Studies of Metal Carbonate Equilibria. Part 16.[1] The Beryllium(II)–Water–Carbon Dioxide(g) System in Neutral-to-alkaline 3.0 mol dm^{-3} Perchlorate Media at 25 °C*

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The complex-formation equilibria in the system Be^{II}–H_2O–CO_2(g) have been studied by potentiometric and solubility measurements in 3.0 mol dm^{-3} $NaClO_4$ at 25 °C. The e.m.f. measurements were performed in the range $6.4 \leqslant -\log h \leqslant 8.5$ (h = free hydrogen-ion concentration), the total metal concentration B was varied from 0.97 to 30 mmol dm^{-3} and the partial pressure of CO_2 from 0.01 to 0.97 atm. The solubility measurements were carried out in the range $4.95 \leqslant -\log h \leqslant 7.0$, at partial pressure of CO_2 of 0.97 and 0.29 atm. The e.m.f. and solubility data can be explained by assuming formation of the mononuclear complexes $Be(OH)_2(CO_2)$, $[Be(OH)_3(CO_2)]^-$, and $[Be(OH)_4(CO_2)]^{2-}$. The potentiometric data can be best explained by also taking into consideration the formation of one polynuclear complex of stoicheiometry $[Be_3(OH)_9(CO_2)_3]^{3-}$ or $[Be_3(OH)_{10}(CO_2)_3]^{4-}$. The set of stability constants obtained from the solubility measurements are $\log K_{s0} = 6.18 \pm 0.03$, $\log \beta_{110} = -6.02 \pm 0.09$, $\log \beta_{131} = -16.82 \pm 0.02$, and $\log \beta_{141} = -24.2 \pm 0.1$. From the potentiometric measurements $\log \beta_{121} = -10.12 \pm 0.06$, $\log \beta_{131} = -16.68 \pm 0.08$, $\log \beta_{141} = -24.22 \pm 0.04$, and $\log \beta_{393} = -45.5 \pm 0.5$ or $\log \beta_{3103} = -52.0 \pm 0.5$. The Raman spectra of concentrated beryllium(II) carbonate solutions in the range pH 7.15—11 indicate that the CO_2 is present as carbonate in the two predominant complexes. Consequently these complexes should be written as $[Be(OH)_2(CO_3)]^{2-}$ and $[Be_3(OH)_3(CO_3)_3]^{3-}$ or $[Be_3(OH)_4(CO_3)_3]^{4-}$. Tentative structures for the two possible polynuclear complexes are proposed and discussed.

In previous publications[1,2] we have investigated the Be^{II}–H_2O–CO_2(g) system in the acid to neutral pH range prior to the precipitation of $Be(OH)_2$(s). We have established the composition and determined the stability constants of the predominant hydroxide and mixed hydroxo–carbonato complexes. Structures for the polynuclear $[Be_p(OH)_q(CO_2)_r]^{(2p-q)+}$ complexes were also proposed, based on the stoicheiometric and spectroscopic information.

It is known that beryllium(II) hydroxide is soluble in bicarbonate solutions. However, the information about the complexes responsible for this phenomenon is scarce, even though some beryllium(II) hydrogencarbonato and carbonato species have been proposed.[3–5] The magnitude of the solubility product of $Be(OH)_2$(s) has been extensively discussed,[6] but no reliable information is available on the solubility of β-$Be(OH)_2$(s), the stable phase of beryllium(II) hydroxide.

Knowledge of the mode of transport of beryllium(II) in natural waters is important for an understanding of the geochemical cycle of this element. Fluoride and hydroxide have been considered to be the predominant complexing agents of Be^{II} in such waters, and hydroxo complexes have been proposed to account for the beryllium(II) speciation in neutral/alkaline waters.[7] The complex formation by the carbonate ion has been disregarded, possibly because of the lack of reliable data. However, it is known that carbonate plays a role in the mobility of beryllium from its ores, and concentrations up to 10^6 times higher than the normal levels (10^{-12} mol dm^{-3}) have been reported under these conditions.[4]

It is known[8] that solids containing the polynuclear anion $[Be_4O(CO_3)_6]^{6-}$ can be obtained from beryllium(II) carbonate solutions at pH $\geqslant$ 10. Hence, we found it of interest to investigate the stoicheiometry and equilibrium constants of the complexes formed at neutral-to-alkaline pH values and their structural arrangements. Two different experimental methods were used, *i.e.* solubility measurements of β-$Be(OH)_2$ and potentiometric titrations in homogeneous solution. We have also attempted to investigate the way in which the CO_2 groups are bonded in the complexes by using Raman spectroscopy.

Experimental and Results

Solubility Measurements.—The solubility of beryllium(II) hydroxide in bicarbonate solutions can be used to obtain information about the solubility product and the complex-formation equilibria. Solubility measurements of a single solid phase do not give information about the nuclearity of the complexes formed, only their charge.[9] However, at low solubilities the mononuclear complexes are often the predominant ones. We measured the dependence of the solubility of β-$Be(OH)_2$(s) on log h, in bicarbonate solutions at constant CO_2(g) partial pressure. The range of free hydrogen-ion concentration, h, investigated was $4.95 \leqslant -\log h \leqslant 7.0$. The experiments were carried out as potentiometric titrations at 25 °C and in 3.0 mol dm^{-3} $NaClO_4$.

The hydrogen-ion concentration was determined by using the same e.m.f. cell, as used previously. In this case the test solution had the general composition h mol dm^{-3} H^+, d mol dm^{-3} HCO_3^-, $(3.0 - h + d)$ mol dm^{-3} Na^+, and 3.0 mol dm^{-3} ClO_4^-, saturated with β-$Be(OH)_2$(s) and at a CO_2(g) partial pressure a. The Nernst equation had the same form as that employed previously.[1]

A typical solubility experiment started with V_0 cm^3 of a solution S_0 of general composition H_0 mol dm^{-3} H^+, $(3.0 - H_0)$ mol dm^{-3} Na^+, and 3.0 mol dm^{-3} ClO_4^-. The initial acidity of the solution, H_0, and the E_0 of the glass electrode, were determined coulometrically by a Gran titration.[10] A stream of

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* *Non-S.I. unit employed:* atm = 101 325 Pa.

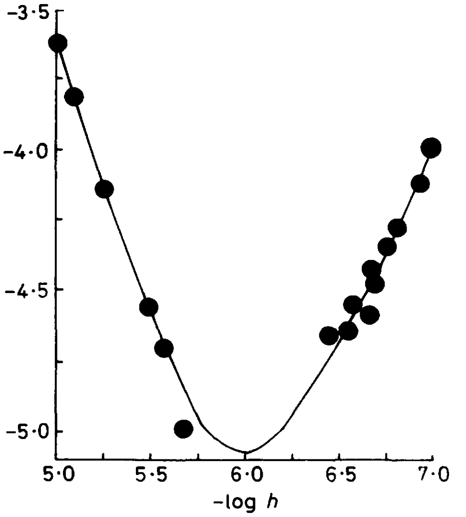

Figure 1. Plot of log B *vs.* $-\log h$ for the experiments at $a = 0.29$ atm. The continuous line was calculated according to the set of constants proposed in this study

N_2–CO_2 gas was then introduced into the titration vessel, and the selected H value was achieved by the addition of a known amount of $NaHCO_3$(s). At this point *ca.* 0.5 g of β-$Be(OH)_2$(s) was introduced into the vessel. The attainment of equilibrium was monitored by measuring the proton concentration. Equilibrium was assumed to be obtained when the potential of the glass electrode remained constant within 0.1 mV over 24 h. The attainment of equilibrium took 4—5 d for the first point and 1 d for the successive points of the titration. When equilibrium was reached, the experiment was discontinued and the total Be^{II} in solution was analysed spectrophotometrically with Chrome-S Azurol in a pyridine–hydrochloric acid buffer, according to Silverman and Shideler.[11]

The beryllium hydroxide was precipitated from alkaline beryllium(II) perchlorate solutions, under a N_2(g) stream. According to Gilbert and Garrett,[12] the α form is initially obtained. This phase was aged and transformed to the β form by stirring the mixture at 70 °C for several days. The solid was characterized by elemental analysis and by its *X*-ray powder diffraction pattern as β-$Be(OH)_2$(s). The composition and morphology of the solid phase in equilibrium with the sample solution were tested before and after the titrations. The diffraction patterns indicated no changes in the β-$Be(OH)_2$(s) phase during its time of contact with the test solution. The data obtained are shown in Figure 1, in the form of log B *vs.* $-\log h$.

The data obtained in the ranges pH 4.95—6 and 6.3—7.2 were analysed separately.

(*a*) *Solubility data in the range* $4.95 \leqslant -\log h \leqslant 6$. In the acid pH range the species responsible for the solubility of β-$Be(OH)_2$(s) are positively charged, as seen from the slope of the plot in Figure 1. The complexes of general form $[Be_p(OH)_q(CO_2)_r]^{(2p-q)+}$ which are expected to predominate have previously been established by e.m.f. measurements in homogeneous solution.[1,2] At $B < 1$ mmol dm^{-3}, these are $[Be(OH)]^+$, $Be(OH)_2$, $Be(OH)_2(CO_2)$, $[Be_3(OH)_3]^{3+}$, and $[Be_3(OH)_3(CO_2)]^{3+}$.

For the solubility experiments performed at constant CO_2(g) partial pressure, a, the total metal concentration, B, in equilibrium with β-$Be(OH)_2$(s) can be expressed as in equation (1).

$$B = b + [Be(OH)^+] + [Be(OH)_2] + [Be(OH)_2(CO_2)] + 3[Be_3(OH)_3(CO_2)^{3+}] + 3[Be_3(OH)_3{}^{3+}] \quad (1)$$

By introducing the conditional stability constants $K_{12}{}^*$ and $K_{33}{}^*$ (ref. 1) and the solubility product K_{s0} for β-$Be(OH)_2$(s) [equations (2) and (3)], where b is the free concentration of

$$Be(OH)_2(s) + 2\,H^+ \rightleftharpoons Be^{2+} + 2\,H_2O \quad (2)$$

$$K_{s0} = bh^{-2} \quad (3)$$

beryllium, equation (1) can be transformed into (4). The values

$$B = K_{s0}h^2 + K_{s0}\beta_{110}h + K_{s0}K_{12}{}^* + 3K_{s0}{}^3K_{33}{}^*h^3 \quad (4)$$

for $K_{12}{}^*$ and $K_{33}{}^*$ have been previously determined [1] at a = 0.97, 0.29, and 0.10 atm. We have used these equilibrium constants and calculated the unknown solubility constant and β_{110} by a least-squares fitting using the MLAB program:[13] log $K_{s0} = 6.2 \pm 0.1$ and log $\beta_{110} = -6.02 \pm 0.09$. The magnitude of β_{110} is in good agreement with our previous estimate from potentiometric measurements.[2]

(*b*) *Solubility data in the range* $6.2 \leqslant -\log h \leqslant 7.0$. Once the solubility product of β-$Be(OH)_2$(s) had been determined, we considered the data obtained in the pH range where negatively charged complexes dominate. If only mononuclear complexes are formed equation (5) is applicable. By combining this

$$B = [Be^{2+}] + \sum_{q,r}[Be(OH)_q(CO_2)_r{}^{(2-q)+}] = b + \sum_{q,r}\beta_{qr}bh^{-q}a^r \quad (5)$$

expression with the solubility equilibrium, we obtain equation (6). Since the measurements were performed at constant a, the

$$B = K_{s0}h^{-2}(1 + \sum_{q,r}\beta_{qr}h^{-q}a^r) \quad (6)$$

conditional constants (7) can be employed. Hence, equation (8) is obtained and rearrangement gives (9). A plot of the

$$K_q{}^* = \sum_r \beta_{qr}a^r \quad (7)$$

$$B = K_{s0}h^{-2}(1 + \sum_q K_q{}^*h^{-q}) \quad (8)$$

$$\log Bh^{-2} = \log K_{s0} + \log (1 + \sum_q K_q{}^*h^{-q}) \quad (9)$$

experimental data in the form log Bh^{-2} against $-\log h$ indicates that the solubility data at the higher $-\log h$ values approach an asymptote of slope -2. This suggests a limiting complex with $q = 4$. From the dependence of these curves on the partial pressure of CO_2 it is possible to deduce that $r = 1$ and consequently that the limiting complex is $[Be(OH)_4(CO_2)]^{2-}$.

In order to determine whether additional species with different values of q were present, the experimental data were compared with polynomial forms of equation (1) which included the terms with $q = 2$ and 3. In this way the total beryllium(II) concentration in solution for a set of experiments at constant CO_2 partial pressure can be written as in equation (10). The conditional constants for the formation of these

$$B = b + \sum_r[Be(OH)_2(CO_2)_r] + \sum_r[Be(OH)_3(CO_2)_r{}^-] + \sum_r[Be(OH)_4(CO_2)_r{}^{2-}] \quad (10)$$

$$K_{1n}{}^* = \sum_r[Be(OH)_n(CO_2)_r]h^n b^{-1}a^{-r} \qquad (n = 2—4) \quad (11)$$

species at constant a are given by equation (11). By combining equations (10) and (11) with (2) and (3) we obtain equation (12).

$$B = K_{s0}h^2 + K_2{}^*K_{s0} + K_3{}^*K_{s0}h^{-1} + K_4{}^*K_{s0}h^{-2} \quad (12)$$

The experimental data were fitted to the general equation (12) by a least-squares procedure using the MLAB[13] program. The following results were obtained. (*a*) The best agreement between experimental and calculated data is obtained for the following sets of parameters: $a = 0.97$ atm, $K_{s0} = (1.513 \pm 0.032) \times 10^6$ dm^3 mol^{-1}, $K_3{}^* = (1.51 \pm 0.15) \times 10^{-17}$ mol^3 dm^{-9}, and $K_4{}^* = (5.25 \pm 0.33) \times 10^{-25}$ mol^4 dm^{-12}; $a = 0.29$ atm, $K_{s0} = (1.513 \pm 0.032) \times 10^6$ dm^3 mol^{-1}, $K_3{}^* = (4.41 \pm 0.24) \times 10^{-18}$ mol^3 dm^{-9}, and $K_4{}^* = (1.82 \pm 0.42) \times 10^{-25}$ mol^4 dm^{-12}. The dependence of $K_3{}^*$ and $K_4{}^*$ on a indicates that $r = 1$. Hence, the values of the solubility and stability constants are log $K_{s0} = 6.18 \pm 0.03$, log $\beta_{131} = -16.82 \pm 0.02$, and log $\beta_{141} = -24.2 \pm 0.1$. (*b*) The data available proved not to be sufficient to define the Be(OH)$_2$(CO$_2$)$_r$ species, and consequently these were not taken into account in the final model.

The theoretical solubilities as a function of pH were calculated by taking into consideration the equilibria and stability constants proposed in equations (1)—(4), (10), and (11). They are plotted and compared with the experimental solubility data in Figure 1.

E.M.F. Measurements.—The Be^{II}–H$_2$O–CO$_2$(g) system was studied in 3.0 mol dm^{-3} (Na)ClO$_4$ using e.m.f. titrations as described before.[2] In this medium the liquid junction potential can be described by $j_1 = -16.8$ dm^3 mV mol^{-1} and $j_2 = 7.34 \pm 0.08$ dm^3 mV mol^{-1}.[1]

In coulometric titrations the total metal concentration B and the CO$_2$(g) partial pressure, a, were kept constant. The total acidity of the test solutions, H, was varied by using the same experimental technique as described before.[1] The ranges of acidity and total metal concentration were $6.4 \leqslant -\log h \leqslant 8.5$ and $0.97 \leqslant B \leqslant 5$ mmol dm^{-3}. The carbon dioxide partial pressure was varied in the range $0.01 \leqslant 0.97$ atm, by using appropriate CO$_2$–N$_2$ gas mixtures.

In volumetric titrations a test solution of general composition d mmol dm^{-3} HCO$_3^-$, B mmol dm^{-3} Be^{II}, $(3\,000 + d - 2B)$ mmol dm^{-3} Na$^+$, and 3.0 mol dm^{-3} ClO$_4^-$ was titrated with a solution of general composition h mmol dm^{-3} H$^+$, B mmol dm^{-3} Be^{II}, $(3\,000 - h - 2B)$ mmol dm^{-3} Na$^+$, and 3.0 mol dm^{-3} ClO$_4^-$. The variation of the e.m.f. with successive additions of the latter solution was measured with the potentiometric cell described in equations (5) and (6) of ref. 1. The partial pressure of CO$_2$(g) was kept constant at $a = 0.97$ atm by bubbling carbon dioxide as described before. The total metal concentrations used were 6, 10, and 30 mmol dm^{-3}, and the acidity range was $6.8 \leqslant -\log h \leqslant 7.4$.

The general experimental methodology was similar to that used in the previous investigations.[1,2]

The investigation of this system at alkaline pH is difficult because of the precipitation of Be(OH)$_2$(s) and a larger error in the Z values. The error in the experimental $Z(-\log h)_{B,a}$ functions is large since both H and d are large numbers. In the volumetric titrations the data collected had an approximately constant value of $Z = 4$ over the entire pH range investigated. Hence, these data allowed us to conclude only that the predominant complex had the general form [Be(OH)$_4$(CO$_2$)$_r$]$_n$. From the solubility measurements we have established that the limiting complex has a charge -2 and $r = 1$, hence n must be equal to one and the stoicheiometry is [Be(OH)$_4$(CO$_2$)]$^{2-}$.

In the coulometric titrations the precipitation of Be(OH)$_2$(s) due to local excess of alkali could be avoided and data were obtained for $Z < 4$, in titrations where $0.97 \leqslant B \leqslant 5$ mol dm^{-3} and $0.97 \leqslant a \leqslant 0.29$ atm. These are plotted in Figure 2 and allow a more detailed analysis.

Graphical treatment. From the data shown in Figure 2 it is obvious that polynuclear species are formed in the range Z 2—4. The stoicheiometry of the limiting complex at $Z = 4$ has already been established as [Be(OH)$_4$(CO$_2$)]$^{2-}$ by both solubility and volumetric titrations. The limiting species at $Z = 2$ has previously been shown to be Be(OH)$_2$(CO$_2$). The fact that the acidity of the solution increases when the total metal concentration, B, decreases indicates that the polynuclear complexes are formed at $Z < 4$. Hence we attempted to compare the experimental data at constant a with normalized[14] functions containing polynuclear terms [Be$_p$(OH)$_q$]$^{(2p-q)+}$ within the limits $1 < p \leqslant 6$ and $3 \leqslant q < 24$. A satisfactory agreement between experimental and normalized functions in the form $Z(-\log h)_{B,b}$ was found for $p = 3$ and $q = 9$ or 10. Consequently, the experimental data can be explained by the formation of [Be(OH)$_2$(CO$_2$)$_r$], [Be$_3$(OH)$_q$(CO$_2$)$_r$]$^{(6-q)}$ ($q = 9$ or 10) and [Be(OH)$_4$(CO$_2$)]$^{2-}$.

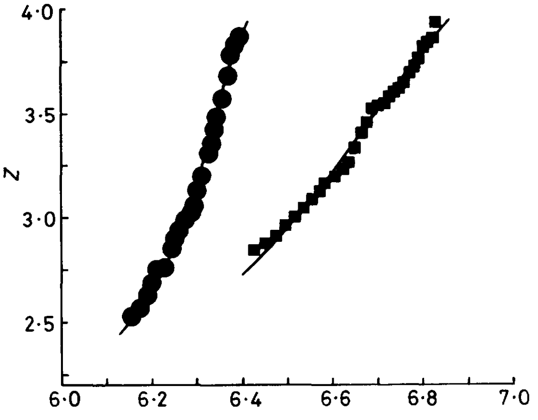

Figure 2. Experimental data in the form Z *vs.* $-\log h$ for the coulometric titrations at $a = 0.97$ atm and $B = 1$ (●) and 4.5 mmol dm^{-3} (■). The theoretical lines were calculated with the model which includes Be(OH)$_2$, Be(OH)$_2$(CO$_2$), [Be$_3$(OH)$_3$(CO$_3$)$_3$]$^{3-}$, and [Be(OH)$_4$(CO$_2$)]$^{2-}$

Numerical treatment. We attempted to refine the model by a least-squares method using the LETAGROP-ETITR program.[15] The experimental data in the form $(E,H,a)_B$ were minimized. Several models were tested, which included the mononuclear complexes Be(OH)$_2$(CO$_2$), [Be(OH)$_3$(CO$_2$)]$^-$, and [Be(OH)$_4$(CO$_2$)]$^{2-}$ and the polynuclear complexes [Be$_3$(OH)$_q$(CO$_2$)$_r$]$^{(6-q)}$ with $q = 9$ or 10 and $r = 1$—3. The best agreement in terms of error-square sums and standard deviations was found for $q = 9$ and $r = 3$. However, the difference between this hypothesis and one with $q = 10$ and $r = 3$ was only 4%.

Hence, we concluded that the experimental data can be explained with the stability constants log $\beta_{121} = -10.12 \pm 0.06$, log$\beta_{131} = -16.68 \pm 0.08$, log$\beta_{141} = -24.22 \pm 0.04$, and log $\beta_{393} = -45.5 \pm 0.5$ or log $\beta_{3103} = -52.0 \pm 0.5$. The agreement between the equilibrium constants for the (1,3,1) and (1,4,1) species obtained by e.m.f. and solubility measurements is good.

Raman Measurements.—As discussed previously,[1] the differences in the Raman spectra of bonded hydrogencarbonate and carbonate can be used to deduce the mode of bonding of the CO$_2$ group. We have recorded the Raman spectra of the following solutions [all containing 50 mmol dm^{-3} Be(ClO$_4$)$_2$]: (1) $a = 0.97$ atm, pH 7.15; (2) $a = 0.97$ atm, pH 7.75; $a = 0.10$ atm, pH 8.67; (4) [HCO$_3^-$]$_T$ = 0.72 mol dm^{-3}, pH 9.6; and (5) [HCO$_3^-$]$_T$ = 0.80 mol dm^{-3}, pH 11.0. The composition of solutions 1—3 was calculated[1] by using the set of constants determined in this work for Be(OH)$_2$-

Table. Summary of the Raman bands. Perchlorate bands have been omitted

Solution	Bands (cm^{-1})
1	1 357s, 1 048m, 1 010s, 368w
2	1 357s, 1 068w, 1 048m, 1 010s, 368w
3	1 357s, 1 068m, 1 048m, 1 010s, 368w
4	1 357m, 1 068s, 1 048m, 1 010s, 368w
5	1 357w, 1 068vs, 1 048(sh), 1 010w

v = Very, s = strong, m = medium, w = weak, sh = shoulder.

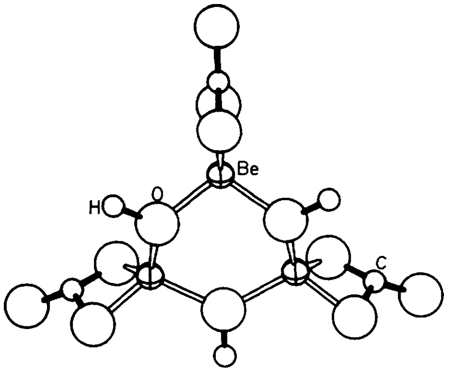

Figure 3. Model of the structure of $[Be_3(OH)_3(CO_3)_3]^{3-}$

(CO_2), $[Be(OH)_3(CO_2)]^-$, $[Be(OH)_4(CO_2)]^{2-}$, and $[Be_3(OH)_9(CO_2)_3]^{3-}$. Solution 1 contained 29% of the bonded carbonate in the form of the polynuclear species, and 71% as $[Be(OH)_4(CO_2)]^{2-}$. In solutions 2 and 3 the limiting complex $[Be(OH)_4(CO_2)]^{2-}$ accounts for practically 100% of the co-ordinated carbonate. The composition of solutions 4 and 5 is more difficult to establish because we did not use pH values higher than 8.5 in our potentiometric measurements. These two solutions were investigated in order to see whether the Raman spectra indicated changes in the CO_2 co-ordination, as compared to the previous solutions. The Raman spectra were recorded by using the same laser source and spectrophotometer as previously described.[1] The resulting spectra are summarized in the Table.

The bands at 1 357 and 1 010 cm^{-1} correspond to ν_2 and ν_1 of free HCO_3^-. They decrease in intensity with increasing pH, as expected. The band at 1 068 cm^{-1} corresponds to ν_1 of free CO_3^{2-}, its intensity increasing with increase in $[CO_3^{2-}]$. The band at 1 048 cm^{-1} is assigned to bonded carbonate, as discussed previously.[1] The fact that this band is obtained throughout the whole pH range indicates that the same type of CO_3^{2-} co-ordination is present in the two predominant beryllium(II)–carbonate complexes. A relative decrease in intensity is observed at the highest pH value, but this may be caused by the increase in intensity of the band at 1 068 cm^{-1} which overlaps the band at 1 048 cm^{-1}. The band at *ca.* 370 cm^{-1} cannot be assigned to carbonate modes. Frequencies in the region 350—380 cm^{-1} have been observed in the Raman spectra of beryllium(II) in acidic aqueous and D_2O solutions.[16,17] The band at 368 cm^{-1} could thus correspond to a Be–OH vibration.

From these results we can conclude that the CO_2 is bonded as CO_3^{2-}, presumably in a bidentate fashion, in the limiting complex $[Be(OH)_4(CO_2)]^{2-}$. Hence, this complex should be written as $[Be(OH)_2(CO_3)]^{2-}$, as expected for tetrahedral co-ordination. The Raman spectra of all the solutions investigated showed the same features, which indicates the same kind of CO_2 bonding also in the mixed polynuclear complex. As mentioned before, we did not observe any change in the band corresponding to bonded carbonate in the solutions (4,5) at higher pH. This only indicates that the same type of Be^{II}–CO_2 bonding is found also in this case. The composition of the complexes formed in the range pH 9—11 is now being investigated by n.m.r. spectroscopy. The results will be presented in a forthcoming publication.[18]

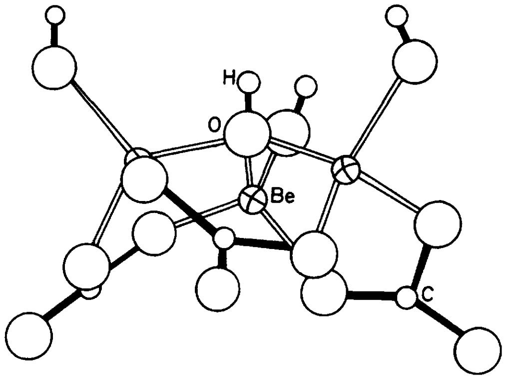

Figure 4. Model of the structure of $[Be_3(OH)_4(CO_3)_3]^{4-}$

Discussion

We have established by solubility and e.m.f. measurements that $[Be(OH)_4(CO_2)]^{2-}$ is the predominant species responsible for the solubility of beryllium(II) hydroxide in bicarbonate solutions. We have also determined that $Be(OH)_2(CO_2)$ and $[Be(OH)_3(CO_2)]^-$ are minor mononuclear species.

The Raman spectra indicate that CO_2 is present as CO_3^{2-} in the predominant complex $[Be(OH)_4(CO_2)]^{2-} \equiv [Be(OH)_2(CO_3)]^{2-}$. We have previously proposed the same type of bonding for $BeCO_3$.[1] It is reasonable to expect the same kind of co-ordination in $[Be(OH)_3(CO_2)]^-$, and this complex should thus be written as $[Be(OH)(CO_3)]^-$.

The data collected at low Z suggest the formation of a polynuclear complex. By a graphical treatment of the data we have established $[Be_3(OH)_9(CO_2)_3]^{3-}$ or $[Be_3(OH)_{10}(CO_2)_3]^{4-}$ as the most probable stoicheiometry. Only a small amount, at most 5%, of the total Be^{II} is present in the polynuclear form. Nevertheless, the fact that Z increases by 50% on going from the mononuclear to the polynuclear species has a pronounced influence on the slope and location of the Z curves (*cf.* Figure 2). This means that the graphical procedures are very sensitive to the nuclearity of the complexes. The graphical method proved to be much better than the least-squares method in defining the minor species. The reason for this is that the total acidity H was used as the error-carrying variable in the refinement of the system, and was not very sensitive to variations in the chemical model unless a good initial estimate of the equilibrium constant for the polynuclear complex was available. With the constant provided by the graphical procedure there were no such problems. However, the amount of data was insufficient to distinguish between a polynuclear complex with nine or ten OH groups.

Reasonable structures can be proposed for both trinuclear complexes (see Figures 3 and 4). In the case of $[Be_3(OH)_9(CO_2)_3]^{3-}$ the structure conserves the original ring structure of $[Be_3(OH)_3]^{3+}$, with the three CO_3^{2-} groups bonded in a bidentate fashion to give a tetrahedral co-ordination around Be^{II}. A similar structure has been determined by *X*-ray diffraction for $[Be_3(OH)_3(C_5H_4NCO_2)_3]\cdot H_2O$, in the solid state,[18] where the three pyridine-2-carboxylate groups chelate in the same way as we propose for the carbonate. In the case of the complex containing ten hydroxo groups the structure

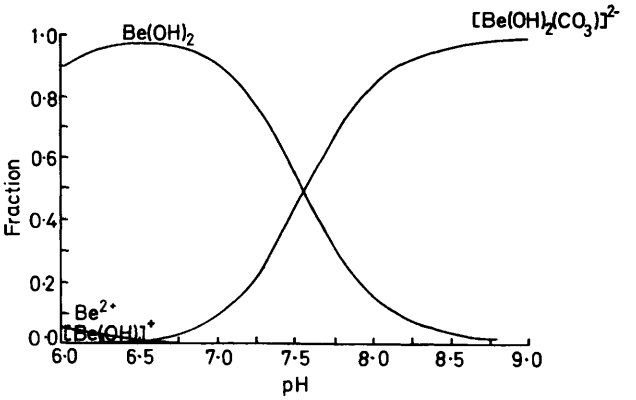

Figure 5. Distribution diagram for the different hydroxo and hydroxo-carbonato complexes of Be^{II} which predominate in average natural water conditions: $B = 10^{-12}$ mol dm^{-3}, total carbonate = 1 mmol dm^{-3}, and pH 6—9

depicted in Figure 4 is related to that found in the solid state for the $[Be_4O(CO_3)_6]^{6-}$ anion.[17]

Mickievicz and Samtschuk have measured the solubility of $Be(OH)_2(s)$ in bicarbonate[3] and carbonate[4] solutions. From the measurements in bicarbonate solutions they proposed a set of complexes $[Be(OH)]^+$, $Be(OH)_2$, $[Be(OH)_2(HCO_3)]^-$, and $[Be(OH)_2(HCO_3)_2]^{2-}$, in partial agreement with our results. Nevertheless, these data are not reliable, as seen from the fact that the constants reported cannot describe the experimental solubility data. No pH measurements were reported and the free bicarbonate concentration was calculated by an iterative process, dependent on the model chosen, which is a less satisfactory method. In the investigation of the solubility of $Be(OH)_2(s)$ in carbonate solutions[4] the authors worked at constant pH (11.0). From the dependence of log B on the concentration of CO_3^{2-} it is possible to conclude that the species responsible for the solubility contain one and two carbonate groups, respectively; $[Be(OH)(CO_3)]^-$ and $[Be(CO_3)_2]^{2-}$ were proposed, but the proton concentration was not varied and consequently there is insufficient information to define the possible mixed complexes. It is interesting, though, that these data suggest a transition from $[Be(OH)_2(CO_3)]^{2-}$ to $[Be(CO_3)_2]^{2-}$ at high $CO_3^{2-}:OH^-$ ratios.

From our solubility measurements of β-$Be(OH)_2(s)$ in 3.0 mol dm^{-3} perchlorate we obtain log $K_{s0} = 6.18 \pm 0.03$, and estimate log $K^0_{s0} = 5.9 \pm 0.1$ at infinite dilution. We can in this way calculate ΔG_{298} for the transformation from the α to the β modifications of $Be(OH)_2(s)$ as -5.5 ± 0.8 kJ mol^{-1}, to be compared with the value estimated by Fricke and Humme[19] of -2.1 kJ mol^{-1}.

The data obtained on the beryllium(II) complex formation in bicarbonate media can also be used to get an idea of the relative effect of carbonate and hydroxide on the complex formation of beryllium in natural waters. We have made a model calculation using the average pH and total carbonate concentration of most natural water systems (pH 6.5—9, $[HCO_3^-] = 1$ mmol dm^{-3}). The total Be^{II} was set at 10^{-12} mol dm^{-3}, the average concentration found in natural waters. The stability constants used were the ones obtained in this study, extrapolated by the specific ion interaction (s.i.t.) approach, to infinite dilution. Those for $[Be(OH)]^+$ and $Be(OH)_2$ were from previous work,[2] and the values of log $\beta^0_{130} = -23.46 \pm 0.05$ and log $\beta^0_{140} = -37.59 \pm 0.05$ were the result of our own recalculation of the solubility data of Gilbert and Garrett.[12] The distribution diagram in Figure 5 shows that the mixed species are important and consequently that they have to be considered in the speciation scheme for beryllium(II) in natural waters.

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