Hydrolytic equilibria of lead(II) at 100 °C in 3.6 mol kg^{-1} LiClO$_4$

Michele Fiore, Santino Orecchio, Vincenzo Romano,* Giuseppe Ruggirello and Roberto Zingales

Department of Inorganic Chemistry, University of Palermo, Via Archirafi 28, I-90123 Palermo, Italy

An *in situ* method, which allows the generation, analysis and measurement of the free hydrogen-ion concentration of aqueous solutions at high temperature (100 °C), has been elaborated. It is based on the use of a galvanic cell without a liquid junction containing a glass electrode and of a cell where controlled external and/or internal electrolysis processes take place. The reliability of the method has been checked by carrying out coulometric acid–base titrations of standard dilute HClO$_4$ solutions in 3 mol dm^{-3} LiClO$_4$ as ionic medium. The high accuracy so obtained has made it possible to study lead(II) hydrolysis at 100 °C. In the whole range of lead(II) concentration investigated (2 × 10^{-3}–0.1 *m*) the collected data ($Z \longrightarrow \log h$) can be explained by assuming the formation of a mononuclear [Pb(OH)]$^+$ ($\log \beta_{11} = -6.05 \pm 0.01$) and a tetranuclear species [Pb$_4$(OH)$_4$]$^{4+}$ ($\log \beta_{44} = -15.94 \pm 0.03$). An increase in temperature from 25 to 100 °C has the effect of increasing the acidic properties of lead(II) solutions and of decreasing the number of hydrolysed species.

Equilibrium analysis has supplied a theoretical and methodological basis in most studies on solution equilibria.[1] The hydrolysis of inorganic cations and anions gives rise to a large array of mono- and poly-nuclear species. Difficulties arise in the study of some of these, such as those of Al^{III}, Cr^{III} and Ga^{III}, due to their extremely slow reactions. This has led to a disagreement between both the speciation patterns and the equilibrium constants reported.[1] So, in the absence of an appropriate catalyst, the experimental study of such equilibria must be carried out at a temperature high enough to ensure rapid attainment of equilibrium.

Systematic studies at high temperatures (300–400 °C) have been performed[2] using cells with a liquid junction containing the hydrogen electrode, held under pressure. The experimental methods reported, including the addition of measured volumes of properly thermostatted reagents, cannot be easily realized. According to our experimental results, accurate studies of equilibria in aqueous solution can be made routinely at 100 °C or even higher temperatures, using a system consisting of an electrolytic cell for the coulometric *in situ* generation of the required reagents together with a potentiometric cell without a liquid junction and containing the usual glass electrode. A similar system was employed[3] to study indium(III) hydrolysis at 25 °C. We now report a study of the hydrolysis of lead(II) ion at 100 °C in 3.6 mol kg^{-1} LiClO$_4$.

Method of Investigation

The method is based on two cells, the galvanic cell (G) and the electrolytic one (C). Solution S$_0$ has the composition B_0 *m*

Glass electrode	Solution S$_0$	Ag	G

PbO$_2$	Solution S$_0$	Ag	C
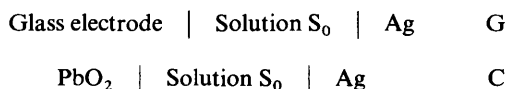
Pb(ClO$_4$)$_2$, A_0 *m* AgClO$_4$, H_0 *m* HClO$_4$, I_0 *m* LiClO$_4$, where *m* is the molality (mol per kg of solvent) and $I_0 = 3.6 - 2 B_0 - A_0 - H_0$. Lithium perchlorate was chosen as ionic medium because it can be obtained in high purity after a double crystallization from water.[4] The temperature-independent value of 3.6 *m* corresponds to about 3 mol dm^{-3} at 25 °C. A commercial glass electrode was employed.

The electrodes of cells G and C were fitted into a five-necked vessel, the necks being long enough to keep at 100 °C not only the solution, but also the electrodes, especially the whole
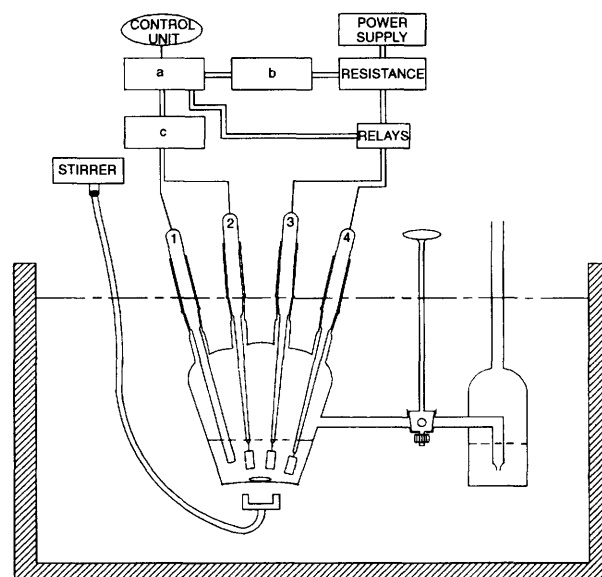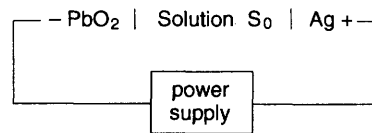

Fig. 1 Sketch of the reaction vessel and of the coulometric–potentiometric system. a, Data acquisition system; b, digital voltmeter; c, high impedance electrometer. Electrodes: 1, glass; 2, silver sheet; 3, silver net; 4, PbO$_2$ net

$$-\,\text{PbO}_2 \mid \text{Solution S}_0 \mid \text{Ag}\,+$$

power supply

Scheme 1

body of the glass electrode. Possible overpressure in the closed vessel was eliminated through a liquid valve connected to a side of the vessel, filled with a small amount of solution S$_0$ (see Fig. 1).

The closed system made up from cells G and C allowed us to determine at 100 °C the hydrogen-ion content of solution S$_0$ by means of a coulometric–potentiometric titration.

Connecting cell C to a direct current power supply gave the electrical circuit shown in Scheme 1, where a current of constant intensity was made to flow for measured intervals of time. In cell C reaction (1) takes place which allowed us to carry out the potentiometric titration by means of stepwise elimination of

Table 1 Experimental data for a coulometric–potentiometric titration at 100 °C. Initial composition of the solution in moles: $n^0{}_{Ag} = 0.505 \times 10^{-3}$, $n^0{}_{Pb} = 0.510 \times 10^{-3}$, $n^0{}_H = 0.328 \times 10^{-3}$. Electrolysis current intensity $i = 2 \times 10^{-3}$ A

t/s	E/mV	$10^3 Q_n/C$	$10^3 n_{Ag}/mol$	$10^5 G$	$10^3 n_H/mol$	E°/mV
0	35.1	0	0.505	17.0	0.328	21.3
600	38.6	1 200	0.518	15.6	0.304	21.5
1 200	42.2	2 400	0.530	14.3	0.279	21.6
1 800	45.9	3 600	0.543	13.0	0.254	21.6
2 100*	47.9	4 800	0.549	12.4	0.242	21.6
2 400	50.0	6 000	0.555	11.7	0.230	21.7
2 700*	52.5	7 200	0.561	11.0	0.217	22.0
3 000	54.3	8 280	0.568	10.5	0.205	21.6
3 300*	56.8	9 600	0.574	9.8	0.192	21.7
3 600	58.6	10 800	0.580	9.4	0.180	21.0
3 900*	61.7	12 000	0.586	8.6	0.167	21.5
4 140	63.5	13 200	0.591	8.2	0.157	21.0
4 500*	67.5	4 200	0.599	7.3	0.143	21.4
4 800	70.6	5 400	0.605	6.7	0.130	21.3
5 100*	74.3	6 600	0.611	6.1	0.118	21.4
5 400	78.4	7 800	0.617	5.4	0.105	21.6
5 700*	82.8	9 000	0.624	4.8	0.093	21.7
6 000	87.1	10 200	0.630	4.2	0.080	21.1
6 300*	94.1	11 400	0.636	3.4	0.068	22.4
6 600	100.2	12 600	0.642	2.9	0.056	21.7

* Refers to reverse electrolysis.

Table 2 Comparison of the hydrogen-ion concentrations obtained at 25 °C with a standard volumetric method (v) and at 100 °C with the coulometric–potentiometric (p) one

Solution	10^3 [H$^+$]/mol dm^{-3}	
	v	p
1	1.439	1.440
2	6.582	6.588
3	12.10	12.04

$$PbO_2(s) + 4H^+ + 2Ag(s) \rightleftharpoons 2Ag^+ + Pb^{2+} + 2H_2O \quad (1)$$

H$^+$, so avoiding any external addition of reagents. After each electrolysis step the electromotive force (emf) E of cell G quickly reached[4] an equilibrium value. Before the neutralization point, the electrode polarization in cell C was reversed to drive reaction (1) in the opposite direction, in order to perform a stepwise electrolytic generation of H$^+$ to restore the initial acidity of solution S_0. Data from a typical titration, collected during both the direct and the reverse electrolysis, are reported in Table 1. The current intensity i, the electrolysis time t and the E of cell G are the measured variables, while Q_n, n_{Ag}, n_H and G were computed as follows.

If $n^0{}_{Ag}$ and $n^0{}_H$ are the amounts in mmol of Ag$^+$ and H$^+$ in solution at the beginning of the titration, and after that a current of i_k mA has passed through cell C for n periods of t_k seconds, according to reaction (1), the actual amount of Ag$^+$, n_{Ag}, will be given by equation (2),

$$n_{Ag} = n^0{}_{Ag} + \sum_{k=0}^{n} i_k t_k / F = n^0{}_{Ag} + (Q_n/F) \quad (2)$$

where

$$Q_n = \sum_{k=0}^{n} i_k t_k$$

is the amount of electrical charge in millicoulombs passed through cell C after n electrolysis steps. The value of the Faraday constant F has been set[5] equal to 9.6485×10^4 mol^{-1}. In the same way equation (3) can be written.

$$n_H = n^0{}_H - 2 \sum_{k=0}^{n} i_k t_k / F = n^0{}_H - (2Q_n/F) \quad (3)$$

According to the approximation of the constant ionic medium,[6] the emf of cell G can be written as in equation (4)

$$E = E^{\circ} + 74.04 \log (n_{Ag}/n_H) \quad (4)$$

where potentials are expressed in millivolts and the constant term E°, reported in the last row of Table 1, has been determined by means of equation (4), from the n_{Ag}, n_H and E data collected in the experiment.

Combining equations (2)–(4) and rearranging we obtain (5).

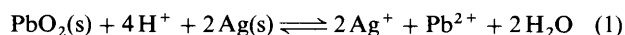$$10^{(E^{\circ}-E)/74.04} n_{Ag} = n^0{}_H - (2Q_n/F) \quad (5)$$

Equation (5) is a particular result of the Gran treatment[7] of potentiometric titration data, used to locate the equivalence point. So, plotting $G = 10^{-E/74.04} n_{Ag}$ versus Q_n one should obtain a straight line, extrapolation of which to $G = 0$ gives the value of Q_e, the amount of millicoulombs needed to titrate the acidity excess in solution S_0. Under these conditions, the left-hand side of equation (5) is equal to 0 and $n^0{}_H = 2Q_e/F$.

Plotting against Q_n the G values reported in Table 1, one indeed obtains a straight line which intercepts the x axis at a value of Q_e which allows calculation of the hydrogen-ion content of solution S_0 at the beginning of the titration. It is worth noting the good agreement of this value with that obtained at 25 °C by volumetric titration of solution S_0 with standard NaOH using the methyl orange–indigo carmine[8] mixed indicator to obtain a sharper end-point. Agreement has also been obtained for different S_0 solutions as reported in Table 2.

The conclusions which can be drawn from these results may be helpfully used to investigate the lead(II) hydrolysis equilibria at 100 °C. The most important of them are as follows.

(1) For a given solution the values of $n^0{}_H$ obtained from volumetric titrations at 25 °C with standard NaOH are in good agreement with those derived at 100 °C with the present procedure (see Table 2).

(2) The values of the emf E of cell G are unequivocally dependent on Q_n, the amount of charge passed through solution S_0.
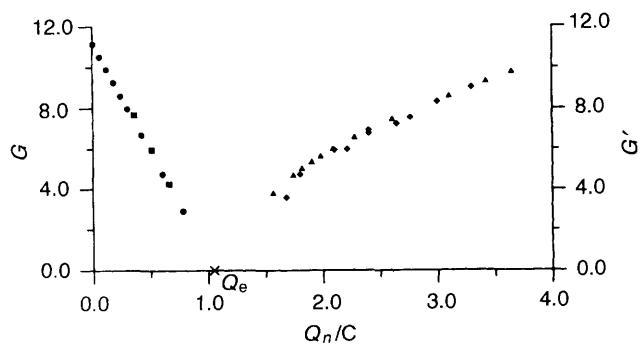
Fig. 2 Gran plot for a complete titration of a S_0 solution. Symbols refer to data from the external electrolysis alkalization (●), external electrolysis acidification (■), internal electrolysis strong alkalization (▲) and external electrolysis neutralization (◆)

(3) There is a nernstian dependence of these emf values on the concentration of the species. This is shown also from the constancy of the term $E^\circ = E - 74.04 \log(n_{Ag}/n_H)$, the standard deviation of which, in the example in Table 1, is ± 0.3 mV.

(4) The emf of cell G quickly attains an equilibrium value, which remains constant, ± 0.05 mV, for periods longer than 24 h.[4]

(5) Reaction (1) is electrochemically reversible in the acid solution S_0: if we let a current (1–50 mA) flow through both cells Ag | Solution S_0 | Ag and PbO_2 | Solution S_0 | PbO_2 for periods as long as 4–5 h, the ionic concentrations in solution S_0 do not undergo any appreciable change.

Measurement of Lead(ii) Hydrolysis at 100 °C

The results so far discussed were always obtained by maintaining an excess of H^+ in solution S_0. Nevertheless, the electrolytic elimination of H^+ can be carried out beyond the equivalence point, so that $2Q_n/F > n^\circ_H$. In the absence of any hydrolytic equilibrium, the excess of OH^- ions given by equation (6) should be equal to the amount of free OH^- ions

$$n_{OH} = 2(Q_n - Q_e)/F \qquad (6)$$

and directly proportional to G', equation (7). Actually, in a plot

$$G' = 10^{(E/74.04)}/n_{Ag} \qquad (7)$$

of G' versus Q_n the experimental points show a negative deviation from the expected straight line. This clearly indicates that lead(ii) hydrolysis is taking place, making the G' values increase less than expected.

Moreover, if the polarity of the electrodes in cell C is reversed in order to increase stepwise the hydrogen-ion content in the hydrolysed solution, the values of G' obtained do not overlap those derived in the previous alkalization step. This could suggest some kinetic complications in the attainment of lead(ii) hydrolysis equilibria at 100 °C, but it is unlikely as at 25 °C the hydrolysis equilibria are set up quickly.[9] The lack of reversibility is more likely due to the occurrence of reaction (8) which,

$$H_2O + e^- \rightleftharpoons \tfrac{1}{2}H_2 + OH^- \qquad (8)$$
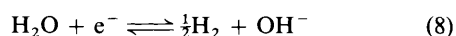
as the acidity of solution S_0 decreases, becomes more and more competitive with (9) at the negative electrode. As a consequence,

$$PbO_2 + 2H_2O + 2e^- \rightleftharpoons Pb^{2+} + 4OH^- \qquad (9)$$
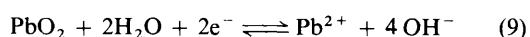
the number of OH^- ions cathodically generated is unpredictably less than that expected on the basis of equation (9). Fortunately this problem can be overcome: by short-circuiting the electrodes, cell C spontaneously delivers a discharge direct current. In this way an *internal electrolysis* takes place which

does not suffer any polarization effect and gives rise only to reaction (1) which proceeds quickly enough. So, in each coulometric titration, as the equivalence point was approached the external power supply was disconnected, the electrodes of cell C short-circuited, and the alkalization reaction went on, *mutatis mutandis*, with a 100% yield. Of course, the inner electrolysis process gives a current of variable intensity i, so that the amount of millicoulombs passed through the cell must be computed by solving the integral $\int i \, dt$ over the considered time interval. In this way, as shown in Fig. 2, G' values obtained from the internal electrolysis overlap those obtained from the external one.

The results discussed so far show that cell C, used both in the external and internal electrolysis processes, represents a simple and accurate system for the controlled generation and/or elimination of H^+, Ag^+ and Pb^{2+}. Provided that solutions S_0 are acidic, cell G represents a simple, accurate and quick system for the measurement of $\log h$ in the hydrolysed lead(ii) solutions. So, the integrated system comprised of cells G and C in the closed vessel at 100 °C allows variation of the analytical composition of solution S_0 and measurement of the equilibrium concentration of H^+.

In order to verify that, during the coulometric alkalization process, oversaturated solutions were not produced, and that accordingly measurements had not been carried out on solutions far from equilibrium, we tried to determine at which value of $\log h$ saturation of PbO occurred at 100 °C. So, for each value of B [the total lead(ii) concentration] we have also investigated S_0 solutions saturated at 100 °C with solid PbO (see Experimental section), to give solutions S_i having a definitely known analytical composition: $(B_0 + H_0/2)$ m $Pb(ClO_4)_2$, A_0 m $AgClO_4$, x_b m PbO, I_0 m $LiClO_4$. The analytical base excess, $2x_b$, in solution S_i, due to the solubility of PbO, can be determined from the lead mass-balance equation (10), where B, the total lead concentration in S_i, was easily

$$B = B_0 + (H_0/2) + x_b \qquad (10)$$

determined by complexometric titration (see Experimental section) and the terms B_0 and H_0 were the same as those for the corresponding S_0 solution. A better evaluation of x_b was obtained from the potentiometric titration.

Potentiometric titration of solution S_i was started by acidifying the solution by external electrolysis. After each electrolysis step the emf E of cell G was measured to a constant value, maintained for at least 15 min. When the base excess $(2x_b)$ had been nearly neutralized, the solution was again stepwise alkalized, using cell C in an internal electrolysis process, nearly to restore the initial value of E. At this point the power supply was again connected to cell C, and the solution stepwise electrolysed to an acidity level high enough to destroy any hydrolysis product in the solution. Finally it was partially neutralized by external electrolysis. In other words, during a complete titration, any S_i solution was: (a) acidified by external electrolysis; (b) alkalized by internal electrolysis; (c) extensively acidified by external electrolysis; (d) partly neutralized by external electrolysis.

Once Q_n millicoulombs had been passed in step (a), the silver content of the solution was given by equation (11) and the total

$$n_{Ag} = n^\circ_{Ag} - (Q_n/F) \qquad (11)$$

excess of hydroxyl ions by equation (12) where P is the weight in

$$n_{OH} = 2x_b P - (2Q_n/F) \qquad (12)$$

kilograms of water contained in the portion of solution S_i taken for the experiment. Equation (4) could then be rewritten as (13), where K_w is the ionic product of water in the ionic medium used, at 100 °C. Both K_w and P are constant during each titration.

and from its intercept on the Q_n axis it was possible to calculate the most accurate value of x_b. Experimental data for a complete titration of a typical S_i solution are collected in Table 3.

The value of x_b so obtained and the data collected in steps (c) and (d) allowed the determination of the constant term E°. This was used in equation (17) to evaluate h, the concentration of

$$h = 10^{(E^\circ - E)/74.04}n_{Ag}/P \quad (17)$$

free H^+ in the hydrolysed solution. As discussed in the next section, h was used in equation (18) to determine Z, the mean

$$Z = (h - H)/B \quad (18)$$

number of H^+ ions set free from each Pb^{2+} ion, equation (19).

$$H = (2Q_n/FP) - 2x_b \quad (19)$$

The titration of each solution S_i, which required a whole working day, was followed by that of the corresponding S_0 solution. This acidic solution, in which the metal content was only slightly lower than that in the corresponding S_i solution, was alkalized stepwise by external electrolysis nearly to the beginning of the lead(II) hydrolysis. In this way it was possible to plot G vs. Q_n, to obtain the value of n°_H, from which to determine E° by equation (4). Then, the alkalization was continued by internal electrolysis, to nearly the maximum extent of hydrolysis, at the starting $\log h$ value of the corresponding S_i solution. The emf data collected in this range were used to obtain values of Z for the hydrolysis of solution S_0, by means of equations (18) and (19). Finally, the power supply was connected and the solution acidified stepwise to the initial acidity content.

Data Treatment

In order to obtain the hydrolysis pattern of Pb^{II} at 100 °C the 426 experimental pairs of data from eight titrations of S_i and S_0 solutions were treated with both graphic and computational methods. Each titration was carried out at least twice.

For each hydrolysis reaction (20) the related equilibrium

$$q\text{Pb}^{2+} + p\text{H}_2\text{O} \rightleftharpoons [\text{Pb}_q(\text{OH})_p]^{(2q-p)+} + p\text{H}^+ \quad (20)$$
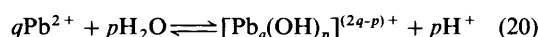
constant, in the limits of validity of the constant ionic medium method,[5] can be expressed as in equation (21). So, the system

$$\beta_{qp} = [\text{Pb}_q(\text{OH})_p^{(2q-p)+}][\text{H}^+]^p/[\text{Pb}^{2+}]^q \quad (21)$$

composition can be determined when the p and q values and the value of each equilibrium constant β_{qp} are known.

The most important features of such a system can be quickly identified in a plot of Z against $-\log h$. As shown in Fig. 3, Z is not a single-value function of h, also being dependent on the B value; this is a clear indication that polynuclear hydrolysis reactions take place,[10] so that the parameter q can assume values different from 1. Moreover the spacing $(dB/d \log h)_z$ between curves in Fig. 3 is not constant, ruling out the hypothesis that at 100 °C the hydrolysis reactions of Pb^{II} follow a 'core + links' pattern. This pattern, proposed by Sillén,[10] correctly explains the hydrolysis of several cations including that of Pb^{II} at 25 °C.[9]

Several graphical approaches[11-15] have been used to find the p, q and β_{qp} values from which we could infer, as the most likely, the formation of $[\text{Pb(OH)}]^+$ and $[\text{Pb}_4(\text{OH})_4]^{4+}$, and determine the values of the related formation constants $\log \beta_{11} = -6.0$ and $\log \beta_{44} = -15.8$, without completely ruling out the existence of other species.

Table 3 Experimental data from a complete coulometric–potentiometric titration on a saturated solution at 100 °C. Initial composition of the S_i solution: $m_{Ag} = 0.0706$, $m_{Pb} = 0.0384$, $x_b = 3.57 \times 10^{-3}$

$10^3 Q_n/C$	E/mV	G	h/mol kg^{-1}	$-\log h$	Z
0ᵃ	291.5	8666	2.38×10^{-5}	4.62	0.093
240ᵃ	290.6	8427	2.44×10^{-5}	4.61	0.086
600ᵃ	288.8	7968	2.57×10^{-5}	4.59	0.077
960ᵃ	286.9	7510	2.72×10^{-5}	4.57	0.067
1320ᵃ	284.7	7014	2.91×10^{-5}	4.54	0.058
1680ᵃ	281.9	6429	3.16×10^{-5}	4.50	0.048
2040ᵃ	278.3	5748	3.53×10^{-5}	4.45	0.038
2400ᵃ	273.3	4920	4.11×10^{-5}	4.39	0.029
2760ᵃ	264.9	3789	5.32×10^{-5}	4.27	0.019
3120ᵃ	247.5	2205	9.12×10^{-5}	4.04	0.010
2582ᵇ	270.2	4468	4.52×10^{-5}	4.34	0.024
2066ᵇ	278.4	5766	3.52×10^{-5}	4.45	0.038
1570ᵇ	283.6	6778	3.00×10^{-5}	4.52	0.051
906ᵇ	288.0	7772	2.63×10^{-5}	4.58	0.069
281ᵇ	291.0	8532	2.41×10^{-5}	4.62	0.085
4320ᶜ	171.5	5.29	9.61×10^{-4}	3.02	
4680ᶜ	160.5	7.43	1.35×10^{-3}	2.87	
5040ᶜ	152.1	9.62	1.75×10^{-3}	2.76	
5400ᶜ	145.6	11.74	2.13×10^{-3}	2.67	
5760ᶜ	140.1	13.89	2.53×10^{-3}	2.60	
6000ᶜ	136.8	15.36	2.79×10^{-3}	2.55	
5640ᵈ	142.4	12.94	2.35×10^{-3}	2.63	
5280ᵈ	148.5	10.74	1.95×10^{-3}	2.71	
4920ᵈ	156.1	8.50	1.55×10^{-3}	2.81	
4320ᵈ	177.5	4.39	7.98×10^{-4}	3.10	

ᵃ Data obtained in the external electrolysis acidification step. ᵇ Data obtained in the internal electrolysis alkalization step. ᶜ Data obtained in the extensive external electrolysis acidification step. ᵈ Data obtained in the external electrolysis alkalization step.
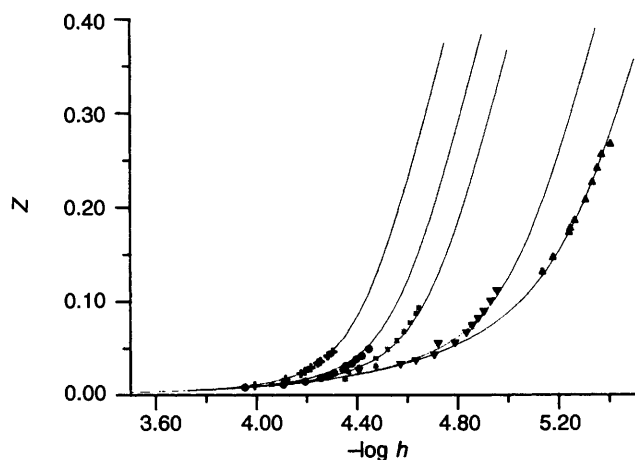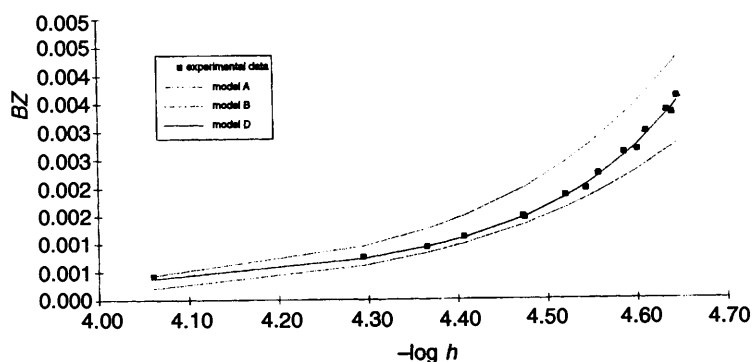

Fig. 3 Plot of Z, defined by equation (18), against $-\log h$ for the hydrolysis of Pb^{II} at 100 °C. Curves calculated from the reported hydrolysis constants are added. Lead(II) concentration: 0.0061 (▲), 0.014 (▼), 0.038 (✳), 0.053 (●) and 0.079 m (+)

Combining equations (12) and (13) and rearranging, one obtains (14). As already stated, a plot of $G' = 10^{(E/74.04)}/n_{Ag}$

$$E = E^\circ + 74.04 \log (n_{Ag}n_H/K_wP^2) \quad (13)$$

$$n_{OH} = 10^{(E-E^\circ)/74.04}K_wP^2/n_{Ag} = 2x_bP - (2Q_n/F) \quad (14)$$

versus Q_n is not linear, but its lower straight portion can be extrapolated to $G' = 0$, giving a good approximation to x_b, equation (15).

$$x_b = Q_n/FP \quad (15)$$

In step (b) the collected data gave G' values overlapping those obtained in step (a).

Step (c) was then carried out and the collected E data used to compute G from equation (16). A plot of G versus Q_n was linear

Fig. 4 Plot of BZ against $\log h$ for a single S_i solution ($B = 0.038\ m$). Some theoretical curves are superimposed on the experimental points

Table 4 Proposed models for the hydrolysis of lead(II) at 100 °C tested by means of the HYPERQUAD computer program

Model	Set of species (qp) Proposed	Found	$\log \beta_{qp} \pm 3s$	σ	χ^2
A	22	22	-9.1 ± 0.2	2.34	27.3
B	11	11	-6.12 ± 0.03	1.72	10.62
	33	33	-12.67 ± 0.03		
C	11	11	-6.05 ± 0.01	1.08	11.03
	34	34	-20 ± 1		
	44	44	-15.94 ± 0.03		
	68	—			
D	11	11	-6.05 ± 0.01	1.08	7.17
	44	44	-15.94 ± 0.03		
E	11	11	-6.05 ± 0.01	1.08	7.17
	33	—			
	44	44	-15.94 ± 0.03		

To overcome this ambiguity, we treated our data by means of the computer program HYPERQUAD.[16] Starting from an input model, the program tries to minimize a particular function of the untreated experimental data, ruling out from the model those species whose equilibrium constants show a standard deviation greater than 33% of their value. At the end of the run, together with the best model and the best values of the equilibrium constants, the output gives the statistical parameters σ and χ^2 (which allow one to check the agreement between the experimental data and the final theoretical model) and the error distribution in order to detect the presence of systematic errors.

As the function whose residual should be minimized, we used that in equation (22). In Table 4 are reported the input models

$$U = \sum_h \sum_i W_{hi}(E_h^{obs} - E_h^{calc})(E_i^{obs} - E_i^{calc}) \qquad (22)$$

used, together with those obtained at the end of the run, and the related statistical parameters, while in Fig. 4 the theoretical curves ($BZ\ vs.\ \log h$) for some of these models are superimposed on the experimental points; BZ represents the concentration of hydroxyl ions bound to Pb^{II}, as derived from equation (18). Model A, despite showing some agreement with the experimental data, has been ruled out because of its high σ and χ^2 values; B was rejected with respect to C and D on the basis of a statistical F test. Nevertheless, the same F test did not allow one to choose between models C (built up according to Olin's results[9]) and D; their χ^2 values were also not appreciably different. However, model D has been chosen as the one which better describes lead(II) hydrolysis at 100 °C for the following reasons: (i) $[Pb_3(OH)_4]^{2+}$ is not present in the distribution diagrams given as output by the computer; (ii) the standard deviation of the estimate of its equilibrium constant β_{34} is much higher than that for the other constants; (iii) the simpler model is always to be preferred.[17] Finally, the addition of one more
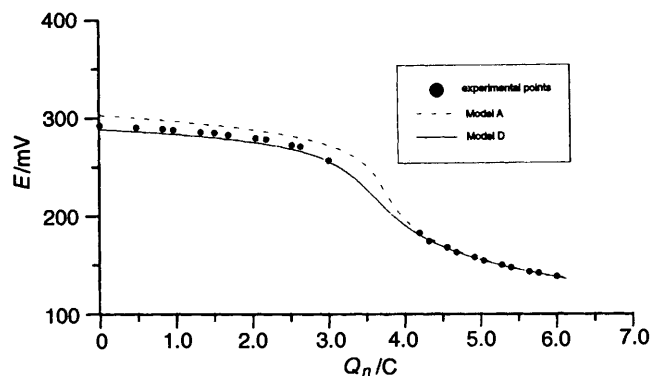

Fig. 5 Plot of primary emf data E against Q_n with curves built up on the basis of models A and D superimposed

species, for example $[Pb_3(OH)_3]^{3+}$, to the input model does not give any improvement, but provides the same output as that from model D.

In Fig. 5, primary E data for a single titration are plotted against Q_n; two curves drawn by using the constant values reported in Table 4 for models A and D are superimposed on them. The curve related to model D shows the best fit over the whole range investigated. This fit can also be checked by means of the appropriate projection maps.[18] On the basis of all these results, we can conclude that at 100 °C the hydrolysis of lead(II) proceeds through the formation of a mononuclear species $[Pb(OH)]^+$ in the dilute solutions and the additional tetranuclear $[Pb_4(OH)_4]^{4+}$ in the more concentrated solutions.

A few words can be said on the probable composition of the solid products, the precipitation of which limits the hydrolysis range of Pb^{II}. For each saturated solution S_i, values of $\log h$ and B have been used to calculate B/h, B/h^2 and B/h^3. Only the quantity B/h does not show any systematic trend with B: the mean value of $\log B/h$ is 3.14 ± 0.08. The constant value of B/h for the most hydrolysed solutions clearly indicates $Pb(OH)ClO_4$ as the simplest formula for the precipitate and it is a clear check of the chemical equilibrium established in the saturated solutions. The logarithm of the solubility product $[Pb^{2+}][ClO_4^-]/h$ is 3.69 ± 0.08.

Discussion

The results reported clearly indicate that the external and internal electrolysis processes using cell C, in the presence of ions having very weak acidic properties, like Ag^I and Pb^{II}, allow the controlled and reversible generation of H^+ at 100 °C, the accuracy and reproducibility of which are limited by those of the measurement of the amount of current passed (1 part in 10 000). Its equilibrium concentration at 100 °C can be measured by means of cell G without a liquid junction, the accuracy and precision of which are limited by the apparatus used for the emf measurements. Efforts to use the lead amalgam

electrode[9] to measure the free lead(II) concentration failed owing to its instability at 100 °C. On the other hand the usual glass electrodes are of great utility under these drastic temperature conditions. The relevant fall of their resistance rising from 25 to 100 °C or more[19] makes cell G very prompt in reaching the equilibrium values in a few minutes. After that, the values remain constant to ±0.1 mV for at least 24–36 h.

As Ag[I] is a much weaker acid, the homogeneous hydrolysis of Pb[II] can be studied without any interference. At the greatest B value it begins at about log $h = -3.9$, and it is completed at about half a log h unit higher when a solid product appears. Great efforts were made to ensure that a true state of equilibrium with the solid phase was reached. In this connection the use of high-purity solid PbO has proven to be of great help. The unusually high-temperature conditions and the great importance of the quantitative electrochemical generation of some reacting species necessitated a limitation on the presence of impurities in the solutions investigated.[11] Furthermore, this method of saturating with solid PbO and the coulometric generation of the reagents has avoided the introduction of ions like hydrogencarbonate or carbonate (always present under the usual basic solutions) for which lead(II), and metal ions generally, has strong affinity.

The fast attainment of constant emf values and the reversibility of the E vs. Q_n curve are acceptable criteria to establish that a true equilibrium was reached during the titrations. We believe that the hydrolysis range and the hydrolysis mechanism are well defined, in spite of the difficulties due to the narrowness of the field of existence of the homogeneous hydrolysed solutions at 100 °C.

The comparison of our results with those of Olin[9] shows that, at higher temperature, the acid strength of Pb[II] increases by nearly two logarithmic units. Moreover, by using the ΔH and log β values reported for the tetramer formation,[20] one obtains a value of log $\beta_{44} = -16.3$ at 100 °C, which is in good agreement with the value of -15.94 found in this investigation.

It can be seen that two species only are enough to describe lead hydrolysis at 100 °C while at 25 °C two more species are necessary. Another important point is that we experienced the formation of a solid product at the highest Z values reached; this does not seem to happen at 25 °C, suggesting that the highly hydrolysed lead(II) solutions at 25 °C are over-saturated.

In conclusion we believe we have set up a useful technique to carry out lead hydrolysis studies at 100 °C and are confident that it can be used for studying the hydrolysis of other metal ions at 100 °C and higher temperatures.[21]

Experimental

Lithium perchlorate was prepared by adding to 70% $HClO_4$ a slight excess of solid Li_2CO_3; the mixture was left to stand for a couple of days and then filtered through a G3 sintered glass funnel without suction. The clear solution was acidified with dilute $HClO_4$, boiled under nitrogen bubbling to drive off CO_2 and concentrated to the first appearance of $LiClO_4$ crystals. Then it was filtered and the filtrate cooled in an ice-bath to give an abundant white precipitate of $LiClO_4$; the crystals were filtered off and washed with the minimum volume of cold water. Finally, they were crystallized twice more from hot water. The solid was used to prepare a stock solution of about 3.5 mol dm[3]. The content of $LiClO_4$ was accurately determined by evaporating a weighed amount at 120 °C in a calibrated weighing bottle. The small amount of $HClO_4$ in this stock solution was determined by a coulometric–potentiometric titration at room temperature. In the coulometric cell Pt | stock solution | 1 mol dm^{-3} $NaClO_4$ | 0.9 mol dm^{-3} $NaClO_4$, 0.1 mol dm^{-3} $AgClO_4$ | Ag a current was passed to destroy stepwise the H^+ ions, according to the reaction $H^+ + e^- \rightleftharpoons \frac{1}{2}H_2$; after each electrolysis step the emf of the potentiometric cell glass electrode | stock solution | 1 mol dm^{-3} $NaClO_4$ | 0.99 mol dm^{-3} $NaClO_4$, 0.01 mol dm^{-3} $AgClO_4$ | Ag was read and the collected data treated according to Gran[7] to locate the equivalence point.

Silver perchlorate was prepared by dissolving 99.99% silver metal in HNO_3 (1:1); on concentrating nearly to dryness, solid $AgNO_3$ was obtained which was then filtered through a sintered glass funnel and twice crystallized from water. It was then dissolved in water and treated with a stoichometric amount of Na_2CO_3: the solid Ag_2CO_3 so obtained was filtered off and washed to remove any NO_3^- trace (sulfuric acid–diphenylamine test).[22] Dilute $HClO_4$ was then saturated with this Ag_2CO_3, kept overnight and then filtered through a G3 funnel. The solution was then made just acidic and boiled to drive off CO_2. After cooling, this stock solution, which was about 1 mol dm^{-3} in $AgClO_4$, was analysed for its content of Ag^+ according to Volhard (ref. 23, p. 344), and for the excess of H^+ by titration with standard NaOH and methyl red as indicator. This determination was also carried out potentiometrically, giving a hydrogen-ion concentration never differing by more than 0.1% from the volumetric one. Their average value was taken as the concentration of the stock solution.

A lead perchlorate stock solution was obtained starting from twice crystallized $Pb(NO_3)_2$ and following the same procedure as for $AgClO_4$. The lead content of the stock solution was determined both by electrodeposition (ref. 23, p. 516) and volumetric titration with ethylenedinitrilotetraacetate and xylenol orange as indicator (ref. 23, p. 588). The excess of H^+ in this stock solution was determined by potentiometric titration with a standard NaOH solution, using the Gran method[7] for the determination of the equivalence point. Independent volumetric titrations in the presence of the methyl orange–indigo carmine indicator[8] gave a hydrogen-ion concentration which differed by less than 0.1% from the potentiometric one.

Saturated lead solutions were obtained by adding, to a volume of solution S_0, an excess of solid PbO, keeping the system under reflux for 12 h at 100 °C. Then a portion of this hot suspension was quickly filtered through a G3 sintered glass filter into the measurement vessel, determining its weight by difference. A clear and homogeneous solution denoted S_i was so obtained. In it the maximum concentration of the hydrolysis products for that total lead content was realized. The remaining part of the saturated solution was filtered and stored for duplicate measurements and for determining the total lead and silver molalities in it.

Electrodes and apparatus

Silver[24] and lead dioxide (ref. 23, p. 516) electrodes were prepared as described. Jena glasswerk Schott and Gerate glass electrodes were used; at 100 °C these came to a steady state within 10–15 min and kept a constant potential within 0.1–0.2 mV.

A Hewlett-Packard model 6186 C direct current power supply was employed. It delivered a constant current, the intensity of which was determined from the emf fall over a standard 100 Ω resistor (Leeds and Northrup), in series with the electrolysis cell. The time interval during which the current was flowing was measured with a simple timer, the lowest detectable value being 0.01 s.

The potentiometric and the electrolysis cells were placed in the titration vessel, the long necks of which were provided with joints. The solution in the vessel was magnetically stirred by a Teflon bar. The vessel and most of its long necks were immersed into a bath (0.075 m[3]) filled with silicon oil (200 Fluid, Dow Company) heated by a 1000 W quartz candle. The oil was kept in continuous motion by a blade stirrer. The temperature was measured by means of a digital thermometer and its fine adjustment at 100 ± 0.1 °C was realized by a lamp and a thermoelectronic switch.

Acknowledgements

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