The Hydrolysis of Metal Ions. Part 3.[1] Lead(II)

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The hydrolysis of lead(II) has been investigated by potentiometric titration at 25 °C in 0.10 mol dm^{-3} K[NO$_3$]. Data treatment by our version of MINIQUAD indicates the formation of the species $[Pb(OH)]^+$, $[Pb_3(OH)_4]^{2+}$, $[Pb_3(OH)_5]^+$, $[Pb_4(OH)_4]^{4+}$, and $[Pb_6(OH)_8]^{4+}$; the $-\log \beta_{pq}$ values for these species are estimated to be 7.86 (0.006), 23.91 (0.02), 31.75 (0.02), 20.40 (0.004), and 43.38 (0.009), respectively, the estimated standard deviations being given in parentheses. The use of low concentrations of total lead (1.000×10^{-4}—2.008×10^{-3} mol dm^{-3}) does not prevent the detection of high polymers and aids the detection of the new species $[Pb_3(OH)_5]^+$.

THE hydrolysis of lead(II) has been investigated by a variety of techniques such as potentiometry, ultracentrifugation, light scattering, Raman spectroscopy, and X-ray diffraction.[2,3] Of these techniques, only potentiometry can stand alone. The apparent complexity of this system [3] together with some uncertainties in earlier work [2] makes re-investigation desirable and we report here the results of such a study carried out at 25 °C in 0.10 mol dm^{-3} potassium nitrate.

EXPERIMENTAL

Reagents.—The source of lead was Univar lead nitrate (analytical reagent). This was twice recrystallised, only the first *ca.* 10% being taken in each case. The final product was dried *in vacuo* over silica gel and was used as a primary standard to prepare the stock solution. The other reagents have been described previously.[1,4]

Procedure.—The previously described procedures [1,4] were followed. Because the experimental pH range was close to neutrality, λ in the expression $[H^+] = 10^{-pH}/\lambda$ could not be sensibly refined and the value 0.850, previously found for uranium(VI), was used.[1] The value of log K_w was taken to be -13.80.[4] All titrations were carried out at 25.0 ± 0.1 °C in 0.10 mol dm^{-3} K[NO$_3$]. Some details of the titrations are given in Table 1; full details are available on request.

TABLE 1

Summary of titrations of lead(II) at 25 °C in 0.10 mol dm^{-3} potassium nitrate

Total (initial) lead concentration (10^{-3} mol dm^{-3})	pH Range	Number of points
2.008	6.418—7.350	60
1.004	6.648—7.498	50
0.502	6.583—7.947	55
0.201	6.697—8.218	55
0.100	6.203—8.297	60

RESULTS

The convention previously adopted [1,4] defines the stoicheiometric equilibrium constants (on the mol dm^{-3} scale) for reaction (1) as in equation (2). Each species is represented by either its formula or a (p,q) pair.

$$p\mathrm{Pb}^{2+} + q\mathrm{H_2O} \rightleftharpoons [\mathrm{Pb}_p(\mathrm{OH})_q]^{(2p-q)+} + q\mathrm{H}^+ \qquad (1)$$

$$\beta_{pq} = [\{\mathrm{Pb}_p(\mathrm{OH})_q\}^{(2p-q)+}][\mathrm{H}^+]^q/[\mathrm{Pb}^{2+}]^p \qquad (2)$$

For relatively simple systems containing, for example, not more than three hydrolytic species, a systematic approach in the numerical treatment of the data is possible.[4] For systems containing as many as five species in a relatively narrow pH range, the view has been expressed [3] that successful equilibrium analysis is not possible with potentiometric data alone. However, as has been demonstrated recently,[1] this view is not valid if the data are sufficiently precise and, hence, sufficiently discriminating. Nevertheless, the problem posed by the numerical analysis of such complex systems is extremely difficult to overcome because of the apparent absence of any suitable systematic strategy. The problem is the selection of the 'correct' model which then needs verification by the data using sufficiently close estimates of the β_{pq} values as starting points in the refinement process. Inadequate estimates of these values can lead to the rejection of a species (and hence the model), even though the species is actually present.

Using our version [1] of MINIQUAD [5,6] we examined a very large number of models involving the species: (1,1), (1,2), (1,3), (1,4), (2,1), (2,2), (2,3), (2,4), (3,4), (3,5), (4,4), (4,6), (4,7), (5,6), (5,8), (5,9), and (6,8). Initial estimates of the β_{pq} values were obtained from a generalised form of the Sylva–Davidson empirical relationship [1,4] [equation (3)] because of the absence of any information on the (2,2) species (see below). In equation (3) β_{pq} represents the

$$A = (r-1)(q+2-2p) - (p-1)(s+2-2r)$$
$$B = (p-1)(u+2-2t) - (t-1)(q+2-2p)$$
$$C = (r-1)(u+2-2t) - (t-1)(s+2-2r)$$
$$\log \beta_{pq} = (A \log \beta_{tu} + B \log \beta_{rs})/C \qquad (3)$$

formation constants of the ***unknown*** species (p,q), and β_{rs} and β_{tu} refer to those of any two ***known*** species (r,s) and (t,u). In the present case (at least initially) the last values were literature values for the (4,4) and (6,8) species. These initial estimates were not necessarily adequate during the *early* stages of the refinement (depending on the model) but they did provide a starting point. If any given estimated constant became relatively independent of the model (see Part 2) [1] and its estimated standard deviation was small (usually less than 5%), the value was temporarily fixed and the search and refinement process continued. In this way, progressively better estimates of the β_{pq} values could often be obtained with which additional models could be examined. Using our earlier criteria,[1,4] namely (*a*) all estimated standard deviations must be less than *ca.* 10% and (*b*) the R factor is *ca.* 0.001, the parameters of what was considered to be the global minimum (*i.e.* the 'best' model) were finally found.

In Table 2 are details of the global minimum (model 5) together with some closely situated local minima. In all these models, all β_{pq} values were refined simultaneously. Model 5 is clearly the ' best ' one and is the only model which meets the above criteria. The data in Table 2, however, are misleading because they do not properly reflect the difficulties of the model selection procedure as outlined above. A remarkable feature of these data is the small variation in the $-\log\beta_{pq}$ values (and the estimated standard deviations) in the various models.

TABLE 2

Comparison of some models of lead(II) hydrolysis *

Model number	Model	$-\log\beta_{pq}$	Estimated standard deviation of $-\log\beta_{pq}$	Estimated relative standard deviation (%) of β_{pq}	10^{10} × error square sum	*R* factor
1	(4,4)	20.23	0.008	2.0	204.1	0.008 0
	(6,8)	43.38	0.01	2.6		
2	(1,1)	8.05	0.03	5.8	88.5	0.005 3
	(4,4)	20.28	0.007	1.7		
	(6,8)	43.20	0.01	2.8		
3	(1,1)	8.04	0.01	3.2	24.9	0.002 8
	(3,4)	23.67	0.02	3.9		
	(4,4)	20.44	0.009	2.1		
	(6,8)	43.57	0.02	4.8		
4	(1,1)	7.79	0.008	1.8	12.2	0.002 0
	(3,5)	31.53	0.02	3.5		
	(4,4)	20.32	0.004	0.8		
	(6,8)	43.20	0.005	1.1		
5	(1,1)	7.86	0.006	1.4	4.3	0.001 2
	(3,4)	23.91	0.02	4.1		
	(3,5)	31.75	0.02	3.7		
	(4,4)	20.40	0.004	0.9		
	(6,8)	43.38	0.009	2.1		

* In 0.10 mol dm^{-3} K[NO$_3$].

TABLE 3

Survey of some results of the potentiometric investigation of the hydrolysis reactions of lead(II) at 25 °C

Medium *	Total lead concentration range (10^{-3} mol dm^{-3})	$-\log\beta_{pq}$ (1,1)	(2,1)	(3,4)	(3,5)	(4,4)	(6,8)	Ref.
B mol dm^{-3} Pb^{2+} (3 − 2*B*) mol dm^{-3} Na$^+$ 3 mol dm^{-3} [ClO$_4$]$^-$	500 990 1 490		6.45 6.45 6.34			19.25 19.23 19.28		7
B mol dm^{-3} Pb^{2+} (1.5 − *B*) mol dm^{-3} Mg^{2+} 3 mol dm^{-3} [ClO$_4$]$^-$	500 1 000 1 450		6.49 6.57 6.45			18.95 18.98 19.04		8
B mol dm^{-3} Pb^{2+} (1.5 − *B*) mol dm^{-3} Ca^{2+} 3 mol dm^{-3} [ClO$_4$]$^-$	500 1 000 1 450		6.30 6.39 6.24			19.12 19.11 9.12		8
B mol dm^{-3} Pb^{2+} (2 − 2*B*) mol dm^{-3} Na$^+$ 2 mol dm^{-3} [ClO$_4$]$^-$	0.1—100	7.93				19.35		13
B mol dm^{-3} Pb^{2+} (2 − 2*B*) mol dm^{-3} Na$^+$ 2 mol dm^{-3} [NO$_3$]$^-$	10—200	8.84	7.11			21.72		13
3 mol dm^{-3} Na[ClO$_4$]	1.25—80.0	7.9		22.87		19.25	42.14	2
0.3 mol dm^{-3} Na[ClO$_4$]	1.25—10.0	7.8		23.35		19.90	42.66	2
0.10 mol dm^{-3} K[NO$_3$]	0.100—2.008	7.86		23.91	31.75	20.40	43.38	This work

* *B* = Total lead(II) concentration.

The variation of the parameters of model 5 with λ was examined and, as in the case of copper(II) [4] [and unlike that of uranium(VI)], the values of the error square sum (which showed no minimum) and the estimated standard deviations of the log β_{pq} values change very little. For $0.75 \leqslant \lambda \leqslant 0.95$, the variations in the refined $-\log\beta_{pq}$ values are between 0.10 and 0.82 log units at most, depending on the species; the (6,8) species shows the greatest variation and this is attributed, at least in part, to its stoicheiometry. The choice of λ = 0.850 is an arbitrary one and is based on earlier work; [1] it is considered to be more realistic than a value determined in the absence of a metal ion.[4]

DISCUSSION

Table 3 provides a survey of some previous potentiometric investigations of the hydrolysis of lead(II) at 25 °C. Systems postulated to contain anionic or neutral species were omitted because these species are apparently not produced under the present experimental conditions. The most important difference between the earlier investigations and the present one is that low total lead(II) concentrations were used in this work.

The relative importance of the five detected species in the present investigation is shown in Figure 1 as a function of pH for a total lead(II) concentration of 2×10^{-3} mol dm^{-3}. Figure 2 presents the same calculations for a total lead(II) concentration of 10^{-4} mol dm^{-3}. In these calculations, true equilibrium was assumed; thus, possible supersaturation and/or precipitation were ignored. A comparison of these two Figures together with the data in Table 1 provides a measure of the relative contributions of the various species to the data.

The dominant hydrolytic species at low lead(II) concentrations (Figure 2) is the (1,1) cation, [Pb(OH)]$^+$. A search for other monomeric species, such as [Pb(OH)$_2$] and [Pb(OH)$_3$]$^-$, proved unsuccessful and it must be assumed that these are produced only at pH values higher than those reached in the present work.

Inclusion of the (2,1) species in model 5 slightly increases the estimated standard deviations of the five species and slightly improves the fit (error square sum, 4.15×10^{-10} compared to 4.3×10^{-10} of model 5), but it has a negligible effect on the refined values of the other constants. The value of $-\log \beta_{21}$ (6.26), however, had an estimated standard deviation of 0.15 (33.7%) and was not considered as making any measurable contribution to the present data. Indeed, when speciation calculations were carried out using all six equilibrium constants, for 2×10^{-3} mol dm^{-3} lead(II), the *maximum* contribution of the (2,1) species (at pH 6.9) is only 0.9% (as lead). Clearly the present experimental conditions do not enable detection of this minor species. Earlier work indicating this species was carried out using the partial self-medium method because of the very high lead(II) concentrations required for its detectable formation.[7,8] Unfortunately, the interpretation of such data can be subject to serious uncertainties because of compositional changes which occur throughout a titration.[1,3]

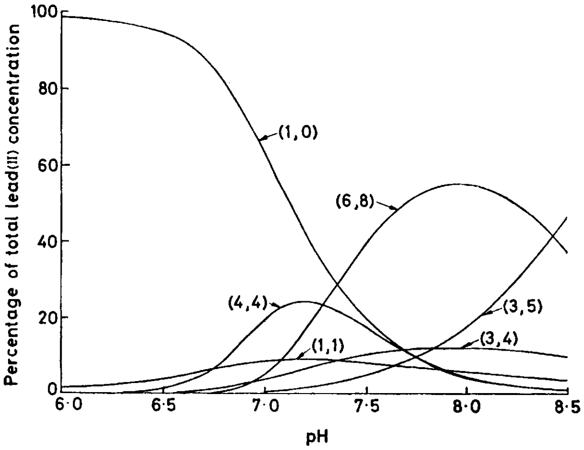

Figure 1 Percentage distribution of lead(II) in various hydrolytic species for a total concentration of 2×10^{-3} mol dm^{-3}, using the constants of model 5. It is assumed that $[H^+] = 10^{-pH}$

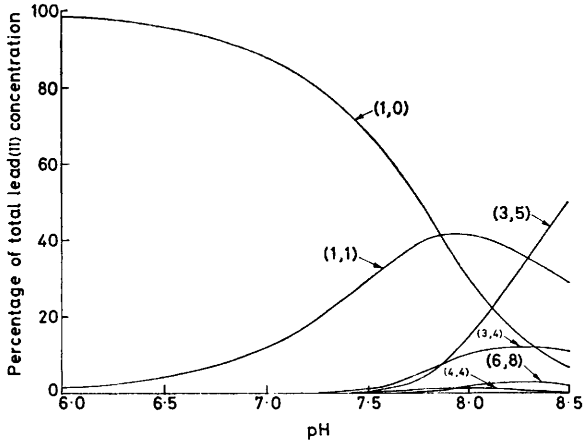

Figure 2 Lead(II) distribution as in Figure 1, but for a total concentration of 10^{-4} mol dm^{-3}

Except in some very early work[9] the dimeric species $[Pb_2(OH)_2]^{2+}$, which is the first 'core-plus-links' species, has not been postulated. Attempts at refining for this species with the present data also failed. Its absence is possibly the result of reaction (4) being heavily favoured

$$2[Pb_2(OH)_2]^{2+} \rightleftharpoons [Pb_4(OH)_4]^{4+} \qquad (4)$$

to the right. All other metals previously claimed[3] to form the (4,4) species also, apparently, do not form the (2,2) species; however, some of these systems require re-examination because of the limitations of the partial self-medium method.

Despite the absence of $[Pb_2(OH)_2]^{2+}$, the second core-plus-links species, $[Pb_3(OH)_4]^{2+}$, is present to a considerable extent. It is more important than the (4,4) and (6,8) species at low lead concentrations at any pH value where all three exist (Figure 2).

A comparison of models 3 and 5 (Table 2) strongly indicates the presence of $[Pb_3(OH)_5]^+$ since the overall precision is improved and the error-square sum is reduced nearly six-fold when it is included in the model. This species has not been detected before. A likely explanation for its previous omission is given in Figure 3, where percentage lead present as the (3,5) species is plotted against total lead concentration. These calculations are for pH values of 7.5—8.0 and are illustrative only, since true solution equilibrium is not always present because of supersaturation and/or precipitation. The present data are obviously in the best region for its detection, whereas those of earlier work (Table 3) were not. At high pH values the (3,5) species becomes one of the more important ones, even at low lead concentrations (Figures 1 and 2).

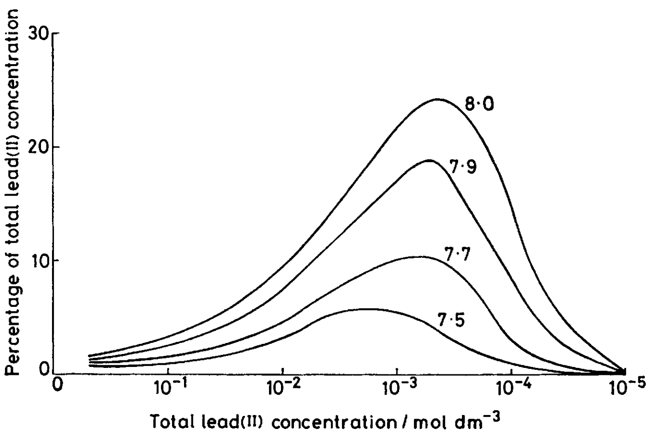

Figure 3 Percentage formation of $[Pb_3(OH)_5]^+$ as a function of lead(II) concentration in the pH range 7.5—8.0, using the constants of model 5

The (4,4) species is the best documented and was originally proposed by Pedersen[10] in 1945. It is a member of the series $[Pb_n(OH)_{2n-4}]^{4+}$ as is the higher species $[Pb_6(OH)_8]^{4+}$ detected by Olin[2] and the present work. The intermediate species, (5,6), is apparently not produced in measurable concentrations under the present experimental conditions. Because hydrolysed lead(II) solutions can be prepared which contain almost exclusively either $[Pb_4(OH)_4]^{4+}$ or $[Pb_6(OH)_8]^{4+}$ at high total metal concentrations, Johansson and Olin[11] studied such solutions using X-ray diffraction. They detected a tetrahedral arrangement of the lead atoms in the (4,4) species and suggested a *non*-octahedral structure for the $[Pb_6(OH)_8]^{4+}$ ion, with the two additional lead atoms being centrally placed over two faces of the tetrahedron.

Application of equation (3) to model 5, using $-\log \beta_{pq}$ values of the (1,1) and (4,4) species (an arbitrary choice), allows the $-\log \beta_{pq}$ of the remaining three species to be predicted (Table 4). The agreement is excellent and suggests once again (see Part 2)[1] that, *for species actually produced*, the energetics of the hydrolysis reactions are dominated by the deprotonation and polymerisation steps[12] and that other aspects such as contributions arising from structural considerations are of minor importance, at least as reflected by the $-\log \beta_{pq}$ values.

As discussed previously,[1] comparison of different investigations is difficult because of the number of differences that occur in the data, in their method of acquisition, and in their numerical analysis. From Table 3 it can be seen that the only comparable investigations, as dictated largely by the total metal concentrations used, are the work of Olin[2] in 3.0 and 0.3 mol dm^{-3} $Na[ClO_4]$, and that of Hugel,[13] in 2.0 mol dm^{-3} perchlorate and nitrate media.

In perchlorate media [10^{-4}—10^{-1} mol dm^{-3} total lead(II)], Hugel[13] detected only the (1,1) and (4,4) species. His failure to detect other species must be attributed to using inappropriate pH ranges, this being readily shown by calculations using the present equilibrium constants. The contribution of the (1,1) species to these data is also mostly negligible. In nitrate media [10^{-2}—2×10^{-1} mol dm^{-3} total lead(II)], the accessible pH range is further reduced by the increased ease of precipitation. In this second investigation, claim was also made for the detection of the (2,1) species, its formation being said to be facilitated by nitrate bonding. This is a doubtful assertion since, using Hugel's β_{pq} values, calculations show that its contribution to the data is negligible.

TABLE 4

Experimentally determined and empirically estimated values of the hydrolysis constants of lead(II) using equation (3)

	$-\log \beta_{pq}$	
Species	Experimental	Estimated
(3,4)	23.91	24.08
(3,5)	31.75	31.94
(6,8)	43.38	44.48

Olin's investigation[2] is the most comprehensive of all earlier work and involved the use of both glass and lead amalgam electrodes. However, it is subject to some unresolved uncertainties, namely: (*a*) the presence of impurities which had to be corrected for; (*b*) the inability to use lead(II) concentrations less than 1.25×10^{-3} mol dm^{-3}, (*c*) the unavoidability of local concentration effects causing a precipitate to form which would not always completely re-dissolve. In addition, these data were analysed graphically and in a stepwise manner, both of which introduce further uncertainties. A computer analysis of some of these data has been reported[14] but complete details were not given. Accordingly, a complete analysis was carried out to assist a comparison with the present work. A standard linear least squares program LSQ[15] was used for all data (507 titration points) and the (3,5) species was also included for comparative purposes. The results of these calculations are given in Table 5.

TABLE 5

Recalculation of Olin's[2] data (25 °C)

Model	$-\log \beta_{pq}$	Estimated standard deviation of $-\log \beta_{pq}$*	Estimated relative deviation (%) of β_{pq}	$10^7 \times$ Error mean square
3.0 mol dm^{-3} $Na[ClO_4]$				
(1,1)	7.94	0.16	35.2	7.79
(3,4)	22.95	0.06	13.2	
(4,4)	19.26	0.001	0.2	
(6,8)	42.13	0.009	2.1	
(1,1)	7.89	0.14	31.0	7.59
(3,4)	23.01	0.07	15.5	
(3,5)	31.62	0.14	30.6	
(4,4)	19.26	0.001	0.2	
(6,8)	42.13	0.009	2.1	
0.3 mol dm^{-3} $Na[ClO_4]$				
(1,1)	7.80	0.14	30.7	2.05
(3,4)	23.15	0.05	11.5	
(4,4)	19.95	0.01	2.3	
(6,8)	42.76	0.01	2.9	
(1,1)	7.79	0.14	30.2	2.04
(3,4)	23.18	0.06	13.2	
(3,5)	32.27	0.73	93.3	
(4,4)	19.94	0.01	2.5	
(6,8)	42.76	0.01	2.9	

* It is assumed that $\sigma(\log \beta) = \frac{1}{2}[\log(\beta + \sigma\beta) - \log(\beta - \sigma\beta)]$.

The agreement between Olin's graphical analysis (Table 4) and the present computer analysis (Table 5) is extremely good; however, the agreement in the estimates of the precision of some of the constants is poor. All eight constants reported by Olin[2] are given uncertanties of ±0.1 log units, which must reflect the inadequacy of the method of their graphical estimation. The results in Table 5 indicate that the precision for the (4,4) and (6,8) species is considerably better than estimated by Olin; that for the (1,1) and (3,4) species, however, is approximately the same and poor (and does not meet our acceptance criteria).

If speciation calculations are carried out using Olin's model and the $-\log \beta_{pq}$ values in Table 5, for Olin's experimental conditions the data are dominated by the (4,4) and (6,8) species, the contribution of $[Pb(OH)]^+$ is mostly negligible (*ca.* 1—4%), and the contribution of $[Pb_3(OH)_4]^{2+}$ is limited. This is a direct result of the inability to use lead(II) concentrations of less than 1.25×10^{-3} mol dm^{-3}, which appears to be the sole cause of the poor detection of $[Pb(OH)]^+$ and the limited detection of (3,4) species, rather than the overall precision of the data. The data in Table 5 also suggest that the same reason underlies the failure of the data to detect satisfactorily the second trimer, $[Pb_3(OH)_5]^+$.

A comparison of Olin's results with the present ones reveals good agreement and, for the (3,4), (4,4), and (6,8) species, the trend in ionic strength dependence is maintained. The present work confirms the earlier suggestion [1] that it is perhaps more prudent to avoid high metal concentrations and hence to vary these within a relatively narrow range. This has not prevented the detection of highly polymerised species, here a hexamer, and has allowed the new species, $[Pb_3(OH)_5]^+$, to be found.

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