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## Thermodynamics of the Zinc Bicarbonate Ion Pair

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Zinc(II) is shown to form a mono complex with bicarbonate in dilute aqueous solution. Values of the log of the equilibrium constant for the reaction  $\text{Zn}^{2+}_{\text{aq}} + \text{HCO}_3^- \rightleftharpoons \text{ZnHCO}_3^+_{\text{aq}}$  are 1.42, 1.40, 1.47, 1.57, and 1.63 at temperatures 10, 25, 40, 55, and 70 °C.

### Introduction

Recent work by Bauman et al.,<sup>1</sup> Almon,<sup>2</sup> and Siebert<sup>3</sup> on  $\text{CaHCO}_3^+$  and  $\text{MgHCO}_3^+$  ion pairs has confirmed the existence of these complexes in dilute aqueous solutions over a temperature range of 10–90 °C. Zinc bicarbonate was selected for study to gain insight into the effects of electronegativity and polarizability on metal bicarbonate interactions. Zinc is more polarizable than calcium or magnesium and has a greater electronegativity. Its ionic radius lies between that of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ .

In parallel with our earlier studies, chloride was selected as the common anion for the determinations. Zinc chloride complexing has been studied by a number of people with differing results.<sup>4–10</sup> The data are summarized by Libus and Tialowska.<sup>10</sup> Our experiments were designed to fall outside the range of  $\text{ZnCl}_x^{2-x}$  complexing. The mean activity coefficients for zinc chloride solutions<sup>11</sup> are virtually identical with those found for calcium chloride up to an ionic strength of 0.6. The single ion activity coefficients calculated for  $\text{Zn}^{2+}$  from the MacInnes assumption using the mean salt method agree to within 1% with those calculated from the Debye–Hückel equation using an  $a_0$  value of 6 Å over a range of ionic strength from 0 to 0.9. This value is suggested by Klotz and Rosenberg.<sup>22</sup>

The hydrolysis of  $\text{Zn}^{2+}$  to form various  $\text{OH}^-$  complexes has been studied by a number of authors.<sup>12–15</sup> The results of their measurements applied to a 0.1 M zinc chloride solution at pH 5.5 (the midpoint of our working range) indicate that less than 0.5% of the total  $\text{Zn}^{2+}$  ion is complexed with hydroxide ion.

One difficulty in the study of  $\text{ZnHCO}_3^+$  as compared with  $\text{CaHCO}_3^+$  or  $\text{MgHCO}_3^+$  is the threat of zinc carbonate (Smithsonite) precipitation;  $\text{p}K_{\text{sp}} = 10.27$ .<sup>16</sup> Smithsonite is 2 orders of magnitude less soluble than calcite ( $\text{p}K_{\text{sp}} = 8.34$ ) and 6 orders less soluble than  $\text{MgCO}_3$  ( $\text{p}K_{\text{sp}} = 4.52$ ), and solutions were often supersaturated with respect to zinc carbonate precipitation by a considerable amount. However, precipitation does not occur rapidly at room temperature and aqueous solutions can maintain supersaturation for long periods of time. In contrast, the equilibrium between the free ions and the zinc bicarbonate ion pair appears to be very rapid; i.e., a solution reaches a stable pH within a few minutes after an addition of  $\text{HCO}_3^-$  or  $\text{Zn}^{2+}$  is made. A paper by Taketatsu<sup>17</sup>

reported that the precipitate formed by the addition of  $\text{KHCO}_3$  or  $\text{K}_2\text{CO}_3$  to a solution containing  $\text{Zn}^{2+}$  ion could be partially redissolved by shaking; the fraction of the zinc which can be redissolved was observed to increase with increasing concentrations of carbonate or bicarbonate. These observations strongly suggest that some soluble carbonate and/or bicarbonate complexes of zinc exist, but no attempt has been made to characterize these complexes or determine equilibrium constants governing their formation.

In order to evaluate the equilibrium constant for the reaction



one must be able to evaluate the activities of the three reacting species. This can be done by utilizing the acid–base properties of  $\text{HCO}_3^-$  and determining its activity from pH measurements as described by Siebert and Hostetler.<sup>3</sup>

The investigation depended on measurements of changes in pH as alternate additions of  $\text{KHCO}_3$  and  $\text{ZnCl}_2$  solutions were made to a solution containing these species in equilibrium with an atmosphere of  $\text{CO}_2$  at constant partial pressure. A slow stream of  $\text{CO}_2$  was bubbled through the solution to maintain a constant  $P_{\text{CO}_2}$  and also provide for stirring. The equations which define the system are

$$m(\text{ZnHCO}_3^+) = m(\text{K}^+) + m(\text{H}^+) - m(\text{HCO}_3^-) \quad (2)$$

and

$$m(\text{Zn}^{2+}) = m(\text{Zn}^{2+}_{\text{T}}) - m(\text{ZnHCO}_3^+) \quad (3)$$

from mass balance, and since

$$K_1 = \frac{a_1(\text{HCO}_3^-)a_1(\text{H}^+)}{a_1(\text{H}_2\text{CO}_3)} = \frac{a_2(\text{HCO}_3^-)a_2(\text{H}^+)}{a_2(\text{H}_2\text{CO}_3)} \quad (4)$$

if  $a(\text{H}_2\text{CO}_3) = K_0 P_{\text{CO}_2}$  it is assumed to remain constant over the entire experiment.

$$a_2(\text{HCO}_3^-) = \frac{a_1(\text{H}^+)a_1(\text{HCO}_3^-)}{a_2(\text{H}^+)} \quad (5)$$

Finally

$$K_f = \frac{a_1(\text{ZnHCO}_3^+)}{a_1(\text{Zn}^{2+})a_1(\text{HCO}_3^-)} = \frac{a_2(\text{ZnHCO}_3^+)}{a_2(\text{Zn}^{2+})a_2(\text{HCO}_3^-)} \quad (6)$$

The subscripts 1 and 2 refer to the molalities or activities in

consecutive steps of the titration. Activity coefficients are calculated on the basis of the Debye-Hückel equation

$$\log \gamma_i = \frac{-AZ_i\sqrt{I}}{1 + B\hat{a}\sqrt{I}}$$

Values of  $A$  and  $B$  are taken from Hamer<sup>18</sup> and  $\hat{a}$  is 6.0 Å.

The most significant assumption made in this treatment is that the activity of aqueous  $\text{CO}_2$  remains constant throughout the titration. The data reduction program systematically sweeps possible values for  $a_1(\text{HCO}_3^-)$ , which is related to  $P_{\text{CO}_2}$ , and converges on the value which gives a minimum internal deviation in the value of  $\log K_f$ . This procedure does not require exact values for  $K_0$  or  $K_1$  which are poorly known above 50 °C; neither does it depend on the absolute pH of the solution which may or may not be accurate. It depends only on changes in pH between successive additions. The value of  $a_1(\text{HCO}_3^-)$  which gives the best convergence of  $\log K_f$  can be used to calculate an optimum  $P_{\text{CO}_2}$ ; it is significant that these "optimum" values for carbon dioxide pressure are usually very close to the expected value of 1 atm at temperatures with known  $K_0$  and  $K_1$  values.

The formation constant,  $K_f$ , for the reaction (1) where

$$K_f = a(\text{ZnHCO}_3^+) / [a(\text{Zn}^{2+})a(\text{HCO}_3^-)] \quad (7)$$

was determined at the temperatures 10, 25, 40, 55, and 70 °C.

### Experimental Section

Stock solutions of zinc chloride were prepared from reagent grade zinc oxide and hydrochloric acid (Mallinckrodt). After approximately equal amounts of the two reagents had been added to a small amount of water, the solution was allowed to stand for several hours to ensure complete reaction and filtered to remove any unreacted zinc oxide and the pH adjusted to about 3 with HCl. The solution was then diluted to volume with deionized distilled water to give a molality of 1.0. Exact values for zinc ion concentration were determined by titration with standard EDTA solutions.

Stock solutions of  $\text{KHCO}_3$  were prepared from dry potassium bicarbonate (Matheson) dissolved in a weighed quantity of deionized distilled water to give the desired molality.

The reaction was carried out in a polypropylene reaction vessel immersed in a constant-temperature water bath.<sup>3</sup> The pH of the reaction solution was monitored by an Orion 801 digital pH meter and an electrode pair consisting of an Orion Model 90-02-00 double junction reference electrode using 10%  $\text{KNO}_3$  solution in the outer chamber and one of several glass membrane pH electrodes: Beckman general purpose (39000 and 41263), Beckman amber glass (43509) for high temperature work, and Fisher (13-639-3) general purpose electrodes.

The reaction vessel was charged with stock  $\text{ZnCl}_2$  and  $\text{KHCO}_3$  solutions and sufficient distilled deionized water to bring the mass to about 1850 g. All water was weighed to 0.5 g. Additions of  $\text{ZnCl}_2$  and  $\text{KHCO}_3$  solutions were made by difference weighing. A container of the solution was weighed to 0.001 g, a 50-mL glass syringe was used to transfer the desired amount of solution into the reaction vessel, and the container was reweighed. The precision of a given addition was about  $\pm 0.05$  g due to erratic delivery by the syringe. The overall precision of a series of additions using the same syringe during a run was also  $\pm 0.05$  g since no solution was lost from the syringe between additions.

The electrode pair was standardized against Beckman standard buffer solutions of pH 4.008 (phthalate) and 7.00 (phosphate); the 25 °C values were adjusted for other temperatures by use of tables supplied by the manufacturer. The electrodes were then placed in the reaction vessel and allowed to equilibrate. Normally at least 1 h was allowed for the pH to reach a stable value in the reaction environment; during this time the  $\text{CO}_2$  atmosphere was circulated through the reaction vessel. Electronic background noise usually caused a variation of  $\pm 0.002$  to  $\pm 0.005$  pH unit in the meter's readings, but one could determine the equilibrium position by observing the meter for about 1 min; when no significant change in this equilibrium position was observed for 15–20 minutes, it was considered safe to proceed with the titration.

**Table I.** Typical Reaction Conditions for a Determination of  $\log K_f$  for the  $\text{ZnHCO}_3^+$  Ion Pair at 25 °C<sup>a</sup>

addition	amt of $\text{KHCO}_3$ , g	amt of $\text{ZnCl}_2$ , g	pH
1	5.964		4.877
2		11.106	4.846
3	5.953		4.926
4		13.700	4.896
5	6.851		4.970
6		17.652	4.933
7	6.850		5.000
8		19.161	4.966
9	6.745		5.023

<sup>a</sup> Initial conditions: concentrations:  $\text{KHCO}_3$ , 22.307 g, 0.101375 m;  $\text{ZnCl}_2$ , 22.053 g, 1.0413 m;  $\text{H}_2\text{O}$ , 1772.4 g; gas phase; pure  $\text{CO}_2$ ; pH 4.777.

**Table II.** Activities of Reaction Species in a Typical Reaction to Determine  $\log K_f$  for the  $\text{ZnHCO}_3^+$  Ion Pair at 25 °C

	activities $\times 10^3$				
$\text{HCO}_3^-$	0.925 59	1.165	1.085	1.304	1.217
$\text{Zn}^{2+}$	5.763	5.718	7.617	7.565	9.840
$\text{ZnHCO}_3^+$	0.138 78	0.171 34	0.216 14	0.260 28	0.302 23
$\log K_f$	1.415	1.410	1.418	1.421	1.402
$\text{HCO}_3^-$	1.444	1.326	1.547	1.430	1.631
$\text{Zn}^{2+}$	9.769	12.353	12.281	14.790	14.712
$\text{ZnHCO}_3^+$	0.369 50	0.433 26	0.494 84	0.556 06	0.624 74
$\log K_f$	1.418	1.423	1.416	1.420	1.416

average  $\log K_f = 1.416$ , average deviation =  $\pm 0.004$

**Table III.**  $\log K_f$  for  $\text{ZnHCO}_3^+$  as a Function of Temperature

temp, °C	$\log K_f$	no. of runs	$\sigma_m^a$
10	1.423	4	0.022
25	1.400	9	0.020
40	1.474	6	0.014
55	1.570	4	0.017
70	1.631	7	0.016

<sup>a</sup>  $\sigma_m$  = standard error of the mean.

The titration sequence of the experiment consisted of alternate additions of  $\text{KHCO}_3$  and  $\text{ZnCl}_2$  stock solutions, beginning and ending with  $\text{KHCO}_3$  for a total of nine additions. The initial solutions, increment sizes, and pH changes for a typical experiment at 25 °C are shown in Table I and the calculated activities of each species for each step in the titration and the calculated values of  $\log K_f$  are shown in Table II. After each titration addition, the reaction mixture was allowed to reach chemical and thermal equilibrium and the pH was recorded as it reached a stable value as soon as the increment was thoroughly mixed with the solution in the reaction vessel; this rarely required more than about 5 min.

All calculations were done in molalities since all additions to the reaction species as well as the initial solutions and water were handled as weighed increments.

Data reduction was done on an IBM 370-165 using a program (XKF) written by the author. The program uses a WATFIV compiler and systematically tests possible values for  $a_1(\text{HCO}_3^-)$  and converges on the value which gives the minimum internal deviation in  $\log K_f$ . When a minimum has been reached, the program excludes points which show a deviation greater than twice the average deviation of the run and converges on a new minimum. The program gives no consideration to the average value of other experiments or a theoretically calculated value for  $\log K_f$ ; it only seeks to minimize the internal deviation within the run. The program also calculates an optimum  $P_{\text{CO}_2}$  on the basis of the optimum value for initial bicarbonate activity and  $K_0$  and  $K_1$  for the temperature under consideration.

### Results and Discussion

The results of the experiments to determine  $\log K_f$  are shown in Table III. No trends were observed in the relationship of  $\log K_f$  values to ionic strength (varied from 0.03 to 0.20) or to the concentration of either zinc or bicarbonate ions. Initial concentrations of reacting solutions were varied by a factor

**Table IV.** Thermodynamic Properties Calculated for the  $\text{ZnHCO}_3^+$  Ion Pair as a Function of Temperature

$t, ^\circ\text{C}$	$-\Delta G^\circ,$ kcal/mol	$\Delta H^\circ,$ kcal/mol	$\Delta S^\circ,$ cal/(mol K)
10	1.84	0.13	6.9
25	1.91	0.85	9.3
40	2.11	1.75	12.3
55	2.36	2.82	14.0
70	2.56	4.06	19.3

of 10 or more, and the pH range varied by nearly 2 units. The chemistry of the system over this range of concentration could be described with one ion pair,  $\text{ZnHCO}_3^+$ , and one equilibrium constant,  $K_f$ . The computer program minimized the internal deviation of  $\log K_f$  values for the different steps of a run. The initial assumption was found to be consistent with the experimental data; had other species played a significant role in the chemistry of these solutions, it is doubtful that the program would have converged as well as it did; one would expect much larger internal deviations.

In order to test for the possible presence of a stable carbonate complex of the form  $\text{ZnCO}_3^0$ , the data reduction program was modified to determine the formation constant of  $\text{ZnCO}_3^0$ , assuming this to be the only ion pair. With the same data as used earlier for the determination of the formation constant of  $\text{ZnHCO}_3^+$ , a "tentative" formation constant of  $\text{ZnCO}_3^0$  was determined to be  $2.91 \times 10^6$  with an average internal standard deviation of  $5.11 \times 10^5$  at  $25^\circ\text{C}$ . On the assumption that the better described system will give smaller internal deviations, these results were compared with the results assuming a  $\text{ZnHCO}_3^+$  ion pair. Because of the large difference in size of the  $K_f$ 's,  $2.91 \times 10^6$  vs. 25.1, a "relative" standard deviation was used, this being the average standard deviation divided by the average  $K_f$ . The smaller relative standard deviation will come from the treatment giving smaller internal deviations of  $K_f$ . Assuming  $\text{ZnCO}_3^0$  as the only ion pair, we have 0.176 as the relative standard deviation. Assuming  $\text{ZnHCO}_3^+$  as the only ion pair, we have 0.0614 as the relative standard deviation.

The program was further modified to determine the formation constant of  $\text{ZnHCO}_3^+$  with the assumption of different values of the  $\text{ZnCO}_3^0$  constant. Values ranging from  $10^1$  to  $10^7$  for  $K_f$  of  $\text{ZnCO}_3^0$  were used with no improvement in the relative standard deviation.

Thus the best fit of the data occurs when no  $\text{CO}_3^{2-}$  complexing is involved. This is not too surprising since in the pH range involved here (4.5–5.6) the concentration of available carbonate ion is too low to effect the stoichiometry of the complexes.

An equation describing the experimental temperature dependence of  $\log K_f$  was derived using least squares

$$\log K_f = 1.413 - 9.187 \times 10^{-4}t + 6.0317 \times 10^{-5}t^2 \quad (8)$$

where  $t$  is in  $^\circ\text{C}$ . The agreement of this equation with the experimental points is shown in Table V. The derivative of eq 8 is readily obtained giving

$$\begin{aligned} (d \log K_f/dt) &= (d \log K_f/dT) \\ &= 1.206 \times 10^{-4}t - 9.18 \times 10^{-4} \end{aligned}$$

Hence

$$\Delta H^\circ = 2.303RT^2(1.206t - 9.18) \times 10^{-4} \text{ cal} \quad (9)$$

where  $t$  is the centigrade temperature and  $T$  is the Kelvin temperature. Table IV presents the results of these calculations. Also shown are the values calculated for  $\Delta H^\circ$  and  $\Delta S^\circ$ .

The formation of  $\text{ZnHCO}_3^+$  is endothermic at all temperatures studied; the driving force in the reaction appears to be the positive entropy change caused by a breakdown of the

**Table V.** Comparison of the  $\log K_f$  Values Calculated by the Fuoss Equation and Least-Squares Fitting with Those Determined Experimentally

$t, ^\circ\text{C}$	$\log K_f$ (Fuoss)	$\log K_f$ (least squares eq 8)	$\log K_f$ (exptl)
10	1.335	1.409	1.423
25	1.403	1.427	1.400
40	1.480	1.472	1.474
55	1.559	1.544	1.570
70	1.649	1.643	1.631
		1.818	

**Table VI.** Relationship of Solubility and  $\log K_f$  with Electronegativity

cation	cation electro- negativity	$\log K_f$ $\text{MOH}^{\text{a}}$	$\text{p}K_{\text{sp}}$ $\text{MCO}_3$	$\log K_f$ $\text{MHCO}_3$
$\text{Ca}^{2+}$	1.00	1.40	8.34	1.228 <sup>b</sup>
$\text{Mg}^{2+}$	1.31	2.56	4.52	1.067 <sup>c</sup>
$\text{Zn}^{2+}$	1.65	4.99	10.27	1.400 <sup>d</sup>

<sup>a</sup> Reference 21. <sup>b</sup> Reference 2. <sup>c</sup> Reference 3. <sup>d</sup> This work.

"iceberg" structure of the coordinated water molecules around the ions leading to a decreased orientation of solvent molecules.

Table V also presents an analysis of the data by the Fuoss equation<sup>19</sup>

$$\log K_f = \log A + \frac{B}{2.303 + \epsilon T} \quad (10)$$

where  $A = 4Na^3/3000$  and  $B = Z_1Z_2e^2/ka$  in which  $a$  is the ion size parameter,  $N$  is Avogadro's number,  $k$  is the Boltzmann constant,  $\epsilon$  is the dielectric constant of water,  $e$  is the electronic charge, and  $Z_1$  and  $Z_2$  are charges on the cation and anion. The equation was fitted at  $25^\circ\text{C}$  by use of an "a" value of 2.02 Å. This parameter was assumed to be invariant with temperature. It should be noted that the so-called ion-size parameters used in the activity coefficient calculations involving  $\text{Zn}^{2+}$  (6 Å) and in the Fuoss ion pairing (2.02 Å) are merely empirical parameters based on best fits of experimental data to simple equations. The equation agrees well with experimental data at 40, 55, and  $70^\circ\text{C}$  but poorly at  $10^\circ\text{C}$ . The Fuoss equation had been shown to fit a number of systems involving  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  quite well.<sup>3</sup> The polarizability of  $\text{Zn}^{2+}$  may prevent the equation from fitting as well for  $\text{Zn}^{2+}$  as it does for the hard cations.

Table VI indicates that the trend between  $\log K_f$  and the electronegativity<sup>20</sup> of the cation which holds for  $\text{OH}^-$  and complexes of  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  does not hold for the  $\text{HCO}_3^-$  complexes. The trend in  $\text{HCO}_3^-$  stability parallels the  $\text{p}K_{\text{sp}}$  values.

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