect the variations of the activity factors to show up for $B = 1.490$ M first. On the other hand the relative concentrations of complexes with a $OH^-/Pb(II)$ ratio < 1 increase with B. We have not tried to achieve a better fit by introducing more complexes than those already considered because of the uncertainty of the activity factors.

The values of E^o obtained by putting $h = H$ in eqn. (1) for $0.010 < H < 0.025$ M may be slightly in error. Actually $h = H + [Pb_2OH^{3+}] + 4[Pb_4(OH)_4^{4+}]$. From the equilibrium constants we find that $[Pb_2OH^{3+}]$ would make h somewhat larger than H. $[Pb_4(OH)_4^{4+}]$ is very small and can be neglected. The error in E^o thus introduced is 0.2 mV at most. Practically this error is without importance for our conclusions and would only mean that the $Z(\log h)_B$ curves are slightly displaced along the $\log h$ axis.

Another error is caused by the neglect of the liquid junction potential between the hydrolysed solution and the solution in the reference half-cell. Using Henderson's equation and unpublished conductance data by G. Biedermann E_j was calculated to be *ca* 0.2 mV for the solutions of highest Z. Thus the error introduced by neglecting E_j is small.

The close agreement between the numerical values of the equilibrium constants for the different lead(II) concentrations is intriguing considering the differences in the cat-ionic part of the medium. The reason might be that the ratios of the activity factors in the law of mass action expression for the formation of these complexes stay constant, even though the individual activity factors vary. Hietanen and Sillén [2] have observed that the differences between the numerical values of equilibrium constants which have been determined both with the inert medium method and with the self-medium method are of the order of 0.1 logarithmic unit. This appears to hold also for the formation constant of $Pb_4(OH)_4^{4+}$.

As was mentioned in the introduction previous measurements[1] with 3 M $(Na)ClO_4$ medium indicated the presence of complexes with a $OH^-/Pb(II)$ ratio < 1 at low Z and $B = 0.080$ M and 0.040 M from the fact that the experimental $OH^-/Pb(II)$ ratio was somewhat smaller than 1. The main complex in these solutions was identified as $Pb_4(OH)_4^{4+}$ but the concentrations of the other complexes with a $OH^-/Pb(II)$ ratio < 1 were so small that their formulas could not be found. Assuming $\beta_{1,2}$ to have the same value in 3 M $(Na)ClO_4$ medium as found here the concentration of Pb_2OH^{3+} was calculated from the previously published data. Except for the 0.080 M and 0.040 M titrations at low Z, $[Pb_2OH^{3+}]$ was found to be very small and, for these concentrations, to be consistent with the experimentally found $OH^-/Pb(II)$ ratios.

The formation of complexes of the general composition Me_2OH appears to be quite common. From measurements on hydrolysed $Pb(NO_3)_2$ solutions Pedersen[9] has earlier found evidence for Pb_2OH^{3+}. The value of $\log \beta_{1,2}$ (extrapolated to zero ionic strength) found by him was -7.3. Other metal ions for which hydrolysis data have indicated such complexes include Be^{2+} (Ref.[8]), Cu^{2+} (Ref.[10]), UO_2^{2+} (Ref. [11]), and Th^{4+} (Ref. [2]). For the last three ions the complex only is present in appreciable concentrations for high values of B.

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