

Studies on the Hydrolysis of Metal Ions

25. The Hydrolysis of Lead(II) in Perchlorate Medium

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The hydrolysis of lead(II) has been studied at 25°C by the inert medium method using 3 M or 0.3 M (Na)ClO₄ and the cells

— Pb-Hg / S / ref. +
— glass / S / ref. +

S had the general composition

B M Pb(II), *H* M H⁺, (*I* - 2*B* - *H*) M Na⁺, *I* M ClO₄⁻

The experimental data *Z* (average number of OH⁻ bound per lead (II)) and *η* (log [Pb(II)]_{tot} / [Pb²⁺]_{free}) as functions of log *h* can be explained by the following reactions and equilibrium constants.

Equilibrium constants

		3 M (Na)ClO ₄	0.3 M (Na)ClO ₄
Pb ²⁺ + H ₂ O ⇌ PbOH ⁺ + H ⁺	log β ₁₁	- 7.9 ± 0.1	- 7.8 ± 0.1
4Pb ²⁺ + 4H ₂ O ⇌ Pb ₄ (OH) ₄ ⁴⁺ + 4H ⁺	log β _{4,4}	- 19.25 ± 0.1	- 19.90 ± 0.1
3Pb ²⁺ + 4H ₂ O ⇌ Pb ₃ (OH) ₄ ³⁺ + 4H ⁺	log β _{4,3}	- 22.87 ± 0.1	- 23.35 ± 0.1
6Pb ²⁺ + 8H ₂ O ⇌ Pb ₆ (OH) ₈ ⁴⁺ + 8H ⁺	log β _{8,6}	- 42.14 ± 0.1	- 42.66 ± 0.1

SURVEY OF PREVIOUS WORK

The two most complete investigations on the hydrolysis of Pb(II) hitherto published are those of Pedersen¹ and Faucherre². Pedersen carried out potentiometric titrations of Pb(NO₃)₂ solutions to which NaOH was added and log *h* followed with a glass electrode. The experimental data could be explained by the formation of the complexes Pb₂OH³⁺, PbOH⁺ and Pb₄(OH)₄⁴⁺. However, the nitrate is not very suitable for this type of investigation since the basic lead nitrates have so low solubility that only one percent of the total Pb(II) was hydrolysed before precipitation started.

This led Faucherre to study lead(II) perchlorate solutions instead, which allow the addition of 4/3 OH⁻ per Pb(II) before precipitation starts. Potentiometric titrations, where NaOH was added and log *h* followed with a glass

electrode, were interpreted as follows. In solutions where less than one OH^- per lead(II) had been added the complex $\text{Pb}_4(\text{OH})_4^{4+}$ was formed. On further addition of alkali the complex $\text{Pb}_9(\text{OH})_{12}^{6+}$ started to form. When $4/3 \text{ OH}^-$ per lead(II) had been added precipitation started. Spectrophotometric and cryoscopic measurements on solutions containing less than one OH^- per lead(II) indicated the complex $\text{Pb}_4(\text{OH})_4^{4+}$ also. Faucherre followed the change in $\log h$ of $\text{Pb}(\text{NO}_3)_2$ solutions upon dilution. These measurements also indicated the complex $\text{Pb}_4(\text{OH})_4^{4+}$. In addition PbOH^+ was indicated in dilute solutions.

Most of the other previous works on the hydrolysis of Pb(II) have been done with so called pure salt solutions, notably with solutions of $\text{Pb}(\text{NO}_3)_2$. Kullgren ³ measured the acidity of $\text{Pb}(\text{NO}_3)_2$ kinetically at 100°C and 85.5°C . He could explain his data by the reaction $\text{Pb}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{PbOH}^+ + \text{H}^+$ ($\beta_{11} = 1.02 \times 10^{-6}$). Denham and Marris ⁴ measured the acidity of $\text{Pb}(\text{NO}_3)_2$ and PbCl_2 solutions with the quinhydrone electrode but did not attempt to explain their findings in terms of a hydrolysis reaction. Cranston and Brown ⁵ made similar experiments with the glass electrode and assuming only the first mononuclear step, calculated from their data $\beta_{11} = 1.7 \times 10^{-8}$ at 15°C and from the earlier data by Denham and Marris $\beta_{11} = 3.8 \times 10^{-8}$ at 25°C . Guiter ⁶ followed colorimetrically the change of $\log h$ in a $\text{Pb}(\text{NO}_3)_2$ solution on dilution. He suggested that the ions $\text{Pb}_2(\text{OH})_2^{2+}$, PbOH^+ and their nitrate complexes were formed, but apparently some of his results contradict the law of mass action.

Reiff and Müller ⁷ suggested the complex $\text{Pb}_2(\text{OH})_2^{2+}$. Their measurements of the concentration of Pb^{2+} by lead amalgam in solutions of analytical composition PbOHClO_4 showed that $[\text{Pb}^{2+}]$ was not negligibly small. Therefore they suggested that the complex was partly dissociated to Pb^{2+} , PbOH^+ and $\text{Pb}(\text{OH})_2$. From a study of the solubility of $\text{Pb}(\text{IO}_3)_2$ in HClO_4 - NaClO_4 mixtures and PbO in HClO_4 , Misra and Pani ⁸ and Pattanaik and Pani ⁹ claimed the existence of PbOH^+ . They interpreted the increase of the solubility of the iodate with increasing acidity as due to the formation of PbOH^+ which contradicts the law of mass action; a more reasonable explanation is the formation of undissociated iodic acid. See also Ref. ¹⁰ where the increase of the solubility of $\text{Cu}(\text{IO}_3)_2$ with acidity was used to determine the dissociation constant for iodic acid. The fact that they were able to dissolve PbO in HClO_4 in a 1:1 ratio is not very convincing evidence for the formation of PbOH^+ since any species $(\text{PbOH}^+)_n$ would give the same result. The formation of PbOH^+ and $\text{Pb}(\text{OH})_2$ has been suggested by Goward ¹¹ from polarographic measurements.

Finally we might cite a report on ultracentrifuge work on lead perchlorate solutions by Johnson and Kraus ¹². "Preliminary ultracentrifugation studies of Pb(II) in perchlorate solution indicate that low-molecular weight polymers are formed in the range of hydrolysis studied, between hydroxyl numbers (n) about 0.5 and 1.4. Interpretation by a simple monomer-tetramer equilibrium does not seem adequate, however, since degrees of polymerization higher than 4 are found for $n = 1.4$. Near $n = 1$ the weight average degree of polymerization is about 4, but existence of a predominant tetrameric species has not yet been established".

From the above survey we might conclude that there is good evidence for the complexes PbOH^+ and $\text{Pb}_4(\text{OH})_4^{4+}$ but comparatively little quantitative work has been done on solutions with a $\text{OH}^-/\text{Pb(II)}$ ratio > 1 . The electro-metric measurements have been done almost exclusively with $\log h$ -sensitive electrodes. It was therefore considered worthwhile to reinvestigate the hydrolysis of Pb(II) in perchlorate solution using both the glass electrode and the amalgam electrode.

SYMBOLS

The commoner symbols used in the text are defined below for reference.

- B total Pb(II) concentration
 b concentration of Pb^{2+}
 H analytical hydrogen ion concentration
 h actual hydrogen ion concentration
 Z average number of hydrogen ions split off by one Pb(II)
 ν average number of OH^- groups bound to one Pb(II) in a complex (5)
 η $\log B/b$
 $\beta_{p,q}$ formation constant of $\text{Pb}_q(\text{OH})_p^{(2q-p)+}$ from Pb^{2+} and H_2O .
 $q \text{ Pb}^{2+} + p \text{ H}_2\text{O} \rightleftharpoons \text{Pb}_q(\text{OH})_p^{(2q-p)+} + p \text{ H}^+$
 $BZ = h - H = \sum p \beta_{p,q} b^q h^{-p}$
 $10\eta = 1 + \sum q \beta_{p,q} b^{q-1} h^{-p}$
 $y(x)$, y as a function of x at constant ν

Other symbols used are defined where they appear in the text. 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.

In the following we shall describe in detail only the experiments done with $3 M$ $(\text{Na})\text{ClO}_4$ as medium and their interpretation. The interpretation of the data with $0.3 M$ $(\text{Na})\text{ClO}_4$ will be discussed briefly at the end of the chapter dealing with the calculations on the $3 M$ $(\text{Na})\text{ClO}_4$ data.

METHOD OF INVESTIGATION

The experiments have been carried out as potentiometric titrations. The analytical hydrogen ion concentration of lead(II) perchlorate solutions with $3 M$ $(\text{Na})\text{ClO}_4$ as the ionic medium was varied by adding sodium hydroxide or perchloric acid. The total lead concentration, B , was kept constant in each run and the hydrogen ion concentration, h , and the concentration of Pb^{2+} , b , were measured with the cells

— glass/equilibrium solution/ ref. + (I)

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

— Pb-Hg/equilibrium solution/ ref. + (II)

$$E = E_{am}^\circ - 29.58 \log b - E_i \quad (2)$$

Eqns. (1) and (2) have been written on the assumption that the activity factors keep constant so that they may be included as constants in the E° 's. However, this is only approximately correct since E_{am}° is not independent of the total lead concentration, B , for B larger than 10 mM. The change in E_{am}° when b was lowered from 80 mM to 5 mM was -0.3 mV but from 5 mM down to 0.5 mM no further change in E_{am}° was observed. No similar trend in E_g° was noted. This may be due to the fact that E_g° cannot be determined with sufficient accuracy (± 0.2 mV). A thorough investigation of these changes in the activity factors has been omitted deliberately since such an investigation by G. Biedermann is now under way at this Institute.

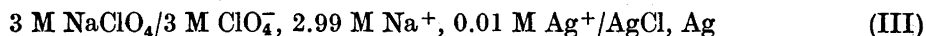
The composition of the solutions measured can be written

$$[\text{Pb(II)}] = B \text{ M}, [\text{H}^+] = H \text{ M}, [\text{Na}^+] = (3 - 2B - H) \text{ M}, [\text{ClO}_4^-] = 3 \text{ M}$$

where H is the analytical hydrogen ion concentration. In the present case H is usually a negative number, so that the solutions are deficient in hydrogen ions.

A p p a r a t u s

The measurements were performed in an oil thermostat at $25^{\circ} \pm 0.1^{\circ}\text{C}$ using the salt bridge described by Forsling, Hietanen and Sillén¹³. The reference half-cell was



Much trouble was experienced before we found a glass electrode which could be used without too large corrections in the $\log h$ range (-2 to -8.5) studied. The glass electrodes were tested against the hydrogen electrode in a series of buffers made up by gradually adding NaOH in 3 M NaClO₄ to a solution, S, containing 0.005 M HClO₄, 0.005 M HAc, 0.005 M H₃PO₄, 0.005 M H₃BO₃, 3 M NaClO₄. The emfs of the cells

$$- \text{Pt}/\text{H}_2/\text{S}/\text{ref} + (E_H) \quad (\text{IV})$$

$$- \text{glass}/\text{S}/\text{ref} + (E_g) \quad (\text{V})$$

were measured. Actually the glass and H₂ electrodes were kept in the same solution. The difference $\Delta E = E_H - E_g$ was thus obtained for different $\log h$ values, which were calculated from E_g and eqn. (1) using an E_g° determined with mixtures of HClO₄ and 3 M (Na)ClO₄. The glass electrode finally selected for the measurements was a Beckman electrode (No. 1190-808) which gave a constant ΔE down to $\log h \simeq -7.5$, thus behaving like a hydrogen electrode. From $\log h \simeq -7.5$ to -8.5 ΔE gradually increased and the corresponding change in ΔE was applied as a correction to the glass electrode. The largest correction (at $\log h = -8.5$) was $+ 0.5$ mV.

The emf of cell (I) was recorded to ± 0.2 mV on a Radiometer valve potentiometer (PHM4). The amalgam emf was measured to ± 0.01 mV by a Cambridge potentiometer.

Experimental details of the emf measurements and titration procedure

The liquid junction potential, E_j , and an estimate of the beginning of the hydrolysis of Pb(II) was obtained in a titration, where standard NaOH was added to a solution containing 10 mM Pb²⁺ and 100 mM HClO₄ in 3 M (Na)ClO₄. Treating the data as an ordinary acid-base titration using Gran's extrapolation method¹⁴ a straight line was obtained almost the whole way down to the equivalence point. This indicates that the hydrolysis of Pb(II) at moderate concentrations is small until an excess of OH⁻ has been added.

The amalgam and glass electrode potentials were also used to determine E_j by the procedure described by Biedermann and Sillén¹⁵. The results obtained were in complete agreement with their findings and E_j has been calculated as $-16.7 h$ mV in subsequent titrations.

E_g^o and E_{am}^o were determined from the potentials in acid solution inserting the analytical concentrations for h and b in eqns. (1) and (2), which is permissible since the hydrolysis is negligible for $H > 2$ mM. For $B > 5$ mM the titrations were started from $H \simeq 20$ mM and the E^o 's calculated from the first points of each titration. This procedure becomes less satisfactory for lower values of B since then most of the alkali added is consumed to neutralize the acid added for the determination of the E^o 's, which is undesirable when Z is to be determined accurately. When B was 5 mM or less the titration was started from the H⁺ concentration ($\simeq 0.3 B$) associated with the lead perchlorate stock solution, NaOH gradually added and the hydrolysis followed till precipitation started. Afterwards a strong perchloric acid solution was introduced to give H values between 5 and 20 mM and E_g^o and E_{am}^o determined from the potentials. In one of the 2.5 mM titrations both methods were used as a check. The values for E_g^o agreed to ± 0.1 mV and those for E_{am}^o to ± 0.05 mV which is as good as can be expected.

In general after each addition of alkali the glass and amalgam emfs took about 20 min to attain a constant value. The time increased somewhat as the degree of hydrolysis increased. Also it was somewhat longer at the lowest B (1.25 mM) measured. A local excess of OH⁻ could not be avoided upon addition of the alkali and a precipitate was formed. The precipitate dissolved rapidly and completely at the beginning of a run but in the most hydrolysed solutions small amounts remained undissolved. This small residue apparently dissolved very slowly, since the potentials remained constant. It may consist of basic lead carbonates formed from the inevitable carbonate content (*ca.* 0.1 % of total OH⁻) of the sodium hydroxide.

In general, the titrations had to be discontinued when Z had reached $\simeq 1.3$ since the solutions became permanently turbid owing to the precipitate of basic lead perchlorates. In the 80 and 40 mM titrations, where rather strong alkali had to be used, the amount of precipitate formed was appreciable when Z had reached 1 and the hydrolysis could not be followed further. The lowest B value that could be used satisfactorily was 1.25 mM. When 0.625 mM was tried reproducible values could not be obtained. When the same lead solution was titrated with the same alkali different results were obtained on different

days. The nonreproducibility occurred with 0.625 mM Pb(II) only and in hydrolysed solution. In acid solution the agreement between different titrations was still good.

The measurements on $B = 0.625$ mM revealed an impurity in the sodium perchlorate. When the very weak NaOH solution used for this titration was standardized potentiometrically against HClO_4 , both solutions containing 3 M $(\text{Na})\text{ClO}_4$, it was found that the Gran extrapolation was not linear near the equivalence point. The 3 M $(\text{Na})\text{ClO}_4$ behaved as if it contained a weak acid (concentration $\simeq 3 \times 10^{-5}$ M). By making the same standardization in 0.3 M $(\text{Na})\text{ClO}_4$, it was established that the disturbance was connected with the NaClO_4 . In this medium the disturbance almost disappeared. The Z measurements in 3 M $(\text{Na})\text{ClO}_4$ have been corrected for this buffer capacity of the ionic medium on the assumption that it is a function of $\log h$ only and not affected by the presence of lead. With the exception of the last few points of the 1.25 and 2.5 mM titrations the correction is less than 1 % in Z . This impurity was not detected until the measurements in 3 M $(\text{Na})\text{ClO}_4$ were almost completed. It was therefore decided to extend the measurements to 0.3 M $(\text{Na})\text{ClO}_4$ to avoid the uncertainty in the Z values for small values of B caused by the impurity.

The reversibility of the hydrolysis reactions was tested by carrying out some back titrations. The results from these titrations in general agreed to better than ± 0.005 in Z and η with those from the forward titrations, thus indicating that true equilibria were measured.

Materials and analysis

Sodium perchlorate was prepared and analysed as described previously¹⁶. The determination of free, strong acid or base in the product has been somewhat modified. Since the method employed can also be advantageously used to determine the analytical hydrogen ion concentration in solutions of metal salts, which do not hydrolyse too strongly, it may be worth a short description. The following solutions are employed

- S_1 Metal salt solution of concentration B M and ionic medium I M
- S_2 Metal salt solution of concentration $2B$ M and ionic medium $2I$ M
- S_3 Solution containing acid or base of known concentration H M

When the acidity of the ionic medium is determined S_1 and S_2 of course, do not contain the metal salt. To a known volume (V_0) of solution S_1 are added equal volumes (V) of solutions S_2 and S_3 , and $\log h$ is measured as a function of V . If the acidity of solution S_1 is δ , it is 2δ in solution S_2 , so that the acidity in each point is given by;

$$h = \frac{V_0\delta + 2V\delta + VH}{V_0 + 2V} = \delta + \frac{VH}{V_0 + 2V} \quad (3)$$

From the measured emf we get;

$$E = E^0 + 59.15 \log h + E_j; 10^{(E-E_j)/59.15} = h \cdot 10^{E^0/59.15} = \text{const} \cdot h = \text{const} \cdot \left(\delta + \frac{VH}{V_0 + 2V} \right) \quad (4)$$

If we plot $10^{(E-E_j)/59.15}$ as a function of $VH/(V_0 + 2V)$ a straight line is obtained which, when extrapolated to $10^{(E-E_j)/59.15} = 0$ gives $-\delta$ on the horizontal axis. The method is a version of the usual Gran extrapolation¹⁴, and a special case of a more general expression derived by Berecki-Biedermann¹⁷.

Perchloric acid solutions were prepared and analysed as described previously¹⁶.

Sodium hydroxide was prepared either from 50 % NaOH by dilution or by the method described by Han and Chao¹⁸ adding $\text{Ba}(\text{OH})_2$. No difference was observed between titrations carried out with NaOH prepared in either way. Base solutions stronger than *ca.*

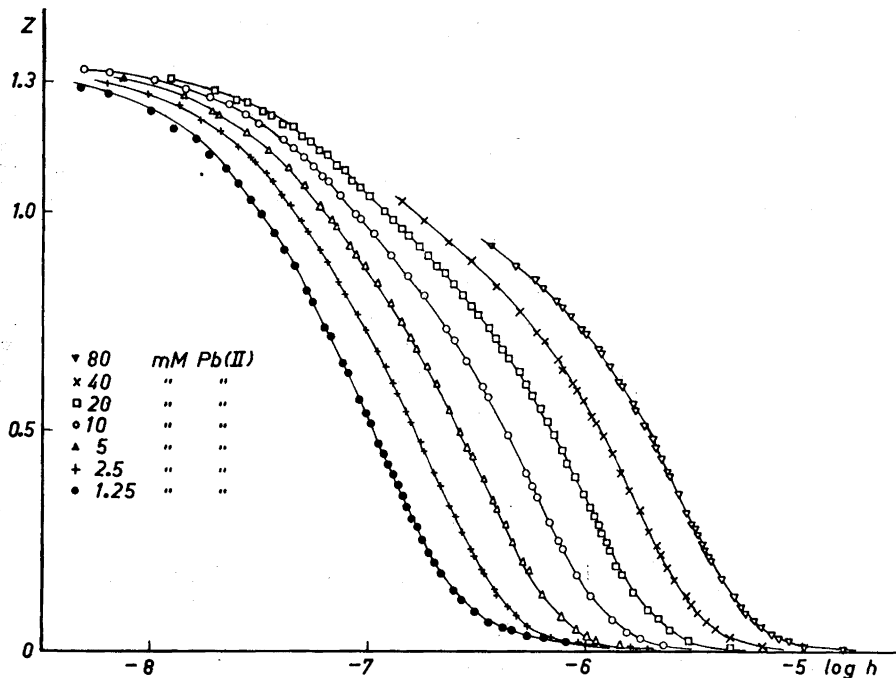


Fig. 1. Average number, Z , of OH^- bound per Pb(II) as a function of $\log h$ with 3 M $(\text{Na})\text{ClO}_4$ as medium. The curves are calculated with the equilibrium constants given in the text.

25 mM were standardized visually against standard acid. Less strong solutions were standardized potentiometrically using Gran's method to determine the end point.

Lead (II) perchlorate solutions were prepared from two different lead sources. One solution was prepared from PbO (Baker p.a.) which was dissolved in perchloric acid and small amounts of tetravalent lead present in the oxide destroyed by H_2O_2 . The other solution was prepared from lead metal (Merck silberfrei) which was dissolved in nitric acid and the nitric acid dispelled by fuming with perchloric acid. Due to the very great solubility of lead perchlorate, this salt could not be satisfactorily recrystallised from water but had to be used without further purification. The Z and η data obtained from solutions made up from the two stock solutions were consistent which would indicate that no impurities were present. Lead was determined as lead sulfate¹⁹ or as lead iodate²⁰. Both methods gave the same results to $\pm 0.1\%$. The analytical hydrogen ion concentration was determined potentiometrically using a Gran extrapolation to obtain the equivalence point.

Lead amalgam was prepared by dissolving lead metal (Merck silberfrei) in mercury. The amalgam was stored under 25 mM HClO_4 in a N_2 atmosphere and the lead concentration in the amalgam was ca. 0.7% (weight).

RESULTS AND CALCULATIONS

The experimental data are presented in Figs 1, 2, 3 and 4 and in Tables 1 and 2 giving Z and η as functions of $\log h$ and B . $Z = (h-H)/B$, i. e. the average number of OH^- groups bound per lead(II), and $\eta = \log B/b$.

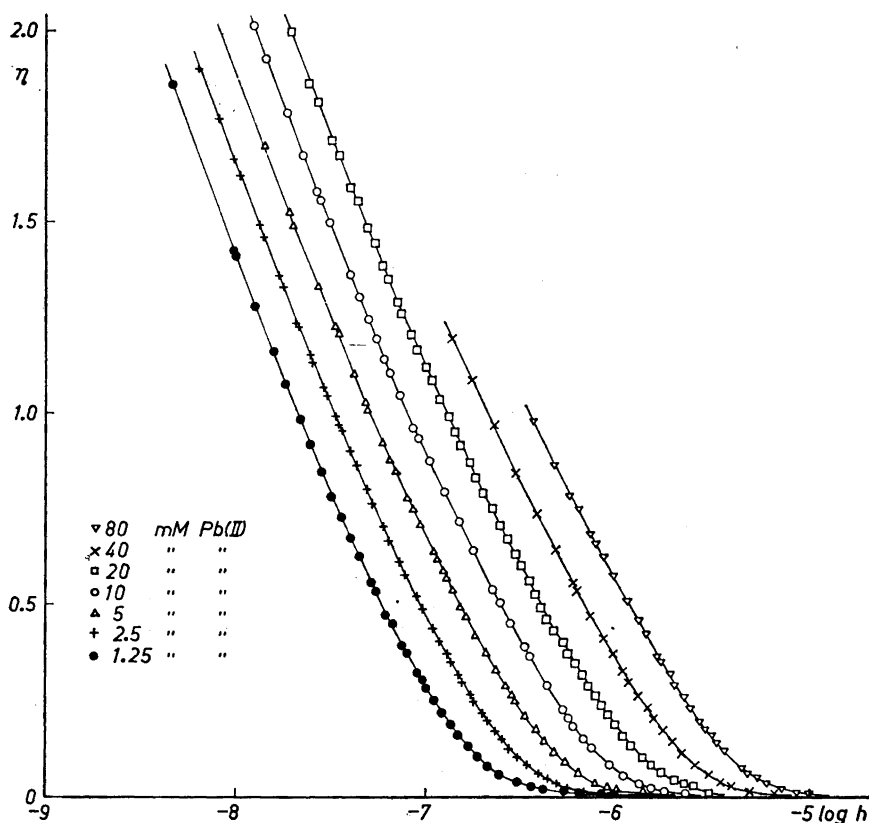


Fig. 2. $\eta = \log B/b$ as a function of $\log h$ with 3 M (Na)ClO₄ as medium. The curves are calculated with the equilibrium constants given in the text.

In those earlier studies, published from this Institute, where it has been possible to determine experimentally both η and Z , these have been treated separately to find the formulas of the hydrolysis products and their formation constants (see for example Ref. ²¹). The fact that the two sets of data have given the same results may be taken as additional evidence for the correctness of the hydrolysis mechanism proposed.

With lead(II), such a procedure certainly would give the main complexes formed, but it is somewhat more difficult to establish the minor products with certainty. When deriving the composition of the complexes formed, we shall prefer to combine the two sets of data. This mode of approach greatly simplifies our task, although we lose the double-check of the previous method. As a check on systematic errors in either set of data the equilibrium constants will be determined from the Z and η data separately.

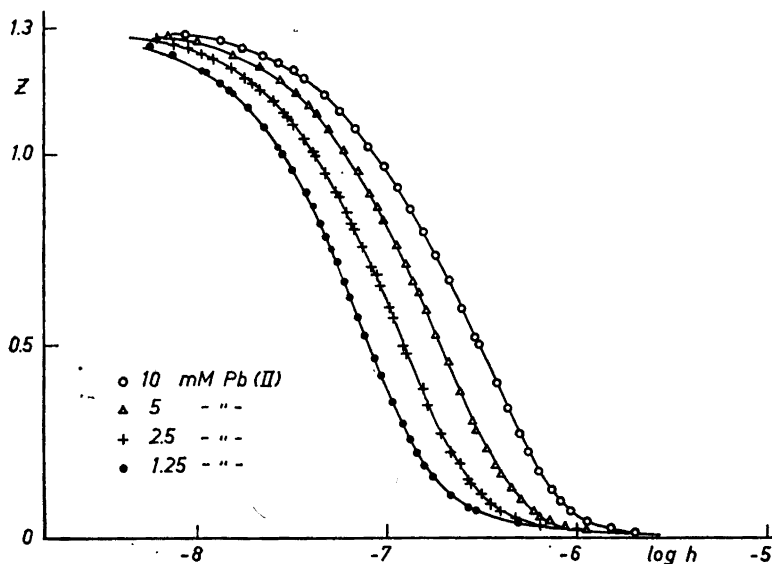


Fig. 3. Z as a function of $\log h$ with 0.3 M (Na)ClO₄ as medium. The curves are calculated with the equilibrium constants given in the text.

It is apparent that polynuclear complexes are formed since Z and η are functions of both B and $\log h$. It is also apparent that more than one complex is formed. The lower the value of B is, the steeper are the Z and η curves. This would indicate that when B is lowered, complexes with a higher $\text{OH}^-/\text{Pb(II)}$ ratio are formed at increasingly early stages of the hydrolysis. The limiting value of this ratio is $4/3$ as indicated by the $Z_{\text{lim}} \cong 1.3$ and $\lim_{b \rightarrow 0} (\Delta\eta/\Delta\log h)_B \cong -1.3$.

Determination of the products of hydrolysis in the region where $\nu = 1$. By combining the Z and η data we can calculate the number of OH^- groups bound per hydrolysed Pb(II) , ν ,

$$\nu = \frac{h-H}{B-b} \quad (5)$$

This quantity gives an average value of the ratio $\text{OH}^-/\text{Pb(II)}$ in the complexes formed. On calculation from Tables 1 and 2, ν is found to have the value 1.00 ± 0.02 in the initial stages of hydrolysis for B values larger than 2.5 mM. After the halt at 1.0, ν steadily increases with $-\log h$ and the largest value of ν registered was 1.33.

For the two lowest concentrations, however, the initial ν values showed irregularities indicating that the data from these concentrations are less reliable at small values of Z . Usually ν started from a value of ca. 1.2 and then decreased to ca. 1.05. Afterwards it steadily increased again in a regular manner. These irregularities are probably connected with the impurity in the NaClO_4 , since they are less pronounced with 0.3 M (Na)ClO₄. But even with this medium the values for the lowest concentrations do not show the

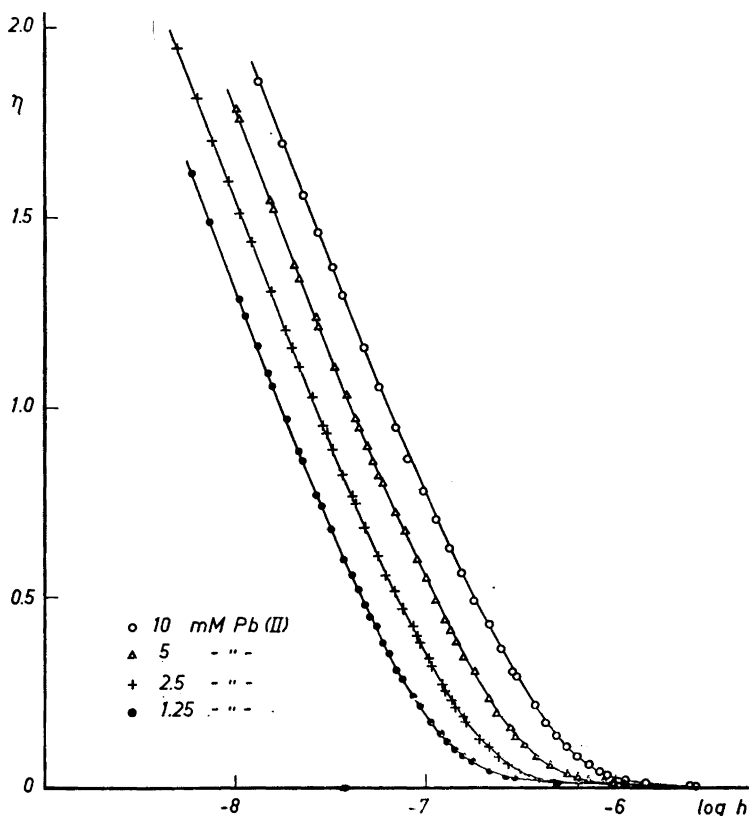


Fig. 4. η as a function of $\log h$ with 0.3 M (Na)ClO₄ as medium. The curves are calculated with the equilibrium constants given in the text.

regular behaviour of those found for the higher values of B . However, it must be pointed out that ν is very sensitive to experimental errors since H and $(B-b)$ are both obtained as differences between numbers which are about equal in magnitude. It is reasonable to assume that even for the two lowest values of B , complexes with a $\text{OH}^-/\text{Pb(II)}$ ratio = 1 are formed in the initial stages of hydrolysis.

We shall start with a determination of the formulas of the complexes formed in the region where $\nu = 1$. In this region complexes with the general composition $(\text{PbOH}^+)_n$ apparently predominate. However, their range of predominance varies greatly with B . For $B = 80$ mM it extends to $Z \simeq 0.8$ but for $B = 5$ mM ν deviates significantly from 1 when $Z > 0.3$. An inspection of the curves for $B \geq 5$ mM shows that they are parallel and that the spacing along the $\log h$ axis

$$\left(\frac{\Delta \log B}{\Delta \log h} \right)_{\eta} \simeq \left(\frac{\Delta \log B}{\Delta \log h} \right)_Z = 1.33 \pm 0.03 \quad (6)$$

Table 1.

Corresponding values of $-\log h$, Z and η with 3 M (Na)ClO₄ medium.

▽ $B = 0.080$ M: Run I. $-\log h$, Z , η ; 4.962, 0.011, 0.0049; 5.108, 0.030, 0.0147; 5.174, 0.050, 0.0238; 5.223, 0.069, 0.0333; 5.260, 0.088, 0.0424; 5.317, 0.125, 0.0617; 5.361, 0.160, 0.0799; 5.422, 0.211, 0.1086; 5.443, 0.228, 0.1174; 5.475, 0.260, 0.1364; 5.507, 0.291, 0.1556; 5.563, 0.351, 0.1935; 5.620, 0.407, 0.2337; 5.674, 0.459, 0.2743; 5.727, 0.509, 0.3169; 5.781, 0.557, 0.3612; 5.836, 0.602, 0.4068; 5.890, 0.644, 0.4552; 5.948, 0.685, 0.5072; 6.007, 0.723, 0.5617; 6.071, 0.760, 0.6201; 6.139, 0.795, 0.6823; 6.207, 0.829, 0.7483; 6.244, 0.845, 0.7834.

Run II. 4.812, 0.004, 0.0025; 4.990, 0.013, 0.0059; 5.059, 0.021, 0.0109; 5.137, 0.037, 0.0184; 5.182, 0.053, 0.0251; 5.221, 0.067, 0.0322; 5.277, 0.096, 0.0461; 5.317, 0.123, 0.0596; 5.351, 0.149, 0.0742; 5.410, 0.196, 0.0992; 5.459, 0.238, 0.1239; 5.495, 0.277, 0.1479; 5.532, 0.312, 0.1692; 5.574, 0.356, 0.1979; 5.615, 0.397, 0.2263; 5.652, 0.436, 0.2557; 5.691, 0.480, 0.2875; 5.770, 0.546, 0.3500; 5.852, 0.612, 0.4190; 5.936, 0.674, 0.4910; 6.022, 0.730, 0.5731; 6.114, 0.784, 0.6573; 6.218, 0.833, 0.7557; 6.330, 0.880, 0.8642; 6.445, 0.924, 0.9798.

× $B = 0.040$ M: Run I. $-\log h$, Z , η ; 5.182, 0.011, 0.0051; 5.334, 0.031, 0.0145; 5.404, 0.051, 0.0237; 5.453, 0.070, 0.0328; 5.486, 0.088, 0.0419; 5.515, 0.106, 0.0511; 5.541, 0.124, 0.0592; 5.588, 0.157, 0.0761; 5.623, 0.188, 0.0926; 5.656, 0.217, 0.1089; 5.683, 0.246, 0.1251; 5.710, 0.272, 0.1403; 5.760, 0.322, 0.1704; 5.804, 0.366, 0.1998; 5.845, 0.407, 0.2289; 5.890, 0.451, 0.2627; 5.933, 0.493, 0.2968; 5.977, 0.534, 0.3320; 6.019, 0.572, 0.3688; 6.068, 0.609, 0.4077; 6.114, 0.645, 0.4486; 6.208, 0.713, 0.5355; 6.311, 0.755, 0.6308; 6.421, 0.832, 0.7350; 6.533, 0.887, 0.8492; 6.646, 0.936, 0.9672; 6.759, 0.984, 1.0859; 6.864, 1.029, 1.1961.

Run II; 5.160, 0.010, 0.0049; 5.304, 0.025, 0.0122; 5.366, 0.039, 0.0189; 5.443, 0.067, 0.0300; 5.527, 0.117, 0.0554; 5.590, 0.163, 0.0788; 5.637, 0.203, 0.1018; 5.676, 0.240, 0.1224; 5.710, 0.274, 0.1420; 5.759, 0.321, 0.1714; 5.845, 0.408, 0.2309; 5.929, 0.488, 0.2939; 5.967, 0.526, 0.3269; 6.049, 0.598, 0.3966; 6.137, 0.664, 0.4723; 6.227, 0.725, 0.5538; 6.322, 0.783, 0.6437; 6.426, 0.836, 0.7417; 6.529, 0.886, 0.8472; 6.641, 0.934, 0.9567.

□ $B = 0.020$ M: Run I. $-\log h$, Z , η ; 5.333, 0.009, 0.0035; 5.497, 0.023, 0.0096; 5.600, 0.045, 0.0197; 5.656, 0.067, 0.0299; 5.703, 0.088, 0.0400; 5.769, 0.130, 0.0603; 5.821, 0.171, 0.0806; 5.868, 0.210, 0.1015; 5.907, 0.249, 0.1228; 5.943, 0.287, 0.1448; 6.012, 0.358, 0.1901; 6.080, 0.426, 0.2371; 6.147, 0.490, 0.2875; 6.212, 0.551, 0.3426; 6.360, 0.664, 0.4606; 6.497, 0.766, 0.5975; 6.651, 0.859, 0.7506; 6.813, 0.944, 0.9176; 6.971, 1.022, 1.0861; 7.123, 1.094, 1.2594; 7.199, 1.129, 1.3510; 7.278, 1.161, 1.4477; 7.361, 1.193, 1.5569; 7.457, 1.223, 1.6742; 7.571, 1.251, 1.8179; 7.716, 1.279, 2.0015; 7.919, 1.306, 2.2658.

Run II; 5.512, 0.022, 0.0109; 5.606, 0.044, 0.0204; 5.708, 0.087, 0.0404; 5.774, 0.129, 0.0610; 5.825, 0.170, 0.0819; 5.848, 0.190, 0.0924; 5.889, 0.229, 0.1140; 5.929, 0.267, 0.1353; 5.967, 0.304, 0.1580; 5.983, 0.322, 0.1688; 6.051, 0.391, 0.2148; 6.115, 0.456, 0.2631; 6.178, 0.518, 0.3145; 6.245, 0.578, 0.3690; 6.279, 0.606, 0.3984; 6.311, 0.634, 0.4274; 6.384, 0.687, 0.4903; 6.420, 0.712, 0.5231; 6.457, 0.737, 0.5576; 6.528, 0.786, 0.6303; 6.570, 0.810, 0.6681; 6.609, 0.832, 0.7070; 6.690, 0.877, 0.7871; 6.729, 0.898, 0.8270; 6.771, 0.919, 0.8676; 6.847, 0.959, 0.9514; 6.886, 0.979, 0.9930; 6.927, 0.998, 1.0364; 7.001, 1.035, 1.1195; 7.043, 1.053, 1.1627; 7.079, 1.071, 1.2063; 7.155, 1.105, 1.2939; 7.231, 1.139, 1.3852; 7.310, 1.171, 1.4839; 7.397, 1.202, 1.5924; 7.495, 1.230, 1.7165; 7.617, 1.258, 1.8676.

○ $B = 0.010$ M: Run I. $-\log h$, Z , η ; 5.831, 0.051, 0.0226; 5.963, 0.114, 0.0527; 6.043, 0.176, 0.0828; 6.110, 0.236, 0.1159; 6.171, 0.295, 0.1497; 6.227, 0.352, 0.1865; 6.281, 0.408, 0.2251; 6.369, 0.495, 0.2910, 6.458, 0.578, 0.3640; 6.556, 0.662, 0.4512; 6.648, 0.736, 0.5380; 6.751, 0.811, 0.6394; 6.893, 0.900, 0.7807; 7.042, 0.985, 0.9368; 7.187, 1.067, 1.1061; 7.353, 1.145, 1.3055; 7.561, 1.220, 1.5610; 7.916, 1.292, 2.0193; 8.327, 1.325, 2.5596.

Run II. 5.644, 0.013, 0.0064; 5.748, 0.027, 0.0128; 5.808, 0.041, 0.0186; 5.884, 0.068, 0.0318; 5.978, 0.122, 0.0581; 6.129, 0.251, 0.1267; 6.251, 0.376, 0.2031; 6.362, 0.492, 0.2896; 6.480, 0.602, 0.3890; 6.612, 0.707, 0.5056; 6.753, 0.807, 0.6416; 6.827, 0.855, 0.7144; 6.903, 0.902, 0.7932; 6.982, 0.948, 0.8753; 7.062, 0.995, 0.9598; 7.136, 1.039, 1.0480; 7.221, 1.082, 1.1433; 7.261, 1.102, 1.1930; 7.304, 1.123, 1.2447; 7.400, 1.164, 1.3626; 7.510, 1.204, 1.5002; 7.578, 1.224, 1.5823; 7.650, 1.243, 1.6749; 7.736, 1.262, 1.7888; 7.847, 1.280, 1.9290; 7.990, 1.299, 2.1206; 8.197, 1.137, 2.4008; 8.335, 1.324, 2.5720.

△ $B = 0.005$ M: Run I. $-\log h$, Z , η ; 5.836, 0.014, 0.0070; 5.999, 0.037, 0.0168; 6.109, 0.071, 0.0327; 6.203, 0.127, 0.0601; 6.274, 0.182, 0.0874; 6.340, 0.243, 0.1206; 6.386, 0.290, 0.1456; 6.436, 0.343, 0.1780; 6.487, 0.395, 0.2115; 6.536, 0.447, 0.2480; 6.587, 0.498, 0.2879;

Table 1. Continued.

6.636, 0.547, 0.3281; 6.688, 0.596, 0.3731; 6.741, 0.645, 0.4201; 6.793, 0.688, 0.4695; 7.162, 0.969, 0.8488; 7.233, 1.013, 0.9262; 7.307, 1.056, 1.0117; 7.381, 1.098, 1.1037; 7.469, 1.140, 1.2095; 7.571, 1.181, 1.3319; 7.699, 1.221, 1.4928; 7.859, 1.261, 1.7010; 8.134, 1.299, 2.0580.

Run II. 5.858, 0.013, 0.0073; 5.955, 0.025, 0.0137; 6.051, 0.047, 0.0239; 6.207, 0.126, 0.0614; 6.337, 0.235, 0.1175; 6.536, 0.446, 0.2521; 6.742, 0.643, 0.4235; 6.974, 0.833, 0.6463; 7.033, 0.876, 0.7115; 7.097, 0.919, 0.7788; 7.163, 0.967, 0.8515; 7.229, 1.011, 0.9282; 7.571, 1.179, 1.3336; 7.856, 1.258, 1.7010; 8.318, 1.310, 2.3024; 7.729, 1.228, 1.5317; 7.488, 1.142, 1.2318; 7.324, 1.063, 1.0320; 7.190, 0.982, 0.8768; 7.075, 0.903, 0.7487; 6.966, 0.825, 0.6368; 6.913, 0.789, 0.5857; 6.867, 0.751, 0.5398; 6.822, 0.714, 0.4962; 6.698, 0.603, 0.3829; 6.555, 0.461, 0.2636; 6.426, 0.328, 0.1720; 6.296, 0.198, 0.0979; 6.115, 0.074, 0.0367.

+ $B = 0.0025$ M: Run I. $-\log h, Z, \eta$; 5.708, 0.007, 0.0030; 6.152, 0.033, 0.0135; 6.264, 0.057, 0.0250; 6.325, 0.081, 0.0362; 6.371, 0.105, 0.0463; 6.409, 0.128, 0.0578; 6.470, 0.173, 0.0794; 6.519, 0.217, 0.1007; 6.562, 0.259, 0.1231; 6.604, 0.300, 0.1467; 6.676, 0.378, 0.1954; 6.744, 0.452, 0.2448; 6.808, 0.518, 0.2961; 6.869, 0.583, 0.3479; 6.928, 0.644, 0.4020; 7.020, 0.729, 0.4861; 7.109, 0.808, 0.5740; 7.195, 0.880, 0.6656; 7.282, 0.948, 0.7620; 7.366, 1.010, 0.8624; 7.462, 1.068, 0.9689; 7.527, 1.105, 1.0456; 7.595, 1.140, 1.1312; 7.673, 1.172, 1.2245; 7.758, 1.203, 1.3327; 7.862, 1.233, 1.4621; 7.985, 1.261, 1.6264.

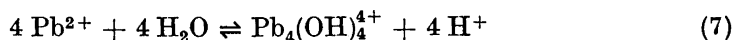
Run II. 5.797, 0.010, 0.0041; 6.029, 0.020, 0.0074; 6.127, 0.030, 0.0115; 6.252, 0.060, 0.0226; 6.316, 0.079, 0.0331; 6.365, 0.102, 0.0443; 6.423, 0.139, 0.0619; 6.482, 0.184, 0.0842; 6.528, 0.227, 0.1072; 6.573, 0.268, 0.1302, 6.633, 0.328, 0.1656; 6.700, 0.405, 0.2137; 6.766, 0.474, 0.2633; 6.827, 0.541, 0.3151; 6.889, 0.604, 0.3675; 6.962, 0.678, 0.4351; 7.053, 0.760, 0.5206; 7.141, 0.836, 0.6092; 7.226, 0.906, 0.7018; 7.312, 0.972, 0.7978; 7.398, 1.034, 0.9003; 7.446, 1.061, 0.9530; 7.476, 1.080, 0.9895; 7.544, 1.116, 1.0673; 7.612, 1.150, 1.1525; 7.689, 1.182, 1.2485; 7.778, 1.212, 1.3597; 7.881, 1.242, 1.4949; 8.016, 1.269, 1.6673; 8.099, 1.282, 1.7724; 8.201, 1.294, 1.9057.

● $B = 0.00125$ M: Run I. $-\log h, Z, \eta$; 6.078, 0.022, 0.0063; 6.271, 0.033, 0.0114; 6.345, 0.042, 0.0158; 6.450, 0.064, 0.0249; 6.514, 0.085, 0.0347; 6.582, 0.115, 0.0499; 6.631, 0.148, 0.0648; 6.698, 0.200, 0.0905; 3.753, 0.251, 0.1168; 6.803, 0.299, 0.1456; 6.847, 0.351, 0.1743; 6.889, 0.400, 0.2041; 6.933, 0.446, 0.2348; 7.016, 0.538, 0.3021; 7.097, 0.628, 0.3721; 7.175, 0.713, 0.4495; 7.260, 0.796, 0.5333; 7.348, 0.876, 0.6263; 7.441, 0.953, 0.7287; 7.547, 1.029, 0.8461; 7.662, 1.099, 0.9860; 7.806, 1.166, 1.1625; 8.002, 1.228, 1.4130; 8.348, 1.282, 1.8623.

Run II. 5.478, 0.011, 0.0016; 6.196, 0.029, 0.0090; 6.387, 0.050, 0.0178; 6.470, 0.072, 0.0266; 6.526, 0.093, 0.0360; 6.573, 0.114, 0.0459; 6.609, 0.136, 0.0557; 6.670, 0.175, 0.0763; 6.727, 0.224, 0.1016; 6.778, 0.278, 0.1283; 6.829, 0.326, 0.1564; 6.871, 0.375, 0.1858; 6.915, 0.422, 0.2162; 6.959, 0.469, 0.2477; 6.996, 0.514, 0.2791; 7.045, 0.568, 0.3204; 7.128, 0.656, 0.3927; 7.209, 0.738, 0.4711; 7.292, 0.819, 0.5570; 7.395, 0.913, 0.6713; 7.493, 0.995, 0.7805; 7.611, 1.066, 0.9191; 7.743, 1.129, 1.0753; 7.902, 1.191, 1.2795.

in the range where $\nu = 1$. This means that the complexes formed can be written as $\text{Pb}(\text{Pb}(\text{OH})_{1.33 \pm 0.03})_n$ (Ref. ²²), where n is variable and unknown and may assume any value which fulfills the requirements that $n(1.33 \pm 0.03)$ are whole numbers. The restriction that the complexes should give a value $\nu = 1$ gives as the only possibility $n = 3$, from the relation $n(1.33 \pm 0.03)/(n + 1) = 1$. Hence the complex formed is $\text{Pb}_4(\text{OH})_4^{4+}$.

In this derivation we have not made use of the shapes of the Z and η curves for the complex. It is therefore necessary to make a comparison with theoretical curves for $\text{Pb}_4(\text{OH})_4^{4+}$ to see if the experimental $Z(\log h)_B$ and $\eta(\log h)_B$ curves are of the correct shapes. At the same time the equilibrium constant for the reaction



is determined.

Table 2.

Corresponding values of $-\log h$, Z and η with 0.3 M (Na)ClO₄ medium.

○ $B = 0.010$ M: Run I. $-\log h$, Z , η ; 5.696, 0.012, 0.0051; 5.943, 0.040, 0.0176; 6.032, 0.067, 0.294; 6.132, 0.119, 0.0558; 6.200, 0.170, 0.0808; 6.303, 0.266, 0.1342; 6.428, 0.399, 0.2167; 6.538, 0.521, 0.3029; 6.675, 0.667, 0.4290; 6.812, 0.796, 0.561; 6.947, 0.912, 0.7035; 7.094, 1.018, 0.8621; 7.244, 1.113, 1.0527; 7.434, 1.200, 1.2951; 7.569, 1.240, 1.4594; 7.752, 1.279, 1.6971; 8.063, 1.316, 2.1045.

Run II. 5.674, 0.012, 0.0037; 5.836, 0.023, 0.0095; 6.087, 0.093, 0.0416; 6.256, 0.219, 0.1051; 6.367, 0.334, 0.1711; 6.521, 0.501, 0.2884; 6.607, 0.596, 0.3631; 6.742, 0.733, 0.4915; 6.878, 0.856, 0.6282; 7.013, 0.967, 0.7765; 7.165, 1.066, 0.9469; 7.331, 1.157, 1.1548; 7.434, 1.200, 1.2884; 7.495, 1.220, 1.3675; 7.647, 1.260, 1.5602; 7.875, 1.298, 1.8594.

△ $B = 0.005$ M: Run I. $-\log h$, Z , η ; 6.061, 0.029, 0.0134; 6.247, 0.079, 0.0357; 6.343, 0.126, 0.0584; 6.540, 0.302, 0.1507; 6.676, 0.455, 0.2460; 6.796, 0.592, 0.3454; 6.901, 0.713, 0.4478; 7.004, 0.822, 0.5546; 7.113, 0.921, 0.6736; 7.224, 1.010, 0.8011; 7.270, 1.041, 0.8538; 7.344, 1.092, 0.9478; 7.413, 1.129, 1.0333; 7.491, 1.166, 1.1270; 7.579, 1.201, 1.2389; 7.682, 1.234, 1.3728; 4.817, 1.266, 1.5459; 8.003, 1.297, 1.7872.

Run II. 6.525, 0.276, 0.1338; 6.617, 0.378, 0.1939; 6.747, 0.528, 0.3021; 6.868, 0.666, 0.4127; 7.020, 0.826, 0.5631; 7.184, 0.966, 0.7369; 7.351, 1.089, 0.9444; 7.588, 1.199, 1.2335; 7.474, 1.154, 1.0932; 7.388, 1.109, 0.9857; 7.251, 1.021, 0.8197; 7.099, 0.892, 0.6388; 6.967, 0.767, 0.5016; 6.817, 0.607, 0.3596; 6.681, 0.453, 0.2463; 6.556, 0.305, 0.1544; 6.408, 0.163, 0.0776; 6.066, 0.026, 0.0134.

+ $B = 0.0025$ M: Run I. $-\log h$, Z , η ; 6.004, 0.018, 0.0081; 6.406, 0.068, 0.0297; 6.504, 0.108, 0.0490; 6.617, 0.192, 0.0821; 6.783, 0.346, 0.1727; 6.895, 0.481, 0.2559; 6.986, 0.601, 0.3404; 7.079, 0.708, 0.4273; 7.165, 0.805, 0.5169; 7.248, 0.892, 0.6122; 7.385, 1.009, 0.7677; 7.490, 1.078, 0.8871; 7.596, 1.142, 1.0270; 7.735, 1.202, 1.2045; 7.917, 1.255, 1.4388; 8.309, 1.317, 1.9517.

Run II. 6.193, 0.031, 0.0129; 6.328, 0.050, 0.0193; 6.457, 0.086, 0.0375; 6.578, 0.151, 0.0693; 6.715, 0.271, 0.1305; 6.842, 0.415, 0.2133; 6.969, 0.575, 0.3212; 7.035, 0.655, 0.3827; 7.121, 0.758, 0.4702; 7.167, 0.805, 0.5155; 7.209, 0.850, 0.5622; 7.320, 0.952, 0.6859; 7.385, 1.009, 0.7664; 7.432, 1.045, 0.8228; 7.540, 1.111, 0.9503; 7.598, 1.142, 1.0254; 7.664, 1.172, 1.1061; 7.817, 1.228, 1.3070; 7.919, 1.255, 1.4369; 7.978, 1.268, 1.5125; 8.039, 1.281, 1.5967; 8.122, 1.293, 1.7022.

● $B = 0.00125$ M: Run I. $-\log h$, Z , η ; 6.308, 0.035, 0.0147; 6.577, 0.076, 0.0337; 6.756, 0.154, 0.0699; 6.922, 0.295, 0.1412; 7.022, 0.420, 0.2125; 7.119, 0.531, 0.2835; 7.197, 0.629, 0.3535; 7.266, 0.719, 0.4245; 7.353, 0.818, 0.5171; 7.439, 0.907, 0.6131; 7.552, 1.001, 0.7389; 7.667, 1.083, 0.8846; 7.806, 1.158, 1.0587; 7.978, 1.223, 1.2832; 8.134, 1.263, 1.4877.

Run II. 6.529, 0.067, 0.0276; 6.663, 0.107, 0.0462; 6.744, 0.145, 0.0648; 6.842, 0.217, 0.0996; 6.972, 0.351, 0.1720; 7.069, 0.468, 0.2413; 7.151, 0.572, 0.3102; 7.222, 0.666, 0.3792; 7.292, 0.751, 0.4502; 7.358, 0.827, 0.5232; 7.427, 0.898, 0.6013; 7.501, 0.962, 0.6821; 7.572, 1.020, 0.7680; 7.648, 1.074, 0.8619; 7.730, 1.124, 0.9711; 7.829, 1.170, 1.0908; 7.883, 1.192, 1.1621; 7.948, 1.214, 1.2399.

This is accomplished in the following way. We start from the equations

$$B = b + 4\beta_{4,4}b^4h^{-4} \quad (8)$$

$$BZ = 4\beta_{4,4}b^4h^{-4} \quad (9)$$

$$10\eta = B/b = 1 + 4\beta_{4,4}b^3h^{-4} \quad (10)$$

and introduce

$$\beta^3 = 4\beta_{4,4} \text{ and } v = \beta B h^{-4/3} \quad (11, 11a)$$

We find after elimination of b

$$\log v = \log B - 4/3 \log h + \log \beta = \eta + 1/3 \log (10\eta - 1) = 1/3 \log Z - 4/3 \log (1 - Z) \quad (12)$$

According to these equations plots of Z and η as functions of $(\log B - 4/3 \log h)$ should give single curves independent of B . Then these are compared with the theoretical $\eta(\log v)$ and $Z(\log v)$ curves and examined for a fit. The difference on the $\log v$ and $(\log B - 4/3 \log h)$ axes in this position gives $\log \beta$ and from eqn. (11) $\log \beta_{4,4}$.

For $B \geq 5$ mM the experimental points in the region with $v = 1$ fell on single curves, which had the shape required by the theoretical curves. The value of the equilibrium constant found from the Z and η data was the same

$$\log \beta_{4,4} = -19.25 \pm 0.03$$

The 2.5 and 1.25 mM curves showed deviations in a direction which indicated that species smaller than $\text{Pb}_4(\text{OH})_4^{4+}$ were also present. However, the deviations are not very large.

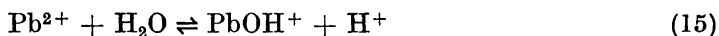
In order to obtain information about the cause of these deviations the terms for the $\text{Pb}_4(\text{OH})_4^{4+}$ ion were subtracted from B and BZ . The following quantities were calculated and plotted as functions of $\log h$

$$\eta_c = \log \frac{B_c}{b} \quad \text{and} \quad Z_c = \frac{BZ - 4\beta_{4,4}b^4h^{-4}}{B_c} \quad (13, 13a)$$

where B_c , a corrected B , is defined by

$$B_c = B - 4\beta_{4,4}b^4h^{-4} \quad (14)$$

These plots showed that η_c and Z_c were independent of B_c and were functions of $\log h$ only, which indicates that the mononuclear complex PbOH^+ is formed. In fact a satisfactory fit was obtained with normalized curves according to Sillén²³. The equilibrium constant for the reaction



was found to be

$$\log \beta_{11} = -7.90 \pm 0.05$$

The equilibrium constants $\beta_{4,4}$ and β_{11} were also determined simultaneously from projection maps by the method described by Biedermann and Sillén²⁴ with $(\log B - 4/3 \log h)$ and $\log h$ as variables on the axes. This approach gave the same values for the equilibrium constants as before, but indicated that the uncertainty in $\log \beta_{11}$ should be increased to ± 0.1 logarithmic unit.

Determination of the products of hydrolysis in the region where $v > 1$. Now we turn to the upper parts of the $Z(\log h)_B$ and $\eta(\log h)_B$ curves. The calculations to be described in the following were made on the Z and η data for $B < 40$ mM. (In the 40 and 80 mM titrations $\text{Pb}_4(\text{OH})_4^{4+}$ is so predominant that little information can be found about the other species present). As has already been mentioned both the Z and η data indicate that complexes with a $\text{OH}^-/\text{Pb(II)}$ ratio = 4/3 are formed. By calculating the concentrations of $\text{Pb}_4(\text{OH})_4^{4+}$ and PbOH^+ for each experimental point and subtracting the terms for these

ions we can find the average number of OH^- groups bound to each Pb(II) in the unknown complexes. This quantity remained constant at 1.33 ± 0.03 in the region where it could be calculated with sufficient accuracy. This region covered more than one $\log h$ unit for each value of B . It is therefore apparent that the complexes predominating in the upper parts of the curves are of the form $(\text{Pb}(\text{OH})_{4/3}^{2/3+})_n$ and the formulas of the complexes have been determined on this assumption.

Approach I. Information about possible species written as $\text{Pb}(\text{Pb}(\text{OH})_t)_n$ is found from the difference quotient $(\Delta \log B / \Delta \log h)_\eta = t$. If one only of the above complexes predominated, we would have $t = 2.0$ for $\text{Pb}_3(\text{OH})_4^{2+}$, $t = 1.6$ for $\text{Pb}_6(\text{OH})_8^{4+}$, $t = 1.5$ for $\text{Pb}_9(\text{OH})_{12}^{6+}$, etc. The spacing along the $\log h$ axis between the experimental η ($\log h$) $_B$ curves for $B = 20, 10$ and 5 mM gave a t value close to 1.6 , but for the two lower concentrations t was somewhat higher. Since the presence of PbOH^+ could be expected to cause such an effect, it was considered possible that the data could be explained by the formation of $\text{Pb}_6(\text{OH})_8^{4+}$ only. To test the hypothesis the following equations were used. We start from

$$B = b + \beta_{11}bh^{-1} + 4\beta_{4,4}b^4h^{-4} + 6\beta_{8,8}b^6h^{-8} \quad (16)$$

$$BZ = \beta_{11}bh^{-1} + 4\beta_{4,4}b^4h^{-4} + 8\beta_{8,8}b^6h^{-8} \quad (17)$$

$$B/b = 10\eta = 1 + \beta_{11}h^{-1} + 4\beta_{4,4}b^3h^{-4} + 6\beta_{8,8}b^5h^{-8} \quad (18)$$

and introduce the corrected dependent variables B_c , η_c and Z_c by

$$B_c = B - \beta_{11}bh^{-1} - 4\beta_{4,4}b^4h^{-4} = b + 6\beta_{8,8}b^6h^{-8} \quad (19)$$

$$B_cZ_c = BZ - \beta_{11}bh^{-1} - 4\beta_{4,4}b^4h^{-4} = 8\beta_{8,8}b^6h^{-8} \quad (20)$$

$$B_c/b = 10\eta_c = 1 + 6\beta_{8,8}b^5h^{-8} \quad (21)$$

With the parameters

$$6\beta_{8,8} = \alpha^5 \text{ and } 8\beta_{8,8} = \gamma^5 \quad (22, 22a)$$

and the variables

$$\alpha B_c h^{-1.6} = v \text{ and } \gamma B_c h^{-1.6} = u \quad (23, 23a)$$

we get

$$\log v = \log B_c - 1.6 \log h + \log \alpha = \eta_c + 0.2 \log (10\eta_c - 1) \quad (24)$$

and

$$\log u = \log B_c - 1.6 \log h + \log \gamma = 0.2 \log Z_c - 1.2 \log (1 - 0.75Z_c) \quad (25)$$

If the hypothesis is valid each of the Z_c and η_c according to eqns. (24) and (25) should give a single curve when plotted as a function of $(\log B_c - 1.6 \log h)$. The terms for PbOH^+ and $\text{Pb}_4(\text{OH})_4^{4+}$ were calculated with the equilibrium constants already determined.

The plots showed that $\text{Pb}_6(\text{OH})_8^{4+}$ alone did not suffice to explain the data. The data for the three highest concentrations fulfilled the requirements for the formation of $\text{Pb}_6(\text{OH})_8^{4+}$ at large values of Z_c and η_c well, but the t value used was too small to bring the data from the 2.5 and 1.25 mM titrations on to the $\eta_c, Z_c(\log B_c - 1.6 \log h)$ curves formed at the higher concentrations. Moreover at low Z_c and η_c the shapes of the experimental and theoretical curves were a little different. The fact that we have to use a larger t value for the lower concentrations to bring the data on to the same curve indicates the presence of $\text{Pb}_3(\text{OH})_4^{2+}$. $\text{Pb}_3(\text{OH})_4^{2+}$ is the only complex with $\nu = 4/3$ and a t value > 1.6 .

From the above discussion it may be considered likely that the data could be explained by the formation of $\text{Pb}_6(\text{OH})_8^{4+}$ and $\text{Pb}_3(\text{OH})_4^{2+}$. However, we shall start with the more general assumption that all members of the series $(\text{Pb}(\text{OH})_{4/3}^{2/3+})_n$ may be present. In order to determine the equilibrium constant for the first member of the series, $\text{Pb}_3(\text{OH})_4^{2+}$, two methods were used.

Approach II. We start from the equations

$$B = b + [\text{PbOH}^+] + 4[\text{Pb}_4(\text{OH})_4^{4+}] + 3[\text{Pb}_3(\text{OH})_4^{2+}] + 6[\text{Pb}_6(\text{OH})_8^{4+}] + \dots \quad (26)$$

$$B_c = B - b - [\text{PbOH}^+] - 4[\text{Pb}_4(\text{OH})_4^{4+}] = 3\beta_{4,3}b^3h^{-4} + 6\beta_{8,6}b^6h^{-8} + \dots = 3\beta_{4,3}x + 6\beta_{8,6}x^2 + \dots \quad (27)$$

$$b^3h^{-4} = x \quad (28)$$

We can calculate $[\text{Pb}_4(\text{OH})_4^{4+}]$ and $[\text{PbOH}^+]$ for each experimental point from the potentials and the equilibrium constants already determined. In addition we can find $b^3h^{-4} = x$. With this quantity as the independent variable, B_c becomes a function of x only.

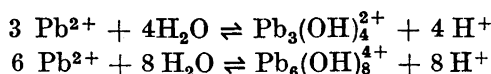
$$B_c = 3\beta_{4,3}x + 6\beta_{8,6}x^2 + \dots \text{ or } B_c x^{-1} = 3\beta_{4,3} + 6\beta_{8,6}x + \dots \quad (27, 27a)$$

The first two coefficients of the above series are found by plotting $B_c x^{-1}$ as function of x . If the first two complexes only are present a straight line should be obtained. The presence of higher complexes should give the line a curvature for the higher x values. The plot is shown in Fig. 5. The points fall with good approximation on a straight line and there appears to be no indication of the presence of $\text{Pb}_9(\text{OH})_{12}^{6+}$ or higher complexes. The intercept and the slope of the line give the following equilibrium constants.

$$\log \beta_{4,3} = -22.89 \pm 0.1$$

$$\log \beta_{8,6} = -42.13 \pm 0.1$$

corresponding to the equilibria



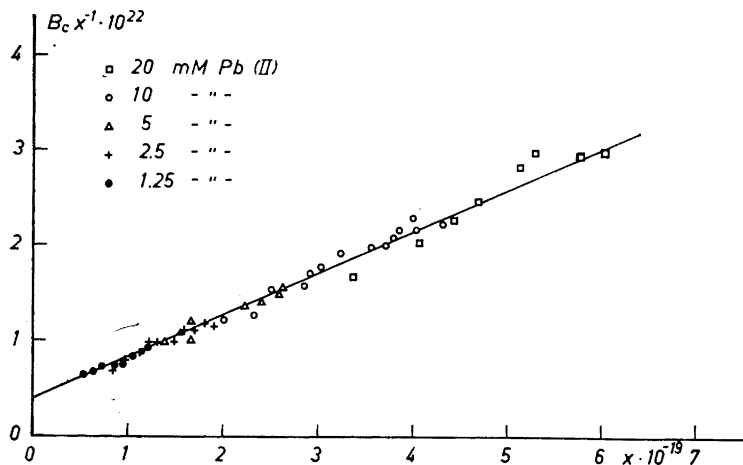


Fig. 5. Determination of $\log \beta_{4,3}$ (and $\log \beta_{8,6}$) from eqn. (27). B_c ; terms for $\text{Pb}_4(\text{OH})_4^{4+}$ and PbOH^+ have been subtracted. The drawn line yields $\log \beta_{4,3} = -22.89$ (and $\log \beta_{8,6} = -42.13$).

Approach III. The above calculations were made on the assumption that $\text{Pb}_4(\text{OH})_4^{4+}$ and PbOH^+ were formed in the initial stages of hydrolysis. If we combine the amalgam data with the Z data the members of the series can be found on the more general assumption, which is strongly supported by the initial ν values, that only complexes of the general type $(\text{PbOH})_n^{n+}$ occur beside $(\text{PbOH}_{4/3})_n^{2/3n+}$ species. The following equations are valid.

$$B = b + \sum n\beta_{n,n}b^n h^{-n} + 3\beta_{4,3}b^3 h^{-4} + 6\beta_{8,6}b^6 h^{-8} + \dots \quad (29)$$

$$BZ = \sum n\beta_{n,n}b^n h^{-n} + 4\beta_{4,3}b^3 h^{-4} + 8\beta_{8,6}b^6 h^{-8} + \dots \quad (30)$$

Subtracting and rearranging we get

$$(BZ + b - B)x^{-1} = \beta_{4,3} + 2\beta_{8,6}x + \dots \quad (31)$$

The plot $(BZ + b - B)x^{-1}$ versus x yields a straight line (Fig. 6) and the equilibrium constants are found to be

$$\log \beta_{4,3} = -22.85 \pm 0.1$$

$$\log \beta_{8,6} = -42.15 \pm 0.1$$

From Figs. 5 and 6 we find that the data for each total lead(II) concentration are gathered in different parts of the lines and do not overlap to any great extent, nor do they cover a broad range in x . This is due to the nature of the functions used. They are based on the concentrations of the $(\text{PbOH})_{4/3}^{2/3+}$ species obtained from the difference between B and the concentrations of the other species present. Of course, when the latter predominate this difference

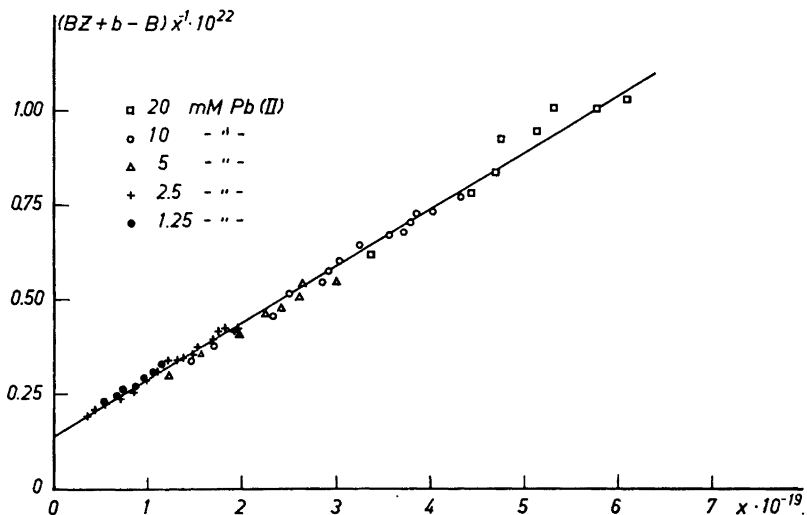


Fig. 6. Determination of $\log \beta_{4,3}$ (and $\log \beta_{8,6}$) from eqn. (31). The drawn line yields $\log \beta_{4,3} = -22.85$ (and $\log \beta_{8,6} = -42.15$).

is not very accurate. This leads to a quite narrow x range where the difference is of sufficient accuracy. Therefore any curvature of the lines may not show up. The value found for $\log \beta_{4,3}$ will be accepted as being correct, but we shall still doubt the value found for $\log \beta_{8,6}$ since higher complexes may also be present.

Now we can subtract the term for $\text{Pb}_3(\text{OH})_4^{2+}$ in eqns. (19,20,21) and obtain

$$B_c Z_c = \sum p \beta_{p,q} b^q h^{-p} \quad (32)$$

$$10^{\eta_c} = 1 + \sum q \beta_{p,q} b^q h^{-1} h^{-p} \quad (33)$$

where the sums represent the terms for the unknown complexes. Since the plots in Figs. 5 and 6 strongly indicated that the term for $\text{Pb}_8(\text{OH})_8^{4+}$ predominates in the sums above we started with the assumption that $p = 8$ and $q = 6$ and eqns. (24) and (25) were used to test it. From Figs. 7 and 8 it is seen that Z_c and η_c are functions of $(\log B_c - 1.6 \log h)$ only as required by the hypothesis. The agreement between the experimental and normalized curves is also good. Hence there is no reason to introduce more new complexes other than $\text{Pb}_3(\text{OH})_4^{2+}$ and $\text{Pb}_8(\text{OH})_8^{4+}$ to explain the upper parts of the η ($\log h$)_B and Z ($\log h$)_B curves. $\log \beta_{8,6}$ was found from eqns. (24, 25) and the difference between the coordinates on the $(\log B_c - 1.6 \log h)$ and the $\log v$ and $\log u$ axes when the experimental and normalized curves overlap.

$$\log \beta_{8,6} = -42.15 \pm 0.1 \quad (\eta \text{ data}) \text{ and } -42.13 \pm 0.1 \quad (Z \text{ data})$$

Final values for $\beta_{4,4}$ and β_{11} . Thus having established the complexes which predominate in the low $\log h$ region and their equilibrium constants it must be remembered that these findings were based partly on the hypothesis that

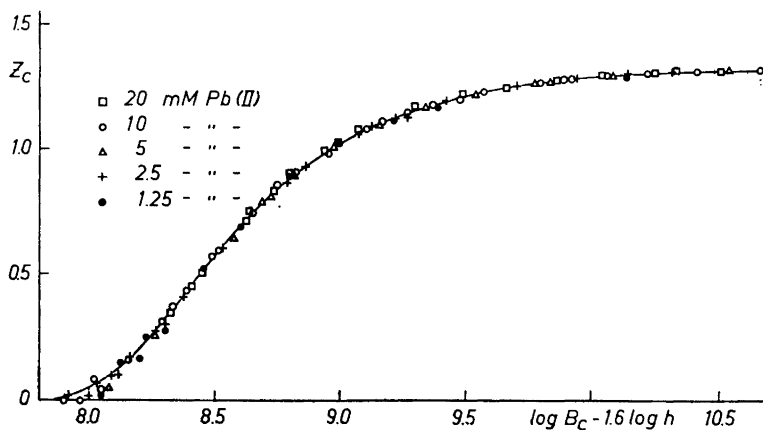


Fig. 7. Z_c as a function of $(\log B_c - 1.6 \log h)$ according to eqn. (25). Z_c , B_c ; terms for $\text{Pb}_4(\text{OH})_4^{4+}$, $\text{Pb}_3(\text{OH})_4^{3+}$ and PbOH^+ have been subtracted. Drawn curve represents normalized curve, calculated from eqn. (25), in position of best fit and giving $\log \beta_{8,6} = -42.13$.

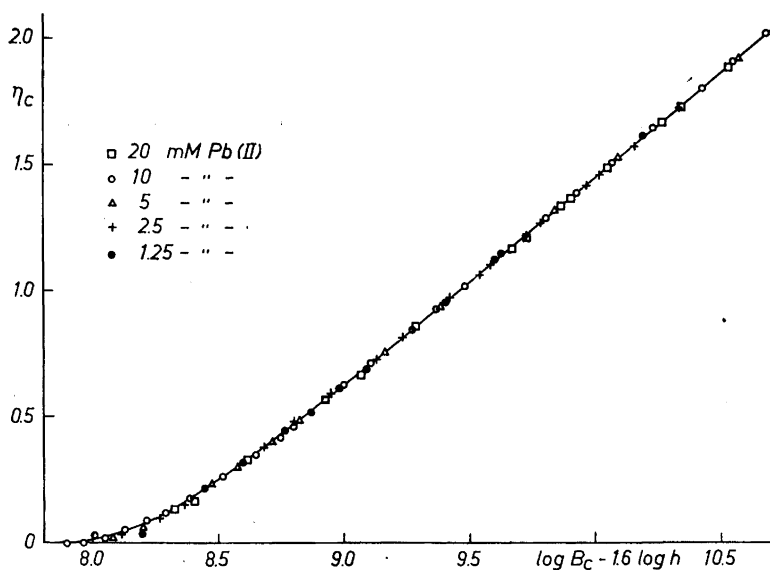


Fig. 8. η_c as a function of $(\log B_c - 1.6 \log h)$ according to eqn. (24). η_c , B_c ; terms for $\text{Pb}_4(\text{OH})_4^{4+}$, $\text{Pb}_3(\text{OH})_4^{3+}$ and PbOH^+ have been subtracted. Drawn curve represents normalized curve, calculated from eqn. (24), in position of best fit and giving $\log \beta_{8,6} = -42.15$.

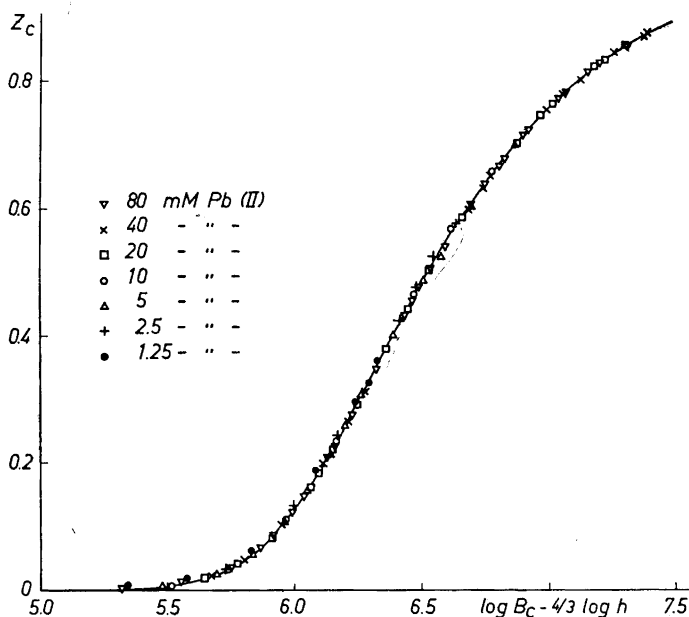


Fig. 9. Z_c as a function of $(\log B_c - 4/3 \log h)$ according to eqn. (12). Z_c , B_c ; terms for $\text{Pb}_6(\text{OH})_8^{4+}$, $\text{Pb}_3(\text{OH})_4^{2+}$ and PbOH^+ have been subtracted. Drawn curve represents normalized curve, calculated from eqn. (12), in position of best fit and giving $\log \beta_{4,4} = -19.26$.

$\text{Pb}_4(\text{OH})_4^{4+}$ and PbOH^+ were formed as the initial hydrolysis products. Therefore it was considered necessary to recalculate the data in the high $\log h$ region to see that this hypothesis is not upset by disturbances from the new complexes. A calculation of the concentrations of $\text{Pb}_3(\text{OH})_4^{2+}$ and $\text{Pb}_6(\text{OH})_8^{4+}$ showed that they give only a small contribution in this region.

In order to follow, separately, the formation curve of $\text{Pb}_4(\text{OH})_4^{4+}$ at low B values and into the region where the contribution of $\text{Pb}_3(\text{OH})_4^{2+}$ and $\text{Pb}_6(\text{OH})_8^{4+}$ is not negligible the following equations were derived

$$B_c Z_c = BZ - \beta_{11} b h^{-1} - 4\beta_{4,3} b^3 h^{-4} - 8\beta_{8,6} b^6 h^{-8} = 4\beta_{4,4} b^4 h^{-4} \quad (34)$$

$$10^{\eta c} = (B - \beta_{11} b h^{-1} - 3\beta_{4,3} b^3 h^{-4} - 6\beta_{8,6} b^6 h^{-8}) b^{-1} = 1 + 4\beta_{4,4} b^3 h^{-4} \quad (35)$$

By subtracting the terms for the other complexes, calculated with the equilibrium constants already determined, we have arrived at equations identical to (9, 10) and the equilibrium constant is determined as described there (Figs. 9, 10). The value found was

$$\log \beta_{4,4} = -19.25 \pm 0.03 (\eta \text{ data}) \text{ and } -19.26 \pm 0.03 (Z \text{ data})$$

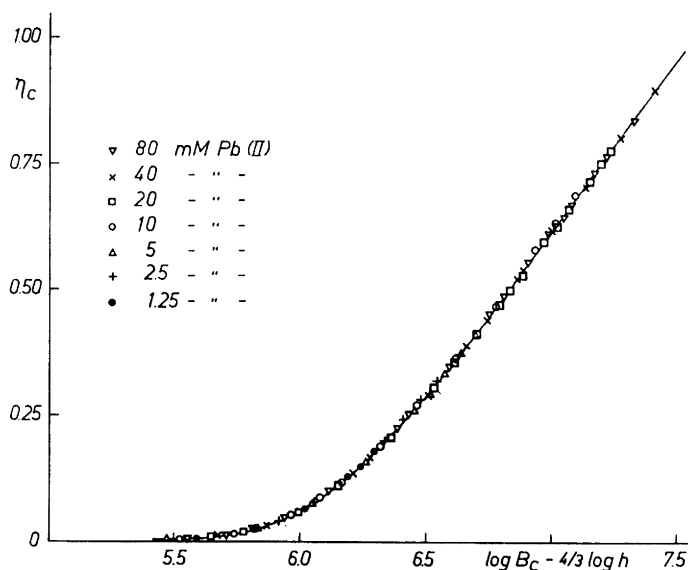


Fig. 10. η_c as a function of $(\log B_c - 4/3 \log h)$ according to eqn. (12). η_c , B_c ; terms for $\text{Pb}_4(\text{OH})_8^{4+}$, $\text{Pb}_3(\text{OH})_4^{2+}$ and PbOH^+ have been subtracted. Drawn curve represents normalized curve, calculated from eqn. (12), in position of best fit and giving $\log \beta_{4,4} = -19.25$.

Determination of the equilibrium constants in 0.3 M (Na)ClO₄. With 0.3 M (Na)ClO₄ as medium the Pb(II) concentrations 10, 5, 2.5 and 1.25 mM were investigated. The interpretation of the data has not been carried out independent of the results which were obtained from the 3 M (Na)ClO₄ data. We have tested only to see if they could be explained by the same mechanism. The calculations were started from eqn. (31) which gave a good straight line from which the equilibrium constants were found as

$$\log \beta_{4,3} = -23.35 \pm 0.1$$

$$\log \beta_{8,6} = -42.66 \pm 0.1$$

Knowing these constants the quantities

$$B_c Z_c = BZ - 4\beta_{4,3} b^3 h^{-4} - 8\beta_{8,6} b^6 h^{-8} \quad (36)$$

$$10^{\eta_c} = (B - 3\beta_{4,3} b^3 h^{-4} - 6\beta_{8,6} b^6 h^{-8}) b^{-1} \quad (37)$$

were calculated and Z_c and η_c plotted as functions of $(\log B_c - 4/3 \log h)$. The data from the 10 and 5 mM titrations fell on the same curve as required by the formation of $\text{Pb}_4(\text{OH})_4^{4+}$, but the data for the other two values of B were slightly off the curve. This is not unexpected since the Z and η curves

for these concentrations clearly indicate the presence of mononuclear species. Log $\beta_{4,4}$ was determined from the 10 and 5 mM titrations by curve-fitting according to eqn. (12) and found to be

$$\log \beta_{4,4} = -19.89 \pm 0.05 (\eta \text{ data}) \text{ and } -19.91 \pm 0.05 (Z \text{ data})$$

With these values for log $\beta_{4,4}$, new $B_c Z_c$ and η_c functions were calculated where the terms for $\text{Pb}_4(\text{OH})_4^{4+}$ had also been subtracted. Plots of Z_c and η_c as functions of log h gave single curves, which fitted the normalized curves for PbOH^+ well. Log β_{11} was found to be

$$\log \beta_{11} = -7.75 \pm 0.1$$

Log β_{11} was estimated also from the lower parts of the Z and η curves of the 2.5 and 1.25 mM titrations. The value found was $\log \beta_{11} = -7.8 \pm 0.1$. With this value for log β_{11} the terms for PbOH^+ were also subtracted in eqns. (36) and (37). The new plots of Z_c and η_c as functions of $(\log B - 4/3 \log h)$ fell on the same curves for all concentrations and the plots gave good agreement with the normalized curves for the formation of $\text{Pb}_4(\text{OH})_4^{4+}$.

With the help of the equilibrium constants thus found theoretical $Z(\log h)_B$ and $\eta(\log h)_B$ curves were calculated for all values of B both in 3 M and 0.3 M $(\text{Na})\text{ClO}_4$. In general very good agreement was found between the experimental and theoretical curves as is seen from Figs. 1, 2, 3 and 4. However, there are two questions that need some discussion.

The first question is concerned with the Z data from the titrations at low values of B . As has been mentioned already the 3 M $(\text{Na})\text{ClO}_4$ contained an acidic impurity. The Z data used in the previous calculation have been corrected for this impurity. If for the moment we assume that the correction is not valid, ν values as high as 1.37 are found for $B = 1.25$ mM. Thus complexes with a $\text{OH}^-/\text{Pb(II)}$ ratio $> 4/3$ must also be present. It is likely that these complexes contain only a few Pb atoms since otherwise the deviations could be expected to be most pronounced at the highest values of B . The simplest explanation that might be suggested is the formation of $\text{Pb}(\text{OH})_2$. We have

$$BZ' - (\beta_{11}bh^{-1} + 4\beta_{4,4}b^4h^{-4} + 4\beta_{4,3}b^3h^{-4} + 8\beta_{8,6}b^6h^{-8}) = p\beta_{p,q}b^qh^{-p} \quad (38)$$

Z' is the Z value which is obtained if no correction is applied for the acidity in the $(\text{Na})\text{ClO}_4$. The quantity in the parenthesis was calculated as a function of log h using the previously determined equilibrium constants and neglecting the term $q\beta_{p,q}b^qh^{-p}$ in B . This approximation was employed since exact calculations would be very time-consuming. Using eqn. (38) $\log \beta_{2,1}$ ($p = 2, q = 1$) was estimated from the 1.25 and 2.5 mM titrations. The value found was $\log \beta_{2,1} \simeq -16$. No other hypotheses were tested.

A value of $\beta_{2,1}$ around 10^{-16} would make the acidity constants of Pb^{2+} and PbOH^+ about equal. This unusual situation has been observed for other metal

ions including Hg^{2+} (Ref. 27), Tl^{3+} (Ref. 25), Fe^{3+} (Ref. 26), In^{3+} (Ref. 28) and Sc^{3+} (Ref. 29). The η data do not show any deviation from the calculated curves either in 3 M or 0.3 M $(\text{Na})\text{ClO}_4$. In 0.3 M $(\text{Na})\text{ClO}_4$ medium, where no correction has been applied for the acidity in the NaClO_4 , there is almost no discrepancy between the experimental and calculated $Z(\log h)_B$ curves, which would indicate the validity of the correction applied to the measurements with 3 M $(\text{Na})\text{ClO}_4$ as medium. Since the presence of $\text{Pb}(\text{OH})_2$ in the investigated $\log h$ region is dubious it has not been included in the explanation of the data.

The second question is concerned with the data at low Z for the 80 and 40 mM titrations. In this region ν is found to be < 1 . It starts from *ca.* 0.9 and increases to 1.00 ± 0.02 . The deviations from $\nu = 1$ for the first points appear to be outside the limits of the experimental error and would indicate the presence of complexes with a $\text{OH}^-/\text{Pb}(\text{II})$ ratio < 1 , for instance $\text{Pb}_2\text{OH}^{3+}$. This is not unlikely since a high value of B and $\log h$ favours the formation of such complexes. The disturbance might be caused by the complex $\text{Pb}_2\text{OH}^{3+}$, for which Pedersen¹ found evidence in concentrated $\text{Pb}(\text{NO}_3)_2$ solutions. A search for this complex is now being made by studying the hydrolysis in concentrated $\text{Pb}(\text{ClO}_4)_2$ solutions.

To sum up we propose the following reactions and equilibrium constants to explain the data.

		Equilibrium constants	
		3 M $(\text{Na})\text{ClO}_4$	0.3 M $(\text{Na})\text{ClO}_4$
$\text{Pb}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{PbOH}^+ + \text{H}^+$	$\log \beta_{11}$	-7.9 ± 0.1	-7.8 ± 0.1
$4\text{Pb}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Pb}_4(\text{OH})_4^{4+} + 4\text{H}^+$	$\log \beta_{4,4}$	-19.25 ± 0.1	-19.90 ± 0.1
$3\text{Pb}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Pb}_3(\text{OH})_4^{2+} + 4\text{H}^+$	$\log \beta_{3,3}$	-22.87 ± 0.1	-23.35 ± 0.1
$6\text{Pb}^{2+} + 8\text{H}_2\text{O} \rightleftharpoons \text{Pb}_6(\text{OH})_8^{4+} + 8\text{H}^+$	$\log \beta_{6,6}$	-42.14 ± 0.1	-42.66 ± 0.1

DISCUSSION

The present investigation agrees with the earlier works by Pedersen¹ and Faucherre² in so far as they also found evidence for the complexes $\text{Pb}_4(\text{OH})_4^{4+}$ and PbOH^+ . The numerical values of the equilibrium constants seem to agree less satisfactorily. However, they have often been determined in different media and are therefore not directly comparable.

Faucherre's values for $\beta_{4,4}$ were obtained from his measurements on $\text{Pb}(\text{NO}_3)_2$ solutions, which also contained $\text{Ba}(\text{NO}_3)_2$ to make the ionic strength, I , 0.6 or 0.06. Pedersen also determined $\beta_{4,4}$ in mixtures of $\text{Pb}(\text{NO}_3)_2$ and $\text{Ba}(\text{NO}_3)_2$ at different I and has given a formula from which $\log \beta_{4,4}$ can be calculated knowing I . In the table below the results of these authors are compared.

I	$\log \beta_{4,4}$ (Faucherre)	$\log \beta_{4,4}$ (Pedersen)
0.6	-18.75	-20.81
0.06	-18.05	-20.61

In perchlorate medium Faucherre did not determine $\beta_{4,4}$ directly. He calculated theoretical Z curves for $\text{Pb}_4(\text{OH})_4^{4+}$ with $\log \beta_{4,4} = -18.75$ obtained with nitrate medium, and from the fact that these curves satisfactorily pass through his experimental points in 1 M NaClO_4 the value in this medium must be close to -18.75 . This value differs by 0.5 units from our value in 3 M NaClO_4 .

The lower value for $\beta_{4,4}$ in nitrate medium, found by Pedersen, is reasonable considering the complex formation between Pb^{2+} and NO_3^- . The values found by Faucherre with the same medium, therefore, seem to be somewhat in error.

The discrepancy between the results obtained by Faucherre and us from measurements on solutions with $Z > 1$ is probably due mainly to his mode of calculation. His calculations were based on the assumption that the lead(II) at $Z = 1$ is present solely as $\text{Pb}_4(\text{OH})_4^{4+}$, which is not correct.

The values for $\log \beta_{11}$ found in the literature range between -6.2 and -8.7 . There is, however, no value from perchlorate solutions.

The complexes found probably have closed structures but we shall at the present stage refrain from any structure proposals.

Acknowledgements. The author is indebted to Professor Lars Gunnar Sillén for his continual interest in this work and to Professor Robert E. Connick, Univ. of Calif., for valuable criticism of the manuscript. He also wishes to thank Dr. George Biedermann for discussions on practical aspects of the research and for comments in the manuscript. Thanks are also due to Mr. György Patzauer for skilful help with some of the measurements and calculations and to Mr. Frans Eriksson for construction of the apparatus. The English of this paper has been corrected by Mr. David Martin. This work has been supported by *Statens Tekniska Forskningsråd (Swedish Technical Research Council)* and the *Air Force Office of Scientific Research of the Air Research and Development Command, United States Air Force*, through its European Office.

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Received August 25, 1959.