Studies on Metal Carbonate Equilibria. 18. Lead(II) Carbonate Complexes in Alkaline Solutions

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Potentiometric measurements with a glass electrode and a Pb amalgam electrode at 25°C have shown that in a 1 M NaClO₄-1 M Na₂CO₃ solution, at acidities ranging from [OH⁻] = 10⁻³⁻⁺ M to [OH⁻] = 10⁻⁹⁻⁺ M, and for 10⁻³⁻⁻ M ≤ [Pb(II)] ≤ 10⁻⁴⁻⁻ M, the prevailing forms of lead(II) are Pb(CO₃)₂⁻⁻, PbCO₃OH⁻ and Pb(OH)₃⁻⁻.

The equilibrium constants, expressed on a 3 M NaClO₄ activity scale, have been evaluated for the following reactions

\[ \text{Pb}^{2⁺} + 2\text{CO}_3^{2⁻} \rightleftharpoons \text{Pb(CO}_3)_2^{2⁻} \]

\[ \log b_{20} = 8.9 \pm 0.1 \]

\[ \text{Pb}^{2⁺} + \text{CO}_3^{2⁻} + \text{OH}⁻ \rightleftharpoons \text{PbCO}_3\text{OH}⁻ \]

\[ \log b_{11} = 10.9 \pm 0.3 \]

\[ \text{Pb}^{2⁺} + 3\text{OH}⁻ \rightleftharpoons \text{Pb(OH)}_3⁻⁻ \]

\[ \log b_{03} = 13.3 \pm 0.3 \]

The stoichiometry of the complexes and the magnitude of the equilibrium constants indicate a coordination geometry with Pb(II) at the apex of a square or trigonal pyramid (as found in many solid structures) and with chelate bonded CO₃²⁻.

In a previous study we have examined the chemical equilibria in the Zn(II)-OH⁻-CO₃²⁻ system in 1 M CO₃⁻⁻. The experimental techniques that might be used to study this system, and the chemical interpretation of the data, are not straightforward. One reason for this is that the low solubilities of ZnCO₃(s) and basic zinc carbonates make it difficult to perform precise potentiometric measurements with metal ion-selective electrodes. We were able to give a reasonable chemical description of the system. Both the nature of the complexes formed, Zn(CO₃)₂⁻⁻, Zn(OH)₂CO₃⁻⁻ and Zn(OH)₄⁻⁻, and their equilibrium constants were in agreement with the known chemical properties of the central ion (four-coordination, presumably in tetrahedral geometry) and the ligand (the formation of chelate complexes as judged by the magnitude of the equilibrium constants).

In the present study we have used the same experimental conditions and the same method to explore the composition of the complexes formed in the Pb(II)-OH⁻-CO₃²⁻ system. Some previous studies have been made of the Pb(II)-CO₃²⁻ system at lower acidities and carbonate concentrations, and a number of different experimental methods have been used, all indicating the formation of PbCO₃ and Pb(CO₃)₂⁻⁻. The equilibrium constants are in rather good agreement, and are given by the values log b₁₀ ~ 6 and log b₂₀ ~ 9. Under the experimental conditions used by us, one expects the formation of mixed hydroxide/carbonate complexes. We use the composition of these for a discussion of the coordination number and coordination geometry of Pb(II).

Pb(II) has a stereochemically “active” lone pair, which often results in pyramidal coordination with Pb(II) at the apex, e.g. in Pb₉O₄(OH)₄, Pb₉O(OH)₆⁺ and Pb₉(OH)₆⁺ (cf. Wells). The stoichiometry of the limiting hydroxide complex Pb(OH)₃⁻⁻ indicates a similar coordination geometry. From a coordination chemical point of view

one might then expect to find the formation of complexes such as \( \text{Pb(OH)}\text{CO}_3^- \) and perhaps \( \text{Pb(OH)}_2\text{CO}_3^2- \), while \( \text{Pb(OH)}_3\text{CO}_3^3- \) and \( \text{Pb(OH)}_4\text{CO}_3^4- \) are less probable. Carbonate is an excellent bridging ligand, but polymeric complexes with bridging carbonates do not seem to be formed at high carbonate concentrations.\(^{10-13}\)

A study of equilibria in the \( \text{Pb}^{2+} - \text{OH}^- - \text{CO}_3^2- \) system may give additional information on the constitution of mononuclear \( \text{Pb}^{2+} \) complexes.

**Notations**

The reacting species, \( \text{Pb}^{2+} \) and \( \text{CO}_3^2- \) form a series of mononuclear (vide infra) complexes, \( \text{Pb(CO}_3\text{)}_p\text{(OH)}_q^{2p-q} \), according to the general reaction:

\[
\text{Pb}^{2+} + p\text{CO}_3^2- + q\text{OH}^- \rightleftharpoons \text{Pb(CO}_3\text{)}_p\text{(OH)}_q^{2p-q},
\]

(1)

\( f_{pq} \) = activity factor of the species \( \text{Pb(CO}_3\text{)}_p\text{(OH)}_q^{2p-q} \) on the 3 M \( \text{NaClO}_4 \) activity scale.

\( B \) = analytical concentration of lead(II)

\( C \) = analytical concentration of \( \text{OH}^- \)

\( c \) = free concentration of \( \text{OH}^- \)

\( \beta_{pq} \) and \( ^0\beta_{pq} \) = formation constants for reaction (1) on the 1 M \( \text{NaClO}_4 \)-1 M \( \text{Na}_2\text{CO}_3 \) and 3 M \( \text{NaClO}_4 \) activity scales, respectively.

\( K_{pq} \) and \( ^0K_{pq} \) = equilibrium constants for the reaction:

\[
\text{Pb(OH)}_q^{2-p} + p\text{CO}_3^2- \rightleftharpoons \text{Pb(CO}_3\text{)}_p\text{(OH)}_q^{2p-q}
\]

on the 1 M \( \text{NaClO}_4 \)-1 M \( \text{Na}_2\text{CO}_3 \) and the 3 M \( \text{NaClO}_4 \) activity scales, respectively.

\( \beta_c \) is the conditional equilibrium constant for the reaction:

**Table 1. Survey of the \( E_b(\log c)_b \) data. \( E_b \) in mV.**

<table>
<thead>
<tr>
<th>log ( B )</th>
<th>( -E_b(\log c) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-3.398</td>
<td>798.2 (2.560), 797.7 (2.644), 797.3 (2.714), 797.1 (2.784), 796.9 (2.893), 796.7 (2.974), 796.5 (3.096), 796.2 (3.180), 795.9 (3.245), 795.6 (3.356), 795.3 (3.432), 794.9 (3.491), 794.4 (3.561)</td>
</tr>
<tr>
<td>-3.398</td>
<td>802.1 (2.105), 797.7 (2.423), 800.2 (2.222), 803.8 (1.970), 806.9 (1.803), 810.0 (1.669), 812.9 (1.573), 815.5 (1.485), 817.8 (1.424), 822.1 (1.319), 825.7 (1.243), 830.3 (1.147), 835.8 (1.051), 838.6 (1.001)</td>
</tr>
<tr>
<td>-3.398</td>
<td>797.3 (2.462), 796.9 (2.525), 796.5 (2.602), 796.3 (2.675), 796.2 (2.734), 796.3 (2.832), 796.2 (3.001), 796.0 (3.091), 795.6 (3.187), 795.4 (3.295), 795.3 (3.365), 795.3 (3.414), 795.6 (3.486)</td>
</tr>
<tr>
<td>-3.398</td>
<td>799.6 (2.278), 803.1 (2.001), 804.3 (1.968), 806.4 (1.864), 807.4 (1.801), 810.2 (1.678), 811.7 (1.617), 814.5 (1.525), 816.5 (1.465), 818.6 (1.402), 822.5 (1.307), 825.4 (1.238), 827.2 (1.201), 831.6 (1.111), 834.9 (1.044)</td>
</tr>
<tr>
<td>-3.222</td>
<td>848.9 (0.772), 847.4 (0.778), 846.0 (0.792), 844.4 (0.807), 844.3 (0.822), 842.0 (0.842), 839.8 (0.875), 836.8 (0.915), 833.8 (0.963), 831.3 (0.995), 828.2 (1.003), 825.4 (1.088), 823.0 (1.128), 820.2 (1.184), 816.9 (1.251), 813.2 (1.316), 812.2 (1.356)</td>
</tr>
<tr>
<td>-3.000</td>
<td>841.4 (0.831), 839.7 (0.836), 838.1 (0.843), 836.7 (0.856), 835.4 (0.871), 834.1 (0.883), 831.7 (0.912), 828.4 (0.951), 827.4 (0.973), 824.6 (1.010), 822.0 (1.042), 820.0 (1.078), 817.8 (1.130), 814.8 (1.189)</td>
</tr>
<tr>
<td>-3.000</td>
<td>832.2 (0.956), 830.4 (0.971), 828.6 (0.991), 827.1 (1.015), 825.7 (1.035), 824.2 (1.054), 821.7 (1.099), 818.2 (1.155), 816.6 (1.165), 813.3 (1.220), 811.0 (1.272), 809.4 (1.326), 807.7 (1.395)</td>
</tr>
<tr>
<td>-2.699</td>
<td>832.2 (0.837), 832.0 (0.837), 831.3 (0.841), 830.4 (0.849), 829.6 (0.859), 828.8 (0.864), 827.2 (0.880), 825.9 (0.903), 824.6 (0.915), 822.2 (0.949), 819.8 (0.983), 818.9 (0.996), 818.1 (1.012), 817.2 (1.025), 816.3 (1.051), 814.6 (1.074), 813.6 (1.104)</td>
</tr>
</tbody>
</table>
“Pb” + qOH− ⇔ “Pb”(OH)q

where “Pb” is the sum over p of all the species Pb(CO3)2−2p, referred to the 1 M NaClO4−1 M Na2CO3 activity scale.

All equilibrium constants are expressed in molar units.

Method

The emfs, $E_a$ and $E_b$, of the cells:

- RE | TS | GE +  
- RE | TS | Pb(Hg),0.02% +  

have been measured at 25°C. RE denotes the reference half cell:

3 M NaClO4 | 0.01 M NaCl,2.99 M NaClO4 | AgCl(s),Ag.

GE is the glass electrode and TS represents the test solution of the following composition:

TS = B M Pb(II), C M OH−, (1−C) M ClO4−, 1 M CO3−2, (3−2B) M Na+.

$B$ ranged from 4 · 10−4 M to 2 · 10−3 M, and the free hydroxide concentration, $c$, from 10−3.5 M to 10−0.78 M.

The $E_b$ (log $c$) data, reported in Table 1, were collected by measuring the emf of cells (A) and (B) after each addition to TS of the titrant solution, T, of composition:

T = B M Pb(II), C T M OH−, (1−C T) M ClO4−, 1 M CO3−2, (3−2B) M Na+.

In addition, the emf, $E_d$, of the cell:

- Pb(Hg) 0.02% | B M Pb(II), (3−2B) M Na+, 1 M CO3−2, 1 M ClO4− | B M Pb2+, (3−2B) M Na+, 3 M ClO4− ([H+] ~ 10−3 M) | Pb(Hg) 0.02%  

was measured, at 25°C, for a series of $B$ values in the range investigated.

Calculations

The deduction of the stoichiometric coefficients $(p,q)$ for the predominant complexes is made in the same way as described previously.  

I. Determination of $q$ and $β_q$. The experimental data, $(E_b − 29.58 \log B) vs. −\log [OH−]$, were tested with normalized functions. The only model that gave an acceptable fit included complexes with $q = 1$ and 3. The normalized function (the full-drawn curve in Fig. 1) was

$$Y = 29.58 \log (1+u+Lu^2) vs \ −\log u,$$

where $u = β_1 · c$ and $L = β_2/β_1^2$.

From the position of best fit and the value $L = 0.028$, we obtain

$$\log β_1 = 1.98 ± 0.05$$

$$\log β_3 = 4.4 ± 0.2$$
Fig. 1. The symbols represent the experimental function \( Y = E_x - 29.58 \log \beta \) vs. \(-\log[OH^-]\). The model curve has been calculated by assuming \( q = 1 \) and 3 and using the values of the equilibrium constants reported in the text.

where the errors are graphically estimated maximum errors.

II. Estimation of the predominant values of \( p \).

From eqn. (6) in Ref. 1 we have

\[
\beta_q = \log \beta_{q,0} f_{p^2+} f_{OH^-} f_q^{-1} (1 - \sum_{p=1}^3 K_{pq}[CO_3^{-2}]^p) \\
\left(1 + \sum_{p=1}^3 \beta_{p} [CO_3^{-2}]^p \right)
\]

where the activity coefficients \( f_i \) in the 1 M NaClO\(_4\)-1 M Na\(_2\)CO\(_3\) solutions are referred to the 3 M NaClO\(_4\) scale. According to the specific ion interaction theory (SIT) the activity coefficients of all species with a negative charge are expected to be equal to unity (cf. Ref. 1).

A value of

\[
\log f_{p^2+} = -8.9 \pm 0.1
\]

was obtained from the measured emf of cell (D). The error was mainly due to the uncertainty in the diffusion potential \( E_i \), which we estimate to be less than 3 mV.

From eqn. (6) in Ref. 1 we have

\[
\log \beta_q = \log \beta_{q,0} + \log \left(1 + \sum_{p=1}^3 K_{p,q}[CO_3^{-2}]^p \right) \\
- \log \left[ \left(1 + \sum_{p=1}^3 \beta_p [CO_3^{-2}]^p \right) / f_{p^2+} \right]
\]

The mononuclear hydrolysis constants \( \log \beta_{01} = 6.3 \pm 0.1 \), \( \log \beta_{02} = 10.9 \pm 0.1 \) and \( \log \beta_{03} = 13.66 \pm 0.05 \) were taken from Olin and Carell\(^{18}\) and Olin.\(^{19}\)

From the SIT\(^{1,20}\) one can easily deduce that \( f_{p^2+} = \beta_p / \beta_{p,0} \). Hence, we have in 1 M CO\(_3^{-2}\)

\[
\log \left[ \left(1 + \sum_{p=1}^3 \beta_p \right) / f_{p^2+} \right] = \log \left(1 + \sum_{p=1}^3 \beta_{p,0} \right)
\]

\[= 8.9 \pm 0.1.\]

From previous equilibrium information we can safely assume that the limiting binary lead(II) carbonate complex in 1 M CO\(_3^{-2}\) is Pb(CO\(_3\))\(_2\)^\(2^-\). The equilibrium constant is then

\[
\log \beta_{20} = 8.9 \pm 0.1
\]

This value is in good agreement with the results of previous investigators.

We can now continue and estimate the composition and the equilibrium constants of the ternary complexes Pb(OH\(_2\))\(_2\)(CO\(_3\))\(_2\).\(^\)\(^\)

For \( q = 3 \) we have \( f_{p(OH)\(_2\)} = 1 \), hence:

\[
\log \beta_3 = 4.4 = \log \beta_{03} + \log \left(1 + \sum_{p=1}^3 \beta_{p,0} \right)
\]

\[= 8.9\]

\[
\log \left(1 + \sum_{p=1}^3 \beta_{p,0} \right) = -0.3 \pm 0.4
\]

i.e. \( \sum \beta_{p,0} \) is not significantly different from zero. This indicates that no mixed complexes such as
Table 2. Summary of the results on the 3 M NaClO₄ activity scale.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
<th>log⁰β</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb²⁺ + 2CO₃²⁻ ⇌ Pb(CO₃)₅⁰⁻</td>
<td>log⁰β₀₀ = 8.9 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>Pb²⁺ + CO₃²⁻ + OH⁻ ⇌ PbCO₃OH⁻</td>
<td>log⁰β₁₁ = 10.9 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>Pb²⁺ + 3OH⁻ ⇌ Pb(OH)₅⁻</td>
<td>log⁰β₃₃ = 13.3 ± 0.3</td>
<td></td>
</tr>
</tbody>
</table>

Pb(OH)₃CO₃⁻ are formed, or at least that the equilibrium constants for the addition of CO₃²⁻ to Pb(OH)₅⁻ are very small.

For q = 1 we have

\[
\log β₁ = 1.98 = \log⁰β₀₁
\]

\[
+ \log \left(1 + \sum_{p=1}^{q} K_{p1}\right) / f_{pOH₁} - 8.9
\]

= 6.3 + \log \left(1 + \sum_{p=1}^{q} K_{p1}\right) - 8.9;

\[
\log \left(1 + \sum_{p=1}^{q} K_{p1}\right) = 4.6 ± 0.2
\]

The previous data indicate that the maximum coordination number in the Pb(II)–OH⁻–CO₃²⁻ system is ≤ 4. Hence, we assume that only one mixed species, Pb(OH)CO₃⁻ is formed. A comparison of the equilibrium constants for the reactions

\[
Pb²⁺ + CO₃²⁻ ⇌ PbCO₃
\]

\[
\log β₀ = 6
\]

and

\[
Pb(OH)⁺ + CO₃²⁻ ⇌ Pb(OH)CO₃⁻ \quad \log⁰K₁₁ = 4.6
\]

supports this assumption.

A summary of the reactions proposed, and of their corresponding equilibrium constants, is given in Table 2.

Conclusions and discussion

The experimental values of log β₃₃, found by different investigators using different experimental methods and different ionic media, are reasonably consistent as judged by the data given in Table 3. The values of log⁰β₃₃ refer to I = O, and have been calculated using the SIT-method. The interaction coefficients ε_{Pb²⁺,CO₃⁻}, ε_{Pb²⁺,NO₃⁻} and ε_{CO₃²⁻,Na⁺} were taken from Ciavatta,²¹ while ε_{PbCO₃OH⁻,Na⁺} ~ −0.1 was estimated from the charge of the complex and comparison with the interaction coefficients of other species of charge −2.

The results obtained in this study strongly indicate the formation of a set of mononuclear binary and ternary complexes in the Pb(II)–OH⁻–CO₃²⁻ system at [CO₃²⁻] = 1 M. A distribution diagram is shown in Fig. 2.

The ratio β₅₀/β₃₃ involving the stepwise constants for the formation of PbCO₃⁰⁻ and Pb(CO₃)₂⁻ taken from the data of Bilinski and Schindler⁶ is around 10¹. This indicates that the chelate formed by the second carbonate is noticeably weaker than that formed by the first. This, in turn, might indicate a preference for three-coordination, as indicated by the stoichiometries

Table 3. Logarithm of the formation constant of Pb(CO₃)₂⁻ in different ionic media (column I). In column II the values of column I are extrapolated to I = O, using the SIT-method, to facilitate comparisons.

<table>
<thead>
<tr>
<th>Method</th>
<th>Medium</th>
<th>Column I</th>
<th>Column II</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.s.v.⁴</td>
<td>0.1 M KNO₃</td>
<td>9.8</td>
<td>10.6</td>
<td>7</td>
</tr>
<tr>
<td>D.p.p.⁵</td>
<td>0.1 M KNO₃</td>
<td>9.1</td>
<td>9.9</td>
<td>7</td>
</tr>
<tr>
<td>Solubility</td>
<td>0.3 M NaClO₄</td>
<td>8.9 ± 0.1</td>
<td>10.1</td>
<td>8</td>
</tr>
<tr>
<td>Solubility</td>
<td>1 M NaClO₄</td>
<td>9.0</td>
<td>10.5</td>
<td>3</td>
</tr>
<tr>
<td>Emf</td>
<td>3 M NaClO₄</td>
<td>8.9 ± 0.1</td>
<td>10.4</td>
<td>This work</td>
</tr>
</tbody>
</table>

⁴Anodic stripping voltammetry. ⁵Differential pulse polarography.
Pb(OH)CO$_3^-$ and Pb(OH)$_5^-$, The stoichiometry of the species Pb(CO$_3$)$_{2}^-$, Pb(OH)CO$_3^-$ and Pb(OH)$_5^-$ strongly indicates a coordination geometry with the Pb(II) at the apex of square or trigonal pyramids. This is in fact the coordination geometry found in several solid Pb(II) compounds, as indicated in the introduction.

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References


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