

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

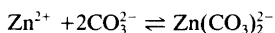
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Potentiometric measurements with glass and Zn amalgam electrodes at 25 °C have shown that in a 1 M NaClO₄–1 M Na₂CO₃ solution, and at hydroxide concentrations ranging from [OH⁻] = 10^{-3.1} M to [OH⁻] = 10^{-0.9} M and for 10^{-3.602} M < [Zn(II)] < 10^{-2.947} M, the predominant forms of zinc(II) are Zn(CO₃)₂²⁻, ZnCO₃(OH)₂²⁻ and Zn(OH)₄²⁻.

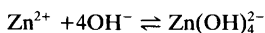
The equilibrium constants, expressed on a 3M NaClO₄ activity scale, for the following reactions have been evaluated:



$${}^0\beta_{20} = [\text{Zn}(\text{CO}_3)_2^{2-}] / ([\text{Zn}^{2+}][\text{CO}_3^{2-}]^2) = 10^{6.9 \pm 0.1}$$



$${}^0\beta_{12} = [\text{ZnCO}_3(\text{OH})_2^{2-}] / ([\text{Zn}^{2+}][\text{CO}_3^{2-}][\text{OH}^-]^2) = 10^{12.2 \pm 0.3}$$



$${}^0\beta_{04} = [\text{Zn}(\text{OH})_4^{2-}] / ([\text{Zn}^{2+}][\text{OH}^-]^4) = 10^{15.1 \pm 0.05}$$

In a previous paper¹ we have reported an investigation of the equilibria in the system Zn(II)–H₂O–CO₂(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(HCO₃)⁺ and Zn₂CO₃²⁺.

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

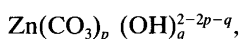
more than one technique. Most of the equilibrium analytical methods require that the concentration of the reacting species be varied in a large interval in order to establish the composition of the products. In the present case, however, the CO₃²⁻ concentration cannot be made much higher or much lower than 1 M because of the limited solubility of Na₂CO₃ 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⁻–CO₃²⁻ at hydroxide concentrations ranging from 10^{-3.1} M to 10^{-0.9} M in 1.00 M carbonate. Owing to the constant CO₃²⁻ 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).

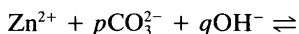
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Notations

The reacting species $Zn^{2+}-OH^{-}-CO_3^{2-}$ form a series of mononuclear complexes



according to the general reaction:



f_{pq} = activity factor for the species $Zn(CO_3)_p(OH)_q^{2-2p-q}$ on the 3 M NaClO₄ activity scale

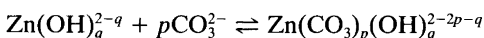
B = analytical concentration of zinc(II)

C = analytical concentration of OH⁻

c = free concentration of OH⁻

β_{pq} and ${}^0\beta_{pq}$ = formation constants for reaction (1) on the 1 M NaClO₄-1 M Na₂CO₃ and 3 M NaClO₄ activity scales, respectively

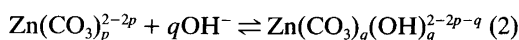
K_{pq} and ${}^0K_{pq}$ = equilibrium constants for the reaction:



on the 1 M NaClO₄-1 M Na₂CO₃ and 3 M NaClO₄ activity scales, respectively

$$\beta_q = \sum_p [Zn(CO_3)_p(OH)_p^{2-2p-q}] / c^q \left(\sum_q [Zn(CO_3)_p^{2-2p}] \right)$$

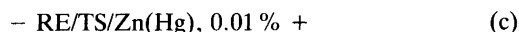
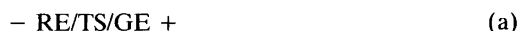
is the equilibrium constant for the reaction:



extended over all the values of p on the 1 M NaClO₄-1 M Na₂CO₃ activity scale.

Method

Complex formation in the system Zn(II)-CO₃²⁻-OH⁻ has been investigated at 25 °C by measuring the emf, E_a and E_c , of the cells:



where RE denotes the reference half cell:

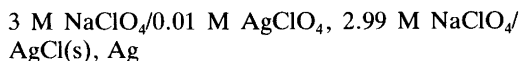


Table 1. Survey of the (E_c , log c)_B data. E_c in mV.

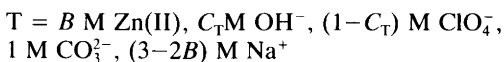
log B	- E_c (-log c)
-2.947	1467.3 (0.862), 1465.1 (0.877), 1463.5 (0.898), 1461.4 (0.917), 1459.6 (0.935), 1458.1 (0.949), 1455.5 (0.976), 1453.8 (0.990), 1451.3 (1.018), 1449.3 (1.024), 1446.0 (1.068), 1443.5 (1.095), 1441.0 (1.123), 1436.9 (1.154), 1432.8 (1.203)
-3.294	1402.5 (1.617), 1400.5 (1.638), 1395.2 (1.698), 1392.4 (1.728), 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)
-3.301	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 (2.834)
-3.301	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 (1.568)
-3.601	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)
-3.601	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:

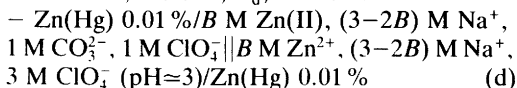


B ranged from $2.5 \cdot 10^{-4}$ M to $1.13 \cdot 10^{-3}$ M and the free hydroxide concentration, c , from $10^{-3.1}$ M to $10^{-0.9}$ M.

The $(E_c, \log c)_B$ 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:



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



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

Experimental

Materials and analysis. A stock solution of $\text{Zn}(\text{ClO}_4)_2$ was prepared by dissolving Zn granules (Merck *p. a.*) in perchloric acid (Merck *p. a.*). The $\text{Zn}(\text{ClO}_4)_2$ 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 Eriochrome Black-T as indicator according to the procedure suggested by Schwarzenbach.² 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 $25.00 \pm 0.01^\circ\text{C}$. 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 $\text{Zn}(\text{ClO}_4)_2$ 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 $\text{Zn}(\text{CO}_3)_p(\text{OH})_q^{2-2p-q}$ 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 ${}^0\beta_{pq}$, 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 $\text{Zn}(\text{II})$ 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 β_q . From the mass balance for zinc(II):

$$B = \sum_p \sum_q [\text{Zn}(\text{CO}_3)_p(\text{OH})_q^{2-2p-q}] \quad (3)$$

and the definitions of β_q and β_{p0} , we obtain

$$B = [\text{Zn}^{2+}] \left(1 + \sum_{p=1} \beta_{p0} [\text{CO}_3^{2-}]^p \right) \left(1 + \sum_{q=1} \beta_q c^q \right) \quad (4)$$

substituting eqn. (4) into the Nernst equation written for cell (c) we obtain:

$$E_c = E_c^\circ + 29.58 \log B + 29.58 \log \left(1 + \sum_{q=1} \beta_q c^q \right) \quad (5)$$

In eqn. (5), E_c° is a constant which includes the factor

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

of eqn. (4) and the liquid junction potential E_j , arising at the boundary between the 3 M NaClO₄ and 1 M NaClO₄-1 M Na₂CO₃ 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 $L = \beta_4 \beta_2^{-2} = 5 \cdot 10^{-3}$, by translations along the coordinate axes. This implies that the predominant q -values are 2 and 4. The values of β_2 and β_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 β_{02} and β_{03} determined by Sekine⁷ in 3 M NaClO₄ are also reported. The value of β_{04} 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 β_q determined above with the corresponding β_{0q} valid for 3 M NaClO₄.

This relation is obtained by substituting

$$\sum_p [\text{Zn}(\text{CO}_3)_p (\text{OH})_q^{2-2p-q}] = [\text{Zn}(\text{OH})_q^{2-q}] \left(1 + \sum_{p=1} K_{pq} [\text{CO}_3^{2-}]^p \right)$$

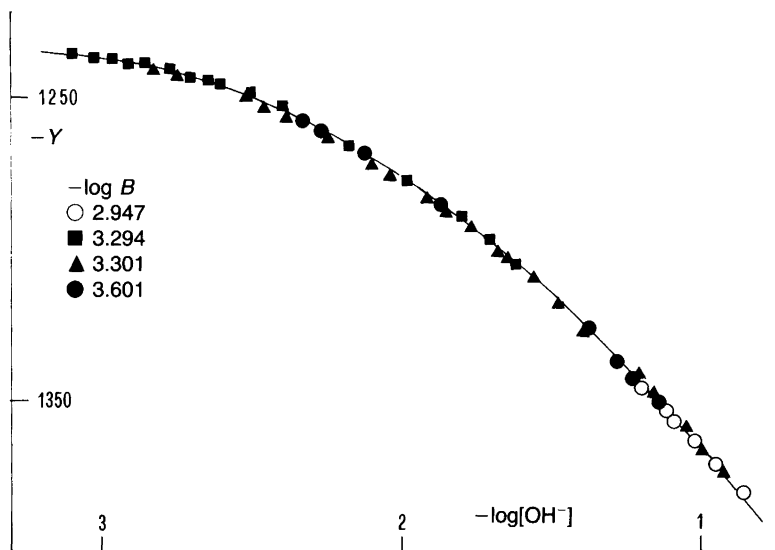


Fig. 1. The symbols represent the experimental function $Y = E_c - 29.58 \log B$ vs. $-\log [\text{OH}^-]$. The model curve has been calculated by assuming $q = 2$ and 4 and using the values of the equilibrium constants reported in the third column of Table 2.

Table 2. Survey of the constants β_{0q} and β_q .

q	$\log \beta_{0q}^a$	$\log \beta_q^b$
2	8.3 \pm 0.1	5.3 \pm 0.03
3	13.8 \pm 0.1	Not determined
4	15.10 \pm 0.05	8.4 \pm 0.05

^aRef. 7. ^bThis work.

and

$$\sum_p [\text{Zn}(\text{CO}_3)_p^{2-2p}] =$$

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

into the definition of β_q [cf. eqn. (2)]. We obtain

$$\beta_q = \beta_{0q} f_{\text{Zn}^{2+}} f_{\text{OH}^-}^{-1} \left(1 + \sum_{p=1} K_{pq} [\text{CO}_3^{2-}]^p \right) /$$

$$\left(1 + \sum_{p=1} \beta_{p0} [\text{CO}_3^{2-}]^p \right) \quad (6)$$

where f_i stands for the activity coefficient of species i referred to the 3 M NaClO₄ activity scale. The ratio

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

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

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

$$= E_d / 29.58 = 6.9 \pm 0.1 \quad (7)$$

The error in eqn. (7) has been calculated by also taking into account the liquid junction potential arising at the boundary between 3 M NaClO₄ and 1 M NaClO₄–1 M Na₂CO₃. We estimate that this does not exceed 3 mV. On the other hand, the ac-

tivities for negatively charged or neutral species are practically coincident in the two media. According to the Specific Interaction Theory⁸⁻¹¹ a 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:

$$\log \beta_q = \log \beta_{0q} +$$

$$\log \left(1 + \sum_{p=1} K_{pq} [\text{CO}_3^{2-}]^p \right) - 6.9 \quad (8)$$

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

$$\log \left(1 + \sum_{p=1} K_{p2} \right) = 3.9 \pm 0.2 \quad (9)$$

$$\log \left(1 + \sum_{p=1} K_{p4} \right) = 0.2 \pm 0.2 \quad (10)$$

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

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

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, $\text{Zn}(\text{CO}_3)_P^{2-P}$, is likely to predominate. Eqn. (7) can then be written:

$$\log (f_{\text{Zn}^{2+}} \beta_{P0}^{-1}) = -6.9 \pm 0.1 \quad (11)$$

If we further consider that the species $\text{Zn}(\text{CO}_3)_P^{2-P}$ 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

$$\beta_{p0} \beta_{p0}^{-1} = f_{Zn^{2+}} \quad (12)$$

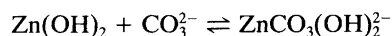
By combining eqns. (11) and (12) we obtain:

$$\log \beta_{p0} = 6.9 \pm 0.1 \quad (13)$$

Zirino and Yamamoto¹² estimated a value of $\log \beta_{10} = 4.1$. The result of eqn. (13) is in good agreement with the statistically expected value for the formation constant of Zn(CO₃)₂²⁻, i.e. $P = 2$. Similar arguments may be extended to eqn. (9), and one finds that $K_{N2} = {}^0K_{N2}$, where N represents the number of carbonates bound to Zn(OH)₂ to form the single species Zn(CO₃)_N(OH)₂^{-2N}. We may then write:

$$\log {}^0K_{N2} = 3.9 \pm 0.2 \quad (14)$$

This value is very close to that of $\log \beta_{10}$ and it is therefore very probable that it refers to the reaction

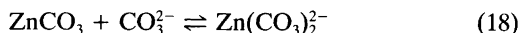
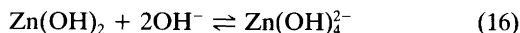
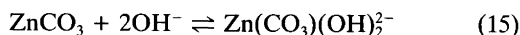


i.e. $N = 1$. This result agrees with the conclusions of a previous paper¹ in which we showed that CO₃²⁻ behaves as a bidentate ligand towards zinc, so that 2 OH⁻ replace 1 CO₃²⁻. Clearly, there is no place in this model for species with an odd number of OH⁻, which, in fact, have not been detected in the present study, whereas they have been found in the absence of carbonate. The overall formation constants, β_{pq} , 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:



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)₂²⁻. 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⁺,¹³ Ce³⁺,¹⁴ UO₂²⁺,¹⁵ 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 β_{20} seems reasonable by comparison with that for the corresponding Cu(II) complex.¹⁸

Acknowledgement. This study has been supported by a grant from the Swedish Natural Science Research Council (NFR).

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

$Zn^{2+} + 2CO_3^{2-} \rightleftharpoons Zn(CO_3)_2^{2-}$	$\log \beta_{20} = 6.9 \pm 0.1$
$Zn(OH)_2 + CO_3^{2-} \rightleftharpoons ZnCO_3(OH)_2^{2-}$	$\log {}^0K_{12} = 3.9 \pm 0.2$
$Zn^{2+} + CO_3^{2-} + 2OH^- \rightleftharpoons ZnCO_3(OH)_2^{2-}$	$\log \beta_{12} = 12.2 \pm 0.3$
$Zn^{2+} + 4OH^- \rightleftharpoons Zn(OH)_4^{2-}$	$\log \beta_{04} = 15.10 \pm 0.05$

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