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The Hydrolysis of the Beryllium Ion in Heavy Water*1,*2

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The hydrolysis of Be^{2+} ion in heavy water containing 3M $NaClO_4$ as an ionic medium was investigated at 25°C by potentiometric titrations, employing a technique of constant-current coulometry. The deuterium-ion concentrations was measured by the use of a commercial glass electrode. The emf data in the range of the total beryllium concentration from 2.5 to 10 mM can be explained on the basis of the following complex formation: $Be_2(OD)^{3+}$, $-\log\beta_{1,2}=3.28\pm0.04$; $Be_3(OD)_3{}^{3+}$, $-\log\beta_{3,3}=9.399\pm0.007$; $Be(OD)_2$, $-\log\beta_{2,1}=11.89\pm0.07$. The composition of the species formed in heavy water is the same as that in light water, but the values of the stability constants are smaller in heavy water than in light water.

Since the discovery of deuterium oxide, many investigations of the chemical reactions in heavy water have been made; these investigations played important roles in the investigation of the mechanisms of chemical reactions.

As for the hydrolytic reactions of metal ions, several investigations have been made in heavy water.[1-4] However, as far as we know, the investigations made so far have been only of the mononuclear hydrolysis species; there have been none of the polynuclear species in heavy water.

The present work was carried out in order to ascertain the differences in the hydrolytic reactions of metal ions in heavy water and in light water.

The hydrolysis of the beryllium ion was chosen as the first of a series of studies of the hydrolysis in heavy water. The hydrolysis of the beryllium ion in light water has been investigated by several researchers,[5-12] and it has been confirmed that $Be_3(OH)_3{}^{3+}$ is the main hydrolysis species. The hydrolysis of the beryllium ion in H_2O-D_2O mixed solvents has previously been studied by the present authors;[13] we found that the composition of the main hydrolysis product is the same as that in light water and that the value of the stability constant of the main species decreases gradually with an increase in the deuterium-atom fraction.

Symbols

B total concentration of Be
b concentration of free Be^{2+}
D total excess concentration of the deuterium ion
d concentration of the free deuteriun ion
Z average number of deuterium ions split off per beryllium $=(d-D)/B$
$\beta_{p,q}$ stability constant of the following reaction:

$$qBe^{2+} + pD_2O = Be_q(OD)_q^{(2q-p)} + pD^+$$

p number of OD groups in hydrolyzed species
q number of beryllium atoms in hydrolyzed species
$\bar{p}$ and $\bar{q}$ average numbers of p and q respectively

Experimental

Reagents and Analysis. *Reagents Used.* These were, unless otherwise stated, prepared and analyzed as has been described in Ref. 5 and Ref. 13.

Beryllium Perchlorate in Heavy Water. This was prepared by the repeated evaporation of beryllium perchlorate in light water (which had itself been prepared and

*1 Ionic Equilibria in Heavy Water. II.

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analyzed as has been described in Ref. 10 under an infrared lamp, while adding heavy water. The beryllium content of the stock solution was determined by the method described in Ref. 5.

Sodium Perchlorate. This was prepared by neutralizing a $HClO_4$ solution with recrystallized Na_2CO_3. The sodium perchlorate was dried at about 120°C and stored in a glass bottle.

Sodium Chloride of Analytical Grade. This was heated for a few hours at 360°C in an electric oven and then stored in a glass bottle.

Apparatus. *Apparatus Used.* These were, unless otherwise stated, the same as those described in Ref. 13.

The Titration Cell. This consisted of a Wilhelm-type half cell[14] for emf measurements and a modified one for constant-current coulometry.

Coulometric Analyzer. Such an analyzer (Leeds & Northrup Co., Philadelphia) was used as a constant-current power source.

Experimental Procedures. All the measurements were carried out in a paraffin-oil thermostat kept at 25.00±0.01°C and placed in a room thermostated at 25±1°C.

The hydrolysis of the Be^{2+} ion in heavy water was followed by measurements of the deuterium-ion concentration.

$NaClO_4$ was added to all the test solutions so that they contained 3M ClO_4^- as an ionic medium; the total Be(II) concentration was kept constant in each series of experiments.

The deuterium-ion concentration of a test solution was measured by means of this cell;

$$\text{Ref}|B\text{M Be}^{2+}, D\text{M D}^{+}, (3-D-2B)\text{M}Na^{+}, 3\text{M ClO}_4^{-}|\text{GE}, \quad \text{(A)}$$

where GE denotes a glass electrode, and Ref, the reference half-cell;

$$|3\text{M NaClO}_4 \text{ in heavy water}|2.99\text{M NaClO}_4 \text{ and } 0.01\text{M AgClO}_4 \text{ in light water}|\text{AgCl-Ag}.$$

The emf of the cell(A) can be denoted as follows:[15]

$$E = E_0 + 59.15 \log d + E_j, \quad (1)$$

where E_0 is a constant and E_j, a liquid junction potential at the junction, test solution | 3M $NaClO_4$ in heavy water. E_j was disregarded since the concentration of the deuterium ion was maintained at less than 0.01M in the present work.[15] Therefore, the emf of the cell (A) can be denoted as follows:

$$E = E_0 + 59.15 \log d. \quad (2)$$

The total beryllium concentration in a test solution was maintained in the 2.5—10 mM range. The concentration of the deuterium ion in the cell (A) was varied by generating D^+ ions or OD^- ions by means of constant-current coulometry, using the same cell assembly as that described by Biedermann and Ciavatta.[16-18]

As an inert salt in the salt bridge, "3M $NaClO_4$ in heavy water" was used. A constant current of 6.43 mA was passed in small steps (a few microfaradays). The potentiometric titrations were conducted in both directions. First, the "forward titration" was carried out by generating OD^- ions, and then the "back titration" was performed to reacidify the hydrolyzed beryllium solution by generating D^+ ions. A steady emf was usually attained within fifteen minutes for $Z \lesssim 0.8$, while in solution with $Z > 0.8$ a steady emf was obtained within two or three hours. During the measurements, a test solution was stirred by a vigorous stream of nitrogen which had been purified by leading it through heavy water and 3M $NaClO_4$ in heavy water.

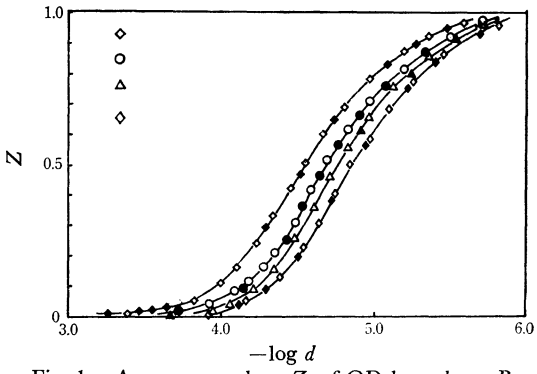

Fig. 1. Average number, Z, of OD bound per Be, as a function of $-\log d$.
Open symbols denote points from forward titrations and filled symbols from back titrations. Drawn curves were calculated with the stability constants given in Table 3.
◇ 0.008358M ○ 0.004969M
△ 0.004000M ◇ 0.002704M

Results and Calculations

The $Z(\log d)_B$ data, which were calculated from the potentiometric measurements by the use of Eq. (2), are shown graphically in Fig. 1.

The experimental data were analyzed by graphical methods and by computer calculations. The hydrolysis data were first submitted to graphical analysis in order to obtain preliminary information on the composition of the hydrolytic species formed; then, on the basis of the information obtained, computer analysis was made to evaluate the most probable hydrolysis scheme and the stability constants of the species formed.

(1) The Evaluation of the Composition of the Hydrolysis Products by Graphical Analysis. The average compositions of the hydrolysis products, $\bar{p}$ and $\bar{q}$, were calculated by the integration method described by Sillén.[19]

The average composition calculated thereby is plotted in Fig. 2 in the form of $\bar{q}$ *vs.* $(2\bar{q}-\bar{p})$.[20]

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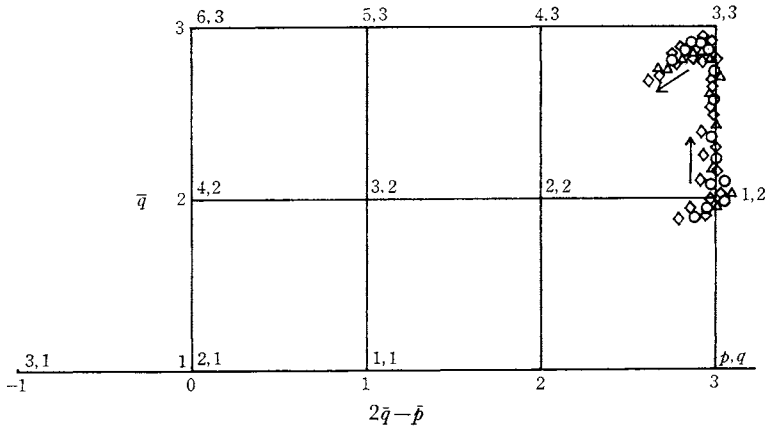

Fig. 2. Average composition of the complexes $\bar{q}(2\bar{q}-\bar{p})$. Direction of an arrow carresponds to the increase in Z. All the points are shown using the same symbols as in Fig. 1.

From this figure, some qualitative information may be obtained on the composition of the hydrolytic species. From Fig. 2, it may be seen that the (1,2) species may be present at low Z and that the (3,3) species is predominant in the main region of Z; moreover, some other minor species may be present at high Z, the composition of which would be either (2,2), (3,2), (2,1) or (3,1), judging from the directions of the plots.

(2) The Evaluation of the Composition and the Stability Constants of the Hydrolysis Products by Computer Analysis. On the basis of the restrictions suggested above, and with the help of an electronic computer (HITAC 5020) the generalized least-squares method was used to determine the most probable hydrolysis scheme containing the lowest number of species which would suffice to account for the experimental data and for the stability constants of the species formed.

The least-squares calculations on the electronic computer were carried out in order to make the error square sum $U=\sum(Z-Z_{calcd})^2$ minimum for the set of stability constants. Z_{calcd} denotes the $Z_{calcd}=\sum\sum p\beta_{p,q}b^q d^{-p}/B$ for a particular set of stability constants.

(2-1) Hydrolysis Scheme in the Lower Region of Z (When Z is less than 0.5). On the basis of the restrictions described in the section of the graphical analysis, we chose the two-species scheme of (1,2)—(3,3). The values for the stability constants of the species calculated by the generalized least-squares method are listed in Table 1, together with the error square sum. In addition, apart from the suggestion made by the graphical analysis and based upon the assumption that the minor species at low Z is less polymerized than the main species, $Be_3(OD)_3^{3+}$, we chose seven different minor species, each of which was paired with $Be_3(OD)_3^{3+}$. The results calculated are also collected in Table 1.

From the results shown in Table 1 and from the fact that the (1,2)—(3,3) scheme gives an excellent fit with the experimental data, it is evident that, at low Z, $Be_2(OD)^{3+}$ is the most probable of the minor species chosen.

(2-2) Hydrolysis Scheme in the Higher Region of Z (when Z is more than 0.5). Based on the information obtained by the graphical analysis, we chose four species, (2,2), (3,2), (2,1), and (3,1); each of them was combined with the (1,2)-(3,3) scheme, which is significant in the $Z<0.5$ region.

Table 1. The error square sums and values of the stability constants for the schemes of $Be_q(OD)_q^{(2q-p)+}$—$Be_3(OD)_3^{3+}$, where $Z\lesssim 0.5$

(p,q)	$\beta_{p,q}$	$\beta_{3,3}$	U
(1,2)	5.33×10^{-4}	4.00×10^{-10}	1.40×10^{-3}
(1,1)	6.33×10^{-3}	3.99×10^{-10}	9.90×10^{-3}
(1,3)	8.12×10^{-2}	4.32×10^{-10}	3.30×10^{-3}
(2,1)	1.09×10^{-14}	4.01×10^{-10}	9.90×10^{-3}
(2,2)	1.21×10^{-10}	4.01×10^{-10}	9.85×10^{-3}
(2,3)	8.29×10^{-6}	3.41×10^{-10}	7.36×10^{-3}
(3,1)	1.22×10^{-8}	3.99×10^{-10}	9.93×10^{-3}
(3,2)	2.27×10^{-17}	4.00×10^{-10}	9.90×10^{-3}

Table 2. The error square sums and the values of the stability constants for the schemes of $Be_2(OD)^{3+}$—$Be_3(OD)_3^{3+}$—$Be_q(OD)_q^{(2q-p)}$, where the values of the stability constants of $Be_2(OD)^{3+}$ and $Be_3(OD)_3^{3+}$ respectively are allowed to vary

(p,q)	$\beta_{1,2}\times10^4$	$\beta_{3,3}\times10^{10}$	$\beta_{p,q}$	U
(2,2)	4.70	4.13	3.71×10^{-10}	7.90×10^{-3}
(3,2)	5.57	3.98	9.98×10^{-15}	2.46×10^{-3}
(2,1)	5.30	3.98	1.28×10^{-12}	2.40×10^{-3}
(3,1)	4.69	4.07	1.04×10^{-18}	3.31×10^{-3}

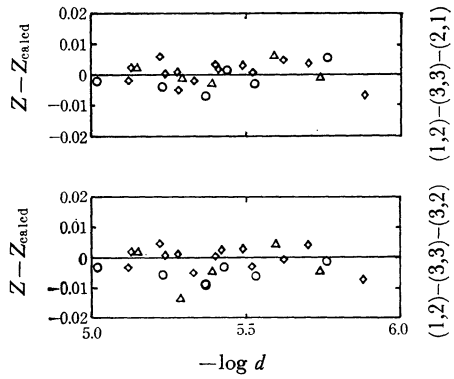

Fig. 3. $(Z-Z_{calcd})$ as a function of $-\log d$ for $Z>0.7$. Symbols are the same as those in Fig. 1.

The values of the stability constants for each set of the three-species schemes were allowed to vary, and the corresponding error-square sums were calculated over the whole range of Z.

The results calculated thereby are listed in Table 2, together with the stability constants of the species. Table 2 shows that the scheme containing the (2,1) species gives rise to the least-error square sum of the schemes chosen, and that the scheme containing the (3,2) species gives rise to the second least-error square sum. Figure 3 shows that the systematic deviations from the experimental data for $Z>0.7$ are slightly less for the scheme containing the (2,1) species than for the scheme containing the (3,2) species.

From the above evidence, it seems reasonable

TABLE 3. THE VALUES FOR THE STABILITY CONSTANTS OF THE HYDROLYSIS SPECIES OF BERYLLIUM ION IN HEAVY WATER AND IN LIGHT WATER CONTAINING 3M $NaClO_4$ AS AN IONIC MEDIUM*

	in heavy water	in light water
$-\log \beta_{1,2}$	3.28 ±0.04	3.16 ±0.05
$-\log \beta_{3,3}$	9.399±0.007	8.662±0.007
$-\log \beta_{2,1}$	11.89 ±0.07	11.16 ±0.06

* The uncertainties of the constants were estimated by multiplying by three the standard deviations.

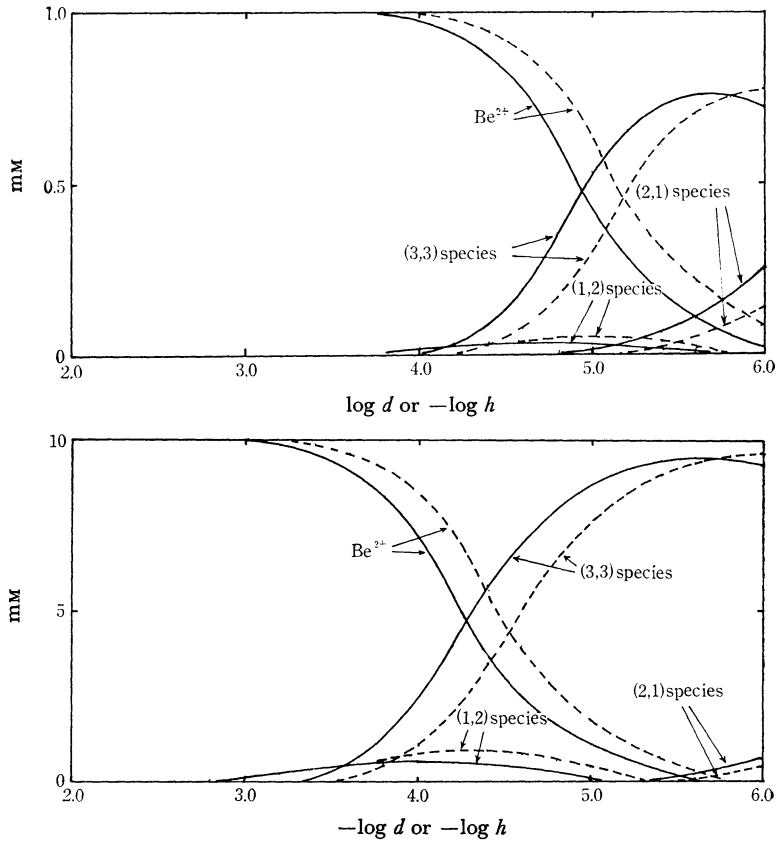

Fig. 4. The calculated distribution of the hydrolytic species in heavy water and in light water at total beryllium concentrations and 1 and 10 mM. Dashed curves represent the distribution of the species in heavy water and full curves the distribution of the species in light water.

to prefer $Be(OD)_2$ as the third species that exists at higher Z values.

The above considerations lead to the conclusion that the data in heavy water can be explained on the basis of the $Be_2(OD)^{3+}$-$Be_3(OD)_3^{3+}$-$Be(OD)_2$ scheme within the limits of accuracy of the present experiments.

The final values for the stability constants are tabulated in Table 3, together with the results we have obtained in light water employing the same method as that used for the heavy-water system.

(3) Distribution of the Species. The distribution of the hydrolytic species in heavy water and in light water, calculated at the total beryllium concentrations of 1 mM and 10 mM, and assuming the values of the stability constants in Table 3, are represented in Fig. 4. There is a general tendency for the species to be less hydrolyzed in heavy water than in light water at a given pH. The dominance of the (3,3) species in the accessible pH region is apparent both in heavy water and in light water. The amount of the (1,2) species increases and the amount of the (2,1) species decreases with an increase in the total concentration of beryllium.

Conclusion

In the present work, it has been found that the compositions of the species formed in heavy water, *i. e.*, $Be_2(OD)^{3+}$, $Be_3(OD)_3^{3+}$, and $Be(OD)_2$, are the same as those in light water, while the values of the stability constants of the hydrolysis products in heavy water are smaller than those in light water.

The fact that the values for the stability constants of the hydrolysis products of the beryllium ion, which can be regarded as a weak acid, are smaller in heavy water than in light water has been seen to be consistent with the results for the dissociation of the weak acids[21] and with those for the mononuclear hydrolytic reactions of the metal ions.[1-3]

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