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Studies on the Hydrolysis of Metal Ions

31. The Complex Formation between Pb^{2+} and OH^- in $Na^+(OH^-, ClO_4^-)$ Medium

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The complex formation between Pb^{2+} and OH^- has been studied in alkaline solution at 25°C. From measurements on the cell

$$\text{Pb (in Hg)}/\ B\ \text{M Pb(ClO}_4)_2,\ A\ \text{M NaOH},\ (I-A)\ \text{M NaClO}_4/\ \text{ref.}$$

it is concluded that the mononuclear species $Pb(OH)_2$ and $Pb(OH)_3^-$ are formed. No evidence of the species $Pb(OH)_4^{2-}$ was found in the $[OH^-]$ range ($[OH^-] < 0.5$ M) studied. The following values of the equilibrium constants were obtained.

		3 M Na(ClO$_4$)	0.3 M Na(ClO$_4$)
$Pb^{2+} + 2OH^- \rightleftharpoons Pb(OH)_2$	$\log \beta_2$	10.90 ± 0.1	10.34 ± 0.1
$Pb^{2+} + 3OH^- \rightleftharpoons Pb(OH)_3^-$	$\log \beta_3$	13.66 ± 0.05	13.29 ± 0.05

The solubility of lead oxide in alkali has been studied by a number of authors [1–6] and found to be proportional to the concentration of free alkali. The results have been interpreted in terms of the formation of $Pb(OH)_3^-$ as the main leadbearing species in alkaline solution. $HPbO_2^-$ or $PbOOH^-$ is equivalent to $Pb(OH)_3^-$ and these species cannot be distinguished by this type of measurement. In the following we shall write $Pb(OH)_3^-$. — The interpretation is not unequivocal since any species $Pb_n(OH)_{2n+1}^-$ would be compatible with the experimental facts (Leden [7]).

Polarographic measurements have been carried out by Heyrovský [8], Lingane [9] and Goward [10] and their results indicated that $Pb(OH)_2$ and $Pb(OH)_3^-$ are formed. Also from polarographic measurements, Akselrud [11] has suggested that Pb(II) is present as a trinuclear anionic complex in alkaline solution.

Johnson and Kraus [12] have concluded from ultracentrifugation studies that the system is monodisperse and mononuclear. They ascribed to the ion present the formula PbO_2^{2-}. According to Johnson [13] $Pb(OH)_3^-$ would also be in agreement with the experimental data.

The reversibility of the lead amalgam electrode in alkaline solution as shown by Lingane [9] and Goward [10] suggested that the complex formation between Pb^{2+} and OH^- could be studied by the titration technique with a stationary lead amalgam electrode as the indicator electrode. This is the aim of the present work.

SYMBOLS

A	total concentration of OH^-.
a	$[OH^-]$, concentration of free OH^-.
B	total concentration of Pb(II).
b	concentration of Pb^{2+}.
Z	average number of OH^- per Pb(II) in complexes.
η	$\log \frac{B}{b}$
β_n	formation constant of $Pb(OH)_n^{(n-2)-}$ from Pb^{2+} and OH^-.
$^*K_n$	acidity constant of $Pb(OH)_{n-1}^{(n-3)-}$

All concentrations in tables and figures are expressed in M (moles/l), and equilibrium constants are given on the M scale. In the text, however, the more convenient unit mM will be used frequently.

METHOD

The concentration of $Pb^{2+}(b)$ has been measured electrometrically, using a lead amalgam electrode, in a large number of equilibrium solutions(S) which had the analytical composition

$$S = B \text{ M } Pb(ClO_4)_2,\ A \text{ M NaOH},\ (I-A) \text{ M } NaClO_4$$

Since the Pb(II) in alkaline solution is present almost exclusively as uncharged and anionic species, the cationic composition of the solutions S is constant and equal to I M Na^+. In the following we shall, therefore, assume that the variations of the activity factors are so small that activities can be replaced by concentrations in the equations expressing the chemical equilibria in our solutions.

The cell used was

$$-\text{Pb(in Hg)} \ / \ \text{S} \ / \ \text{ref.} + \tag{I}$$

$$E_{Pb} = E^{\circ}_{Pb} - 29.58 \log b - 29.58 \log f_{Pb^{2+}} - E_j \tag{1}$$

the reference half-cell was

$$/I \text{ M } NaClO_4/\ (I - 0.01) \text{ M } Na^+,\ 0.01 \text{ M } Ag^+,\ I \text{ M } ClO^- /\ Ag, AgCl \tag{II}$$

and the salt bridge was of the "Wilhelm" type [14].

Eqn.(1) is the simplest relation between the measured potential and the concentration of one of the lead species in solution. It also offers a simple means of putting the results of the emf measurements on an absolute scale by determining E°_{Pb} in acid solution.

Attempts were made to measure $\log[OH^-]$ in these solutions, but we were unsuccessful in finding a glass electrode which functioned like a hydrogen electrode when $\log [OH^-] > -3$. This failure is not serious since $[OH^-]$ can readily be calculated from the analytical OH^- concentrations and the amalgam data.

The liquid junction potential (Ej) in cell (I) was determined on the assumption that it has the same value as in the cell

$$-Pt/H_2,\ A \text{ M NaOH},\ (I-A) \text{ M } NaClO_4/ \text{ ref } + \tag{III}$$

$$E_H = E^{\circ}_H + 59.15 \log A + 59.15 \log f_{OH^-} - E_j \tag{2}$$

E_j, or rather $(59.15 \log f_{OH^-} - E_j)$ was obtained from the measurements by the method described by Biedermann and Sillén [15]. It was found to be 7.8 $[OH^-]$ mV. This agrees well with the result obtained by Ingri *et al.*[16] who got 8 $[OH^-]$ mV.

The amalgam electrode [17], which consisted of a pool on the bottom of the titration vessel, was quite slow in attaining its equilibrium value. We had to wait 0.5 to 1 h after each addition before a constant reading was obtained.

Chemicals. The chemicals used in this work were prepared and analysed as described previously [17].

PRELIMINARY EXPERIMENTS

Since previous work on the behaviour of Pb(II) in alkaline solution indicated that the main lead-bearing species is mononuclear with a charge of —1, some preliminary measurements were carried out in order to verify these results.

Measurements at constant a and varying B. These measurements were carried out at $a = (A—3B) = 0.25$ M and B was varied between 0.1 and 10 mM. The results were plotted as $\log B(\log b)$. The plot was linear with a slope close to unity, which shows that the complexes are mononuclear.

Measurements at constant B and varying a. These measurements were made with the values of $B = 0.2$ and 0.5 mM and $0.1 < [OH^-] < 0.5$ M. The results were plotted as $\eta(\log(A—2B))$. The actual OH^- concentration is unknown, but it is reasonable to assume at least two OH^- groups attached to a Pb(II). The use of a high ligand concentration and low metal ion concentrations makes $(A—2B)$ a good approximation for a. The experimental data when plotted as described fell on a single straight line of slope $\simeq 3$.

The concentration of Pb^{2+} in these solutions is very small and we therefore have

$$B = \Sigma\beta_n b a^n; \quad \eta = \log \Sigma\beta_n a^n \tag{3) (3a}$$

and from (3a)

$$\frac{d\eta}{d \log a} = \frac{\Sigma n\beta_n a^n}{\Sigma\beta_n a^n} = Z \tag{4}$$

The invariance of the difference quotient $\Delta\eta/\Delta\log a$ with a suggest the presence of only one complex and with $Z = 3$. The preliminary measurements thus show that $Pb(OH)_3^-$ is formed as the main species in strongly alkaline solution.

A numerical calculation on the data, however, showed that they were not entirely satisfactory. $\Delta\eta/\Delta\log a$ was found to reach a maximum value of $\simeq 2.97$ and then it started to decrease and reached the value 2.9 at $[OH^-] = 0.5$ M. This would contradict the law of mass action and we began to search for the cause of this behavior. The measurements had been carried out in unprotected glass vessels and dissolution of silica was therefore suspected to occur. A titration carried out in a vessel covered with paraffin gave, however, the same results. The constancy of the amalgam potential for long periods of time would also indicate that no dissolution occurs (see also Ref.[18]).

Contamination of the alkali from the polyethylene bottles used to store the alkali was next considered. Titrations with alkali which had been stored in bottles covered with paraffin gave the same results. A very large contamination of the alkali by carbonate could also be responsible for the observed effect, but this is unlikely since tests with Ba^{2+} gave no precipitate of $BaCO_3$. A titration with alkali to which Na_2CO_3 has been added to give a OH^-/CO_3^{2-} ratio = 10 gave the same results as the other titrations. We were thus unable to find a simple explanation in terms of faulty experimental technique, for this apparent contradiction of the law of mass action as applied by us and we have been led to the conclusion that deviations in the activity factors occur when the ionic medium is changed considerably.

FINAL EXPERIMENTS

The equilibrium solutions were prepared by a titration technique. Usually the experiments were started from an acid solution of the following composition

$$B \text{ M } Pb(ClO_4)_2, \; H \text{ M } HClO_4, \; I \text{ M } NaClO_4$$

To the starting solution, 50 ml by volume, equal volumes of solution from two burets were added. One buret contained an A M NaOH solution and the other contained a solution of composition $2B$ M $Pb(ClO_4)_2$, $(2I—A)$ M $NaClO_4$. Thus the concentrations of Pb(II) $= B$ and of $Na^+ = I$ M were maintained constant during a run.

In order to ensure a broad range in $[OH^-]$ we always attempted to start with an OH^- concentration close to the solubility limit of $Pb(OH)_2$, although no particular care was taken to be very close to it. The solubility data by Garrett, Vellenga and Fontana [6] were used as a guidance. No troubles were experienced on passing from the acid to the alkaline range from the intermediate formation of lead hydroxide. The precipitate dissolved rapidly and completely in the excess alkali.

Titrations were frequently made on alkaline starting solutions prepared a couple of days before an experiment was performed in order to see if there was any difference between fresh and aged alkaline solutions. The results from these titrations did not differ from the other titrations. As a further check on the reversibility of the equilibria, back-titrations were made. The initial solution was made strongly alkaline and acid was added. These titrations gave the same results as the preceding ones. It is therefore likely that true equilibria were measured.

RESULTS WITH 3 M $Na(ClO_4)$ AS MEDIUM

With 3 M $Na(ClO_4)$ as medium the following total Pb(II) concentrations were used; $B = 10, 5, 2.5, 1, 0.5$ and 0.25 mM. Since log $[OH^-]$ was not measured it had to be calculated. Hedström [19] has given formulas which allow the calculation of the free ligand concentration from a knowledge of the total ligand concentration and the free metal ion concentration only. The preliminary measurements had shown that the complexes formed were mononuclear and moreover the concentration of free ligand is large compared to B. In our case, therefore, the method developed by Leden [20] easily leads to the goal. With our notations we have

$$\frac{\partial \eta}{\partial \log a} = Z \tag{4}$$

$$a = A—BZ \tag{5}$$

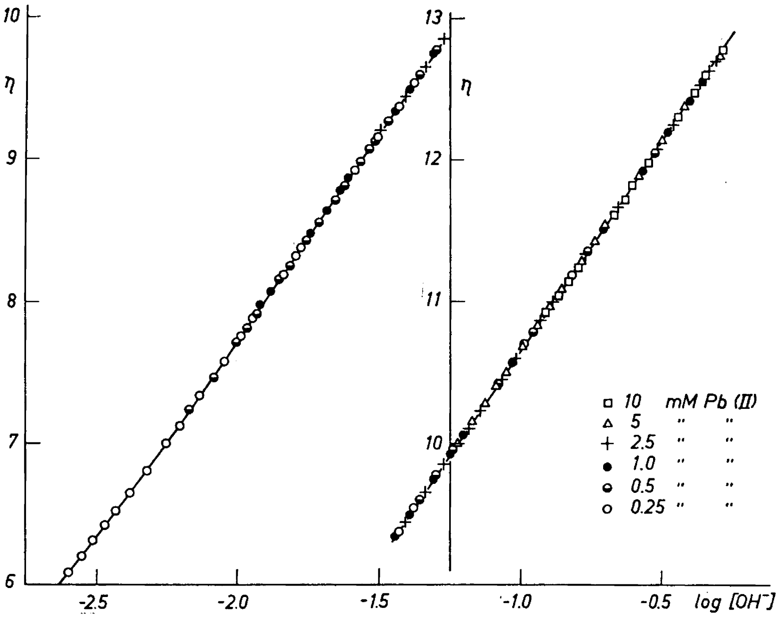

Fig. 1. $\eta = \log [\mathrm{Pb(II)}]_{\mathrm{tot}}/[\mathrm{Pb}^{2+}]$ as a function of $\log[\mathrm{OH}^-]$. The solid line is calculated with $\log \beta_2 = 10.9$ and $\log \beta_3 = 13.66$.

Neighbouring points were used to find $\Delta\eta/\Delta\log a$ and as a first estimate of a, $(A—3B)$ was used. The successive approximations were repeated till the third place in $\log a$ did not change on a further calculation.

The η values at low B and $[\mathrm{OH}^-]$ have been corrected for the presence of small amounts of PbOH^+ and $\mathrm{Pb}_3(\mathrm{OH})_4^{2+}$, which still persist in these solutions [17]. The data plotted as $\eta(\log [\mathrm{OH}^-])$ fall on a single curve as can be seen from Fig. 1.

Determination of the equilibrium constants. The mononuclear complexes present are most likely to be only $\mathrm{Pb(OH)}_3^-$ and $\mathrm{Pb(OH)}_2$, whereas $\mathrm{Pb(OH)}_4^{2-}$ and higher complexes cannot be present in larger amounts since Z never exceeds 3. We have

$$B = \beta_2 b a^2 + \beta_3 b a^3 + \beta_4 b a^4 + \text{———} \qquad (6)$$

$$B a^{-2} b^{-1} = \beta_2 + \beta_3 a + \beta_4 a^2 + \text{———} \qquad (7)$$

By plotting $Ba^{-2}b^{-1}$ as a function of a, β_2 is found from the intercept on the $Ba^{-2}b^{-1}$ axis and β_3 from the slope of the straight line which should be obtained if the hypothesis is valid. The presence of $\mathrm{Pb(OH)}_4^{2-}$ *etc.* should make the line bend upwards at high a. The plot is shown in Fig. 2.

It is obvious that the data can not be fitted to a straight line over the whole $\log[\mathrm{OH}^-]$ studied. This leads to a certain ambiguity when fitting the data to

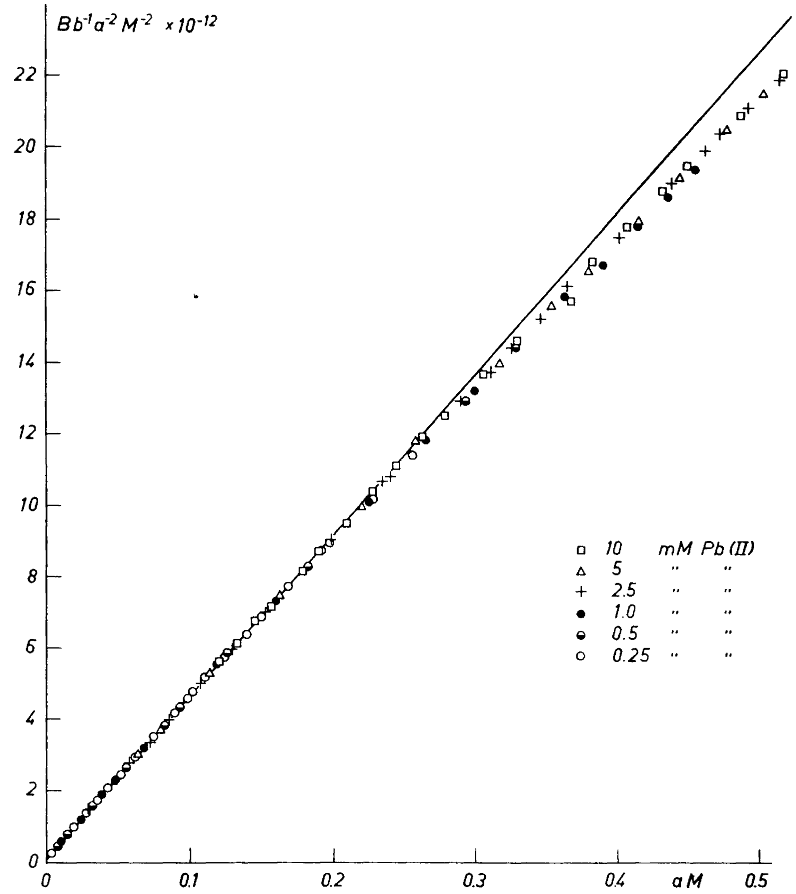

Fig. 2. $[Pb(II)]_{tot}/([Pb^{2+}][OH]^2)$ as a function of $[OH^-]$. The straight line gives $\log \beta_2 = 10.9$ and $\log \beta_3 = 13.65$.

the best straight line. Two such lines have been drawn. The first line was drawn so as to fit all the data for $[OH^-] < 0.2$ M best (Fig. 2). For $[OH^-] > 0.2$ M the deviations from linearity are so large that these data can not be used for the determination of the equilibrium constants. The values of the constants obtained from the line were

$$\log\beta_2 = 10.9 \pm 0.1$$

$$\log\beta_3 = 13.65 \pm 0.05$$

The deviations are in a direction opposite to that expected for the formation of $Pb(OH)_4^{2-}$. A tentative explanation could be variations in the activity factors when the composition of the medium has been changed considerably.

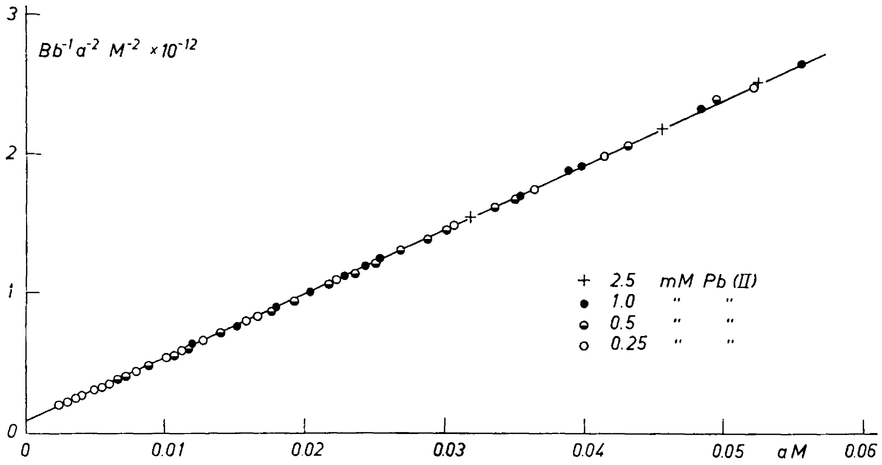

Fig. 3. $[Pb(II)]_{tot}/([Pb^{2+}][OH^-]^2)$ as a function of $[OH^-]$. The straight line gives $\log \beta_2 = 10.9$ and $\log \beta_3 = 13.66$.

This would suggest that the data at low $[OH^-]$ give better values of the equilibrium constants. A straight line drawn through the points for $[OH^-] < 0.05$ M (Fig. 3) gave

$$\log\beta_2 = 10.9 \pm 0.1$$

$$\log\beta_3 = 13.66 \pm 0.05$$

The deviations at large $[OH^-]$ are somewhat surprising in view of the measurements of Garrett, Vellenga and Fontana[6]. They determined the equilibrium constant for the reaction

$$PbO\ (s) + OH^- \rightleftharpoons Pb(OH)_3^-$$

$$K = \frac{[Pb(OH)_3^-]}{[OH^-]} \tag{8}$$

and calculated K by inserting analytical concentrations in (8). For $[OH^-] < 1$ M, K did not vary systematically with $[OH^-]$ and this would indicate that $f_{Pb(OH)_3^-}/f_{OH^-}$ is close to unity. We have calculated the activity factor ratio by combining the measurements from the cells (I) and (III). The variation in the water activity is very small and is neglected.

From eqn. (2) we obtain

$$E_H - E_H^0 - 59.15\log a = 59.15\log f_{OH^-} - E_j = -7.8\,a \tag{2a}$$

and substituting $bf_{Pb^{2+}}$ from

$$\beta_3 = \frac{[Pb(OH)_3^-]}{ba^3} \frac{f_{Pb(OH)_3^-}}{f_{Pb^{2+}}f^3_{OH^-}} \tag{9}$$

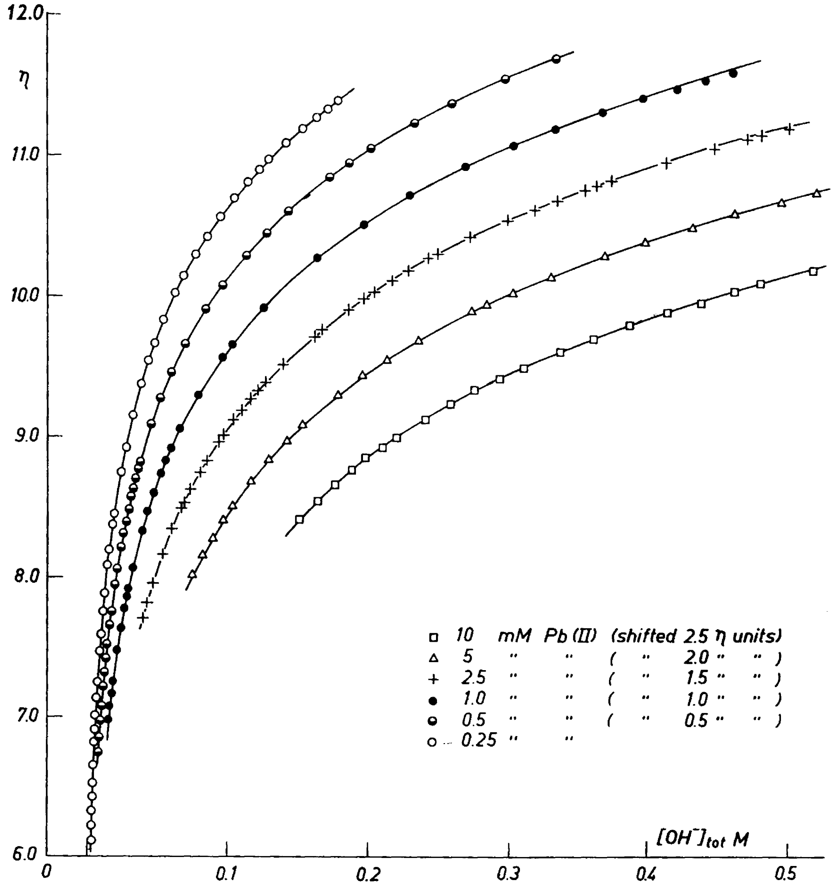

Fig. 4. η as a function of $[\mathrm{OH}^-]_{\mathrm{tot}}$. The solid lines are calculated using log β_2 = 10.9 and log β_3 = 13.66.

in eqn. (1) and putting $a = (A - 3B)$ and $[\mathrm{Pb(OH)}_3^-] = B$ we get

$$\log f_{\mathrm{OH}^-}/f_{\mathrm{Pb(OH)}_3^-} = (E_{\mathrm{Pb}} - E^{\mathrm{O}}_{\mathrm{Pb}})/29.58 + \log B - \log\beta_3 - $$
$$- 3 \log (A - 3B) + 7.8\,(A - 3B)/29.58 \qquad (10)$$

The expression is valid for $[\mathrm{OH}^-] > 0.2$ M where $[\mathrm{Pb(OH)}_2]$ can be neglected. $f_{\mathrm{OH}^-}/f_{\mathrm{Pb(OH)}_3^-}$ was found to decrease from unity to $\simeq$ 0.93 at 0.5 M OH^-.

If the assumption of constant activity factors is still upheld the result would have to be explained in terms of incomplete dissociation of NaOH. It would, however, be necessary to assume that "$(\mathrm{OH})_2^{2-}$" complexes are formed. The formation of NaOH although leading to a $f_{\mathrm{OH}^-}/f_{\mathrm{Pb(OH)}_3^-}$ ratio different from unity, would not give a ratio varying with $[\mathrm{OH}^-]$.

The previous measurements [17] on the hydrolysis of Pb(II) in acid and neutral solution had been discontinued at $\log h \simeq -8.5$ when a precipitate of basic lead perchlorates started to form. Thus there is a gap between the old and the new sets of data of *ca.* 3 log$h$ units. We have tried to fill this gap by measurements with $B = 0.1$, 0.2 and 0.4 mM in 0.3 M $\mathrm{Na(ClO_4)}$. We were, however, unsuccessful and could not obtain stable potentials when $\log[\mathrm{OH^-}] < -3$. In more alkaline solutions the potentials were stable and yielded the following values of the equilibrium constants.

$$\log\beta_2 = 10.34 \pm 0.1$$
$$\log\beta_3 = 13.29 \pm 0.05$$

In order to show the agreement between the experimental data and the values calculated from the equilibrium constants given, Fig. 4 was constructed. Note that the $\eta(A)_B$ curves have been successively displaced by 0.5 η unit in order to increase the clarity of the figure.

DISCUSSION

With the exception of Akselrud's work, all investigations on the behavior of Pb(II) in alkaline solution point to the formation of $\mathrm{Pb(OH)_2}$ and $\mathrm{Pb(OH)_3^-}$. The table gives the values of $\log\beta_2$ and $\log\beta_3$ found in the literature.

			$\log\beta_2$	$\log\beta_3$
Heyrovský [8]	var. NaOH		———	12.15
Lingane [9]	var. NaOH	25°C	———	12.9
Goward [10]	1 M $\mathrm{KNO_3}$	25°C	10.77	13.31
This work	3 M $\mathrm{NaClO_4}$	25°C	10.90	13.66
This work	0.3 M $\mathrm{NaClO_4}$	25°C	10.34	13.29

From solubility measurements we may calculate

$$K_3 = \frac{[\mathrm{Pb(OH)_3^-}]}{[\mathrm{Pb(OH)_2}]\,[\mathrm{OH^-}]} = \frac{\beta_3}{\beta_2} \qquad (11)$$

and find from the data by Garrett, Vellenga and Fontana [6] $\log K_3 = 2.86$ for the yellow oxide and 3.06 for the red oxide. Our value of $\log K_3$ is 2.76 (3 M $\mathrm{NaClO_4}$) and 2.95 (0.3 M $\mathrm{NaClO_4}$).

Considering that the constants have been obtained under different experimental conditions the agreement between the numerical values may be considered satisfactory.

Published values of the solubility product of lead oxide vary considerably [22]. The highest value of $\log K_{s0}$ is -13.96 and the smallest value is -19.96. From our value of β_2 in 3 M $\mathrm{Na(ClO_4)}$ and the solubility of $\mathrm{Pb(OH)_{2(aq)}}$ ($1 \cdot 10^{-4}$ M for the yellow oxide and $4 \cdot 10^{-5}$ for the red oxide[6]) we may estimate $\log K_{s0} \simeq -14.9$ and -15.3. This agrees fairly well with the value of $\log K_{s0} = -15.04$ and -15.23 found by Applebey and Reid [3] from measurements of the cell Pb, PbO/1 M NaOH/ HgO, Hg.

From the β values and the ionic product of water ($\log K_w = -14.22$ in 3 M $\mathrm{NaClO_4}$ (Ingri *et al.*[15]) and $\log K_w = -13.76$ in 0.3 M $\mathrm{NaClO_4}$ (determined by us) we find the following values of the acidity constants of $\mathrm{Pb^{2+}}$.

	3 M $NaClO_4$	0.3 M $NaClO_4$
$\log {}^*K_1$	-7.9	-7.8
$\log {}^*K_2$	-9.6	-9.4
$\log {}^*K_3$	-11.5	-10.8

The regular sequence of the $\log {}^*K_n$ values shows an interesting break after $\log {}^*K_3$. The value of $\log {}^*K_4$ must be much smaller than expected from the sequence. The ratio between the successive acidity constants of Pb^{2+} ($10^{-1.4}$ to $10^{-1.9}$) is considerably larger than for hydroxide acids (such as H_3PO_4), where the ratio is around 10^{-5}, but smaller than found for other metal ions. For a large number of metal ions $\log {}^*K_1$ and $\log {}^*K_2$ have about the same value (Sillén [21]).

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