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# The Hydrolysis of the Copper(II) Ion in Heavy Water[*1]

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The hydrolysis equilibria of the copper(II) ion in heavy water have been studied at 25°C by measuring the deuterium-ion concentration by means of a commercial glass electrode. The total copper(II) concentration was varied between 50 and 90 mM, while the concentration of the perchlorate ion was held constant at 3M by the addition of $NaClO_4$. A hydrolyzed copper(II) perchlorate solution was gradually acidified up to the point where hydrolysis was negligible by the use of constant-current coulometry. The experimental data, which indicate a slight hydrolysis in the $\log d$ range from $-4.0$ to $-5.26$, can be explained by assuming these equilibria;

$$Cu^{2+} + D_2O = CuOD^+ + D^+, \log \beta_{1,1} = -7.71 \pm 0.07;$$

$$2Cu^{2+} + 2D_2O = Cu_2(OD)_2{}^{2+} + 2D^+, \log \beta_{2,2} = -11.46 \pm 0.04.$$

It has been found that the hydrolytic reactions of metal ions in heavy water can be studied with the same accuracy as in light water.[1] We have previously reported on our studies of the hydrolysis of the beryllium ion and the uranyl ion in heavy water.[2–4]

The present work was carried out in order to obtain information on the hydrolysis species of the copper(II) ion in heavy water and to estimate their stability constants.

The hydrolysis equilibria of the copper(II) ion in light water have been studied by a number of investigators,[5–9] using glass electrodes. It has been concluded that the main product is the binuclear complex, $Cu_2(OH)_2{}^{2+}$, but the minor one is not yet precisely known.

## Symbols

| | |
|---|---|
| $B$ | total concentration of copper(II) |
| $b$ | concentration of free copper ions |
| $D$ | analytical excess of deuterium ions$=[ClO_4{}^-]-2B-[Na^+]$ |
| $d$ | concentration of free deuterium ions |
| $h$ | concentration of free hydrogen ions |
| $Z$ | average number of deuterium ions set free per copper atom |
| $p$ | number of OD groups bound to hydrolyzed species |
| $q$ | number of Cu groups present in hydrolyzed species |
| $\beta_{p,q}$ | stability constant of the following reaction: $q\,Cu^{2+} + p\,D_2O = Cu_q(OD)_p{}^{(2q-p)+} + p\,D^+$ |
| $v$ | number of $\mu$F passed through the test solution |
| $E$ | emf |
| $v$ | volume of a test solution, m$l$ |
| [ ] | concentration of the relevant species |

## Experimental

**Reagents and Analysis.** *The reagents used* were, unless otherwise stated, prepared and analyzed as has

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[*1] Ionic Equilibria in Heavy Water (Part 5).

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1) H. Kakihana, M. Maeda and T. Amaya, This Bulletin, **43**, 1377 (1970).

2) H. Kakihana and M. Maeda, *ibid.*, **42**, 1458 (1969).

3) H. Kakihana and M. Maeda, *ibid.*, **43**, 109 (1970).

4) H. Kakihana and M. Maeda, *ibid.*, **43**, 1097 (1970).

5) H. Hagisawa, *Rikagaku Kenkyusho Iho*, **18**, 275 (1939).

6) K. J. Pedersen, *Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd.*, **20** (7), 1 (1943).

7) C. B. Biedermann, *Arkiv Kemi*, **9**, 175 (1956).

8) D. D. Perrin, *J. Chem. Soc.*, **1960**, 3189.

9) H. Ohtaki, *Inorg. Chem.*, **7**, 1205 (1968).

been described in Ref. 2.

*The copper(II) perchlorate solution* was prepared by dissolving copper(II) oxide of a commercial *p. a.* reagent in an excess of hot $HClO_4$ (*p. a* 70%) and by then recrystallizing it twice. The $H_2O$ was expelled by evaporating the solution under an infrared lamp until crystals had formed, whereupon $D_2O$ was added. No chloride or sulfate ions could be detected in the stock solution. The copper content of the stock solutions was measured by electrodeposition,[10] and the total perchlorate concentration was determined by neutralization after passing a definite amount of the solution through a column of the cation exchange resin, Dowex 50W-12, of the $H^+$ form.

**Apparatus.** All the apparatuses used were the same as those described in Ref. 3.

**Procedures.** Earlier investigations[7,9] have indicated that the hydrolysis becomes appreciable at $\log h < -4.0$, and that only a small part of $Cu^{2+}$ can be transformed to hydrolysis products before precipitation starts. Under such conditions, it is imperative to avoid contamination of the solutions to be studied by foreign protolytes. Furthermore, it has been pointed out that copper hydroxide precipitates slowly with a small excess of alkali.[7]

In the present work, in order to avoid contamination by foreign protolytes and the formation of any precipitates during titration, a "*back titration*" technique[9,11,12] was employed: a test solution saturated with copper(II)-hydrolyzed products was prepared and acidified by generating $D^+$ ions coulometrically.

The saturated solutions were prepared by employing apparatuses similar to those described in Refs. 9 and 12. A copper(II) perchlorate solution containing 3M $ClO_4^-$ was put into a vessel. Then a NaOD solution prepared by the electrolysis of a 3M $NaClO_4$ solution was added until pale blue precipitates of copper(II) hydroxides were formed. The solution was stirred at least 40 hr by the use of a magnetic stirrer and filtered through G4 glass filters into a flask.

The turbidity was examined for several months with an aliquot of the filtered solution, but no suspended particles could be detected. Another portion was used for potentiometric titration.

All the preparations were carried out under a nitrogen atmosphere. Nitrogen gas was presaturated by passing it through $D_2O$ and $NaClO_4$ in $D_2O$.

**Emf Measurements.** The general composition of a test solution is written as: *B*M Cu(II), *D*M $D^+$, $(3-2B-D)$M $Na^+$, 3M $ClO_4^-$, where *D* may be negative. For each titration, a definite volume of the test solution (*v* m*l*) was taken and the value of *D* was increased in a step-by-step fashion by constant-current coulometry, using the cell assembly reported as in Refs. 3 and 13.

After $\nu\mu F$ have been passed through the test solution, *D* is equal to:[13]

$$D = D_0 + (\nu/v) \times 10^{-3} \qquad (1)$$

where $D_0$ is the analytical excess of the deuterium-ion concentration in the starting test solution.

The deuterium ion concentration, *d*, was measured by the use of the cell assembly described in Ref. 3.

The emf of the cell may be written as follows:[1]

$$E = E_0 + 59.15 \log d \text{ (at 25°C)} \qquad (2)$$

where $E_0$ is the constant which includes the standard potential for the glass electrode and the term for the activity factor of the $D^+$ ion.

Each of the potentiometric titrations may be divided into two parts. In the first part, $D_0$ and $E_0$ were determined by measuring the emf in the region where $\log d > -3.5$; they were calculated by means of the Gran plot,[14] $10^{E/59.15}$ *vs.* $\nu$. In the second part, measurements were made at $\log d < -3.5$, where the hydrolysis becomes appreciable. Then $Z = (d-D)/B$, the average number of OD groups bound per copper atom, was calculated by the use of Eqs. (1) and (2).

All the emf measurements were carried out at 25.00±0.01°C in a paraffin oil thermostat, and the test solution was stirred by nitrogen gas presaturated by passing it through $D_2O$ and $NaClO_4$ in $D_2O$.

## Results and Calculations

The $Z(\log d)_B$ data are shown graphically in Fig. 1. The experimental data were analyzed by the graphical method. At first, the analysis was made in order to obtain information on the composition of the hydrolysis species and the approximate stability constants, then, on the basis of the

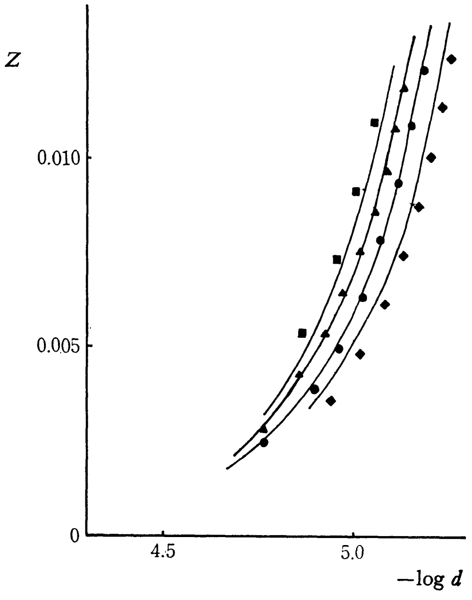

Fig. 1. Average number, *Z*, of OD bound per Cu, as a function of −log *d*. Drawn curves were calculated with the stability constants given in Table 1.

*B*

■ 90.58 mM ▲ 76.20

● 62.12 ◆ 47.65

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[10] E. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. 2, John Wiley & Sons, New York (1955), p. 156.

[11] G. Biedermann and S. Hietanen, *Acta Chem. Scand.*, **14**, 711 (1960).

[12] G. Biedermann and L. Ciavatta, *ibid.*, **16**, 2221 (1962).

[13] L. Ciavatta, *Arkiv Kemi*, **20**, 417 (1962).

[14] G. Gran, *Analyst*, **77**, 661 (1952).

information thus obtained, the accurate stability constants were determined.

**1) The Evaluation of the Composition of the Hydrolysis Species.** When we take into account the fact that, in test solutions, the maximal value of $Z$ never exceeds 0.015, then, without introducing any appreciable error, we may simplify the preliminary calculations by using the approximation:

$$[\mathrm{Cu}^{2+}] = b \cong B = \text{constant}. \tag{3}$$

The concentration of the deuterium ions set free by hydrolysis, $BZ$, is expressed by the equation:

$$BZ = \sum_p\sum_q p\,[\mathrm{Cu}_q(\mathrm{OD})_p{}^{(2q-p)+}] = \sum_p\sum_q p\,\beta_{p,q}b^q d^{-p}. \tag{4}$$

Using Eq. (3), Eq. (4) can be written:

$$Zd = \sum_p\sum_q p\,B^{q-1}\beta_{p,q}d^{-(p-1)} = \sum_p p\,d^{-(p-1)}K_p. \tag{5}$$

where:

$$K_p = \sum_q B^{q-1}\beta_{p,q}. \tag{6}$$

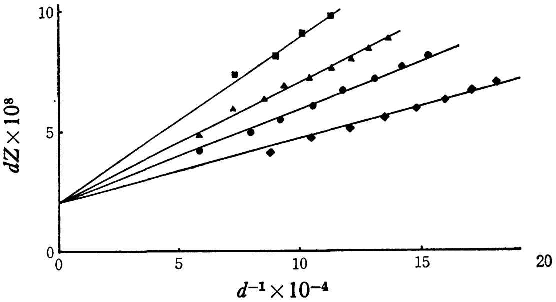

Fig. 2. $dZ$ as a function of $d^{-1}$ (see Eq. (5)). The straight lines are given by the stability constants; log $\beta_{1,1}$=−7.69 and log $\beta_{2,2}$=−11.47.

*B*
■ 90.58 mM ▲ 76.20
● 62.12 ◆ 41.65

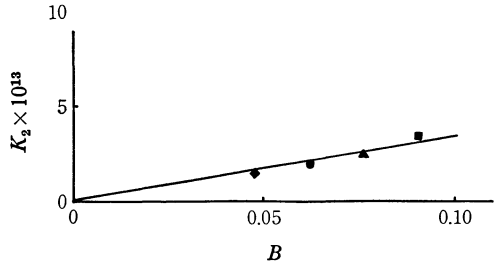

Fig. 3. $K_2$ as a function of $B$ (Eq. (6)). The straight line represents the equation $K_2$=3.42×$10^{-12}B$.

*B*
■ 0.09058 M ▲ 0.07620
● 0.06212 ◆ 0.04765

In order to find the prevailing values of $p$, plots of $Zd$ against $d^{-1}$ were constructed;[9] they are shown in Fig. 2. The plots closely approximate a set of straight lines with a common intercept. This result indicates that the prevailing values of $p$ are 1 and 2.

Next, to determine the values of $q$, the data were compared at different values of $B$. The common intercept, $K_1=\sum_q B^{q-1}\ \beta_{1,q}$, of the previous plots shows that one of the prevailing values of $q$ is 1. The other values were obtained from their slopes. The slope of the line is represented as $2K_2=2(\beta_{2,1}+B\beta_{2,2}+\cdots)$ at each value of $B$. Figure 3 shows a plot of these $K_2$ values against $B$, which gives a straight line passing through the point of

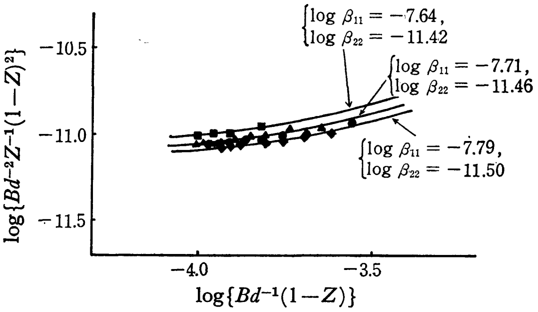

Fig. 4. −log $\alpha$ as a function of −log $\omega$, see Eq. (9). The curves were calculated with the log $\beta_{1,1}$ and log $\beta_{2,2}$ values given in the figure.

*B*
■ 90.58 mM ▲ 76.20
● 62.12 ◆ 47.65

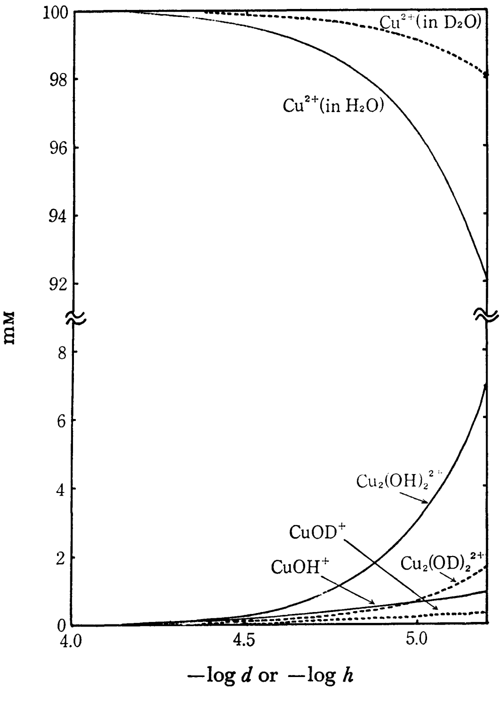

Fig. 5. The calculated distribution of the hydrolytic species in heavy water and in light water at total copper(II) concentrations of 100 mM. Dotted curves represent the distribution of the species in heavy water and full curves in light water.

origin. This indicates that another value of $q$ is 2.

From the results, it can be concluded that the compositions of the hydrolysis species of the copper(II) ion are $CuOD^+$ and $Cu_2(OD)_2^{2+}$, and the approximate stability constants can be estimated to be $\log \beta_{1,1} = -7.69$ and $\log \beta_{2,2} = -11.47$.

**2) The Evaluation of the Stability Constants of the Hydrolysis Species.** The above analysis involved some approximation. It is, therefore, desirable to compare the data directly with the normalized function similar to that described in Ref. 15. We start from the fundamental equations:

$$Z = (\beta_{1,1}d^{-1}+2\beta_{2,2}bd^{-2})/(1+\beta_{1,1}d^{-1}+2\beta_{2,2}bd^{-2}) \tag{7}$$

$$B = b(1+\beta_{1,1}d^{-1}+2\beta_{2,2}bd^{-2}). \tag{8}$$

From Eqs. (7) and (8), and by eliminating $b=B\times(1-Z)$, the following equation is obtained:

$$\begin{aligned}\alpha &= Zd^2B^{-1}(1-Z)^{-2} = \beta_{2,2}(2+\beta_{1,1}\beta_{2,2}^{-1}dB^{-1}(1-Z)^{-1}) \\ &= \beta_{2,2}(2+\beta_{1,1}\beta_{2,2}^{-1}\omega)\end{aligned} \tag{9}$$

If we set $\alpha_1=\alpha\beta_{2,2}^{-1}$ and $\omega_1=\omega\beta_{1,1}\beta_{2,2}^{-1}$, Eq. (9) may be compared with the normalized function:

$$\log \alpha_1 = \log (2+\omega_1). \tag{10}$$

A plot of the $\log \{Bd^{-2}Z^{-1}(1-Z)^2\}$ against $\log \{Bd^{-1}(1-Z)\}$, which will be independent of $B$, can be fitted to a plot of $\alpha_1$ against $\log (2+\omega_1)$ at the particular values of $\beta_{1,1}$ and $\beta_{2,2}$. As shown in Fig. 4, we can obtain the following values:

$$-\log \beta_{1,1} = 7.71 \pm 0.07 \text{ and } -\log \beta_{2,2} = 11.46 \pm 0.04$$

These values are listed in Table 1, together with the values obtained by us in light water.

TABLE 1. THE VALUES FOR THE STABILITY CONSTANTS OF THE HYDROLYSIS SPECIES OF COPPER(II) ION IN HEAVY WATER AND IN LIGHT WATER CONTAINING 3M $NaClO_4$ AS AN IONIC MEDIUM

| | in heavy water | in light water |
|---|---|---|
| $\log \beta_{1,1}$ | $-7.71\pm0.07$ | $-7.22\pm0.03$ |
| $\log \beta_{2,2}$ | $-11.46\pm0.04$ | $-10.75\pm0.02$ |

**3) Distribution of the Species.** The distribution of the hydrolysis species in heavy water and in light water, calculated at the total copper(II) concentration of 100 mM and assuming the values of the stability constants obtained by us, is shown in Fig. 5.

As has been mentioned earlier,[3,4] the species are less hydrolyzed in heavy water than in light water.

A more detailed discussion must be postponed until other hydrolytic reactions of metal ions have been investigated.

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[15] G. Biedermann, N. C. Li and J. Yu, *Acta Chem. Scand.*, **15**, 555 (1961).