Studies on Metal Carbonate Equilibria. 17. Zinc(II) Carbonate Complexes in Alkaline Solutions

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Potentiometric measurements with glass and Zn amalgam electrodes at 25 °C have shown that in a 1 M NaClO 4 –1 M Na 2 CO 3 solution, and at hydroxide concentrations ranging from [OH −] = 10 −3.1 M to [OH −] = 10 −0.7 M and for 10 −3.862 M < [Zn(II)] < 10 −2.967 M, the predominant forms of zinc(II) are Zn(CO 3 ) 2 2− , ZnCO 3 (OH) 2 2− and Zn(OH) 2 2−.

The equilibrium constants, expressed on a 3 M NaClO 4 activity scale, for the following reactions have been evaluated:

\[
\begin{align*}
\beta_{20} &= [\text{Zn(CO}_3\text{)}_2^{2-}] / ([\text{Zn}^{2+}] [\text{CO}_3^{2-}]^2) = 10^{6.04 \pm 0.1} \\
\beta_{12} &= [\text{ZnCO}_3\text{(OH)}_2^{2-}] / ([\text{Zn}^{2+}] [\text{CO}_3^{2-}] [\text{OH}^-]^2) = 10^{12.2 \pm 0.3} \\
\beta_{04} &= [\text{Zn(OH)}_3^{2-}] / ([\text{Zn}^{2+}] [\text{OH}^-]^4) = 10^{15.1 \pm 0.05}
\end{align*}
\]

In a previous paper, we have reported an investigation of the equilibria in the system Zn(II) –H 2 O–CO 2 (g) at acidities ranging from [H + ] = 10 −3 M, where complexing is negligible, to [H + ] = 10 −6 M, where a precipitate of Zn(II) carbonates starts to form. The data could be explained by assuming the formation of the species Zn(HCO 3 ) 2 + and Zn 2 CO 3 2−.

It was found that the precipitate was fairly soluble in excess of carbonate and that stable solutions could be prepared containing about 1 mM Zn(II) at [OH −] > 10 −3 M. However, the zinc content of the solution drops to trace levels when the carbonate concentration is appreciably lower than 1 M.

There is no doubt that extensive complexing of zinc by carbonate occurs in 1 M carbonate. The full investigation of the equilibria involved requires some strategy and very likely the use of more than one technique. Most of the equilibria analytical methods require that the concentration of the reacting species be varied in a large interval in order to establish the composition of the products. In the present case, however, the CO 3 2− concentration cannot be made much higher or much lower than 1 M because of the limited solubility of Na 2 CO 3 and because of the decrease in the concentration of the complexes at lower carbonate concentrations.

In this paper we report the results of an emf investigation of the system Zn(II)–OH −–CO 3 2− at hydroxide concentrations ranging from 10 −3.1 M to 10 −0.9 M in 1.0 M carbonate. Owing to the constant CO 3 2− concentration, the emf method alone cannot give a unique chemical model. We have therefore combined the emf data with previous data on the hydrolysis of Zn(II).

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Notations

The reacting species Zn\(^{2+}\)–OH\(^-\)–CO\(_3^{2-}\) form a series of mononuclear complexes

\[
\text{Zn(CO}_3\text{)}\text{p(OH)}_{q}^{2-2p-q},
\]

according to the general reaction:

\[
\text{Zn}^{2+} + p\text{CO}_3^{2-} + q\text{OH}^- \rightleftharpoons \text{Zn(CO}_3\text{)}_{p}^{2-2p-q} \text{OH}_{q}^{2-2p-q}
\]

(1)

\(f_{pq}\) = activity factor for the species

\[
\text{Zn(CO}_3\text{)}_{p}(\text{OH})_{q}^{2-2p-q}
\]

on the 3 M NaClO\(_4\) activity scale

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

\(C = \) analytical concentration of OH\(^-\)

\(c = \) free concentration of OH\(^-\)

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

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

\[
\text{Zn(OH)}_{q}^{2-2q} + p\text{CO}_3^{2-} \rightleftharpoons \text{Zn(CO}_3\text{)}_{p}(\text{OH})_{q}^{2-2p-q}
\]

extended over all the values of \(p\) on the 1 M NaClO\(_4\)–1 M Na\(_2\)CO\(_3\) activity scale.

Table 1. Survey of the \((E_v, \log c)_{pq}\) data. \(E_v\) in mV.

<table>
<thead>
<tr>
<th>(\log B)</th>
<th>(-E_v) ((\log c))</th>
</tr>
</thead>
</table>
| -2.947   | 1467.3 (0.862), 1465.1 (0.877), 1463.5 (0.898), 1461.4 (0.917), 1459.6 (0.935), 1458.1 (0.949), 1455.5 (0.976), 1453.8 (0.990), 1451.3 (1.018), 1449.3 (1.024), 1446.0 (1.068), 1443.5 (1.095), 1441.0 (1.123), 1436.9 (1.154), 1432.8 (1.203), 1402.5 (1.167), 1400.5 (1.168), 1395.2 (1.198), 1392.4 (1.278), 1386.6 (1.804), 1381.5 (1.884), 1375.7 (1.977), 1364.0 (2.188), 1350.6 (2.433), 1347.7 (2.54), 1342.3 (2.665), 1340.4 (2.717), 1339.3 (2.772), 1335.5 (2.865), 1331.0 (2.958), 1408.9 (1.557), 1407.2 (1.566), 1404.6 (1.593), 1402.6 (1.621), 1400.6 (1.650), 1398.1 (1.682), 1395.6 (1.708), 1390.3 (1.773), 1385.4 (1.856), 1380.7 (1.924), 1373.8 (2.040), 1370.9 (2.111), 1362.2 (2.254), 1355.3 (2.386), 1351.8 (2.470), 1348.5 (2.528), 1341.4 (2.748), 1338.8 (2.894), 1473.1 (0.904), 1471.5 (0.918), 1469.8 (0.924), 1468.1 (0.949), 1466.7 (0.967), 1463.5 (0.993), 1460.7 (1.022), 1456.2 (1.052), 1452.1 (1.096), 1445.6 (1.163), 1439.6 (1.214), 1424.3 (1.388), 1415.5 (1.473), 1407.6 (1.588), 1358.6 (2.408), 1355.0 (2.509), 1350.7 (2.649), 1349.8 (2.707), 1348.4 (2.776), 1347.5 (2.815), 1346.3 (2.875), 1345.6 (2.916), 1344.5 (2.968), 1343.0 (3.032), 1341.0 (3.100), 1359.3 (2.418), 1363.5 (2.332), 1366.6 (2.279), 1374.7 (2.116), 1392.3 (1.856), 1400.1 (1.766), 1406.7 (1.694), 1411.4 (1.635), 1432.7 (1.395), 1444.8 (1.278), 1449.5 (1.222), 1456.6 (1.140), 1462.7 (1.068), 1466.5 (1.036).
GE the glass electrode and TS the test solution of the following composition:

\[ TS = B \ M \ Zn(II), \ C \ M \ OH^-, \ (1-C) \ M \ ClO_4^-, \ 1 \ M \ CO_3^{2-}, \ (3-2B) \ M \ Na^+ \]

\( B \) ranged from \( 2.5 \cdot 10^{-4} \ M \) to \( 1.13 \cdot 10^{-3} \ M \) and the free hydroxide concentration, \( c \), from \( 10^{-3.1} \ M \) to \( 10^{-0.9} \ M \).

The \((E_c, \ log c)_p\) data, reported in Table 1, were obtained by measuring the emf of cells (a) and (c) after each addition to TS of the titrant solution T of composition:

\[ T = B \ M \ Zn(II), \ C_T M \ OH^-, \ (1-C_T) M \ ClO_4^-, \ 1 M \ CO_3^{2-}, \ (3-2B) M \ Na^+ \]

In addition, the emf, \( E_{ds} \), of the cell:

- \( Zn(Hg) \ 0.01 \% / B \ M \ Zn(II), \ (3-2B) M \ Na^+ \),
- \( 1 M \ CO_3^{2-}, 1 M \ ClO_4^- / B \ M \ Zn^{2+}, (3-2B) M \ Na^+ \),
- \( 3 M \ ClO_4^- (pH=3) / Zn(Hg) 0.01 \% \) (d)

was measured at 25°C for a series of \( B \) values in the range investigated.

**Experimental**

**Materials and analysis.** A stock solution of \( Zn(ClO_4)_2 \) was prepared by dissolving \( Zn \) granules (Merck p.a.) in perchloric acid (Merck p.a.). The \( Zn(ClO_4)_2 \) crystals which separated from the acid solution on evaporation were collected and dissolved in doubly distilled water. The zinc concentration was determined by complexometric titration with EDTA using Erichrome Black-T as indicator according to the procedure suggested by Schwarzenbach.\(^3\) \( NaClO_4 \) stock solutions were prepared and analyzed as described elsewhere.\(^3\) \( Na_2CO_3 \) (Merck p.a.) was used without further purification. NaOH solutions were prepared and analyzed according to Ref. 4.

**Measurements.** All the measurements were performed in an oil bath at 25.00 ± 0.01°C. The cell arrangement was similar to that described by Forsling et al.\(^5\) The Ag, AgCl electrodes were prepared according to Brown.\(^6\) Metrohm glass electrodes were employed. They were calibrated versus the hydrogen electrode in separate experiments in the acidity range investigated. A small correction for sodium error had to be introduced only at the lowest acidities.

Zinc amalgam was prepared by electrolysis of \( Zn(ClO_4)_2 \) solutions. The electrolysis (at 3 mA constant current) was carried out for the time required to obtain a 0.0100 % amalgam. Emf measurements were performed with a precision of 0.1 mV, using the apparatus described elsewhere.\(^4\)

**Data and calculations**

It is shown later in this section that only mononuclear species of general composition \( Zn(ClO_4)_p(OH)_{2-p-q} \) are formed. The deduction of the \((p, q)\) coefficients in reaction (1) is carried out in two steps. First, the relevant \( q \) values are determined; then, with the aid of these results the most probable values of \( p \) are deduced. Finally, the formation constants \( \beta_pq \), valid in 3 M \( NaClO_4 \), are derived.

A solution of zinc(II) in 1 M \( NaClO_4 \)−1 M \( Na_2CO_3 \) medium is actually a three component system. However, it may be formally reduced to a two component system if the concentration of one component is kept constant. This is the case in our test solutions where the concentration of \( CO_3^{2-} \) is in such great excess relative to those of \( Zn(II) \) and \( OH^- \) that no appreciable decrease in its concentration occurs on establishment of equilibrium (1). This greatly simplifies the interpretation of the experimental data.

We have defined the reference state in such a way that the activity coefficient of each reacting species tends to unity when the composition of the solution approaches that of the solvent, i.e. 1 M \( NaClO_4 \)−1 M \( Na_2CO_3 \). We can then replace the activities by concentrations.

**I. Determination of q and \( \beta_p \).** From the mass balance for zinc(II):

\[
B = \sum_p \sum_q [Zn(ClO_4)_p(OH)_{2-p-q}] \tag{3}
\]

and the definitions of \( \beta_q \) and \( \beta_p \), we obtain

\[
B = [Zn^{2+} + \sum_{p=1}^{\beta_p \cdot CO_3^{2-}} \left( 1 + \sum_{q=1}^{\beta_q} \right)].
\tag{4}
\]
substituting eqn. (4) into the Nernst equation written for cell (c) we obtain:

\[ E_c = E'_c + 29.58 \log B + 29.58 \log \left( 1 + \sum_{q=1}^{u} \beta_q c^q \right) \tag{5} \]

In eqn. (5), \( E'_c \) is a constant which includes the factor

\[ \left( 1 + \sum_{p=1}^{\beta_{p0}} [CO_3^{2-}]^p \right) \]

of eqn. (4) and the liquid junction potential \( E_j \), arising at the boundary between the 3 M NaClO_4 and 1 M NaClO_4–1 M Na_2CO_3 solutions. In Fig. 1, the experimental data are plotted in the form of \( E_c - 29.58 \log B \) versus \( \log c \). We observe that the points lie on a single curve regardless of the value of \( B \). This indicates (as we have anticipated) that only mononuclear species are formed.

The experimental data may be fitted with the normalized function (Fig. 1, full line):

\[ Y = 29.58 \log(1 + u + Lu^2) \text{ vs. } 1/2 \log u \]

where \( u = \beta_2 c^2 \) and \( L = \beta_4 \beta_2^{-2} = 5 \times 10^{-3} \), by translations along the coordinate axes. This implies that the predominant \( q \)-values are 2 and 4. The values of \( \beta_2 \) and \( \beta_4 \) estimated in the position of best fit are reported in Table 2. The errors are maximum deviations obtained from the limiting positions of the plots and the values of \( L \) which still give an acceptable fit. In Table 2, the values of \( \beta_{02} \) and \( \beta_{04} \) determined by Sekine\textsuperscript{7} in 3 M NaClO_4 are also reported. The value of \( \beta_{u4} \) has been evaluated accurately in a separate study of the hydrolysis of Zn(II) in alkaline solution which is now in progress in our laboratory and which will be reported in the near future.

II. Estimation of the predominant values of \( p \). In this section we describe the estimation of the predominant \( p \) coefficients in reaction (1) by comparison of the values of \( \beta_p \) determined above with the corresponding \( \beta_{pq} \) valid for 3 M NaClO_4.

This relation is obtained by substituting

\[ \sum_{p} [Zn(CO_3)_p(OH)_q]_{2-p-q}^{2-q} = [Zn(OH)_q]_{2-q} \left( 1 + \sum_{p=1}^{K_{eq}} [CO_3^{2-}]^p \right) \]

![Fig. 1. The symbols represent the experimental function \( Y = E_c - 29.58 \log B \) vs. \( -\log [OH^+] \). The model curve has been calculated by assuming \( q = 2 \) and 4 and using the values of the equilibrium constants reported in the third column of Table 2.](image-url)
Table 2. Survey of the constants $\beta_{iq}$ and $\beta_i$.

<table>
<thead>
<tr>
<th>$q$</th>
<th>$\log \beta_{iq}$</th>
<th>$\log \beta_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>8.3 $\pm$ 0.1</td>
<td>5.3$\pm$0.03</td>
</tr>
<tr>
<td>3</td>
<td>13.8 $\pm$ 0.1</td>
<td>Not determined</td>
</tr>
<tr>
<td>4</td>
<td>15.10$\pm$0.05</td>
<td>8.4$\pm$0.05</td>
</tr>
</tbody>
</table>

$^a$Ref. 7. $^b$This work.

and

$$
\sum_p [\text{Zn(CO}_3^2-]^p] = [\text{Zn}^{2+}] \left(1 + \sum_{p=1}^{\infty} \beta_{p0}[\text{CO}_3^2-]^p\right)
$$

into the definition of $\beta_i$ [cf. eqn. (2)]. We obtain

$$
\beta_i = \frac{\beta_{iq} [\text{Zn}^{2+}] f_{oi} f_{q}^{-1} \left(1 + \sum_{p=1}^{\infty} K_{pq}[\text{CO}_3^2-]^p\right)}{\left(1 + \sum_{p=1}^{\infty} \beta_{p0}[\text{CO}_3^2-]^p\right)}
$$

(6)

where $f_q$ stands for the activity coefficient of species $i$ referred to the 3 M NaClO$_4$ activity scale. The ratio

$$
f_{\text{Zn}^{2+}i} \left(1 + \sum_{p=1}^{\infty} \beta_{p0}[\text{CO}_3^2-]^p\right)
$$

in eqn. (6) may be estimated with good approximation from the emf of cell (d) according to eqn. (7):

$$
\log f_{\text{Zn}^{2+}i} \left(1 + \sum_{p=1}^{\infty} \beta_{p0}[\text{CO}_3^2-]^p\right) = E_{d'} - 0.05916 = 6.9 \pm 0.1
$$

(7)

The error in eqn. (7) has been calculated by also taking into account the liquid junction potential arising at the boundary between 3 M NaClO$_4$ and 1 M NaClO$_4$—1 M Na$_2$CO$_3$. We estimate that this does not exceed 3 mV. On the other hand, the activities for negatively charged or neutral species are practically coincident in the two media. According to the Specific Interaction Theory$^{k+1}$, the difference of about 0.005 $z^2$ in $\log f_i$ for a species of negative charge $z$ is to be expected between the two scales. We may thus assume, with the present experimental accuracy, that $f_{\text{OH}^-} = 1$ and $f_q = 1$. Eqn. (6) may then be written:

$$
\log \beta_i = \log \beta_{iq} + 
\log \left(1 + \sum_{p=1}^{\infty} K_{pq}[\text{CO}_3^2-]^p\right) = -6.9
$$

(8)

By using the values reported in Table 2 and considering that [CO$_3^{2-}$] = 1 M we obtain:

$$
\log \left(1 + \sum_{p=1}^{\infty} K_{p2}\right) = 3.9 \pm 0.2
$$

(9)

$$
\log \left(1 + \sum_{p=1}^{\infty} K_{p4}\right) = 0.2 \pm 0.2
$$

(10)

Eeqns. (7) and (9) suggest that extensive complexing of the species Zn$^{2+}$ and Zn(OH)$_2$ by the carbonate ion takes place in the solutions studied, whereas the species Zn(OH)$_4^{2-}$ does not seem to be bound to carbonate, as eqn. (10) indicates. Within the accuracy of the present data we can assume that

$$
\sum_{p=1}^{\infty} K_{p4} = 0,
$$

i.e. $p=0$ when $q=4$. If we now consider that the ratio of carbonate to zinc in our test solutions varies between 885 and 4000, it appears reasonable to assume that the coefficient $p$ in eqn. (7) represents the upper limit, $P$, for the number of carbonates bound to zinc, i.e. a single species, Zn(CO$_3$)$_2^{2-}$, is likely to predominate. Eqn. (7) can then be written:

$$
\log (f_{\text{Zn}^{2+}i}^{-1}) = -6.9 \pm 0.1
$$

(11)

If we further consider that the species Zn(CO$_3$)$_2^{2-}$ may either be neutral or negatively charged, then its activity coefficients in the two
media (1 M NaClO₄–1 M Na₂CO₃ and 3 M NaClO₄) coincide and are equal to unity, as we have stated above. Consequently

$$\beta_{P0}^{\text{aq}} q_{p0}^{-1} = f_{Zn^{2+}}$$

(12)

By combining eqns. (11) and (12) we obtain:

$$\log q_{p0}^{\text{aq}} = 6.9 \pm 0.1$$

(13)

Zirino and Yamamoto estimated a value of $$\log q_{p0}^{\text{aq}} = 4.1$$. The result of eqn. (13) is in good agreement with the statistically expected value for the formation constant of Zn(CO₃)²⁻, i.e. $$P = 2$$. Similar arguments may be extended to eqn. (9), and one finds that $$K_{X2} = q_{X2}$$, where $$N$$ represents the number of carbonates bound to Zn(OH)₂ to form the single species Zn(CO₃)ₙ(OH)₂. We may then write:

$$\log q_{X2} = 3.9 \pm 0.2$$

(14)

This value is very close to that of $$\log q_{p0}^{\text{aq}}$$ and it is therefore very probable that it refers to the reaction

$$\text{Zn(OH)}_2 + \text{CO}_3^{2-} \rightleftharpoons \text{ZnCO}_3(\text{OH})_2^{2-}$$

i.e. $$N = 1$$. This result agrees with the conclusions of a previous paper in which we showed that CO₃²⁻ behaves as a bidentate ligand towards zinc, so that 2 OH⁻ replace 1 CO₃²⁻. Clearly, there is no place in this model for species with an odd number of OH⁻, which, in fact, have not been detected in the present study, whereas they have been found in the absence of carbonate. The overall formation constants, $$q_{p2}^{\text{aq}}$$, of the species found are summarized in Table 3.

**Conclusions**

The procedure described in this paper for establishing the stoichiometry and formation constants of the species formed in the system investigated may appear unusual to the cautious reader. Some may even think that a certain amount of “equilibrium art” and personal bias have been employed to formulate the equilibrium model. A careful examination, however, will show that the critical step in the deduction of the number of carbonate ions, $$p$$, is the assumption that only statistical factors are operative in determining the ratio of the stepwise formation constants. One may further substantiate this by computing (from Tables 2 and 3) the equilibrium constants for the following reactions:

$$\begin{align*}
\text{ZnCO}_3 + 2\text{OH}^- & \rightleftharpoons \text{Zn(CO}_3(\text{OH})_2^{2-} \\
\text{Zn(OH)}_2 + 2\text{OH}^- & \rightleftharpoons \text{Zn(OH)}_3^{2-} \\
\text{Zn(OH)}_2 + \text{CO}_3^{2-} & \rightleftharpoons \text{ZnCO}_3(\text{OH})_2^{2-} \\
\text{ZnCO}_3 + \text{CO}_3^{2-} & \rightleftharpoons \text{Zn(CO}_3)_2^{2-}
\end{align*}$$

A little thought will show that, on statistical grounds, the ratios of the equilibrium constants for reactions (15) and (16), and (17) and (18) should coincide with the ratio of the first (Ref. 12) to the second stepwise formation constant of Zn(CO₃)₂⁻. This is verified within the experimental error!

As we have mentioned in a previous section, carbonate appears to behave as a bidentate ligand towards zinc; this is consistent with observations on other metal carbonate systems (La³⁺, Ce³⁺, UO₂⁺, Be²⁺, 16, 17). The stoichiometric compositions of the zinc complexes also indicate that zinc(II) has tetrahedral coordination geometry in these complexes. The magnitude of $$q_{p0}^{\text{aq}}$$ seems reasonable by comparison with that for the corresponding Cu(II) complex. 18

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**Table 3.** Summary of the results on the 3 M NaClO₄ activity scale.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Log of Equilibrium Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn²⁺ + 2CO₃²⁻ ⇌ Zn(CO₃)₂⁻</td>
<td>6.9 ± 0.1</td>
</tr>
<tr>
<td>Zn(OH)₂ + CO₃²⁻ ⇌ ZnCO₃(OH)₂⁻</td>
<td>3.9 ± 0.2</td>
</tr>
<tr>
<td>Zn²⁺ + CO₃²⁻ + 2OH⁻ ⇌ ZnCO₃(OH)₂⁻</td>
<td>12.2 ± 0.3</td>
</tr>
<tr>
<td>Zn²⁺ + 4OH⁻ ⇌ Zn(OH)₄⁻</td>
<td>15.10 ± 0.05</td>
</tr>
</tbody>
</table>
References


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