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Ionic Equilibria in Mixed Solvents. XI. A Critical Survey of Hydroxo Complexes of Beryllium in Aqueous and Aqueous Mixed Solvents

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Hydrolytic reactions of beryllium ion were studied in water–methanol, water–ethanol, and water–acetone mixtures, 0.2 mole fraction of an organic component being contained. In all the solutions containing 3M $LiClO_4$ as an ionic medium at 25 °C, we found the Be_2OH^{3+}, $Be_2(OH)_2{}^{2+}$, $Be_3(OH)_3{}^{3+}$, and $Be(OH)_2$ complexes. However, in a supplementary work in a 3M $LiClO_4$ aqueous medium in which the solution had been equilibrated with precipitates of beryllium hydroxide and the supernatant was subjected to titration, we found $Be_6(OH)_8{}^{4+}$ instead of $Be(OH)_2$. From a very slow equilibrium observed in the high pH region, we concluded that the $Be(OH)_2$ complex formed by the addition of an alkaline solution gradually polymerizes to $Be_6(OH)_8{}^{4+}$ by releasing some OH^- ions. Through these observations a critical survey is described for the species reported by various authors. The solvent effect on the formation constants of hydroxo complexes is also discussed.

According to simple electrostatic theories, an equilibrium constant of a non-isoelectric reaction such as the dissociation of a neutral acid molecule and the hydrolysis of a metal ion might be affected by the dielectric constant of a solvent. However, studies of hydrolytic reactions of beryllium,[2,3)] copper,[4,5)] nickel,[6)] and aluminium[7)] ions in various aqueous dioxane solutions revealed that formation constants of the complexes were very insensitive to the solvent composition over a relatively wide range of the dioxane concentration, 0—85% w/w, in contrast with dissociation constants of carboxylic acids and phenols.[8,9)]

In a reaction in which protons or hydroxide ions are liberated, the acid-base property of a solvent might also contribute to the equilibrium of the reaction beside the dielectric constant and the concentration of water in the solvent. Since studies carried out so far in this series of metal hydrolysis were restricted to aqueous dioxane solutions, we undertake to examine the effect of changing the solvent component on the hydrolysis equilibrium of a metal ion. In the present work we use water–methanol, water–ethanol, and water–acetone mixtures in which 0.2 mole fraction of an organic solvent is contained. The beryllium ion is chosen as an example.

Experimental

Reagents. The methods of preparation and purification of the chemicals used were the same as those described previously.[2,3)] Methanol, ethanol, and acetone (reagent grade) were distilled twice. The solvent mixtures contained 0.2 mole fraction of an organic component, *i.e.*, 30.77% w/w methanol, 38.99% w/w ethanol, and 44.62% w/w acetone, respectively.

Apparatus. Beckman glass electrodes Nos. 40495 and 40498 were used in combination with a silver–silver chloride electrode which was set in an improved type of the "Wilhelm" half-cell (see Fig. 1). An Orion Digital pH Meter 801 was used for emf measurements. A Metrohm *E 211 A* type coulometer was employed as a current source after the current indicator was calibrated with a Yokogawa Decade Resistance Box 2786 as a standard resistance. The method of emf measurements was essentially the same as that in the previous studies.[2,3)]

Results

The plots of Z (average number of hydrogen ions set free per beryllium atom) against $-\log h$ (h denotes the concentration of hydrogen ion at equilibrium) were shown in Figs. 2—4. The concentration of free beryllium ion b was calculated according to the equation[10)]

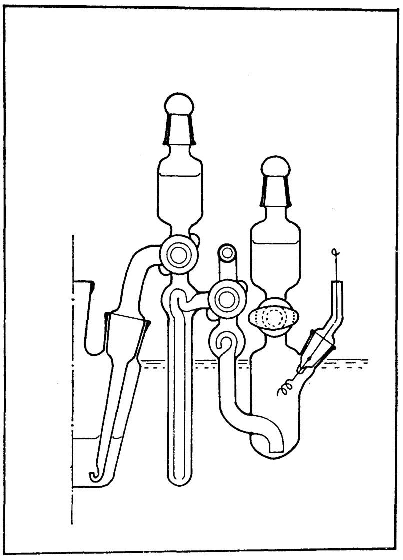

Fig. 1. Cell with silver-silver chloride electrode, salt bridge and titration vessel.

$$\ln b = \ln B + \int_{\infty}^{\ln h}\left[Z+\left(\frac{\partial Z}{\partial \ln B}\right)_h\right]\mathrm{d}\ln h \qquad (1)$$

where B denotes the total concentration of beryllium ion in solution. The calculation was carried out on the basis of the data in Figs. 2—4 assuming $\int_{\infty}^{-2.0}[2.303Z+(\partial Z/\partial \log B)_h]\,\mathrm{d}\log h=0$.

Application of the core-links hypothesis[11)] and calculations of the average numbers of metal and hydroxyl ions in complexes, $\bar{p}$ and $\bar{q}$, respectively, showed that the main product of the reaction was $Be_3(OH)_3{}^{3+}$. Minor components formed in the lower pH range were estimated by computer calculations.

The plot of $(BZ-3{}^*\beta_{3,3}b^3h^{-3})/2bh^{-2}$ against b in a high pH range gave a straight line independent of the total concentration of beryllium. This shows the formation of the $Be_2(OH)_2{}^{2+}$ and $Be(OH)_2$ complexes.

Computer calculations also supported the formation

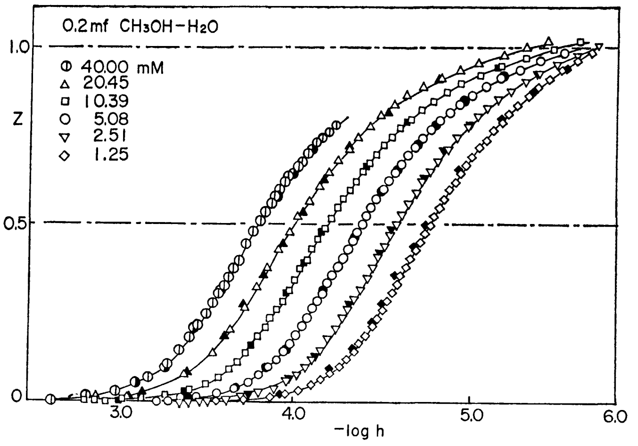

Fig. 2. Z as a function of $-\log h$ in 0.2 mole fraction methanol-water mixture.

Points with open symbols were obtained by forward titrations and points with black symbols, by back titrations. Drawn curves were calculated with the final values of the formation constants listed in Table 4.

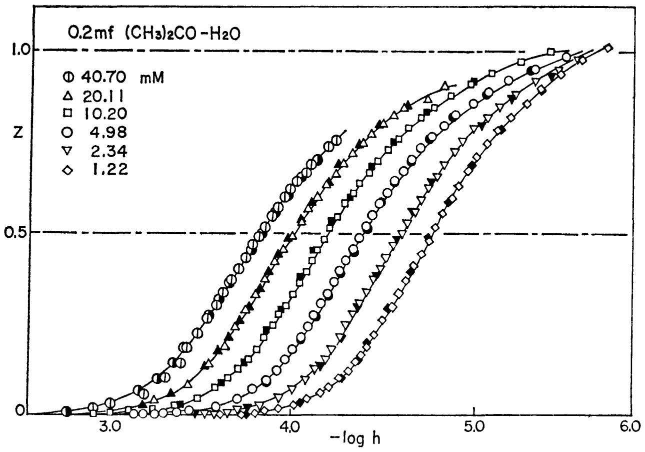

Fig. 4. Z as a function of $-\log h$ in 0.2 mole fraction acetone-water mixture.

The symbols are the same as those in Fig. 2. Drawn curves were calculated with the values of the formation constants listed in Table 4.

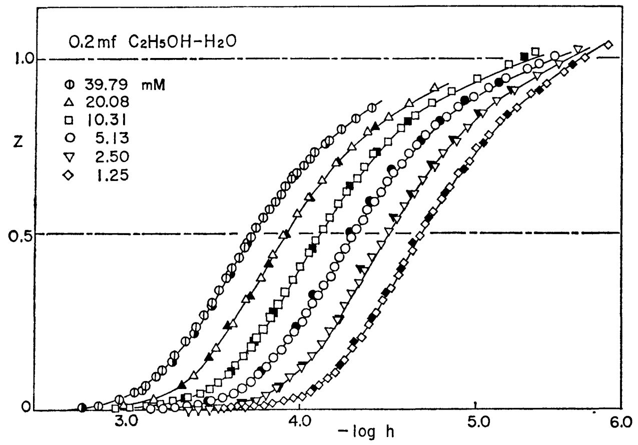

Fig. 3. Z as a function of $-\log h$ in 0.2 mol fraction ethanol-water mixture.

The symbols are the same as those in Fig. 2. Drawn curves were calculated with the values of the formation constants listed in Table 4.

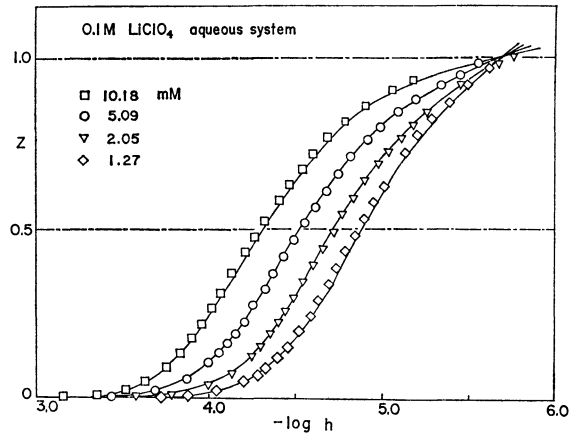

Fig. 5. Z as a function of $-\log h$ in a 0.1 M $LiClO_4$ aqueous solution.

Only the points obtained by forward titrations are shown. Drawn curves were calculated with the values of the formation constants given in Table 5.

TABLE 1. THE ERROR-SQUARE SUMS (U) AND THE FORMATION CONSTANTS ($-\log{}^*\beta_{p,q}$) IN 0.2 MOL FRACTION METHANOL-WATER MIXTURE

$BeOH^+$	Be_2OH^{3+}	$Be(OH)_2$	$Be_2(OH)_2^{2+}$	$Be_3(OH)_3^{3+}$	$Be_3(OH)_4^{2+}$	$Be_6(OH)_8^{4+}$	$U\times10^3$
—	3.52	11.39	7.35	8.54	—	—	3.57
7.44	3.51	11.39	7.34	8.54	—	—	3.58
—	—	11.41	7.22	8.58	—	—	5.67
6.26	—	11.41	7.32	8.57	—	—	5.98
—	3.25	11.33	—	8.46	—	—	7.88
—	3.20	—	—	8.46	14.83	—	10.5
—	3.24	11.46	—	8.46	15.30	—	8.07
—	3.30	—	7.54	8.51	14.82	—	6.26
—	3.24	—	—	8.45	—	26.19	20.5

of these complexes. In Tables 1—3 the results of the calculations of minimum error-square sums are summarized, where $U=\sum(Z_{\text{calc}}-Z)^2$ and the formation constants in the tables are given as $\log{}^*\beta_{p,q}=\log[Be_q(OH)_p{}^{(2q-p)+}][H^+]^p/[Be^{2+}]^q$.

The final values of the formation constants proposed are tabulated in Table 4, together with those in the aqueous dioxane solution.[2]

A similar experiment was carried out in a 0.1 M $LiClO_4$ aqueous solution. Analysis of the data (see

Table 2. The error square-sums (U) and the formation constants ($-\log {}^*\beta_{p,q}$) in 0.2 mole fraction ethanol-water mixture

$BeOH^+$	Be_2OH^{3+}	$Be(OH)_2$	$Be_2(OH)_2^{2+}$	$Be_3(OH)_3^{3+}$	$Be_3(OH)_4^{2+}$	$Be_6(OH)_8^{4+}$	$U\times10^2$
—	3.39	11.12	7.13	8.31	—	—	0.862
6.41	3.22	11.09	7.50	8.27	—	—	1.17
—	—	11.15	6.97	8.37	—	—	1.09
6.26	—	11.14	7.07	8.35	—	—	1.16
—	3.14	11.06	—	8.23	—	—	1.43
—	3.07	—	—	8.23	14.35	—	1.52
—	3.08	11.45	—	8.23	14.53	—	1.38
—	3.09	—	7.50	8.26	14.33	—	1.13
—	3.13	—	—	8.22	—	25.22	2.66

Table 3. The error square-sums (U) and the formation constants ($-\log {}^*\beta_{p,q}$) in 0.2 mole fraction acetone-water mixture

$BeOH^+$	Be_2OH^{3+}	$Be(OH)_2$	$Be_2(OH)_2^{2+}$	$Be_3(OH)_3^{3+}$	$Be_3(OH)_4^{2+}$	$Be_6(OH)_8^{4+}$	$U\times10^2$
—	3.28	11.24	7.21	8.58	—	—	1.41
8.11	3.30	11.23	7.23	8.57	—	—	1.35
—	—	11.27	7.02	8.67	—	—	1.63
5.64	—	11.25	7.51	8.59	—	—	2.37
—	3.06	11.17	—	8.47	—	—	2.50
—	3.01	—	—	8.47	14.62	—	3.03
—	3.00	11.42	—	8.47	14.92	—	2.61
—	3.07	—	7.42	8.53	14.63	—	2.04
—	3.01	—	—	8.45	—	25.90	5.27

Table 4. The formation constants ($-\log {}^*\beta_{p,q}$) of the hydrolytic reactions of beryllium ions in 0.2 mole fraction methanol, ethanol, acetone, and dioxane-water mixtures[a]

	$BeOH^+$	Be_2OH^{3+}	$Be(OH)_2$	$Be_2(OH)_2^{2+}$	$Be_3(OH)_3^{3+}$
Methanol-water	—	3.50±0.05	11.38±0.03	7.35±0.02	8.541±0.002
Ethanol-water	—	3.39±0.06	11.12±0.04	7.13±0.03	8.310±0.002
Acetone-water	$\gtrsim 8$	3.28±0.05	11.24±0.04	7.22±0.02	8.578±0.004
Dioxane-water	$\gtrsim 6.0$	3.64±0.05	10.76±0.03	7.11±0.02	8.763±0.005

a) The uncertainties of the formation constants were estimated by multiplying by three the standard deviations.

Table 5. The formation constants ($-\log {}^*\beta_{p,q}$) of the hydrolytic reactions of beryllium ions in aqueous solutions containing various ionic media at 25 °C

	BeOH	Be_2OH^{3+}	$Be(OH)_2$	$Be_2(OH)_2^{2+}$	$Be_3(OH)_3^{3+}$	$Be_3(OH)_4^{2+}$	$Be_6(OH)_8^{4+}$	$Be_6(OH)_9^{3+}$
1 *m* NaCl[13]	—	3.42± 0.07	—	—	8.907± 0.007	—	27.46± 0.03	—
2 M KNO_3[14]	—	3.28	—	—	8.900	16.0	27.5	34.5
3 M $NaClO_4$[12]	—	3.24± 0.02	10.9± 0.2	—	8.66± 0.03	—	—	—
3 M $NaClO_4$ (60 °C)[20]	—	2.9± 0.2	—	6.25± 0.05	7.7± 0.1	13.22± 0.15	—	—
3 M $LiClO_4$[3]	$\gtrsim 5.4$	3.27± 0.10	11.5± 0.5	—	8.74± 0.05	—	—	—
3 M $LiClO_4$ (this work)	—	3.04± 0.03	—	—	8.671± 0.002	—	27.337± 0.006	—
0.1 M $LiClO_4$ (this work)	$\gtrsim 6.3$	3.32± 0.14	11.35± 0.06	—	8.807± 0.005	—	—	—

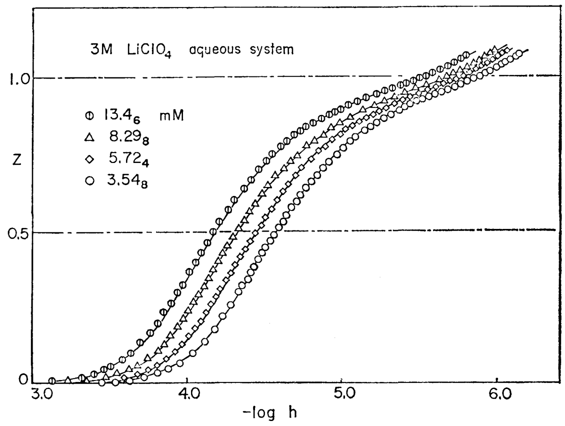

Fig. 6. Z as a function of $-\log h$ in a 3 M LiClO$_4$ aqueous solution.
Only the points obtained by back titrations are shown. Drawn curves were calculated with the values of the formation constants given in Table 5.

Fig. 5) led to a conclusion of the formation of Be_2OH^{3+}, $Be_3(OH)_3^{3+}$, $Be(OH)_2$, and probably $BeOH^+$. The formation constants obtained are listed in Table 5.

Discussion

In 1967 Mesmer and Baes[13] proposed $Be_5(OH)_7^{3+}$ or $Be_6(OH)_8^{4+}$ instead of $Be(OH)_2$ in 1 *m* NaCl solution at 25 °C. The $Be_6(OH)_8^{4+}$ complex was also found by Lanza and Carpéni.[14] Recently Baes and Mesmer[15] critically reviewed studies on the hydrolysis of beryllium ion and pointed out that the formation constant of $Be(OH)_2$ cannot be so large as reported previously[3,12,16] as long as the solubility data by Gilbert and Garrett[17] and by Schindler and Garrett[18] are accepted. The formation constant of $Be(OH)_2$ determined by means of solvent extraction was $\log {}^*\beta_{2,1}=-13.65$[19], which was consistent with the value expected from the solubility product of $Be(OH)_2$.[17,18] The $Be_2(OH)_2^{2+}$ was not detected by these authors.

Ciavatta and Grimaldi[20] also denied the formation of $Be(OH)_2$ in aqueous solution at an elevated temperature (60 °C) and proposed $Be_3(OH)_4^{2+}$ and $Be_2(OH)_2^{2+}$, together with the main product $Be_3(OH)_3^{3+}$.

In spite of negative conclusions for the formation of $Be(OH)_2$ by some authors, our data could still be well explained in terms of the formation of $Be_2(OH)_2^{2+}$ and $Be(OH)_2$ at a relatively high pH. In order to elucidate the reasons of the diverse conclusions for the minor components at a high pH, we carried out supplementary titrations in a 3 M LiClO$_4$ aqueous medium in which titration procedures were slightly modified.

Test solutions were prepared as follows: pH of a beryllium perchlorate solution (the total concentration of the perchlorate ion was kept constant at 3 M) was increased by reduction of hydrogen ions by electrolysis until beryllium hydroxide precipitated. The solution was left to stand for several days under a nitrogen atmosphere while agitating and the supernatant was subjected to titration by coulometric generation of hydrogen ions. The reverse titration was also performed by alkalifying the solution after the preceding titration over the same pH range. In titrations in which pH decreased (open symbols in Fig. 6) a rapid equilibrium was attained at each point of measurements. On the other hand, a very slow equilibrium was observed at a high pH in the reverse titration (pH of the solution increased), and the emf changed slowly in such a manner that pH increased. It took 10—12 hr until an emf in a reverse titration fell on the titration curve obtained by the preceding titration. The results shown in Fig. 6 were explained in terms of the formation of Be_2OH^{3+}, $Be_3(OH)_3^{3+}$, and $Be_6(OH)_8^{4+}$. Replacement of $Be_6(OH)_8^{4+}$ by any of $Be(OH)_2$, $Be_2(OH)_2^{2+}$, and $Be_3(OH)_4^{2+}$ did not improve values of the error-square sum. Addition of any of these complexes to the set of Be_2OH^{3+}, $Be_3(OH)_3^{3+}$, and $Be_6(OH)_8^{4+}$ did not decrease the error-square sum. The formation of $BeOH^+$ was not conclusive. The final values of the formation constants are tabulated in Table 5, along with values reported by previous authors.

From these observations and the results obtained previously by other workers, we conclude that the $Be(OH)_2$ complex readily formed by the addition of hydroxyl ions is an "over-saturated" species and slowly changes to a polymerized species by releasing some hydroxide ions. The polymerization reaction progresses so slowly that the $Be(OH)_2$ complex is recognized as an equilibrium species in the pH range studied when titrations are carried out with an ordinary speed. Although the equilibrium species at a high pH where $Be(OH)_2$ is detected is expected to be $Be_6(OH)_8^{4+}$ as shown in Table 5, the doubt that the $Be_6(OH)_8^{4+}$ complex could be another intermediate species in the polymerization reaction may hardly be dispelled yet in the present stage of investigation.

Since many hydrolytic reactions proceed very slowly (*e.g.*, as seen in aluminium, iron (III), and even in cadmium[21]), rapid titrations may sometimes cause erroneous conclusions. In order to give a complete scope of hydrolysis equilibria of a metal ion, knowledge of reaction kinetics of slow processes as well as precipitation equilibria and hydrolysis equilibria at low concentrations of the metal ions (where only mononuclear complexes are formed) must be needed.

Although some of the complexes listed in Tables 4 and 5 may not be equilibrium species, the $Be_3(OH)_3^{3+}$ is no doubt the main product and an equilibrium species of the hydrolytic reaction of beryllium ion. The formation constant of the complex practically remained unchanged when an aqueous solvent is replaced with an aqueous organic mixture containing various concentrations of an organic solvent. The change of the organic component in the mixture was also insensitive to the formation constant.

It is widely accepted that the equilibrium constant of an association reaction of a positive and a negative ions increases with an increase in the concentration of an organic solvent in aqueous mixtures. In an isoelectric reaction such as an association reaction of a proton and a neutral molecule, on the other hand, the equilibrium constant is decreased and then steeply increased after passing through a minimum. The change of the equilibrium constant was accounted for in terms of the medium effect on protons which are distributed in water and organic solvent molecules through the solvation equilibrium.[22] In a non-isoelectric reaction of the hydrolytic reaction of beryllium ion,

$$3\mathrm{Be}^{2+} + 3\mathrm{H_2O} = \mathrm{Be_3(OH)_3}^{3+} + 3\mathrm{H}^+$$

as well as those of other metal ions, the free energy change of transfer of three moles of Be^{2+} ion from the aqueous phase to a mixture may not be completely compensated for the sum of the free energy changes of transfer of one mole of $\mathrm{Be_3(OH)_3}^{3+}$ and three moles of protons from the mixture to the aqueous phase. The rest of the free energy changes may be further cancelled with the medium effect of protons.

We can rewrite the formation constant of a beryllium hydroxo complex $*\beta_{p,q}$ to $\beta_{p,q}$ as follows:

$$\beta_{p,q} = [\mathrm{Be}_q(\mathrm{OH})_p{}^{(2q-p)+}]/[\mathrm{Be}^{2+}]^q[\mathrm{OH}^-]^p = *\beta_{p,q}/K_1{}^p \tag{2}$$

Here K_1 denotes the autoprotolysis constant of a solvent mixture of a constant ionic medium

$$K_1 = [\mathrm{H}^+][\mathrm{OH}^-] \tag{3}$$

The values of K_1 in the mixed solvents were determined as 14.128±0.003 mol^2 l^{-2} (in 0.2 mole fraction methanol–water mixture) and 14.396±0.008 mol^2 l^{-2} (in 0.2 mole fraction ethanol–water mixture).[23] In the acetone-system K_1 was not determined due to unstable emf's. Acetone may be reduced with hydrogen according to the following equilibrium.[24,25]

$$(\mathrm{CH_3})_2\mathrm{CO} + \mathrm{H_2} = (\mathrm{CH_3})_2\mathrm{CH_2O}$$

By insertion of the values of K_i into Eq. (2) we see the changes of $\beta_{p,q}$ with the solvent composition. The formation constant $\beta_{p,q}$ markedly increased with the increase in the concentration of an organic solvent from 0 to 0.2 mole fraction. The fact showed that the association reaction

$$q\mathrm{Be}^{2+} + p\mathrm{OH}^- = \mathrm{Be}_q(\mathrm{OH})_p{}^{(2q-p)+} \tag{4}$$

is subjected to the solvent effect essentially similar to that in the usual ionic association reaction and that the free energy changes due to the distribution of a proton to water and organic solvent molecules must be taken into account as well as the free energy changes of species in the reaction in order to interprete the variation of equilibrium constants with varying solvent compositions.

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