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Studies on the Hydrolysis of Metal Ions

XVI. The Hydrolysis of the Beryllium Ion, Be^{2+}

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The hydrolysis of the ion Be^{2+} has been studied by electrometric titrations at constant ionic medium (3 M ClO_4^-), using quinhydrone and hydrogen electrodes. A mathematical analysis was made of the curves $Z (\log h)_B$ giving Z, the average number of OH bound per Be, as a function of $\log h$, at various total beryllium concentrations B. It was concluded that the main product is $Be_3(OH)_3^{3+}$; for the equilibrium constant of the reaction $3Be^{2+} + 3H_2O \rightleftharpoons Be_3(OH)_3^{3+} + 3H^+$, $\log K_{33} = -8.66 \pm 0.03$ was obtained. No evidence was found of the complexes $(BeOH)_2^{2+}$ and $(BeOH)_4^{4+}$ proposed by previous workers.

Deviations at low values of B and Z indicate the presence of Be_2OH^{3+} and $Be(OH)_2$. The best value for the equilibrium constants were: $2Be^{2+} + H_2O \rightleftharpoons Be_2OH^{3+} + H^+$, $\log K_{12} = -3.24 \pm 0.02$; $Be^{2+} + 2H_2O \rightleftharpoons Be(OH)_2 + 2H^+$, $\log K_{21} = -10.9 \pm 0.2$. Slight deviations at $Z > 0.9$ where equilibrium is achieved very slowly may be due to precipitation or to higher complexes.

Solutions of beryllium salts are acidic, and Berzelius[1] noticed that a solution of beryllium sulfate can dissolve considerable quantities of beryllium hydroxide. Thus the existence of beryllium hydroxo or oxo complexes seems very probable. Several quantitative investigations of the hydrolysis of Be^{2+} have been reported. Most workers agree[2–10] that clear solutions can be obtained up to $Z = 1.0$ (Z = average number of OH^- bound per Be^{2+}). At higher values of Z, precipitation begins. With halogenide ions[2] it is completed by $Z = 2.0$. With other ions precipitation is complete by $Z = 1.8$ to 1.9, which indicates that in these cases the precipitate is not pure $Be(OH)_2$ but contains sulfate[2,8], nitrate[7] or perchlorate[7] ions as well.

The fact that the precipitate appears only when Z exceeds 1.0 suggests the formula $(BeOH)_n^{n+}$ for the soluble complexes. The main reaction would then be (*cf.* eqn. 4 below)

$$n\ Be^{2+} + n\ H_2O \rightleftharpoons (BeOH)_n^{n+} + n\ H^+;\ K_{nn} = [(BeOH)_n^{n+}]\ h^n[Be^{2+}]^{-n} \quad (1)$$

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Prytz [2-4] has compared pH titrations carried out with different beryllium concentrations in the presence of various anions. Testing for $n = 1$ and $n = 2$, she found a variable value for K_{11} whereas K_{22} seemed to be fairly constant. The average value of $10^7\ K_{22}$ was 1.4 for sulfate [2], 1.7 for chloride [2], 5.9 for bromide [3], and 4.4 for iodide [3] solutions. According to Prytz, the complex would then not be $BeOH^+$ but $(BeOH)_2^{2+}$ or Be_2O^{2+}; as usual, equilibrium data cannot distinguish between species containing different amounts of the solvent.

In connection with his work on metal ammine complexes, J. Bjerrum [5, p. 173] studied solutions containing Be^{2+} and NH_3 in 2 M NH_4NO_3. He concluded that his data should rather be explained by the formation of OH complexes than of NH_3 complexes. Following Prytz, he also assumed the equilibrium (1) with $n = 2$, but since his values of K_{22} varied, he suggested that in addition to Be_2O^{2+} also Be_2OH^{3+} and small amounts of a trimer are present.

From pH titration curves for total beryllium concentrations from 10 to 100 mM, and with the ionic medium 1 M $NaClO_4$ or 1 M KNO_3, Schaal and Faucherre [6,7] concluded that n should rather be 4. Teyssèdre and Souchay [8] made a mathematical analysis of the titration curves of 200 and 40 mM Be in 1 M Na_2SO_4 between $Z = 1.0$ (clear solution) and 1.9 (complete precipitation). They also concluded that $n = 4$ in the solution with $Z = 1$. Souchay [9] titrated $BeSO_4$ with NaOH in a solution saturated with Na_2SO_4, and measured the change in temperature of formation of solid $Na_2SO_4(H_2O)_{10}$. From these data he also concluded that $n = 4$. Faucherre [7] studied the depression of the NH_4NO_3-ice eutectic point in the presence of beryllium hydroxo complexes; no figures seem to be given, but he claims that the tetramer, with $n = 4$, is formed. Thus, according to the French workers, the predominant complex would be $(BeOH)_4^{4+}$ or $Be_4O_2^{4+}$.

The existence of ions $(BeOH)_n^{n+}$ is confirmed by the finding of Puche and Josien [10] that $Be(OH)_2$ dissolves in $Be^{2+}SO_4^{2-}$ solutions until the ratio OH/Be becomes 1, and by the thermometric titration of Haldar [11]. Ion exchange data obtained by Honda [12] were explained in terms of the species $(BeOH)_2^{2+}$ in solution. However, Honda's data may equally well be explained by assuming the presence of any species $(BeOH)_n^{n+}$.

Diffusion and conductivity measurements by Heukeshoven and Winkel [13] give an almost linear transition from Be^{2+} to the region with one OH per Be; these data give no evidence for complexes with less than one OH group per Be.

Using a glass electrode, Mattock[14] made "static" titrations of $Be(ClO_4)_2$ solutions of concentration from 1 mM to 30 mM, with NaOH using the ionic medium 1 M $NaClO_4$. He seems to have had considerable difficulties with irreversible equilibria, and his data differ in some respects from those obtained by ourselves and other workers. His conclusions are that there are rapid equilibria up to $Z = 0.5$ whereas the equilibria between $Z = 0.5$ and 1.0 are reached only after about two months at 25°C. Equilibrium constants are given for the formation of $BeOH^+$ and Be_2OH^{3+}: $[BeOH^+][H^+][Be^{2+}]^{-1} = (3 \pm 1) \cdot 10^{-7}$; $[Be_2OH^{3+}]\ [H^+][Be^{2+}]^{-2} = (3.1 \pm 0.6) \cdot 10^{-4}$.

From all other data, including our own, it seems that equilibrium is established very rapidly, as long as a clear solution is obtained. When a precipitate of $Be(OH)_2$ has already been formed, *e.g.* by local high pH, it can only be redissolved rather slowly, and the attainment of equilibrium is retarded. Mattock's equilibrium constants were calculated from data in the lowest pH region, where equilibrium was rapidly obtained, and his value for log K_{12} (-3.5) is in fair agreement with ours (-3.24).

The present work was carried out to throw a little more light on the hydrolysis of Be^{2+}, using the techniques previously developed in this laboratory[15-31].

Symbols

B	total concentration of Be
B	normalized value of B (29)
b	concentration of free Be^{2+} (9a)
c_{pq}; c_n	concentration of complex $Be_q(OH)_p$ (4); of n:th complex (10)
E	emf; E_0 constant, E_j liquid junction emf (2)
F, F_r, F_q	functions of experimental data (7), (19), (22), (23)
g	defined in (9b)
H	total (analytical) excess concentration of H^+
h	concentration of free H^+
j	constant in $E_j = -jh$
k, k_0	constants in hypotheses "II" and "IIIa" (14) and ff
K_{nn} K_{pq},	equilibrium constants (1) (4)
k_n	$= K_{tn,\ n+1}$, equilibrium constants (9)
N	singular value of n in (1) or (9c); (14)
n	integer (1); number of links in "core + links" complex (9c)
$\bar{n}$	average number of links (10)
p_1, p_2	constant parameters to be determined (29)
p, q	integers: number of OH and Be in complex (4)
r	integer (19)
s_n	constants (18)
t	number of OH in "link" (5)
u	auxiliary functions (9a), (17) or (30)
X, Y	normalized x and y (29)
x, y	experimental functions (6a, b) or (28)
Z	average number of OH bound per Be
α	auxiliary function (29), (30)
δ	residual integral in (12)

In the calculations and especially in the equilibrium constants, M (mole/l) is used as unit throughout. Sometimes in the text or headings, however, the convenient unit mM (millimole/l) is used.

METHOD

The present investigation consisted of a series of potentiometric titrations at 25° C. In each titration, the total concentration of beryllium, B, was kept constant, while the total concentration of acid in the system was varied. All solutions were made to contain 3 M ClO_4^- by the addition of $NaClO_4$. Since the concentrations of hydrogen and beryllium ions were low, Be at most 48 mM, H^+ usually much less, compared with the concentrations $\approx$ 3 000 mM of Na^+ and ClO_4^-, it can be assumed with good approximation that the activity factors of all reacting species remain constant[17], and hence that true stoichiometric constants may be calculated from the measurements.

It would be desirable to know the concentrations of both free H^+ and free Be^{2+}. However, no electrode reversible to Be^{2+} is known, so the titrations were followed only by measuring h, the free hydrogen ion concentration. A quinhydrone electrode was used, in combination with the reference electrode

$$SE// = Ag\ /\ 0.01\ M\ AgClO_4,\ 2.99\ M\ NaClO_4\ /\ 3\ M\ NaClO_4$$

To check that no error is introduced by the use of quinhydrone, the hydrogen electrode was used in a few titrations.

Thus the cells for measuring h may be written:

$$\text{SE//H}^+ \ (h),\ \text{QH}_2,\ \text{Q/Pt} \quad (25^\circ\,\text{C})$$

or

$$\text{SE//H}^+ \ (h)\,/\,\text{H}_2(\text{g}),\ \text{Pd} \quad (25^\circ\,\text{C})$$

For each of these cells, the measured emf, E, is related to h by

$$E = E_0 + E_j + 59.16 \log h \tag{2}$$

Here E_0 is a constant, different for each type of cell, and E_j is the liquid junction potential[17], which is approximately given by $E_j = -jh$, where j is a constant, around 0.018 ± 0.001 mV mM^{-1}. The values for E_0 and j were checked for each titration, either by a preliminary acid-base titration in the absence of beryllium, or by titration in the presence of a small amount of beryllium ($B = 1.00$ or 2.56 mM) in the range $0.1\ \text{M} > h > 0.01$ M, where the hydrolysis is negligible.

When E_0 and j are known, and E is measured, h can be obtained from equation (2). From the composition of the solution, the total beryllium concentration B is known, and the analytical excess of hydrogen ions H can be obtained (assuming all beryllium to be present as Be^{2+}). Z, the average number of OH per Be, may then be calculated for any point of the titration:

$$Z = (h - H)\ B^{-1} \tag{3}$$

(part 8[20], eqn. 6; $[\text{OH}^-]$ is negligible in all beryllium solutions studied here).

The data may conveniently be discussed in terms of the variation of Z with log h.

EXPERIMENTAL DETAILS

Reagents

Beryllium perchlorate solutions were prepared as follows: Beryllium carbonate (Kebo puriss) was moistened with water and dissolved in dilute HCl, and sufficient water was added to make $[\text{Be}^{2+}] \approx 0.1$ M and $[\text{H}^+] \approx 0.1$ M. The solution was passed through a column containing the H+ forn of the cation exchange resin, Amberlite IR-120. In the effluent beryllium was obtained completely free from impurities such as aluminium, iron and calcium, which have a far stronger affinity for the cation exchange resin than beryllium ion[32]. An excess of dilute NH_3 was added dropwise to the effluent. The precipitate was centrifuged, dissolved in dilute HNO_3 (p.a.), and reprecipitated with dilute NH_3, freshly prepared from NH_3 gas. This precipitate was again centrifuged, washed free from NO_3^- ions, and dried at 300°C for 12 hours. Each batch of the porous oxide contained about 2 % of water; it was divided into three portions.

The purity of the first portion was checked by the alizarin drop test for aluminium and the thiocyanate test for iron[33]; both tests were negative. The second portion was weighed and ignited at 1 200°C for 8 hours; the accurate content of BeO in the batch was obtained from the constant weight. The third portion was weighed and dissolved in a weighed excess of perchloric acid. The clear solution was completely transferred into a standard flask, and made up to a known volume. The concentration of beryllium in the solution was checked by gravimetric determination as BeO. The result agreed with the expected value within the experimental error. Dilute solutions of $\text{Be(ClO}_4)_2$ for titration were prepared by weight.

Perchloric acid solutions were prepared from perchloric acid (p.a.) and standardized against potassium hydrogen carbonate (Merck p.a.) which was free from Na+, and had been dried in an atmosphere of CO_2.

Sodium hydrogen carbonate solutions were prepared from the p.a. product of Merck. The concentrations were determined against standard HClO_4, both by potentiometric titration using Gran's method for calculating the end-point[34], and by visual titration to the methyl-red end-point.

Sodium perchlorate was prepared by neutralising a solution of $HClO_4$ with $NaHCO_3$. The solutions were analysed by evaporating and drying to constant weight at 125°C. No chloride, chlorate, aluminium or iron could be detected in the product.

Silver perchlorate solutions were prepared by adding an excess of Ag_2O to a boiling solution of $HClO_4$. The solution was filtered, and the concentration of Ag^+ determined by Volhard's method.

Quinhydrone (Merck p.a.) was used without purification since no positive reaction was found for acid, alkali, or iron.

Apparatus

The titration cell was of the "Wilhelm" type described by Forsling, Hietanen, and Sillén [16]. It was kept in a paraffin oil thermostat, 25.0 ± 0.1°C, which was placed in a room thermostated at approximately 25°C.

In the cells with quinhydrone, a Pt foil was used as the inert electrode. It was first cleansed in HNO_3 (1:1), washed with water, and ignited in an alcohol flame. The hydrogen electrodes were lightly palladinated Pt foil [35]. The silver reference electrodes were first prepared as recommended by Brown [36] and then coated with AgCl by electrolysis for half an hour in 0.1 M HCl with a current of 0.3 mA per electrode. The emfs (E) were measured with a Jensen compensator, type 10A, or a Vernier potentiometer. Hundredths of a mV were estimated in each case.

The solutions were introduced into the titration cell from burets which had been calibrated by weighing, using 3 M $NaClO_4$ solution. When a quinhydrone electrode was used, the titration solution was stirred by means of nitrogen which had passed through 10 % H_2SO_4, 10 % NaOH, and 3 M $NaClO_4$ solutions. When a hydrogen electrode was used, the solution in the cell was stirred by a stream of hydrogen which had passed through a column filled with activated copper [37], and then through 10 % H_2SO_4, 10 % NaOH, and 3 M $NaClO_4$ solutions.

Titration procedure

In the following it will be tacitly understood that all solutions contained 3 M ClO_4^-, and in addition Na^+.

Preliminary titrations with NaOH (0.1 M) showed that local precipitation occurred. To avoid this, $NaHCO_3$ (Hedström [19]) was used as the base. To get preliminary values for E_0 and j (eqn. 2), 25.0 or 50.0 ml of 24.92 or 99.43 mM $HClO_4$ was titrated with 100.65 mM $NaHCO_3$. In the main experiments, eleven titrations were made with $B = 48.7_4$, $19{,}2_7$, 10.02_5, 5.05_7, 2.56_0, and 1.00 mM.

Almost all titrations were carried out as follows: 25.0 ml of "neutral medium" (3 M $NaClO_4$), or of 24.92 mM $HClO_4$ was added to 25.0 ml of a solution T_1, containing Be^{2+} (concentration 2 B) and H^+. This mixture, solution S, was titrated, always adding equal volumes of 100.65 or 30.25 mM $NaHCO_3(T_2)$, and of solution T_1. In a few cases, the experiment was continued with a back titration, adding equal volumes of 24.92 mM H^+ and of solution T_1, to confirm that equilibrium had been obtained (see below). The total concentration of beryllium, B, always remained constant throughout the titration.

For the highest value of B, 48.7_4 mM, a different procedure was adopted. To 25.0 ml of a solution T_1, containing Be^{2+} (concentration 2 B) and 113.5 mM H^+, 25.0 ml of 100.65 mM $NaHCO_3(T_2)$ was at first added in portions. This mixture was titrated with equal volumes of 264.0 mM $NaHCO_3(T_3)$ and solution T_1.

At the end of one titration, with 10 mM Be, the equilibrium emf was noted, and the stream of nitrogen replaced by a stream of CO_2. The system was left for an hour, and then nitrogen was bubbled through the solution for two minutes. The emf was the same as before, indicating that the measurements are not invalidated by complex formation between beryllium and carbonate ions.

A steady E was usually attained within half an hour for $Z \leq 0.8$, thus in the main part of the range studied. When hydrolysed solutions (with $Z \leq 0.8$) were back-titrated with acid, the points $Z(\log h)$ fell on the same curve as points obtained by forward titration with HCO_3^-, indicating that the equilibria are reversible in this region. (Fig. 1, 19 mM and 48 mM). In solutions with $0.8 < Z < 0.9$, equilibrium was reached more slowly. A steady E was obtained within one or two hours, and remained constant for at least four

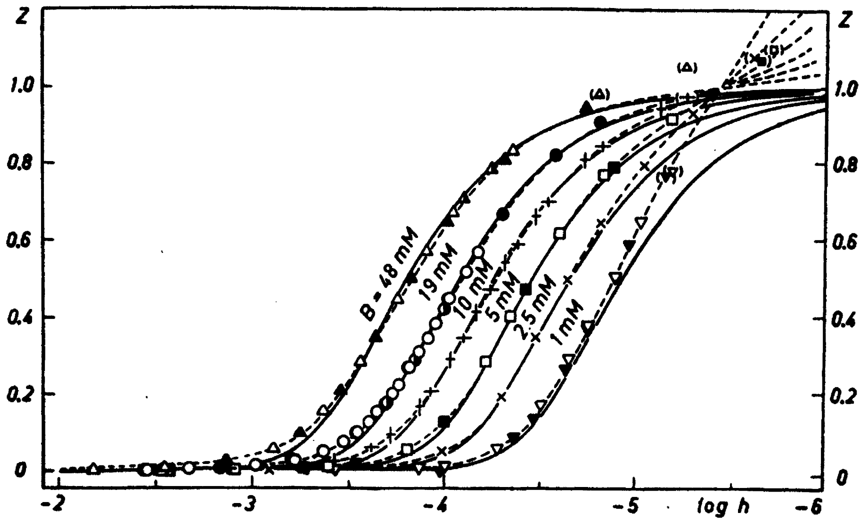


Fig. 1. Average number, Z, of OH bound per Be, as a function of log h. *All experimental points are given. Filled or open symbols represent points from different titrations, half-filled symbols from backtitrations. Total Be concentration B:* ▲ △ ◭ *48.7_4 mM;* ● ○ ◑ *19.2_7 mM;* + *10.0_3 mM;* ■ □ *5.05_7 mM;* × *2.5_8 mM;* ▼ ▽ *1.00 mM. Hydrogen electrode used for* ● *and* ■, *quinhydrone for other symbols. Full curve: calculated for $K_{21} = K_{12} = 0$, log $K_{33} = -8.66$. Broken curves: calculated for log $K_{12} = -3.25$, log $K_{21} = -10.87$, log $K_{33} = -8.66$.*

hours. With $Z \geqq 1$, E was always unsteady, even before a visible precipitate appeared, so that titration was discontinued. With the lowest metal concentration, $B = 1$ mM, a steady emf was only obtained up to $Z = 0.6$; with higher values of Z, E kept drifting even after three hours; it seems practically impossible to get accurate values in this region.

With hydrogen electrodes, the $Z(\log h)$ curves for $B = 19$ and 5 mM agreed, within 0.15 mV, with those obtained with quinhydrone electrodes throughout the whole region of hydrolysis (see Fig 1). Hence, there is no reason to assume an appreciable error due to beryllium-quinhydrone complexes.

THE MAIN PRODUCT OF HYDROLYSIS

Fig. 1 gives the data $Z(\log h)_B$, calculated from the potentiometric measurements, using eqns. (2) and (3). Table 1 gives the values of log h and Z for one titration at each of the six values of B, and for one titration with a hydrogen electrode. If only mononuclear complexes were formed, Z would be a function of h only, and all points would lie on the same Z (log h) curve, regardless of the value of B. As this is not the case, at least one polynuclear hydroxo complex must be formed.

The polynuclear species may be written in the general form $Be_q(OH)_p^{(2q-p)+}$, where p and q are positive integers; we shall by K_{pq} denote the equilibrium constant of the reaction

$$pH_2O + qBe^{2+} \rightleftharpoons Be_q(OH)_p^{(2q-p)+} + pH^+, \quad K_{pq} = c_{pq}h^pb^{-q} \qquad (4)$$

Table 1. Experimental data Z (log h)$_B$ for typical titrations.

Titration 1.
B = 48,74 mM

$-\log h$	Z
2.170	0.005
3.100	0.057
3.366	0.153
3.554	0.277
3.753	0.442
3.907	0.569
4.047	0.671
4.104	0.706 *
4.251	0.784 *
4.360	0.831
(4.816)	(0.976)
(5.276)	(1.054)

Titration 3.
B = 19.27 mM

$-\log h$	Z
2.445	0.000
2.664	0.004
3.011	0.013
3.213	0.027
3.365	0.049
3.468	0.075
3.542	0.101
3.599	0.127
3.646	0.152
3.692	0.177
3.728	0.201
3.761	0.224
3.818	0.267
3.865	0.308
3.911	0.346
3.953	0.382
4.029	0.447
4.112	0.518
4.175	0.568
3.999	0.418 *
3.848	0.288 *
3.695	0.173 *

Titration 4 **
B = 19.27 mM

$-\log h$	Z
2.444	0.000
2.828	0.006
3.199	0.028
3.540	0.102
3.810	0.267
4.025	0.447
4.304	0.667
4.582	0.821
4.818	0.907

Titration 5.
B = 10.02_5 mM

$-\log h$	Z
2.483	0.000
2.884	0.004
3.619	0.062
3.931	0.206
4.103	0.344
4.244	0.472
4.388	0.588
4.544	0.698
4.824	0.844
(5.264)	(0.975)

Titration 7
B = 5.05_7 mM

$-\log h$	Z
2.564	0.000
2.900	0.003
3.393	0.011
3.799	0.056
4.214	0.287
4.340	0.401
4.599	0.617
4.834	0.771
5.183	0.916
(5.709)	(1.100)

Titration 9
B = 2.56_0 mM

$-\log h$	Z
2.571	0.000
3.086	0.001
3.990	0.049
4.298	0.192
4.474	0.375
4.640	0.496
4.816	0.646
5.047	0.796
5.293	0.936
(5.615)	(1.080)

Titration 10
B = 1.00_3 mM

$-\log h$	Z
2.916	0.000
3.424	0.002
3.868	0.006
4.006	0.013
4.281	0.064
4.509	0.169
4.653	0.287
4.754	0.316
4.897	0.503
5.031	0.651
(5.193)	(0.776)

* Values of back-titration.
** Hydrogen electrodes were used. ( ) no steady potential obtained.

A quite general method for computing the various K_{pq}, which has been suggested by Hedström [27] could not be used in the present work, since the data have not the extreme accuracy needed. Therefore, two other approaches were attempted: the "core + links" approach and the assumption that all complexes are $(\mathrm{BeOH})_n^{n+}$. When the main product of hydrolysis had thus been determined, the secondary products were considered.

"Core + links" approach

It has previously been found that the main hydrolysis products of a number of metal ions [20-23] may be written in a general "core + links" form $Me((OH)_tMe)_n$, where t is a constant, and n is a constant or variable integer; then $p = t\ (q—1)$. If all the complexes present in appreciable amounts can be written in such a "core + links" form, a set of parallel $Z(\log h)_B$ curves should be obtained [25, 20], and the value of t is given by

$$t = (\partial \log B / \partial \log h)_Z \qquad (5)$$

Indeed, the data in Fig. 1 for the hydrolysis of Be^{2+} seem to lie on parallel curves $Z\ (\log h)_B$, in the range $0.1 < Z < 0.8$. In Fig. 2, $\log B$ is plotted against $\log h$ for values of Z between 0.05 and 0.8. From the slope, and (5), a value of $t = 1.5$ may be obtained, neglecting the slight deviations at high and low values of Z.

Again, if only "core + links" species $Be((OH)_tBe)_n$ are formed, all experimental points should lie on the same curve $y\ (x)$ with the coordinates [26, 20]

$$x = \log B — t \log h; \quad y = Z / t \qquad (6a, b)$$

The experimental plot of $y = Z/1.5$ against $x = \log B — 1.5 \log h$ is shown in Fig. 3. It is seen that the points for $48\ mM \geq B \geq 5\ mM$ lie on a single curve except these for very low values of Z. Small deviations are observed for the lowest values of B, 2.5 and 1 mM, which may indicate the presence of mononuclear complexes.

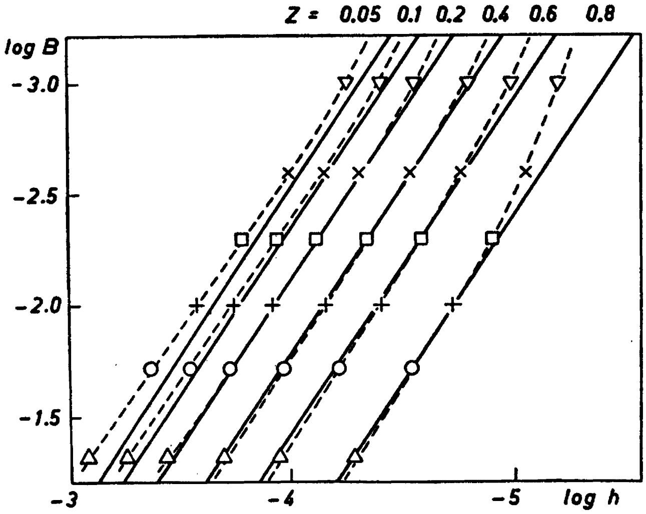


Fig. 2. Log B *as a function of log* h, *for different values of* Z. *Full lines are calculated for log* $K_{33} = -8.66$, *and no other complexes than* $(BeOH)_3^{3+}$. *Broken curves are calculated for same set of constants as in Fig 1; they also represent the best fit with the "normalized projection map" (29).*

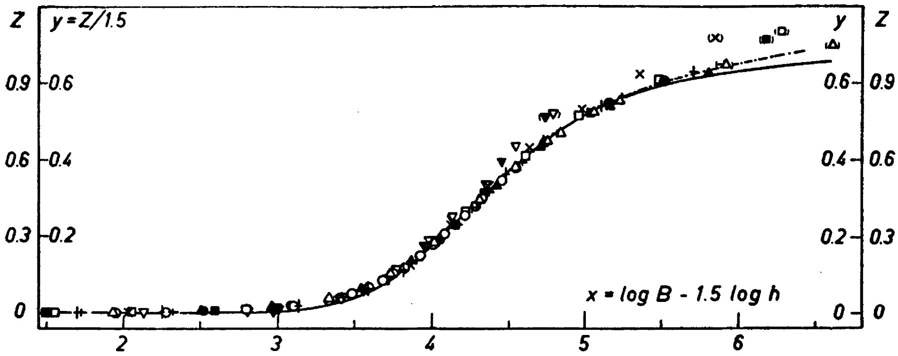


Fig. 3. Z, *or* y = Z/1.5, *as a function of* x = *log* B − *1.5 log* h. *All experimental points are shown using the same symbols as in Fig. 1. Full curve: calculated for log* K_{33} = *−8.66; dot-dash curve: calculated for log* K_{33} = *−8.68, log* K_{56} = *−19.14 etc (IIIa,* k_0 = *60).*

Although these deviations for low values of Z or B seem to be beyond the experimental errors, it seems reasonable to postpone a discussion of them, and to start by discussing the main reaction in the range where the y (x) curves coincide for $t = 1.5$.

To test for the other values of t, plots were made of $Z/2$ against $(\log B - 2 \log h)$, of $3Z/5$ against $(\log B - \frac{5}{3} \log h)$ and of $3Z/4$ against $(\log B - \frac{4}{3} \log h)$. With $t = 2$, the spread of the points was too severe. With $t = \frac{5}{3}$ and $\frac{4}{3}$, the spread of the points was not so bad as with $t = 2$, but far worse than with $t = 1.5$.

With $t = 1.5$, the complexes formed in appreciable amounts would be of the type $\mathrm{Be}((\mathrm{OH})_{1.5}\mathrm{Be})_n^{(2+0.5n)+}$. To decide whether n is a constant or a variable, the curve y (x) must be investigated further.

Direct analysis of the curve y (x)

It may be shown (AB II [26], eqns. 14 and 15) that from data y (x) one can calculate

$$\log F = y \log e + \int_{-\infty}^{x} y \, \mathrm{d}x \tag{7}$$

$$u = 10^x F^{-1}; \qquad g = F(1-y)-1; \tag{8a, b}$$

where in our case

$$u = [\mathrm{Be}^{2+}]h^{-1.5} = bh^{-1.5}; \quad g = \Sigma\, k_n u^n \tag{9a, b}$$

and k_n is the equilibrium constant for the reaction

$$(n+1)\mathrm{Be}^{2+} + 1.5\,n\,\mathrm{H_2O} \rightleftharpoons \mathrm{Be}((\mathrm{OH})_{1.5}\mathrm{Be})_n^{(2+0.5n)+} + 1.5\,n\,H^+; \quad k_n = K_{1.5n,n+1} \tag{9c}$$

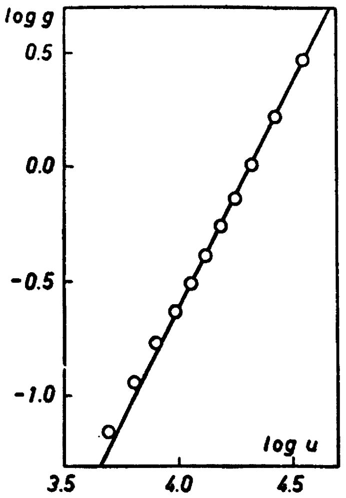


Fig 4. Direct analysis of the curve y(x) *in Fig. 3: log* g *as a function of log* u, *together with the best straight line of slope 2.*

(In passing we may note that log F = log $\frac{B}{b}$ and is thus identical with the quantity that has been denoted by η in other papers [20, 25 etc]).

The average number of $((OH)_{1.5}Be)$ links per complex is defined by

$$\bar{n} = \Sigma n c_n \,/\, \Sigma c_n \tag{10}$$

where c_n is the equilibrium concentration of the complex with n links. One may calculate $\bar{n}$ either by differentiating log g (log u), or directly[29] from y and F:

$$\bar{n} = \frac{d \log g}{d \log u} = \frac{y}{1 - y - F^{-1}} \tag{11a, 11b}$$

A smooth curve was drawn through the experimental points (y, x); where deviations occurred at low y, the lowest value of y was always used for each

Table 2. Direct analysis of curve $y(x)$

			$\delta = 0$					$\delta = -0.05$	
y	x	$\int_a^x y\,dx$	F	$\log u$	$\log g$	$\bar{n}$	$-\log k_2$	$\bar{n}$	$-\log k_2$
0.1	3.760	0.0323	1.190	3.685	−1.149	1.67	8.52	4.35	8.99
0.15	3.925	0.0531	1.313	3.807	−0.935	1.71	8.55	2.68	8.80
0.2	4.070	0.0786	1.464	3.904	−0.767	1.71	8.58	2.15	8.72
0.25	4.200	0.1077	1.646	3.983	−0.631	1.76	8.60	2.03	8.70
0.3	4.330	0.1424	1.874	4.058	−0.506	1.81	8.62	1.97	8.70
0.35	4.455	0.1844	2.170	4.119	−0.387	1.85	8.63	1.97	8.68
0.4	4.600	0.2388	2.585	4.187	−0.259	1.88	8.63	1.94	8.68
0.45	4.745	0.3006	3.134	4.249	−0.140	1.95	8.64	1.99	8.67
0.5	4.930	0.3888	4.037	4.324	+0.008	1.98	8.66	2.01	8.66
0.55	5.200	0.5312	5.890	4.430	+0.218	1.96	8.64	1.97	8.66
0.6	5.550	0.7329	9.853	4.556	+0.468	2.01	8.64	2.01	8.65

value of x. By graphical integration from $x = 2$ and using (7), (8), and (11 b), the values of F, log g, log u and $\bar{n}$ in Table 2 were calculated. The residual integral

$$\delta = \int_{-\infty}^{2.0} y\mathrm{d}x \qquad (12)$$

was assumed to be zero. In Fig. 4, log g is plotted against log u; a straight line of slope 2.0 was obtained in almost the whole range, which according to (11a) means that only the complex with $n = 2$, *i. e.* $\mathrm{Be_3(OH)_3^{3+}}$, is formed. The same conclusion is drawn from the values for $\bar{n}$ calculated directly and given in Table 2. If the residual integral δ is assumed to be —0.05, a still better constancy of $\bar{n}$ is obtained. (Last two columns of Table 2). Since at low values of x there are also secondary reactions, we need not be surprised at a negative value of δ.

If higher complexes were formed, the slope d log g/d log u should increase with increasing log u; however, no such curvature can be observed in the region with $y \leq 0.6$ ($Z \leq 0.9$). In the range $y \leq 0.25$, where $\bar{n}$ is very sensitive to small errors in y, a slight deviation from the straight line is observed, which may be due to the presence of other complexes.

If only the complex with $n = 2$ is formed, then from equation (9b)

$$\log g - 2 \log u = \log k_2 \qquad (13)$$

and a value of log k_2 can be obtained for each point (log g, log u) from eqn. (13). The average values

$$\begin{aligned}\log k_2 = \log K_{33} &= -8.64 \pm 0.02 \ (\text{for } \delta = 0)\\ &= -8.67 \pm 0.03 \ (\text{for } \delta = -0.05)\end{aligned}$$

were obtained using points in the range $0.25 \leq y \leq 0.60$ (Table 2).

Comparison with simple mechanisms

Following AB II[26] and part 8 of this series[20], the experimental curve $y(x)$, Fig. 3, was compared with families of cures $y(X)$, calculated for the simple mechanisms I—III. With hypothesis I (no soluble complex, precipitate formed), no agreement was found.

With hypothesis II (only one complex formed, with $n = N$), only $N = 2$ gave an acceptable agreement in the main part of the curve (even then small deviations were seen for high and low values of y) (Fig. 3). This agreement again makes it very probable that the main complex is $\mathrm{Be_3(OH)_3^{3+}}$. Thus we may apply AB II[26], eqn. (24).

$$x_{\frac{1}{2}} = \log 2 - \log k + \log N - (1 + N^{-1}) \log (N - 1) = \log 4 - \log k \qquad (14)$$

From the value $x_{\frac{1}{2}} = 4.93 \pm 0.015$, where $y = \frac{1}{2}$, eqn. (14) gives $\log k = -4.33 \pm 0.015$. Since the equilibrium constant $k_2 = k^2$, we find

$$\log k_2 = \log K_{33} = -8.66 \pm 0.03$$

With a repeated mechanism like IIIa, the equations in AB II[26] must be modified because n must be even to give an integral number of atoms per complex. Curves were constructed of the $y(X)$ functions calculated for the modified hypothesis IIIa and various values of k_0. Suitable equations are given in the appendix of a paper of Rossotti and Rossotti [31]. For $k_0 \approx 60$, the agreement for high values of y was improved (dot-dash curve in Fig. 3). For $y < 0.53$ ($Z < 0.8$) the curve practically coincides with the full curve for a single complex; the first complex $Be_3(OH)_3^{3+}$ would predominate over all the following complexes $Be((OH)_3Be_2)_{\frac{1}{2}n}^{(\frac{1}{2}n+2)+}$, with $n = 4$, 6 etc. Since the equilibria are very slow for high Z, we do not consider the existence of the higher complexes as certain. The value obtained for log K_{33}, —8.68 ± 0.03, is the same as with other methods.

Although they do not give coincident curves, the experimental diagrams $y(x)$, assuming $t = \frac{4}{3}$ and $\frac{5}{3}$, were also compared with calculated curves for mechanisms I, II and IIIa. No agreement could be found.

Approach assuming polymers $(BeOH)_n^{n+}$

It is remarkable that the present work has indicated $(BeOH)_3^{3+}$ as the main product, whereas previous workers have decided upon either $(BeOH)_2^{2+}$ (Prytz [2-4]), or $(BeOH)_4^{4+}$ (Faucherre [6,7], Souchay [8,9]). It thus seemed worthwhile to test the assumption that all complexes formed are of the general formula $(BeOH)_n^{n+}$. This approach might give an independent check on our conclusion about the main complex ($n = 3$), and also test to what extent complexes $(BeOH)_n^{n+}$ with $n = 2$ or 4 might be formed. (These complexes would not be covered by the "core + links" formula with $t = 1.5$.)

We shall develop this approach along lines given in AB I[25], p. 313. If we have a series of equilibria

$$n\ Be^{2+} + n\ H_2O \rightleftharpoons (BeOH)_n^{n+} + n\ H^+;\ [(BeOH)_n^{n+}] = K_{nn}b^nh^{-n} \qquad (1)$$

we find

$$BZ = \Sigma\ nK_{nn}b^nh^{-n};\quad B = b + \Sigma\ nK_{nn}b^nh^{-n} \qquad (15)$$

hence

$$b = B\ (1 - Z) \qquad (16)$$

We introduce the auxiliary variable u and a series of constants s_n:

$$u = bh^{-1};\ s_n = nK_{nn} \qquad (17)$$

From (15), (16) and (17) we obtain

$$BZ = \Sigma\ s_nu^n;\quad u = B(1—Z)h^{-1} \qquad (18)$$

We may find the constants s_n by the aid of a family of functions F_r which can be obtained from the experimental data:

$$F_r = BZu^{-r} = BZ[B(1—Z)h^{-1}]^{-r} = \Sigma\ s_nu^{n-r} \qquad (19)$$

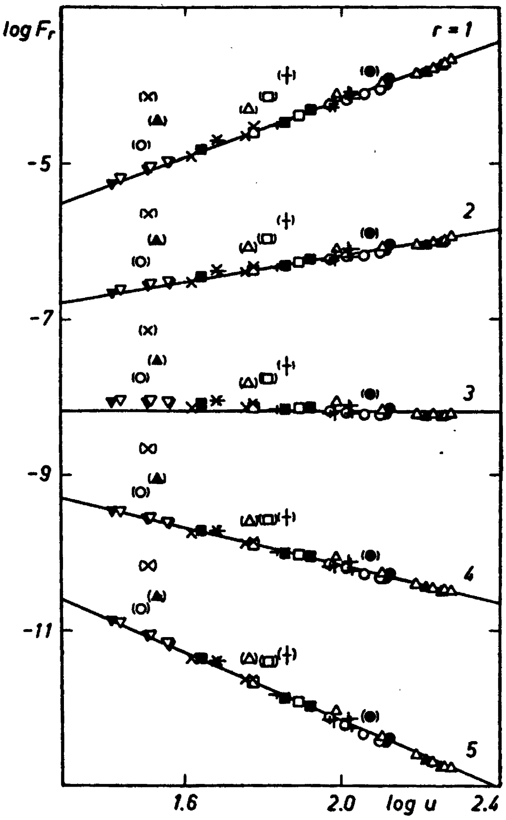


Fig 5. Log F_r*, eqn (19), for* r = *1 to 5, as functions of log* u*, eq (18), and best lines of slope 3* — N*. About one half of the experimental points, which were chosen at random, are given.*

If only one complex $(\text{BeOH})_N^{N+}$ is formed, log $F_N(\log u)$ should be a horizontal line at $\log F_N = \log s_N$.

Fig. 5 gives plots of log F_1 to log F_5 against log u. Indeed, log F_3 gives a horizontal line, indicating that the main complex formed in the solution is $(\text{BeOH})_3^{3+}$, but not $(\text{BeOH})_2^{2+}$ or $(\text{BeOH})_4^{4+}$. If the two latter complexes were present in appreciable amounts, (19) would give $F_3 = s_2u^{-1} + s_3 + s_4u$. One would then expect the log F_3 plot to form a single curve, independent of B, with upward bends at one or both ends. This is, however, not observed. There are deviations at $Z < 0.15$ and $Z > 0.9$, but they are not independent of B and should be due either to experimental errors (the function in rather sensitive to small errors) or to other complexes than the polymers $(\text{BeOH})_n^{n+}$.

From the constant value of $\log F_3 = \log 3 + \log K_{33}$ we obtained

$\log K_{33} = -8.68 \pm 0.05$

Likewise, from the straight lines $\log F_1 = \log s_3 + 2 \log u$ and $\log F_2 = \log s_3 + \log u$, the same value was obtained from both lines

$$\log K_{33} = -8.66 \pm 0.05$$

Conclusion on K_{33}

For the main reaction, $3\ \mathrm{Be}^{2+} + 3\ \mathrm{H_2O} \rightleftharpoons \mathrm{Be_3(OH)_3^{3+}} + 3\ \mathrm{H}^+$, the equilibrium constant K_{33} has been found by a number of methods, which give values that agree very well:

Method	log K_{33}	
Direct analysis	-8.64 ± 0.02	($\delta = 0$); -8.67 ± 0.02 ($\delta = -0.05$)
Curve-fitting	-8.66 ± 0.03	(hyp. II); -8.68 ± 0.03 (IIIa, $K_0 = 60$)
Polymer approach	-8.66 ± 0.05	(F_1 or F_2); -8.68 ± 0.05 (F_3)
Normalized proj.map (see below)	-8.65 ± 0.03	

As an average we may use the value log $K_{33} = -8.66 \pm 0.03$.

THE SECONDARY REACTIONS

Although the main part of the Z (log $h)_B$ curves is compatible with the existence of a single complex $\mathrm{Be_3(OH)_3^{3+}}$, there are deviations, especially at low values of Z and B, indicating the presence of secondary products. To find the formulas of these products we shall use a method which will be discussed by Kakihana [38] in a subsequent paper.

Formulas of complexes

Let us first assume that besides $\mathrm{Be_3(OH)_3^{3+}}$ there is only one more complex, $\mathrm{Be}_q\mathrm{(OH)}_p$, and try to find the values of p and q. The equilibrium constants of formation are K_{pq} and K_{33} and

$$B = [\mathrm{Be}^{2+}] + q[\mathrm{Be}_q(\mathrm{OH})_p] + 3[\mathrm{Be_3(OH)_3}] = b + qh^{-p}b^qK_{pq} + 3h^{-3}b^3K_{33} \quad (20)$$

$$BZ = ph^{-p}b^qK_{pq} + 3h^{-3}b^3K_{33} \quad (21)$$

For small values of Z, where the deviations are most pronounced, we may approximately set $b \approx B$ in (21) and study the function

$$F = Zh^3B^{-2} - 3K_{33} \approx ph^{3-p}B^{q-3}K_{pq} \quad (22)$$

Fig. 6 gives a plot log h(log $F)_B$ calculated using log $K_{33} = -8.66$. As h increases the curves tend to straight lines with d log F/d log $h = 3 - p = 2$;

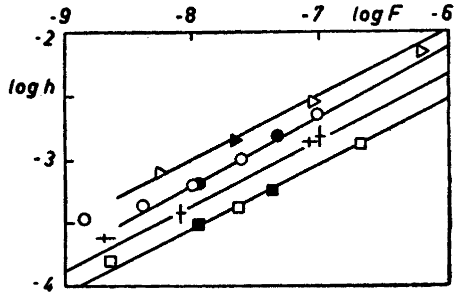


Fig 6. Log F, *eqn.* (*22*) versus *log* h. *Straight lines of slope* ½, *calculated with log* K_{12} = = −*3.25. All experimental points are given within the range shown.*

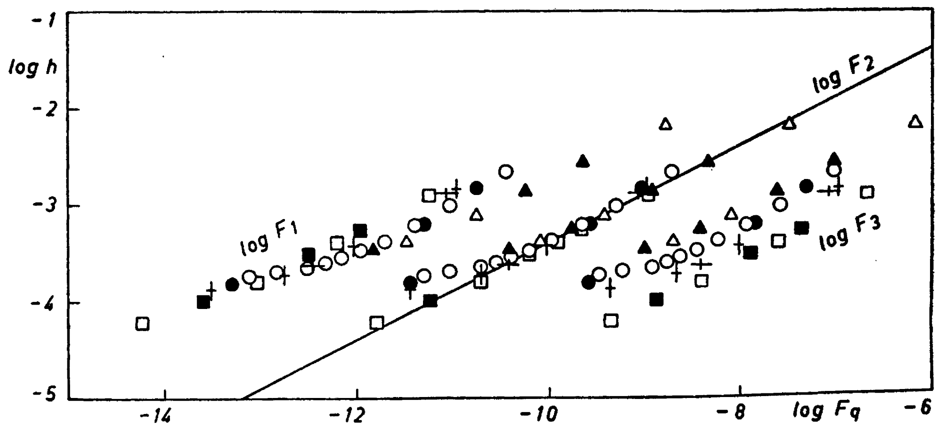


Fig 7. $\log F_1$, $\log F_2$, *and* $\log F_3$, *eqn. (23)* versus $\log h$. *Straight line:* $\log h$ ($\log F_2$) *calculated using* $\log K_{12} = -3.25$. *All experimental points are given within the range shown.*

from the spacing between the lines for various values of B, between 48.74 and 5.06 mM, we may calculate $q - 3 = -1.0$. Changes in log K_{33} by $\pm$ 0.03 do not affect the values obtained for p or q.

We might then conclude that the most important complex in this range, next to $\mathrm{Be_3(OH)_3^{3+}}$, is $\mathrm{Be_2OH^{3+}}$; from the position of the curves in Fig. 6 we may calculate log $K_{12} = -3.25 \pm 0.07$.

To check this result we may try another approximation in (21), namely $b \approx B(1-Z)$; in fact in most of our solutions $B > b > B(1-Z)$. We may then study the function

$$F_q = [Z(1-Z)^{-3}h^3B^{-2} - 3K_{33}]\,[B(1-Z)]^{3-q} \approx pK_{pq}h^{3-p} \qquad (23)$$

We have inserted in turn $q = 1$, 2, 3 and used the data to plot in Fig. 7 log F_q *versus* log h. With $q = 2$ the data with B between 5 and 48 mM fitted a straight line with d log F_2/d log $h = 3 - p = 2.0$. With $q = 1$ or 3, points with different values of B spread out considerably. Thus we once more conclude $p = 1$ and $q = 2$; the position of the line gives log $K_{12} = -3.25 \pm 0.05$.

It still remains to explain the deviations as to the two lowest values of B, 2.56 and 1.00 mM. The only reasonable explanation (besides experimental errors) would be the presence of one or more mononuclear complexes $\mathrm{Be(OH)}_n$. We would then have

$$BZ = \Sigma n[\mathrm{Be(OH)}_n] + [\mathrm{Be_2OH}] + 3[\mathrm{Be_3(OH)_3}] = \Sigma nh^{-n}bK_{n1} + h^{-1}b^2K_{12} + 3h^{-3}b^3K_{33} \qquad (24)$$

Again, we may approximately set $b \approx B\,(1-Z)$ in (24) and calculate the function $F = Z(1-Z)^{-1} - K_{12}(1-Z)h^{-1}B - 3K_{33}(1-Z)^2h^{-3}B^2 \approx \Sigma nK_{n1}h^{-n}$ (25)

Inserting the previously determined values of log $K_{33} = -8.66$ and log $K_{12} = -3.25$, in (25) log F was calculated as a function of log h (Fig. 8).

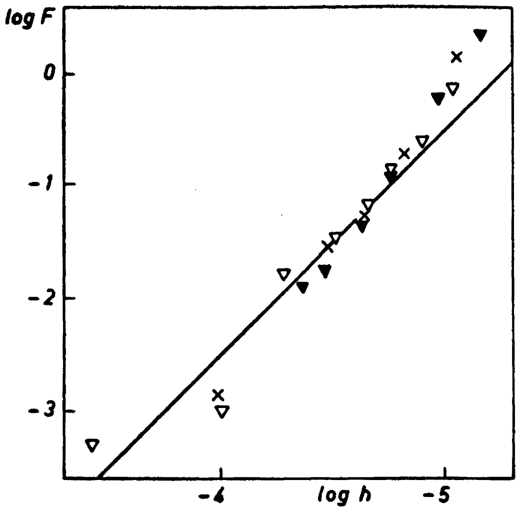


Fig 8. Log F, *eqn. (25), as a function of log* h. *Straight line: calculated for* $K_{11} = 0$, *log* $K_{21} = -10.8$.

Even up to $Z \approx 0.65$, the points seem to fall on a straight line of slope —2, in a position corresponding to log $K_{21} = -10.8$. We may conclude that the main mononuclear complex formed is $Be(OH)_2$; however, the spread of the data certainly does not permit one to exclude the presence of small amounts of $BeOH^+$.

This is not so surprising. For several ions, mercury(II)[15], thallium(III)[18], iron(III)[19], indium(III)[23, 24] the intermediate complex MOH has a remarkable tendency to split up to M and $M(OH)_2$, in marked contrast to the intermediate ion of most dibasic acids.

Calculation of equilibrium constants with normalized projection maps

Now that the formulas of the main and secondary products of hydrolysis were known, we set out to refine the values of the constants, using the method of normalized projection maps for three-variable data[30, 28].

In the present case, the quantities directly measured are h, B, and Z. We have

$$B = b + K_{21}h^{-2}b + 2K_{12}h^{-1}b^2 + 3K_{33}h^{-3}b^3 \tag{26}$$

$$BZ = 2K_{21}h^{-2}b + K_{12}h^{-1}b^2 + 3K_{33}h^{-3}b^3 \tag{27}$$

It is convenient to compare projection maps $y(x)_Z$ of the experimental variables

$$x = -\log h; \qquad y = \log B \tag{28}$$

with calculated normalized projection maps $Y(X)_Z$ of the normalized variables

$$X = \log \alpha = -\log h + p_1; \quad Y = \log \mathbf{B} = \log B + p_2 \tag{29}$$

From the best fit of the maps one may obtain $X—x = p_1$ and $Y—y = p_2$. We shall introduce the auxiliary variables (''normalized h^{-1} and b'')

$$\alpha = h^{-1} \cdot 10^{p_1}; \quad u = b \cdot 10^{p_2} \tag{30}$$

In order to get simple formulas for calculation, we want to choose the constants p_1 and p_2 so that all equilibrium constants are eliminated except for a constant k, which replaces the smallest correction term K_{21}. We thus set

$$\mathbf{B} = B \cdot 10^{p_2} = u + k\alpha^2u + 2\alpha u^2 + 3\alpha^3u^3 \tag{31}$$

$$\mathbf{B}Z = 2k\alpha^2u + \alpha u^2 + 3\alpha^3u^3 \tag{32}$$

Inserting (30) into (31) and comparing with (26) we find

$$\log K_{33} = 3p_1 + 2p_2; \quad \log K_{12} = p_1 + p_2; \quad \log K_{21} = 2p_1 + \log k \tag{33}$$

To construct the necessary graphs $Y(X)_Z$ we used the formulas, derived from (31) and (32).

$$(2—Z)\mathbf{B} = u(2 + 3\alpha u + 3\alpha^3u^2) \tag{34}$$

$$Z = 2 — (2 + 3\alpha u + 3\alpha^3u^2)\,(1 + k\alpha^2 + 2\alpha u + 3\alpha^3u^2)^{-1} \tag{35}$$

Auxiliary diagrams were constructed: $\log\,[(2—Z)\mathbf{B}]\,(\log u)_\alpha$ which is independent of k, and $Z\,(\log u)_\alpha$ for a number of different values of k. From these diagrams, $Y(X)_Z$ or $\log \mathbf{B}\,(\log \alpha)_Z$ was constructed for various values of k, namely $10^7k = 0$, 2, 3, 5 and 10.

The best agreement was found for $k = 3.10^{-7}$, thus $\log k \approx —6.5_3$. In the position of the best fit, the parameters were

$p_1 = \log \alpha + \log h = —2.17 \pm 0.01$; $p_2 = \log \mathbf{B} — \log B = —1.07 \pm 0.01$;
$\log k = —6.5_3 \pm 0.2$

whence with (33)

$\log K_{33} = 3p_1 + 2p_2 = —8.65 \pm 0.03$.
$\log K_{12} = p_1 + p_2 = —3.24 \pm 0.02$
$\log K_{21} = 2p_1 + \log k = —10.9 \pm 0.2$.

The value for $\log K_{33}$ agrees well with the average —8.66 obtained by several methods in the previous sections. Also the values for $\log K_{12}$ and $\log K_{21}$ are in good agreement with the values obtained from the diagrams in Figs. 6—8. We shall accept the values for $\log K_{12}$ and $\log K_{21}$ from the projection maps as our final values.

The dashed curves $Z\,(\log h)_B$ in Fig. 1 were calculated with $\log K_{33} = —8.66$, $\log K_{12} = —3.25$ and $\log K_{21} = —10.87$, thus practically the final set of constants K_{33}, K_{12} and K_{21}. The agreement seems to be as good as can be expected except in the region with $Z > 0.9$. However, in this region the equilibrium emf was obtained much more slowly than for lower values of Z, which may be explained by the presence of either higher species (*e. g.* according to hypothesis IIIa above), or of an invisible precipitate; both might give rise to

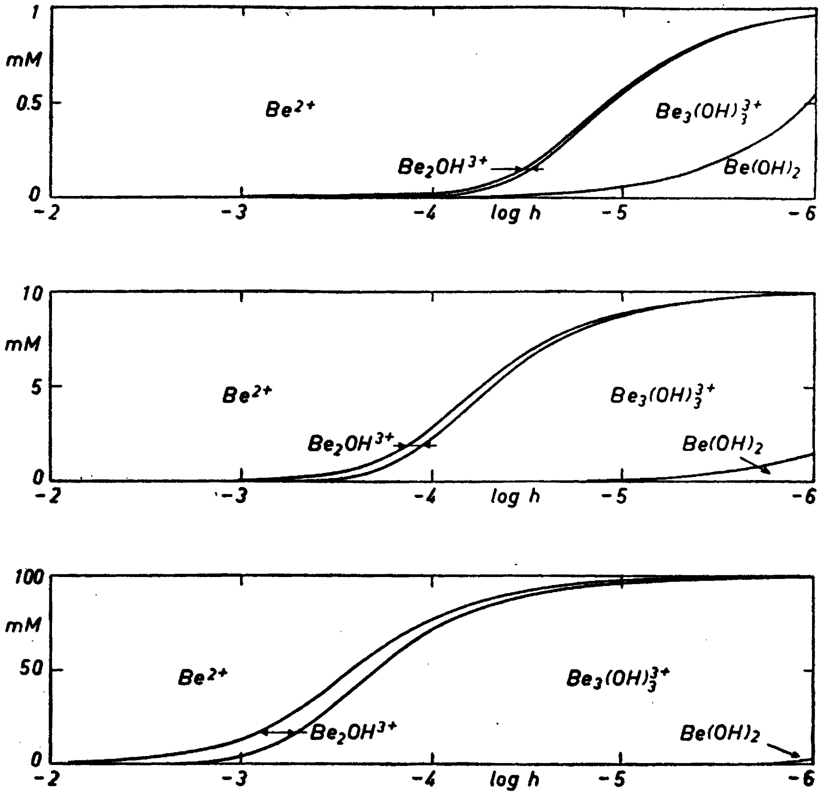


Fig 9. Distribution of complexes for total beryllium concentration $B = 1$, 10, and 100 mM, as a function of log h. *If a vertical line is drawn for a given value of* h, *the segment of this line falling in a certain area, e.g.* Be_2OH^{3+}, *represents the concentration of Be present as this complex in the solution at equilibrium.*

the slight positive deviation in the observed value of Z. The accuracy of the present work does not permit any certain conclusion.

Fig. 9 shows the distribution of the total beryllium over the various species, as a function of log h, for the total concentrations $B = 1$ mM, 10 mM and 100 mM, assuming the equilibrium constants obtained here.

ON THE STRUCTURE OF THE COMPLEXES

Four-coordination of Be^{2+}

Two- or three-coordinated beryllium occurs in some organoberyllium compounds like $Be(C_6H_5)_2$ and $Be(C_6H_5)_3^-$, but with O and F, the coordination always appears to be tetrahedral. The proof of this is to be found in certain simple crystal structures, since beryllium is light and thus rather difficult to locate with X-ray methods. For complicated structures, it has generally been taken for granted that Be is in the centre of a BeO_4 or BeF_4 tetrahedron.

Phenakite, Be_2SiO_4, has a rhombohedral structure built up of SiO_4 and BeO_4 tetrahedra [39]; Be_2GeO_4 is isomorphous [40]. The structure of hambergite, Be_2BO_3OH, is built up of BO_3 triangles and BeO_3OH tetrahedra, sharing corners [41]. In β-$Be(OH)_2$, each Be is surrounded [42] by a somewhat distorted tetrahedron of 4 OH. The structure of $BeSO_4(H_2O)_4$, is built up [43] of tetrahedra $Be(H_2O)_4^{2+}$ and SO_4^{2-}. The stable complexes with organic acids, $Be_4O(OCOR)_6$, where R = CH_3, C_2H_5, C_6H_5 etc., have a symmetrical structure [44] with a central O surrounded by 4 Be. Each Be is in contact with the central O, and with 3 O from three different RCOO groups. The two oxygen atoms of a RCOO group are parallel with an edge of the Be_4 tetrahedron and in contact each with one Be.

With the exception of these volatile substances, which are rather rapidly hydrolysed by water, with the formation of RCOOH, and the rather special Be_2BO_3OH, no structures of beryllium hydroxo- or oxo-compounds seem to be known that would give an easy clue to the structure of the soluble complexes.

In the fluoride complexes, Be and F are very often found to give compounds isomorphous to corresponding compounds with Si and O. For instance, BeF_2 seems to be isomorphous with cristobalite [45], $BaBeF_4$ with $BaSO_4$ [46], the five forms of Na_2BeF_4 with different forms of Ca_2SiO_4 (Thilo and Liebau [47]), and $NaBeF_3$ with β-$CaSiO_3$ [48]. It may thus be expected that the structures contain BeF_4 tetrahedra connected by sharing corners (but not edges), just like the SiO_4 tetrahedra in the corresponding silicon compounds.

Similarly, in Be-OH complexes one may expect the BeO_4 tetrahedra to share corners but not edges.

In the older literature, a number of "basic" beryllium salts have been described. Later work has thrown considerable doubt on their existence as well-defined compounds [49]. Slavvo [50] has recently prepared halogenomercurates as hygroscopic crystals. In addition to $Be(H_2O)_5HgCl_4$ and $Be(H_2O)_5HgBr_4$, he also prepared crystalline $BeOH(H_2O)_2HgCl_3$, $BeOH(H_2O)_2HgBr_3$, and $Be_3(OH)_3(H_2O)_6Hg_2I_7$. It is interesting to note that the three last mentioned salts may all contain the ringshaped complex $Be_3(OH)_3(H_2O)_6^{3+}$ proposed below.

Possible structure of the hydrolysis products

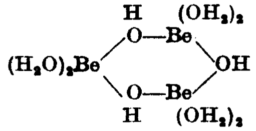
From what is known on the structure of other beryllium compounds it seems reasonable that the complex Be_2OH^{3+} consists of two BeO_4 tetrahedra, sharing a corner, which is very probably OH. The complex would thus be: $(H_2O)_3BeOHBe(OH_2)_3$

The mononuclear complex $Be(OH)_2$ is probably also a tetrahedron, $(H_2O)_2Be(OH)_2$. There is, however, a possibility that the molecule may be linear, forming *sp* bonds: HOBeOH. Alternation between tetrahedral to linear coordination may occur in some Hg^{2+}-complex systems [51] and might be related to the unusually small stability of the complex with one ligand.

The equilibrium constant for the formation of the main complex, $Be_3(OH)_3^{3+}$ from the mono- and dinuclear complexes is

$$Be_2OH^{3+} + Be(OH)_2 \rightleftharpoons Be_3(OH)_3^{3+};\ K_{33}K_{12}^{-1}K_{21}^{-1} = 10^{5.5}.$$

The very high value of this constant, and the predominance of $Be_3(OH)_3^{3+}$ make it extremely unlikely that this complex would have an open chain structure. The most likely structure seems to be a six-membered ring, three tetrahedra being linked by sharing OH corners:



If the tetrahedra are filled out with water, one would get the formula $Be_3(OH)_3(OH_2)_6^{3+}$, which corresponds very well to the formulas of the halogenomercurates prepared by Slavvo [50].

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