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Effect of the Deuterium Atom Fraction on the Stability Constant of the Main Hydrolysis Product of the Beryllium Ion

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It has been confirmed by several investigators that $Be_3(OH)_3^{3+}$ is the main hydrolysis product of the beryllium ion.

The present work was carried out in order to examine the variation in the stability constant of the main hydrolysis species with a variation in the deuterium atom fraction.

First, the composition and the stability constant of the main hydrolysis species were evaluated in 20% and 80% heavy water; next, the variation in the stability constant of the main species with a variation in the deuterium atom fraction(0—0.8) was studied.

Symbols

B total concentration of beryllium
L total excess concentration of lyonium ions*
l total concentration of free lyonium ions
Z average number of lyonium ions split off per beryllium
$\bar{p}$ and $\bar{q}$ average number of OL groups and beryllium atoms respectively in hydrolyzed species
$\beta_{3,3}$ stability constant of the following reaction:

$$3\,Be^{2+}+3\,L_2O=Be_3(OL)_3^{3+}+3\,L^+$$

* Besides, L will be used throughout to mean both H and D.

Experimental

All the reagents used were prepared and analyzed by procedures similar to those described in Ref. 1 and Ref. 2.

Heavy water was redistilled from an alkaline permanganate solution.

A Wilhelm-type half cell[3] was used for the emf measurements.

Glass electrodes of the Beckman type No. 40498 were used in combination with **a Radiometer PHM-4C(Copenhagen)**.

Silver - silver chloride electrodes were used as references.

Procedures. The hydrolysis was investigated by measurements of the total concentration of free lyonium ions using a glass electrode. $NaClO_4$ was added to all the test solutions so that they contained 3M ClO_4^-. The lyonium ion concentration was measured by the use of the cell assembly described in Ref. 3.

It was proved experimentally that the emf of the cell could be denoted as follows:

$$E = E_0 + 59.15 \log l + E_j \text{ (at 25°C)} \qquad (1)$$

where E_0 is a constant, and E_j a liquid junction potential, which was found to be approximated by $E_j=-13\,l$ for the system of 20% heavy water and by $-8\,l$ for the system of 80% heavy water.

In the present work, two kinds of experiments were carried out.

The first were "constant B titrations," the experimental details of which were similar to those presented in Ref. 1.

The second were "constant B and Z titrations," where B was maintained at 20 mM and 40 mM and where Z was adjusted to around 0.5, while only the deuterium atom fraction was varied from 0 to 0.8.

All the measurements were made in a paraffin-oil thermostat kept at 25.00±0.01°C in a room kept by a thermostat at 25±1°C.

Results and Discussion

(1) The Composition and the Stability

1) H. Kakihana and L. G. Sillén, *Acta Chem. Scand.*, **10**, 985 (1956).
2) H. Ohtaki, *Inorg. Chem.*, **6**, 808 (1967).
3) W. Forsling, S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, **6**, 901 (1952).

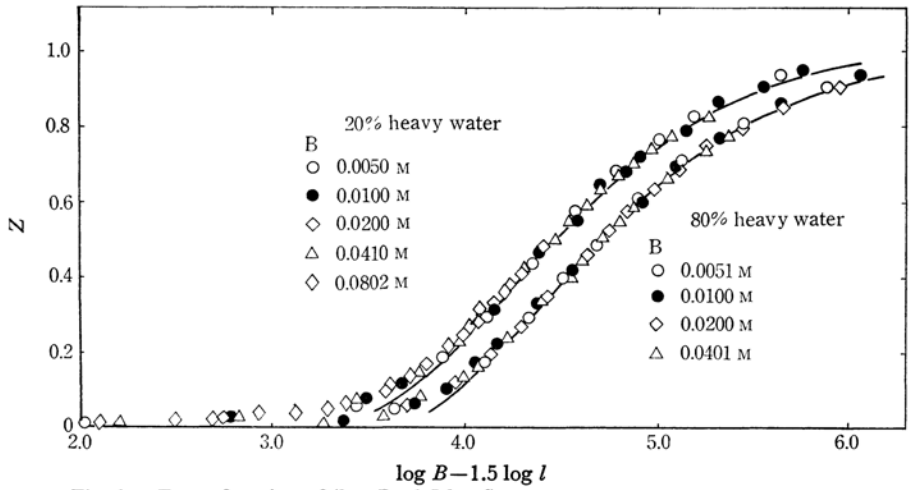

Fig. 1. Z as a function of $(\log B - 1.5 \log l)$.
The drawn curves for the system of 20% heavy water and 80% heavy water were calculated for $-\log \beta_{3,3}=8.75$ and 9.28 respectively.

Constant of the Main Species in 20% Heavy Water and 80% Heavy Water. From the $Z(\log l)_B$ data which were calculated from the potentiometric measurements by the use of Eq.(1), the composition of the hydrolysis species was estimated by the integration method presented by Sillén.[4]

A plot of $\bar{q}$ *vs.* $(2\bar{q}-\bar{p})$[5] suggested the presence of the (3,3) species as the main one in the region of $0.2<Z<0.8$. From this evidence, it may be said that the composition of the main species in H_2O-D_2O mixed solvents is the same as that in light water.

The values of the stability constant of the (3,3) species were calculated by the curve-fitting method described in Ref. 2.

If only the (3,3) species is present in appreciable amounts, the following equation can be derived:

$$\log X = 1/2 \log Z - 3/2 \log(1-Z)$$
$$= 1/2 \log 3 + 1/2 \log \beta_{3,3} + \log B - 3/2 \log l \quad (2)$$

A plot of Z as a function of $(\log B - 3/2 \log l)$ should lie on a single curve, independent of B; the experimental plots are shown in Fig. 1. The experimental plots in Fig. 1 can be fitted with a normalized curve of Z *vs.* $\log X$.

The values of the stability constant for the system of 20% and 80% heavy water were found to be $-\log \beta_{3,3}=8.75\pm0.05$ and 9.28 ± 0.05 respectively.

(2) The Variation in the Stability Constant of the Main Species with the Deuterium Atom Fraction from 0 to 0.8. The differentiation of

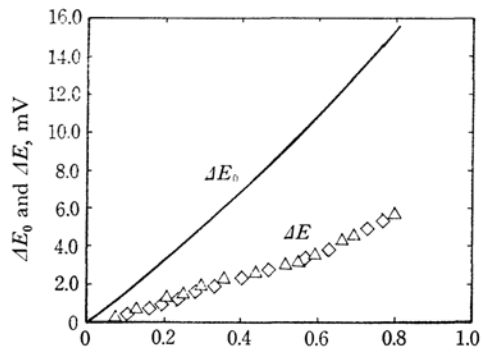

Fig. 2. The plots of ΔE_0 and ΔE *vs.* deuterium atom fraction.
△ $B=0.040$M, $Z=0.499$
◇ $B=0.020$M, $Z=0.516$

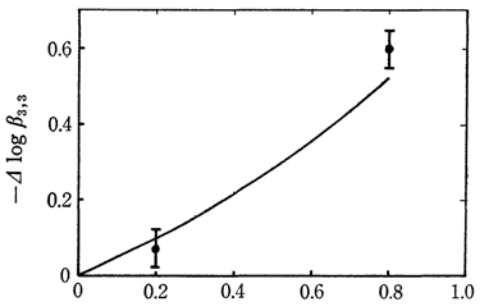

Fig. 3. The change in the stability constant with varying deuterium atom fraction.
The symbol ⊕ denotes the values calculated from Fig. 1.
The value of the stability constant of the (3,3) species in light water was assumed to be $-\log \beta_{3,3}=8.68$, which was obtained by the authors.

4) L. G. Sillén, *ibid.*, **15**, 1981 (1961).
5) H. S. Dunsmore, S. Hietanen and L. G. Sillén *ibid.*, **17**, 2644 (1963).

Eq. (2) with respect to the deuterium atom fraction at constant B and Z values give the following equation:

$$\partial \log \beta_{3,3} = 3\, \partial \log l \qquad (3)$$

The variation in the stability constant can be calculated by the use of Eq. (3) if the change in l with the deuterium atom fraction is measured.

The variation in E_0, ΔE_0, with the deuterium atom fraction is graphed in Fig. 2. The change in E, ΔE, with a variation in the deuterium atom fraction at constant B and Z values is also shown in Fig. 2. The variation in the stability constant, $\Delta \log \beta_{3,3}$ was evaluated from Fig. 2 by the use of Eq. (3), which is shown graphically in Fig. 2.

From the above results, it may be said that the value of the stability constant of the (3,3) species decreases gradually with an increase in the deuterium atom fraction.