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Studies on Metal Carbonate Equilibria. 12. Zinc(II) Carbonate Complexes in Acid Solutions

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The complex formation equilibria were studied at 25 °C by measuring the hydrogen ion concentration of zinc perchlorate solutions saturated with CO_2-N_2 gas mixtures of known composition. The [Zn(II)] ranged from 0.3 to 1 M, the partial pressures of CO_2 investigated were 0.3 and 1 atm and $[H^+]$ from $10^{-5.8}$ to $10^{-4.2}$ M. In the test solutions the ClO_4^- concentration was kept at the 3 M level by the addition of $NaClO_4$. The emf data were explained by assuming the following equilibria. $Zn^{2+}+H_2O+CO_2(g) \rightleftharpoons ZnHCO_3^+ + H^+$ log $^*\beta_{111}=-7.70\pm0.05$ $2Zn^{2+}+H_2O+CO_2(g) \rightleftharpoons Zn_2CO_3^{2+}+2H^+$ log $^*\beta_{221}=-13.47\pm0.05$. The equilibrium constants refer to 3 M $NaClO_4$ as the solvent.

The carbonate and hydrogen carbonate ions are two of the most important ligands in ground and surface water systems, and they are strongly affecting the concentration and migration of several of the metal ions present in these systems. There is a fair amount of information available in the literature about the solubility products of various solid carbonate containing phases.[1] However, the information about soluble carbonate containing species is much more limited.[1] In this and a following communication, we will describe chemical equilibria in the Zn(II)–H_2O-carbonate systems. The first part describes the chemistry in acid solutions, while the second part describes the corresponding systems in the alkaline range.

The solubility product of $ZnCO_3(s)$ has previously been studied by a number of authors.[1] The most precise data seem to be those of Schindler and his co-workers.[2–4] Chemical information about metal carbonate complex formation is of interest both from the fundamental and applied points of view. The stoichiometry of the complexes and the magnitude of their stability constants give information about the mode of bonding of the ligand,[5] these data are also necessary for equilibrium modelling of *e.g.* metal ion migration in natural water systems. The data obtained in the $[H^+]$ range studied here ought to be particularly relevant for the modelling of zinc(II) migration as a result of mining or other industrial operations. Most zinc ores are of sulfidic origin. Hence, both drainage water from the mines and effluents from tailing dams from the ore dressing plants will be acidic as a result of sulfide [and Fe(II)] oxidation. $[H^+]$ values in the range 10^{-5} to 10^{-3} M are not uncommon in these cases.

We have chosen to perform the experiments in a medium of high ionic strength, *viz.* 3 M ClO_4^-, in order to get optimal conditions for establishing the proper chemical model for the

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systems investigated. This condition is, in general, very much different from those encountered when making an equilibrium modelling of a natural water system. However, we have previously shown,[5-7] that one can recalculate equilibrium constants determined in a medium of high ionic strength to other conditions, *e.g.* a pure water solvent, by using the specific ion interaction theory.[8-10] This theory is also useful when establishing the proper chemical model for the system studied when one has rather large changes in the composition of the test solutions, as is the case here, *c.f.* Ref. 5.

NOTATIONS

The reacting species Zn^{2+}, H_2O and $CO_2(g)$ can form a series of (pqr) complexes $Zn_p(OH)_q(CO_2)_r^{2p-q}$

$$pZn^{2+} + qH_2O + rCO_2(g) \rightleftarrows Zn_p(OH)_q(CO_2)_r^{2p-q} + qH^+ \qquad (1)$$

β_{pqr} is the conditional equilibrium constant of (1) in the molar scale, at constant B. $^*\beta_{pqr}$ is the corresponding constant in the reference state, 3 M $NaClO_4$.

a = partial pressure of $CO_2(g)$ in atm
B,b = molar concentrations of Zn(II) an Zn^{2+}, respectively
H = analytical excess of $H^+ = [ClO_4^-] - [Na^+] - 2B$
h = molar concentration of H^+
Y = $[h(h-H)B^{-2} - \beta_{210}]a^{-1}$
Y_o = $\lim\ (Y)_B \quad h^{-1} \rightarrow 0$
m_i, M_i = molality and molarity of species i, respectively.
$\varepsilon(i,k)$, $\tilde{\varepsilon}(i,k)$ = interaction coefficient between ions i and k in $kg \cdot mol^{-1}$ and $dm^3 \cdot mol^{-1}$, respectively
I = ionic strength in $mol \cdot dm^{-3}$

$(OH)CO_2^- \equiv HCO_3^-$ and $(OH)_2CO_2^{2-} \equiv CO_3^{2-}$

EXPERIMENTAL

Method. The $Zn(II)-H_2O-CO_2(g)$ system was investigated in the ranges $0.3\ M < B < 1\ M$, $a = 0.2632$ atm and 0.982 atm, and $4.2 < -\log h < 5.8$. An outline of the experimental method used is given in part 3 of this series.[5] However, most titrations were made by using a volumetric technique instead of the coulometric one previously used. The test solutions had the following analytical composition TS:BM Zn^{2+}, H M H^+, $(3-2B-H)$M Na^+, 3 M ClO_4^- saturated with $CO_2(g)$ of partial pressure a atm. The log $h(H)_{B,a}$ data were collected by performing experiments in the form of titrations, and they are available on request from the authors (D.F.). In order to avoid precipitation, equal volumes of two solutions of composition T_a: 2 B M Zn^{2+}, H_a M H^+, $(3-4B-H_a)$ M Na^+, 3 M ClO_4^-; T_b: H_b M H^+, $(3-H_b)$ M Na^+, 3 M ClO_4^- were used as the titrant. A suitable negative value of H_b made it possible to decrease the acidity in the test solution from a value where the complex formation is negligible to values where solid metal carbonate started to form. The partial pressure of $CO_2(g)$ was measured as before.[11] All measurements were made at 25.00±0.02 °C by using the equipment described earlier.[11] The burettes used were mechanical piston burettes of type Metrohm.

Chemicals used. Solutions of $NaClO_4$, $NaHCO_3$, $AgClO_4$ and $HClO_4$ were prepared from reagents of analytical grade. They were analyzed as described earlier.[12] $Zn(ClO_4)_2$ stock solutions were made either by dissolving zinc granules or zinc oxide, both Merck *p.a.*, in a slight excess of $HClO_4$. The zinc perchlorate was purified by recrystallization and the stock solutions analyzed by titration with EDTA. The hydrogen ion concentration in the zinc perchlorate solutions was determined potentiometrically by using Gran plots.[13]

CALCULATIONS

The calculation method has been described earlier.[5] Plots of $(h-H)/a$ *vs.* $\log h$ turn out to be independent of a at a given value of B. Hence, the predominant species have $r=1$.

At most 3 % of B is present as complexes before precipitation of $ZnCO_3(s)$. Hence, $[Zn^{2+}]=b=B$, and

$$\frac{h-H}{a} = \sum_p \sum_q \beta_{pq1} \cdot B^p h^{-q} \tag{2}$$

We have previously pointed out that it is necessary to take the activity factor changes of reactants and products into account when one has to make such large variations in the composition of the test solutions as is the case in the type of experiment performed here. The activity factors are calculated by using the specific ion interaction theory as described before.[5-7] whereas the activity of water, a_{H_2O}, may be considered constant in the present study.

The zinc data are slightly affected by the hydrolysis of Zn^{2+}. The predominant hydrolysis product is Zn_2OH^{3+}. We corrected for the presence of this species by using the value of $\log \beta_{210}=-8.7$ given by Biedermann and Row.[14]

Plots of

$$Y=\frac{h(h-H)}{a\,B^2} - \frac{\beta_{210}}{a} = \sum_p \sum_q q\beta_{pq1}\, B^{p-2} h^{-q+1} \tag{3}$$

versus h^{-1}, gave a series of parallel straight lines, *c.f.* Fig. 1, indicating that one predominant dinuclear species $Zn_2(OH)_2CO_2^{2+}$ ($\equiv Zn_2CO_3^{2+}$) is formed. The parallel lines also indicate

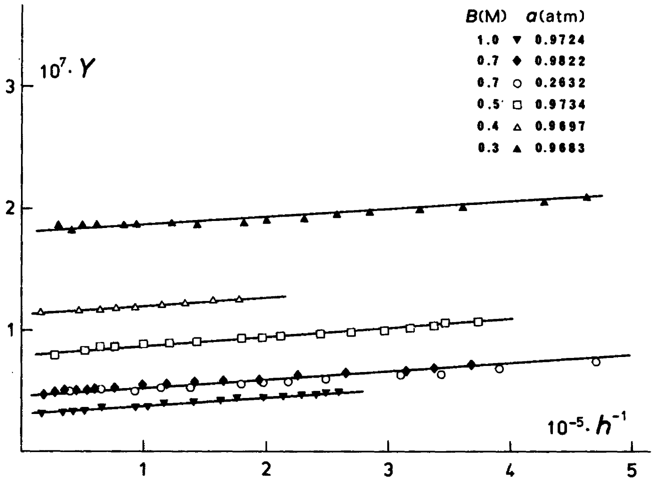

Fig. 1. The data $Y=[h(h-H)B^{-2}-\beta_{210}]a^{-1}$ as a function of h^{-1}. The straight lines represent the expression $10^{-7.99} \cdot B^{-2} + 10^{-7.70} \cdot B^{-1} + 10^{-13.47} \cdot h^{-1}$.

that the value of β_{221} is independent of the changes in the composition of the ionic medium, *i.e.* of B. This simple interpretation can be explained by the specific ion interaction theory.[8–10] The equilibrium constants β_{221} at different levels of B, calculated from the slope of the lines, are related to $^*\beta_{221}$, the corresponding constant in the reference state, *i.e.* pure $NaClO_4$, by

$$\log(\beta_{221}/^*\beta_{221}) = 2[D(I)-D(3)] + [2\bar{\varepsilon}(H^+,ClO_4^-) \\ + \bar{\varepsilon}(Zn_2CO_3^{2+},ClO_4^-) - 2\bar{\varepsilon}(Zn^{2+},ClO_4^-)]\Delta M_{ClO_4^-} \tag{4}$$

where $D=0.5109\sqrt{I}/(1+1.5\sqrt{I})$ is the Debye-Hückel term at ionic strength I mol·dm^{-3} and $\bar{\varepsilon}(i,ClO_4^-)$ are the interaction coefficients between the positive ions, i, with perchlorate.

No variation of the molar concentration of perchlorate takes place in our experiments, *i.e.* $\Delta M_{ClO_4^-}=0$. Thus, in eqn (4) only the difference $[D(I)-D(3)]$ remains and this does not exceed 0.01 units. This implies that the replacement of 2 moles of Na^+ by 1 mole of Zn^{2+} does not influence the value β_{221} which remains substantially constant and coincides with $^*\beta_{221}$ within the experimental error, as long as we keep the ClO_4^- concentration at the 3 M level.

We obtained

$$\log {}^*\beta_{221} = -13.47 \pm 0.05$$

The intercepts $Y_o(B)$ at $h^{-1}=0$ of the plot given in Fig. 1 are equal to $\beta_{011}B^{-2} + \beta_{111}B^{-1} + \beta_{211}$.

The function

$$W = Y_oB^2 = \beta_{011} + \beta_{111}B + \beta_{211}B^2 \tag{5}$$

vs. B (*c.f.* Fig. 2) yields a straight line of intercept β_{011} and slope β_{111}.

The linear dependence of W on B suggests that the species Zn_2OHCO_2 ($\equiv Zn_2HCO_3$) never attains a measurable concentration and that β_{111} does not change appreciably when replacing Na^+ with Zn^{2+}. The latter implication is explained satisfactorily with the aid of eqn. (6)

$$\log(\beta_{111}/^*\beta_{111}) = 2[D(I)-D(3)] + [\bar{\varepsilon}(H^+,ClO_4^-) + \bar{\varepsilon}(ZnHCO_3^+, ClO_4^-) + \\ - \bar{\varepsilon}(Zn^{2+},ClO_4^-)] \cdot \Delta M_{ClO_4^-} \tag{6}$$

For the same reasons invoked when discussing eqn. (4), we can conclude that $\beta_{111} = {}^*\beta_{111}$ throughout our measurements.

We obtained

$$\log {}^*\beta_{111} = -7.70 \pm 0.05$$

In Fig. 2, we can also observe that the intercept β_{011} coincides with the value of $^*\beta_{011}$ determined in 3 M $NaClO_4$ in a previous study.[12]

By analyzing eqn. (7)

$$\log(\beta_{011}/^*\beta_{011}) = 2[D(3)-D(I)] + \bar{\varepsilon}(H^+,ClO_4^-)\Delta M_{ClO_4^-} + \\ + \bar{\varepsilon}(HCO_3^-,Na^+)\Delta M_{Na^+} + \bar{\varepsilon}(HCO_3^-,Zn^{2+})B \tag{7}$$

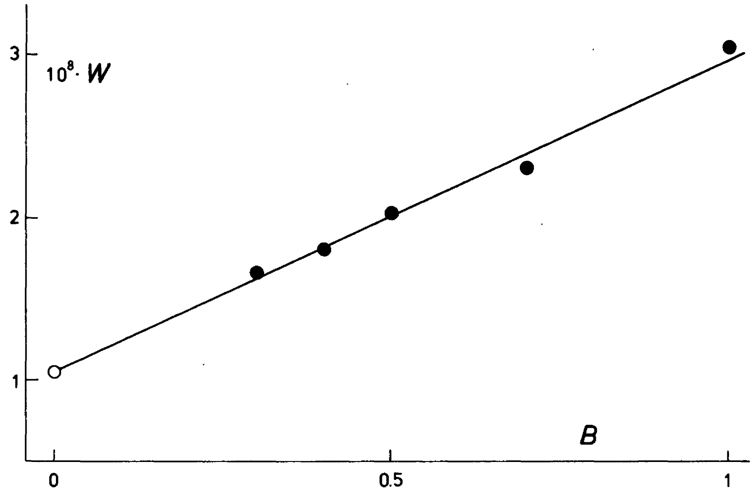

Fig. 2. The data $W=Y_0B^2$ as a function of B. The straight line is calculated using the expression $10^{-7.99}+10^{-7.70}\cdot B$. The point at $B=0$ (○) has been determined in separate experiments.[12]

we observe that the second term on the right hand side of eqn. (7) is zero because $\Delta M_{\mathrm{ClO_4^-}}=0$, furthermore, the third term is close to zero as $\bar{\varepsilon}(\mathrm{HCO_3^-},\mathrm{Na^+})$ is approximately zero.[7] Since the difference of the Debye-Hückel terms attains a maximum value of 0.01, we can conclude that $\bar{\varepsilon}(\mathrm{HCO_3^-},\mathrm{Zn^{2+}})$ cannot differ appreciably from zero.

DISCUSSION

If molalities instead of molarities are used in eqns. (4) and (6), the interaction coefficients $\varepsilon(\mathrm{Zn_2CO_3^{2+}},\ \mathrm{ClO_4^-})$ and $\varepsilon(\mathrm{ZnHCO_3^+},\ \mathrm{ClO_4^-})$ can be obtained since $\varepsilon(\mathrm{H^+},\ \mathrm{ClO_4^-})$ and $\varepsilon(\mathrm{Zn^{2+}},\mathrm{ClO_4^-})$ are known.[15]

We calculated

$$\varepsilon(\mathrm{Zn_2CO_3^{2+}},\mathrm{ClO_4^-})=0.3_5\ \mathrm{kg\ mol^{-1}}$$

and

$$\varepsilon(\mathrm{ZnHCO_3^+},\mathrm{ClO_4^-})=0.2\ \mathrm{kg\ mol^{-1}}$$

The first one is in good agreement with the values of the interaction coefficients of $\mathrm{ClO_4^-}$ with several bivalent positive ions, such as $\mathrm{Cu^{2+}}$, $\mathrm{Zn^{2+}}$, $\mathrm{Hg^{2+}}$, $\mathrm{Mg^{2+}}$, $\mathrm{Co^{2+}}$ (0.32–0.34)[15] and $\mathrm{YHCO_3^{2+}}$ (0.40).[6]

The second one is not far from the values of the interaction coefficients of $\mathrm{ClO_4^-}$ with $\mathrm{HgCl^+}$ (0.20), $\mathrm{CdCl^+}$ (0.25) and $\mathrm{CdI^+}$ (0.27) reported by Ciavatta.[15]

The estimated interaction coefficients were used to extrapolate our results to zero ionic strength. We obtained

$$\log \beta_{221}^{\circ}=-13.0\pm0.1_5$$

and

$$\log \beta_{111}^{\circ}=-\ 7.1\pm0.1_5$$

From these values the formation constants β°_{MHA} and $\beta^{\circ}_{M_2A}$ at zero ionic strength, for the reactions (8) and (9), respectively, can be calculated

$$Zn^{2+} + HCO_3^- \rightleftarrows ZnHCO_3^+ \qquad \log \beta^{\circ}_{MHA} = 0.8 \pm 0.2 \qquad (8)$$

$$2Zn^{2+} + CO_3^{2-} \rightleftarrows Zn_2CO_3^{2+} \qquad \log \beta^{\circ}_{M_2A} = 5.1 \pm 0.2 \qquad (9)$$

The value of log β°_{MHA} is of the same order of magnitude as those generally found for acetate complexes of bivalent metal ions[1] such as Ca^{2+}, Ba^{2+}, Sr^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+}, indicating a similar type of coordination, presumably unidentate, in the two ligands.

We can formally consider the reaction (9) as a sum of

$$Zn^{2+} + CO_3^{2-} \rightleftarrows ZnCO_3^0 \qquad (10)$$

and

$$ZnCO_3^0 + Zn^{2+} \rightleftarrows Zn_2CO_3^{2+} \qquad (11)$$

If the carbonate bridge is formed *via* two unidentate Zn–O bonds we do not expect the values of the equilibrium constants for reactions (10) and (11) to be very different from that of reaction (8), *i.e.* of the order of magnitude of 10. Then the value of log $\beta^{\circ}_{M_2A}$ ought to be around 2 which is much smaller than the value found experimentally. Hence, we conclude that the carbonate ligand is not bonded in this way, but rather with one set of bidentate and one set of monodentate bonds, in the same way as was previously[5,7] suggested for the corresponding lanthanoid complexes.

Zirino and Yamamoto[16] have estimated the value of log $\beta^{\circ}_{MA} = 4.1$ for the equilibrium constant of reaction (10). This value is reasonable as judged from our value of log $\beta^{\circ}_{M_2A}$.

It is not surprising to find that binuclear M_2A complexes are formed both by divalent and trivalent metal ions. This stoichiometry seems to be the most efficient way of using all the donor sites of the carbonate ligand when it is present in solutions with a very large metal ion excess.

One can also observe that the value of log β°_{MHA} is much smaller for Zn^{2+} than for the lanthanoids.[5,7] This indicates that the $ZnCO_3^0$ complex also must be much weaker than the corresponding lanthanoid complex[5,7] (*c.f.* Zirino and Yamamoto[16]). We will return to this question in a following communication.

We can calculate that with a Zn(II) concentration of 10^{-4} M and a total carbonate concentration of $2 \cdot 10^{-3}$ M, $ZnHCO_3^+$ accounts for about 0.5 % of the total zinc in solution at log $h = -6$, whereas the concentrations of the binuclear $Zn_2CO_3^{2+}$ and Zn_2OH^{3+} are negligible.

This finding indicates that soluble carbonate species are of minor importance for the transport of zinc ions in slightly acid solutions.

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