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Ionic Equilibria in Mixed Solvents.   I.   Hydrolysis of Beryllium Ion in a 0.2 Mole Fraction Dioxane–Water Mixture Containing 3 M LiClO$_4$ as an Ionic Medium

BY HITOSHI OHTAKI

The hydrolytic reaction of beryllium ion was studied at 25° in a 0.2 mole fraction dioxane–water mixture (55.009% w/w dioxane) containing 3 M LiClO$_4$ as an ionic medium.   In the range of the total beryllium concentration of 2.5–80 mM, the emf data can be explained in terms of the formation of the following complexes: BeOH$^+$, log $*\beta_{1,1} \lesssim -6.0$; Be$_2$OH^{3+}, log $*\beta_{1,2} = -3.66 \pm 0.05$; Be(OH)$_2$, log $*\beta_{2,1} = -10.84 \pm 0.1$; Be$_2(OH)_2^{2+}$, log $*\beta_{2,2} = -7.15 \pm 0.1$; Be$_3(OH)_3^{3+}$, log $*\beta_{3,3} = -8.75 \pm 0.03$.

Introduction

The majority of investigations on ionic equilibria have been done in aqueous solutions and results obtained have been discussed quantitatively on the basis of the mass action law with reasonable estimation of activity factors.   In these cases, however, the numbers of water molecules in reactions usually remained in the background, despite their important roles in reactions in which water molecules take part, *e.g.*, ion hydration and ion combination involving liberation of some water molecules.   It is only in recent years that water concentration has been taken into account in the discussions on dissociation of organic acids in aqueous organic mixtures.[1–3]

In a series of aqueous mixed-solvent systems with varying compositions of the solvent, water must be considered as a reactant in a chemical equation, provided that water molecules participate in the ionic reaction.   Studies on ionic equilibria in mixed solvents have been undertaken to elucidate the effect of changes in the macroscopic dielectric constant of the solvent on ionization.   However, interpretation of the variation of dissociation constants in terms of the reciprocal of the dielectric constant has not always been successful, although the dielectric constant might be an important factor in ion combination in solution.
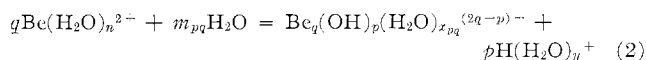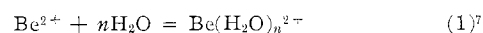
The present study was undertaken to throw more light on the contribution of water molecules to ionic reactions in solution through observations of phenomena in mixed aqueous organic solvents.   In this connection the variation of activity factors of ionic species with changing composition of solvents should certainly be taken into consideration.   Hydrolytic reaction of beryllium ions in aqueous dioxane was chosen as the first topic of the series.

The hydrolysis of beryllium ions in aqueous solution has been studied by many authors, and the historical survey has been described by Kakihana and Sillén.[4]   Carell and Olin[5] confirmed the results by Kakihana and

Sillén, ambiguity about the composition of the main species formed in aqueous solutions seems to have disappeared, and the formation of Be$_3$(OH)$_3^{3+}$ is now established to be the main reaction.[6]   Problems still remain, however, on the structure of the species and on the minor components.   In order to make clear the structure of the species in solution, the number of water molecules in the species must be known.   A six-membered ring (I) proposed by Kakihana and Sillén[4] for Be$_3$(OH)$_3^{3+}$ was not based on any evidence of the existence of water molecules in the species.


I
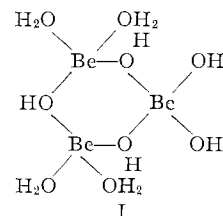
The hydrolytic reaction of beryllium ions may, in general, be written as

$$Be^{2+} + nH_2O = Be(H_2O)_n^{2+} \qquad (1)^7$$

$$qBe(H_2O)_n^{2+} + m_{pq}H_2O = Be_q(OH)_p(H_2O)_{x_{pq}}^{(2q-p)+} + pH(H_2O)_y^+ \qquad (2)$$

assuming that perchlorate ions do not associate with any species.

In aqueous dioxane solution, it may reasonably be assumed that solvation of dioxane with beryllium or hydrolyzed beryllium ions is negligible under conditions where the concentration of dioxane is not so high compared with that of water.   Under such conditions, the hydrolytic reaction of beryllium ion in the aqueous dioxane mixtures may also be written as (2).

For the sake of simplicity, omitting hydrated water molecules, (1) and (2) were rewritten as

$$qBe^{2+} + pH_2O = Be_q(OH)_p^{(2q-p)+} + pH^+ \qquad (3)$$
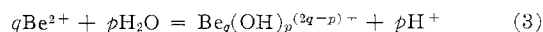
$$*\beta_{p,q} = [Be_q(OH)_p^{(2q-p)+}][H^+]^p/[Be^{2+}]^q$$

(1) M. Yasuda, *Bull. Chem. Soc. Japan*, **32**, 429 (1959).
(2) J. Koskikallio and S. Syrjäpalo, *Suomen Kemistilehti*, **B37**, 120 (1964).
(3) D. J. Glover, *J. Am. Chem. Soc.*, **87**, 5275, 5279 (1965).
(4) H. Kakihana and L. G. Sillén, *Acta Chem. Scand.*, **10**, 985 (1956).
(5) B. Carell and Å. Olin, *ibid.*, **15**, 1875 (1961).

(6) E. Matijević, *J. Colloid Sci.*, **20**, 322 (1965).
(7) The value of n in aqueous solution has been reported to be 4 by means of nmr methods by R. E. Connick and D. N. Fiat (*J. Chem. Phys.*, **39**, 1349 (1963)) and by M. Alei, Jr., and J. J. A. Jackson (*ibid.*, **41**, 3402 (1964)).

Symbols Used in the Text

h	Hydrogen ion concentration at equilibrium
H	Analytical excess of hydrogen ions = $[ClO_4^-] - 2B - [Li^+]$
B	Total concentration of beryllium
b	Concentration of free beryllium ions
Z	Average number of hydrogen ions set free per beryllium atom = $(h - H)/B$
p	Number of OH groups bound to hydrolyzed species
q	Number of Be atoms present in hydrolyzed species
$\bar{p}, \bar{q}$	Average number of p and q, respectively
$*\beta_{p,q}$	Equilibrium constant of the formation of $Be_q(OH)_p{}^{(2q-p)+}$
ν	Ratio of $\bar{p}$ to $\bar{q} = \bar{p}/\bar{q}$.
E	Emf
[ ]	Concentration

The Method of Measurement

During a potentiometric titration, B was kept constant; the studied range of B values was from 0.0025 to 0.0800 M. Lithium perchlorate was used as an ionic medium in order to keep constant the total ionic equivalent concentration (3 M). The potentiometric titration was performed following two different methods. In one way, into a solution, S_1, equal volumes of solutions, T_1 and T_1', were added; the compositions of these solutions were: $S_1 = B$ $Be(ClO_4)_2$, H_0 $HClO_4$, $(3 - 2B - H_0)$ $LiClO_4$; $T_1 = A$ $LiOH$, $(3 - A)$ $LiClO_4$; and $T_1' = 2B$ $Be(ClO_4)_2$, X $HClO_4$, $(3 - 4B - X)$ $LiClO_4$. Values of H_0, the initial concentration of acid in the solution taken in a titration vessel, were controlled to fall in the range between 0.01 and 0.05 M. Concentration of the added hydroxide ion was calculated from the difference of A and X. In the other way, hydrolyzed beryllium perchlorate solution (S_2) taken in a titration vessel was titrated with a perchloric acid solution containing the same concentration of beryllium (T_2). The compositions of the solutions may be written as: $S_2 = B$ $Be(ClO_4)_2$, A_0 $LiOH$, $(3 - 2B - A_0)$ $LiClO_4$; and $T_2 = B$ $Be(ClO_4)_2$, X' $HClO_4$.

All solutions, unless otherwise noted, were prepared with a 0.2 mole fraction dioxane–water mixture (55.00₉% w/w dioxane). The titration was performed under an atmosphere of nitrogen, which was free from carbon dioxide and was preequilibrated with the solvent.

Neither precipitates nor turbidness was noticed at any point of the experiments and a stable emf was established within 10 min after the addition of the titrants and remained unchanged for at least 5 hr within the accuracy of ±0.1 mv. Furthermore, as shown in Figure 1, the reaction was reversible.

The hydrogen ion concentration was measured by means of the cell

$$(-)GE\,|\,solution\,|\,Ref(+) \qquad (A)$$

where GE denotes a glass electrode and Ref the reference half-cell (B)

3.000 M LiClO_4 in 0.2 mole fraction aqueous dioxane	2.990 M LiClO_4 and 0.010 M AgClO_4 in aqueous solution	AgCl–Ag	(B)

The emf of cell A can be written (at 25°)

$$E = E_0' - 59.15 \log h - 59.15 \log f_H + E_j(h,B) \quad (4)$$

where E_0' is a constant and h is the hydrogen ion concentration at equilibrium. f_H represents the activity factor of H^+. The standard state is defined so that f_H, as well as the activity factors of the other reacting species, tends to unity as the composition of the solution approaches to 3 M LiClO_4 in the 0.2 mole fraction aqueous dioxane. $E_j(h,B)$ denotes the liquid junction potential at the junction, solution|3 M LiClO_4 in the 0.2 mole fraction aqueous dioxane. The liquid junction potential at the other junction, 3 M LiClO_4 in aqueous dioxane|2.99 M LiClO_4, 0.01 M AgClO_4 in aqueous solution, can be assumed to be constant throughout a series of titrations.

In such a case where the total ionic concentration, B, and the solvent composition were kept constant, a constant f_H may reasonably be assumed. Then (4) may be rewritten

$$E = E_0 - 59.15 \log h + E_j(h,B) \qquad (5)$$

where

$$E_0 = E_0' - 59.15 \log f_H$$

From emf measurements of the cell

$$GE\,|\,h\ H^+,\ (3.000 - h)\ Li^+,\ 3.000\ M\ ClO_4^-\,|\,Ref \qquad (C)$$

at various h, the total concentration of HClO_4, $E_j(h,0) = -8.3h$ mv was obtained. Supplementary emf measurements were carried out with the cell

$$GE\,|\,H_0\ H^+,\ B\ Be^{2+},\ (3.000 - 2B - H_0)\ Li^+,\ 3.000\ M\ ClO_4^-\,|\,Ref \qquad (D)$$

at various B, H_0 being kept constant, and $E_j(0.2176, B) = 12.3B$ mv was found at $H_0 = 0.2176$ M. Thus $E_j(h,B)$ is assumed to be expressed in the formula $E_j(h,B) = -8.3h + 12.3B$.

By means of density measurements using a pycnometer, no volume change was found within an accuracy of experiments where $(3 - H_0)$ LiClO_4, H_0 HClO_4 solution was mixed with $(1.5 - 0.5H_0)$ $Be(ClO_4)_2$, H_0 HClO_4 solution at $H_0 = 0.2176$ M. It may be concluded from this result that an appreciable volume change does not occur during a titration.

Experimental Details

Reagents and Analysis. Beryllium perchlorate was prepared as follows. Beryllium oxide (Johnson Matthey Co. Ltd., 99% purity) was heated for several hours with excess perchloric acid, nitrogen gas being passed through the slurry. Residual beryllium oxide was filtered off with a glass filter and beryllium perchlorate was recrystallized three times from water. Beryllium ion concentration of the stock solution was determined as BeO after ignition of beryllium hydroxide at about 1100°.[8] Perchlorate ion concentration of the stock solution was determined by the ion-exchange method, and approximate hydrogen ion concentration of the solution was calculated as $[ClO_4^-] - 2B$. The corrected value of the hydrogen ion concentration of the solution was determined by titration with a standard lithium hydroxide solution. The end point was located by means of the Gran plot.[9] Neither chloride nor iron(III) was detected.

Lithium hydroxide solution was prepared by electrolysis of lithium perchlorate solution. About 3 M lithium perchlorate

(8) W. W. Scott, "Standard Method of Chemical Analysis," Vol. 1, 5th ed, D. Van Nostrand Co. Inc., New York, N. Y., 1939, p 139.
(9) G. Gran, *Analyst*, **77**, 661 (1952).

aqueous solution with a slight excess of perchloric acid was taken in a polyethylene bottle and electrolyzed at about 30 ma with platinum-foil electrodes. The polyethylene bottle was connected with an anode chamber by a bridge containing LiClO₄. Nitrogen gas was bubbled continuously in the solution during the electrolysis. About 0.12 *M* lithium hydroxide solution was obtained. The concentration of hydroxide ion was determined by means of titration with standard perchloric acid using a bromocresol green–methyl red mixed indicator. The concentration of lithium in the solution was determined by adding H_2SO_4 to the lithium hydroxide–lithium perchlorate solution, fuming off $HClO_4$, and weighing as the sulfate. The difference of total lithium and [OH^-] was estimated as [ClO_4^-].

The concentration of hydroxide in 0.2 mole fraction aqueous dioxane was determined by titrating with standard $HClO_4$ when each test solution was prepared. The concentration of hydroxide was around 0.05 *M*.

Perchloric acid of reagent grade was used in order to prepare perchloric acid solution. The solution was standardized with potassium hydrogen carbonate using the mixed indicator.

All stock solutions were analyzed on the scale of moles per gram of solution, so that the amount of water in the solution was given as the difference of the total weight of the solution and the weight of the solutes in the solution.

Lithium perchlorate was prepared as described by Biedermann and Ciavatta.[10] The lithium perchlorate was dried at about 200° and stored in a glass bottle. The crystals were again dried at 200° for about 2 days just before preparing a test solution. No detectable amount of chloride was found with the silver nitrate test.

The amount of protolytic impurities in 3 *M* LiClO₄ in 0.2 mole fraction aqueous dioxane was estimated using 5,5-diethylbarbituric acid as a reference substance.[11] The total amount of protolytic impurities of 45 μ*M* concentration and the apparent dissociation constant of the impurities of p*K* = 4.5 were evaluated.

Dioxane of reagent grade was refluxed for 8 hr with 10% HCl solution, a stream of nitrogen being passed through the mixture. Pellets of potassium hydroxide were added. The upper layer of dioxane was decanted, refluxed over freshly cut metallic sodium in an atmosphere of nitrogen, and distilled over sodium through a 70-cm column with glass pieces. The distilled dioxane was stored over sodium in a dark bottle filled with nitrogen gas. Freshly distilled dioxane was used to prepare test solutions.

Water was redistilled from alkaline permanganate solution.

Silver perchlorate solution was prepared from HClO₄ and Ag₂CO₃ which was precipitated from AgNO₃ solution with Na₂CO₃. The Ag₂CO₃ precipitate was repeatedly washed by decantation until no Na⁺ could be detected with a flame test. The concentration of silver ion in the silver perchlorate solution was determined gravimetrically, silver chloride being dried at about 120°.

Potassium hydrogen carbonate was recrystallized twice from water and stored in a desiccator over silica gel in an atmosphere of carbon dioxide.

Apparatus. Glass Electrodes.—Beckman (No. 40498) and Radiometer (G 202 C) glass electrodes were used. No essential difference was found in the electrodes.

Silver–silver chloride electrodes were prepared according to Brown.[12]

The "Wilhelm" type of half-cell described by Forsling, Hietanen, and Sillén[13] was set for emf measurements.

A Radiometer PHM-4d (Copenhagen) calibrated against a P-1 potentiometer (Yokogawa Electric Works, Ltd., Tokyo) was used.

All titrations were performed at 25.00 ± 0.01° in a paraffin oil thermostat, which was placed in a room thermostated at 25 ± 1°.

Evaluation of the Composition and the Stability Constants of Hydrolysis Products

Values of Z and log h at each series of B are summarized in Table I and represented graphically in Figure 1. The results in the present work are corrected for protolytic impurities which existed in solution.

Calculation of b and Qualitative Consideration on the Compositon of the Hydrolysis Products

Concentration of free beryllium ion, b, was calculated by the method described by Sillén[14] using the equations

$$B = b + \sum_p \sum_q q^* \beta_{p,q} b^q h^{-p} \tag{6}$$

$$BZ = \sum_p \sum_q p^* \beta_{p,q} b^q h^{-p} \tag{7}$$

$$S = \sum_p \sum_q {}^* \beta_{p,q} b^q h^{-p} \tag{8}$$

where B, h, and Z were determined experimentally. A parameter R defined in (9) was calculated by (10) at constant B, and then b was obtained using (11).

$$BR = b + S \tag{9}$$

$$R = 1 + \int_\infty^{\ln h} \left(\frac{\partial Z}{\partial \ln B} \right)_h d \ln h \tag{10}$$

$$\ln b = \ln B + R + \int_\infty^{\ln h} Z \, d \ln h =$$

$$\ln B + \int_\infty^{\ln h} \left[Z + \left(\frac{\partial Z}{\partial \ln B} \right)_h \right] d \ln h \tag{11}$$

Integration was carried out with intervals of 0.1 log h unit assuming

$$\int_\infty^{-2.0} \left[2.303Z + \left(\frac{\partial Z}{\partial \log B} \right)_h \right] d \log h = 0$$

The average number of p and q are denoted as $\bar{p}$ and $\bar{q}$, respectively, and estimated as

$$\bar{p} = BZ/(BR - b)$$
$$\bar{q} = (B - b)/(BR - b) \tag{12}$$

and then

$$\nu = \bar{p}/\bar{q} \tag{13}$$

was calculated.

Values of ν plotted against $-\log h$ at various B are shown in Figure 2. Variation of $\bar{p}$ and $\bar{q}$ is visualized in Figure 3 as a plot of $\bar{q}$ vs. $2\bar{q} - \bar{p}$, according to Dunsmore, Hietanen, and Sillén.[15] From the figure some qualitative considerations may be made on the composition of the species formed. At $B \geq 0.01$ *M* where only low Z values were obtained, the presence of 1:1, 1:2, and 3:3 complexes is anticipated. In the region of

(10) G. Biedermann and L. Ciavatta, *Acta Chem. Scand.*, **15**, 1347 (1961); *Arkiv Kemi*, **22**, 253 (1964).

(11) (a) G. Biedermann, L. Newman, and H. Ohtaki, to be published; (b) H. Ohtaki, H. Kato, and K. Kunda, *Bull. Chem. Soc. Japan*, in press.

(12) A. S. Brown, *J. Am. Chem. Soc.*, **56**, 646 (1934).

(13) W. Forsling, S. Hietanen, and L. G. Sillén, *Acta Chem. Scand.*, **6**, 901 (1952).

(14) L. G. Sillén, *ibid.*, **15**, 1981 (1961).

(15) H. S. Dunsmore, S. Hietanen, and L. G. Sillén, *ibid.*, **17**, 2644 (1963).

TABLE I

SUMMARY OF THE EXPERIMENTAL RESULTS FOR Z AND $-\log h$ AT VARIOUS B

$\underline{B} = 0.0800M$ (Back titration): $-\log \underline{h}$, $\underline{Z}$;
2.230, 0.0026_1; 2.358, 0.0036_3; 2.428, 0.0035_9; 2.484, 0.0060_0;
2.544, 0.0087_4; 2.617, 0.0114; 2.690, 0.0149 ; 2.749, 0.0198 ;
2.835, 0.0282 ; 2.948, 0.0442 ; 3.028, 0.0635 ; 3.079, 0.0800 ;
3.141, 0.103_5 ; 3.185, 0.124_4 ; 3.226, 0.145_6 ; 3.266, 0.167_3 ;
3.298, 0.189_3 ; 3.331, 0.211_8 ; 3.363, 0.234_3 ; 3.395, 0.257_3 ;
3.418, 0.280_5 ; 3.440, 0.294_6 ; 3.478, 0.328_1 ; 3.506, 0.352_2 ;
(Back titaration):
2.265, 0.0026_5; 2.558, 0.0088_9; 2.854, 0.0321 ; 3.043, 0.0672 ;
3.158, 0.106_7 ; 3.243, 0.148_3 ; 3.315, 0.191_3 ; 3.378, 0.235_6 ;
3.432, 0.281_3 ; 3.493, 0.327_8 ; 3.549, 0.375_8 ; 3.606, 0.425_0 ;
3.665, 0.475_2 .

$\underline{B} = 0.0400M$ (Back titration): $-\log \underline{h}$, $\underline{Z}$;
2.407, 0.0015_5; 2.478, 0.0025_0; 2.566, 0.0031_5; 2.668, 0.0058_5;
2.784, 0.0093_5; 2.896, 0.0165 ; 3.023, 0.0251 ; 3.194, 0.0510 ;
3.246, 0.0664 ; 3.298, 0.0822 ; 3.381, 0.115_4 ; 3.413, 0.133_3 ;
3.501, 0.186_8 ; 3.579, 0.242_7 ; 3.648, 0.300_9 ; 3.694, 0.341_1 ;
3.738, 0.382_3 ; 3.789, 0.424_6 ; 3.838, 0.468_1 ; 3.890, 0.512_6 ;
3.948, 0.558_2 ; 4.009, 0.605_5 ; $4.044, 0.629_5$; 4.085, 0.653_7 .
(Back titration):
2.933, 0.0166 ; 3.226, 0.0624 ; 3.364, 0.116_5 ; 3.464, 0.174_8 ;
3.557, 0.229_6 ; 3.626, 0.295_6 ; 3.703, 0.365_8 ; 3.774, 0.428_1 ;
3.902, 0.533_3 ; 3.997, 0.605_5 ; 4.052, 0.644_7 .

$\underline{B} = 0.0200M$ (Forward titration): $-\log \underline{h}$, $\underline{Z}$;
2.717, 0.0085_0; 2.884, 0.0089_9; 3.090, 0.0158 ; 3.280, 0.0315 ;
3.347, 0.0410 ; 3.407, 0.0535 ; 3.489, 0.0778 ; 3.599, 0.125_7 ;
3.691, 0.181_8 ; 3.770, 0.242_7 ; 3.844, 0.306_1 ; 3.912, 0.362_2 ;
3.966, 0.412_5 ; 4.025, 0.463_2 ; 4.078, 0.508_4 ; 4.134, 0.553_8 ;
4.184, 0.594_2 ; 4.227, 0.626_2 ; 4.272, 0.655_1 .
(Back titration):
2.758, 0.0023_0; 3.158, 0.0159 ; 3.555, 0.0970 ; 3.767, 0.229_2 ;
3.934, 0.367_9 ; 4.098, 0.509_9 ; 4.233, 0.618_7 ; 4.293, 0.655_1 .

$\underline{B} = 0.0100M$ (Forward titration): $-\log \underline{h}$, $\underline{Z}$;
2.688, 0.0036_3; 2.791, 0.0030_1; 2.911, 0.0052_8; 3.063, 0.0091_9;
3.270, 0.0154 ; 3.478, 0.0329 ; 3.623, 0.0598 ; 3.719, 0.0913 ;
3.789, 0.123_4 ; 3.843, 0.155_6 ; 3.932, 0.218_9 ; 4.007, 0.279_1 ;
4.076, 0.336_7 ; 4.134, 0.392_6 ; 4.193, 0.445_2 ; 4.254, 0.495_6 ;
4.311, 0.543_8 ; 4.370, 0.588_8 ; 4.426, 0.633_4 ; 4.524, 0.696_3 ;
4.621, 0.755_4 ; 4.744, 0.811_1 ; 4.876, 0.863_6 ; 5.053, 0.913_1 ;
5.199, 0.945_2 ; 5.368, 0.975_8 .
(Back titration):
3.606, 0.0557 ; 3.853, 0.155_1 ; 4.012, 0.264_6 ; 4.132, 0.380_7 ;
4.272, 0.499_6 ; 4.429, 0.623_0 ; 4.632, 0.750_7 ; 4.952, 0.882_3 ;
5.244, 0.950_3 .

$\underline{B} = 0.00500M$ (Forward titration): $-\log \underline{h}$, $\underline{Z}$;
2.735, 0.0042_4; 3.035, 0.0064_7; 3.312, 0.0067_9; 3.471, 0.0196 ;
3.667, 0.0368 ; 3.910, 0.100_3 ; 3.987, 0.136_4 ; 4.049, 0.173_3 ;
4.107, 0.209_8 ; 4.193, 0.283_9 ; 4.274, 0.356_3 ; 4.313, 0.391_7 ;
4.389, 0.460_1 ; 4.457, 0.528_3 ; 4.539, 0.594_9 ; 4.617, 0.659_9 ;
4.712, 0.723_0 ; 4.818, 0.784_6 ; 4.940, 0.844_7 ; 5.008, 0.874_2 ;
5.085, 0.903_1 ; 5.170, 0.932_3 ; 5.283, 0.960_3 ; 5.403, 0.988_6 .
(Back titration):
3.780, 0.0585 ; 4.039, 0.157_5 ; 4.166, 0.250_8 ; 4.298, 0.370_0 ;
4.426, 0.489_5 ; 4.565, 0.608_0 ; 4.730, 0.734_9 ; 4.948, 0.850_1 ;
5.227, 0.948_5 .

$\underline{B} = 0.00250M$ (Forward titration): $-\log \underline{h}$, $\underline{Z}$;
3.036, 0.0036_1; 3.187, 0.0117 ; 3.435, 0.0130 ; 3.806, 0.0374 ;
4.122, 0.112_2 ; 4.281, 0.208_7 ; 4.397, 0.313_2 ; 4.506, 0.406_5 ;
4.602, 0.504_7 ; 4.708, 0.601_2 ; 4.832, 0.696_0 ; 4.967, 0.788_8 ;
5.057, 0.844_5 ; 5.160, 0.899_4 ; 5.292, 0.953_0 .
(Back titration):
3.699, 0.0442 ; 4.129, 0.125_0 ; 4.332, 0.258_6 ; 4.489, 0.395_2 ;
4.646, 0.535_8 ; 4.812, 0.680_2 ; 5.026, 0.827_1 ; 5.369, 0.977_0 .
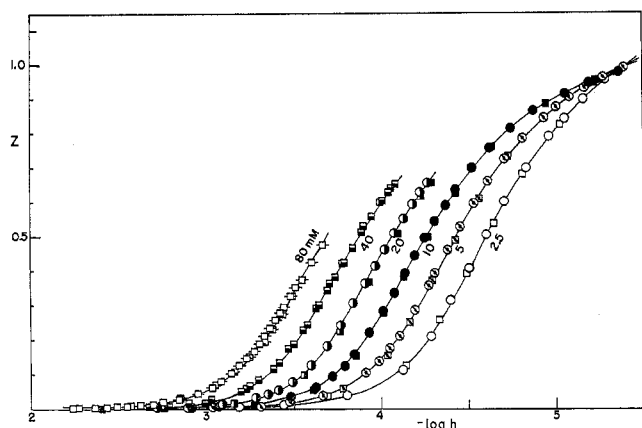

Figure 1.—Z, average number of OH$^-$ bound per beryllium atom, as a function of $-\log h$. Circles denote experimental points obtained by forward titrations, and squares, by back titrations. Drawn curves were calculated with the final values of the stability constants given in Table III.
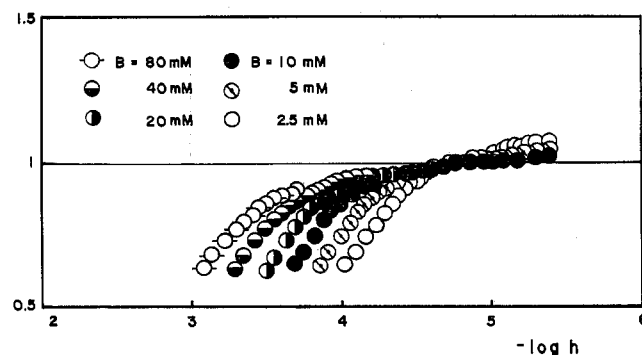

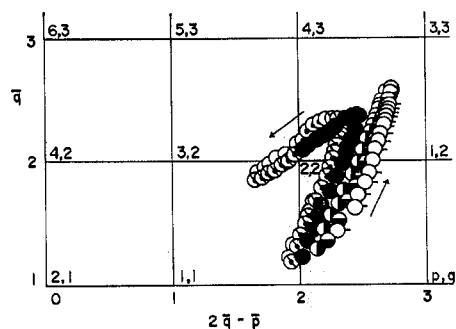Figure 2.—Plot of $\nu = \bar{p}/\bar{q}$ against $-\log h$ at various B.

Figure 3.—Average composition of the complexes shown with the scale of $\bar{q}$ plotted against $2\bar{q} - \bar{p}$. Direction of an arrow corresponds to the increase in Z. Symbols are the same as those in Figure 2.

lower B, the formation of 2:2 and 2:1 complexes seems appreciable at high Z.

A plot of log B vs. log h gave additional evidence for the presence of the 3:3 complex as the main species. At $B \geq 0.01$ M and $Z < 0.6$, straight lines with a slope 1.5 fitted well with experimental results. This can be explained only in terms of the formation of the species having a composition formulated as $Be(Be(OH)_{1.5})_n$. Since ν was found to be 1.00 $\pm$ 0.05 at 4.5 $< -\log h < 5.5$, n must be 2, thus $Be_3(OH)_3{}^{3+}$ (Figure 2).

Exclusion of the 3:1 complex may be reasonable, because $\bar{p}$ approaches 2 passing through a maximum at $\bar{p} = 2.2$–2.5, while $\bar{q}$ decreases to a value apparently lower than 2. Consequently, it can be concluded that the 2:1 complex is the final product and the 3:1 complex may not be appreciably present at the highest Z studied.

On the basis of the consideration described above, the data will be treated to determine the stability constants of the 3:3, 1:1, 1:2, 2:2, and 2:1 complexes. The other species could not be detected within the accuracy of the experiments, as will be described in a later section.

Determination of the Stability Constants of the Complexes

The stability constant of the main species, Be_3-$(OH)_3{}^{3+}$, was first determined. Since the concentration of minor components is small in the region of $B \geq 0.01$ M and $Z \leq 0.6$, the following equations can be derived with a good approximation

$$B = b + 3{}^*\beta_{3,3}b^3h^{-3}$$
$$BZ = 3{}^*\beta_{3,3}b^3h^{-3} \qquad (14)$$

Eliminating b, (15) is obtained

$$\log v = \frac{1}{2}\log Z - \frac{3}{2}\log(1 - Z)$$
$$= \log \beta + \log B + \frac{3}{2}\log h \qquad (15)$$

where

$$\beta = \sqrt{3{}^*\beta_{3,3}} \qquad (16)$$

Since plots of Z as a function of $(\log B - {}^3/_2 \log h)$ should give a single curve independent of B, the plot was compared with the theoretical curve of Z vs. $\log v$ for a fit. The difference on the $\log v$ and $(\log B - {}^3/_2 \log h)$ axes in this position gives $\log \beta$ which leads to $\log {}^*\beta_{3,3}$ (eq 16). The value of the equilibrium constant was found to be: $\log {}^*\beta_{3,3} = -8.70 \pm 0.04$.

In the region where Z is very low, a small deviation is obvious, which is certainly caused by the presence of 1:1 and 1:2 complexes. Taking into account these species, we get

$$B = b + {}^*\beta_{1,1}bh^{-1} + 2{}^*\beta_{1,2}b^2h^{-1} + 3{}^*\beta_{3,3}b^3h^{-3}$$
$$BZ = {}^*\beta_{1,1}bh^{-1} + {}^*\beta_{1,2}b^2h^{-1} + 3{}^*\beta_{3,3}b^3h^{-3} \qquad (17)$$

and substitution and rearrangement lead to

$$\frac{BZ - 3{}^*\beta_{3,3}b^3h^{-3}}{bh^{-1}} = {}^*\beta_{1,1} + {}^*\beta_{1,2}b \qquad (18)$$

A plot of $(BZ - 3{}^*\beta_{3,3}b^3h^{-3})/(bh^{-1})$ vs. b, which was calculated with (11), will give the values of ${}^*\beta_{1,1}$ and ${}^*\beta_{1,2}$ as the intercept and the slope of the straight line, respectively. The values obtained were

$$\log {}^*\beta_{1,1} \lesssim -6.0$$
$$\log {}^*\beta_{1,2} = -3.6_0 \pm 0.1$$

At $B < 0.01$ M and $Z > 0.6$, a large deviation occurred from the theoretical curves drawn assuming only the 3:3 complex. The deviation may be explained in terms of the formation of 2:2 and 2:1 complexes and some others. The presence of the 2:2 and 2:1 complexes was postulated from Figure 3. The sum of the concentrations of the additional complexes being denoted

as δ, the following equation was derived for determining the stability constants of the 2:2 and 2:1 complexes

$$BZ = b + 3{}^*\beta_{3,3}b^3h^{-3} + 2{}^*\beta_{2,2}b^2h^{-2} + 2{}^*\beta_{2,1}bh^{-2} + \delta \qquad (19)$$

From a plot of $\log[(BZ - 3{}^*\beta_{3,3}b^3h^{-3})/2bh^{-2}]$ vs. $\log b$, the following values were found

$$\log {}^*\beta_{2,2} = -7.1 \pm 0.1$$
$$\log {}^*\beta_{2,1} = -10.8 \pm 0.1$$
$$\delta = 0$$

Therefore, it was concluded that the species of Be_2-$(OH)_2{}^{2+}$ and $Be(OH)_2$ are important in this pH region and the other complexes are not present in detectable amounts within the accuracy of experiments.

Finally the data have been treated by the generalized least-squares method with a help of an electronic computer HITAC 5020 in order to make the error square sum $(U = \sum(Z - Z_{calcd})^2)$ minimum for the set of stability constants: ${}^*\beta_{1,1}$, ${}^*\beta_{1,2}$, ${}^*\beta_{2,1}$, ${}^*\beta_{2,2}$, and ${}^*\beta_{3,3}$. Z_{calcd} denotes the value $Z_{calcd} = \sum_p \sum_q p{}^*\beta_{p,q}b^q h^{-p}/B$ for a particular set of the constants, ${}^*\beta_{p,q}$. The values of stability constants chosen and error square sum calculated are listed in Table II. Neglect of ${}^*\beta_{1,1}$ gave rise to only a slightly larger error square sum than that of the five constants, so the existence of $BeOH^+$ was not conclusive. However, neglect of the formation of the 2:2 complex, i.e., the use of only three constants, ${}^*\beta_{1,2}$, ${}^*\beta_{2,1}$, and ${}^*\beta_{3,3}$, gave a rather large error square sum. The conclusion we may draw is that the present data are certainly better explained with the set of ${}^*\beta_{1,2}$, ${}^*\beta_{2,1}$, ${}^*\beta_{2,2}$, and ${}^*\beta_{3,3}$ than with the set of ${}^*\beta_{1,2}$, ${}^*\beta_{2,1}$, and ${}^*\beta_{3,3}$. For ${}^*\beta_{1,1}$ only a probable maximum value may be given. The final values of the constants are given in Table III together with values obtained by graphical methods and by previous workers.[4,5,16]

TABLE II
RESULTS OF CALCULATION OF ERROR SQUARE SUM

$10^7{}^*\beta_{1,1}$	$10^4{}^*\beta_{1,2}$	$10^{10}{}^*\beta_{2,1}$	$10^8{}^*\beta_{2,2}$	$10^9{}^*\beta_{3,3}$	$10^2 U$
9.84	2.19	1.44	7.02	1.76	1.749
0.00	2.29	1.48	7.65	1.75	1.808
0.00	3.47	1.56	0.00	2.34	3.990

Discussion

In the work by Kakihana and Sillén[4] and Carell and Olin[5] the formations of $Be_3(OH)_3{}^{3+}$, Be_2OH^{3+}, and $Be(OH)_2$ were reported in aqueous solutions. Recently, Hietanen and Sillén[16] have refined their results with a LETAGROP VRID program and reported, besides these species, the formation of the $BeOH^+$ complex with the stability constant of $\log {}^*\beta_{1,1} < -6.1$ (see Table III).

The present work, though performed in a very different solvent system from the earlier work, gave results which agreed with the previous ones[4,5,16] for not only the composition of the species but also the values of the stability constant of the complex, although varia-

(16) S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, **18**, 1015 (1964).

TABLE III

THE EQUILIBRIUM CONSTANTS OF THE HYDROLYTIC REACTIONS OF BERYLLIUM ION

Equil const	Ref 4	Ref 5	Ref 16	Present work Graphical	HITAC 5020	Final value
$\log *\beta_{1,1}$	...	...	< -6.1	$\lesssim -6.0$	$-6.0_1 \pm 0.10$	$\lesssim -6.0$
$\log *\beta_{1,2}$	-3.24 ± 0.02	-3.22 ± 0.05	-3.22 ± 0.03	$-3.6_0 \pm 0.1$	-3.66 ± 0.03	-3.66 ± 0.10
$\log *\beta_{3,3}$	-8.66 ± 0.03	-8.66 ± 0.03	-8.664 ± 0.007	-8.70 ± 0.04	-8.75 ± 0.01	-8.75 ± 0.04
$\log *\beta_{2,2}$	...	...	...	-7.1 ± 0.1	-7.15 ± 0.05	-7.15 ± 0.1
$\log *\beta_{2,1}$	-10.9 ± 0.2	...	-10.87 ± 0.04	-10.8 ± 0.1	-10.84 ± 0.05	-10.84 ± 0.1

tion of ionic activity factors with solvent composition still remains uncertain.

The $Be_2(OH)_2{}^{2+}$ complex has not been found by the authors quoted above, but some workers have reported the existence of this species.[17,18] Gilbert and Garrett[18] have studied the complex formation by solubility measurements or, in other words, at the highest Z region. In the present work, the formation of the complex in question becomes more important at higher pH region.

In order to discuss why the values of the stability constants (especially that of the 3:3 complex) in very different solvent systems (or in media of very different macroscopic dielectric constant) agree and how water

(17) M. Prytz, *Z. Anorg. Allgem. Chem.*, **180**, 355 (1929); **197**, 103 (1931); **231**, 238 (1937).
(18) R. A. Gilbert and A. B. Garrett, *J. Am. Chem. Soc.*, **78**, 5501 (1956).

molecules participate in the formation of the complexes, it is necessary to know results in other systems of different composition of aqueous dioxane with the same ionic medium and to estimate the variation of ionic activity factors with composition of the solvent. These studies are in progress in our laboratory and results will be presented in the subsequent papers of this series.

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Spectroscopic Studies of Some Compounds with Octahedral Polynitrite Anions

BY D. M. L. GOODGAME AND M. A. HITCHMAN

It is shown that the orange-brown compound previously formulated as $K_4Ni(NO_2)_6$ is a monohydrate. This has been dehydrated but the spectral properties of the red product suggest that the anion is then of the form $Ni(NO_2)_4(ONO)_2{}^{4-}$. The compounds $[(CH_3)_4N]Ni(NO_2)_3$ and $Cs_3Mn(NO_2)_5$ have been prepared, and the electronic and infrared spectra of these and also $Cs_3Ni(NO_2)_5$ are reported. The pentanitrite complexes contain both nitrogen- and oxygen-bonded nitrite groups, and possible structures are suggested. The trinitrite complex appears to be polymeric with Ni–N(O)O–Ni bridges.

Introduction

Complexes with anions of the type $M(NO_2)_6{}^{n-}$, where M is a first-row transition metal ion, have been long known. From extensive X-ray diffraction studies Ferrari and his co-workers found[1] that most of these compounds have similar structures, in which the six nitrite groups coordinate to M through nitrogen. However, much less is known about anions of stoichiometry $M(NO_2)_x{}^{n-}$ where $x < 6$. We report here the preparation of $Cs_3Mn(NO_2)_5$ and $[(CH_3)_4N]Ni(NO_2)_3$, the results of spectral studies on these and the compound $Cs_3Ni(NO_2)_5$, and also an unexpected observation concerning the compound previously formulated as $K_4Ni(NO_2)_6$.[2-4]

(1) A. Ferrari, L. Cavalca, and M. Nardelli, *Gazz. Chim. Ital.*, **81**, 982 (1951), and references therein.
(2) A. Ferrari, L. Cavalca, and M. Nardelli, *ibid.*, **81**, 945 (1951).
(3) M. Le Postollec and J.-P. Mathieu, *Compt. Rend.*, **254**, 1800 (1962).
(4) M. Le Postollec, J.-P. Mathieu, and H. Poulet, *J. Chim. Phys.*, **60**, 1319 (1963).

Experimental Section

Preparations. $K_4Ni(NO_2)_6 \cdot H_2O$.—This orange-brown compound was obtained by adding a concentrated, aqueous solution of nickel bromide to an excess of a saturated, aqueous solution of potassium nitrite and was dried for several days *in vacuo* over P_2O_5. *Anal.* Calcd for $K_4Ni(NO_2)_6 \cdot H_2O$: K, 30.71; Ni, 11.53; $NO_2{}^-$, 54.24. Found: K, 30.99; Ni, 11.49; $NO_2{}^-$, 53.93.

$K_4Ni(NO_2)_6$.—This hygroscopic, red compound was obtained by heating the monohydrate at 100° for several hours. Weight loss: calcd, 3.94; found, 4.00%. *Anal.* Calcd for $K_4Ni(NO_2)_6$: Ni, 11.95; $NO_2{}^-$, 56.19. Found: Ni, 11.86; $NO_2{}^-$, 55.85.

$Cs_3Ni(NO_2)_5$.—Aqueous solutions of nickel nitrite and cesium nitrite were mixed in 1:3 molar ratio, filtered, and allowed to stand over H_2SO_4. After several days dark red crystals formed, and these were washed with a little ice-cold water and dried *in vacuo* (5% yield). *Anal.* Calcd for $Cs_3Ni(NO_2)_5$: Ni, 8.54; $NO_2{}^-$, 33.46. Found: Ni, 8.57; $NO_2{}^-$, 33.16.

$Cs_3Mn(NO_2)_5$.—A methanolic solution of manganese(II) nitrite, prepared from manganese(II) bromide and excess silver nitrite, was added to one of excess cesium nitrite (5:1 molar