BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1735—1738 (1972)

Ionic Equilibria in Mixed Solvents. VII. Hydrolysis of Copper(II) Ion in Dioxane-Water Mixtures containing 3 M (Li)ClO$_4$ as an Ionic Medium

Hitoshi Ohtaki and Takayoshi Kawai

Department of Electrochemistry, Tokyo Institute of Technology, O-okayama, Meguro, Tokyo

(Received October 2, 1971)

The hydrolytic reactions of copper(II) ion were studied at 25°C in water, in 0.1 and 0.5 mole fraction dioxane-water mixtures, each containing 3 M (Li)ClO$_4$ as an ionic medium. Emf measurements were carried out in the range of the total copper(II) concentration of 0.01125—0.07106 M (in water), 0.01548—0.1356 M (in the 0.1 mole fraction dioxane-water mixture), and 0.02257—0.1231 M (in the 0.5 mole fraction dioxane-water mixture), respectively. Species formed and their formation constants determined (log $^*\beta_{p,q}$) are: CuOH (-7.54 ± 0.02), Cu$_2$OH (-6.22 ± 0.02), Cu$_2$(OH)$_2$ (-11.12 ± 0.05), and Cu$_3$(OH)$_2$ (-10.36 ± 0.05) in water; CuOH (-7.44 ± 0.02), Cu$_2$OH (-6.22 ± 0.02), Cu$_2$(OH)$_2$ (-11.35 ± 0.05), and Cu$_3$(OH)$_2$ (-10.12 ± 0.08) in the 0.1 mole fraction dioxane-water mixture; CuOH (-7.74 ± 0.02), and Cu$_2$OH (-6.40 ± 0.02) in the 0.5 mole fraction dioxane-water mixture.

From the hydrolytic reaction of beryllium ion in dioxane-water mixtures, Ohtaki and Kato[1,2] found that the composition and formation constants of hydrolyzed species of beryllium ions change little even though the dioxane concentration is varied from zero to 0.2 mole fraction (55.01 wt%). Thus, dissociation constants of aquated metal ions, which are weak acids, vary in different manner from those of carboxylic acids[3,4] and of ammonium ions[5,6].

In the present work, the hydrolytic reaction of copper(II) ion was studied by emf measurements in water, in 0.1 and 0.5 mole fraction dioxane-water mixtures, and the chemical species formed and their formation constants were determined.

If we neglect solvated solvent molecules and electric charges of the species for the sake of simplification, the hydrolytic reaction of copper(II) ions can be written as follows, no association of perchlorate ions with any species being assumed;

$$\begin{aligned} q\text{Cu} + p\text{H}_2\text{O} &= \text{Cu}_q(\text{OH})_p + p\text{H} \\ ^*\beta_{p,q} &= [\text{Cu}_q(\text{OH})_p][\text{H}]^p/[\text{Cu}]^q \end{aligned} \tag{1}$$

h	Hydrogen ion concentration in equilibrium.
H	Analytical excess of hydrogen ion concentration $=[\text{ClO}_4]=2B=[\text{Li}]$.
B	Total concentration of copper(II) ion.
b	Concentration of free copper(II) ion.
Z	Average number of hydrogen ions set free per copper ion$=(h-H)/B$.
p	Number of hydroxyl groups bound to hydrolyzed species.
q	Number of copper atoms present in hydrolyzed species.
$^*\beta_{p,q}$	Equilibrium constant for the formation of Cu$_q$(OH)$_p$.
E	Emf.
[ ]	Concentration.

The Method of Measurements. B was kept constant during the course of potentiometric titration. Lithium perchlorate was used as an ionic medium in order to keep the total ionic equivalent concentration constant (3 M). Potentiometric titrations were carried out by the following two methods.

1) Water and the 0.1 mole fraction dioxane-water mixture. Ordinary titration method was employed for the cases of water and the 0.1 mole fraction dioxane-water mixture. Thus a titrant was added from a buret to a test solution prepared as follows. Copper(II) perchlorate solution was neutralized with an alkaline solution prepared by electrolysis, until a certain amount of copper hydroxide was precipitated. The turbid solution was bubbled for several days with nitrogen gas which was presaturated with solvent vapor. The solution was then filtered through G3 and G4 glas filters covered with platinum powder, a clear test solution being obtained. The total concentration of copper(II) ion in this solution was determined by means of gravimetry with salicylaldoxime.[7] An acidic titrant with the same concentration of copper(II) ion as that of the test solution was added. The composition of the titrant was B M of Cu(ClO$_4$)$_2$, H_0 M of HClO$_4$ and ($3-2B-H_0$) M of LiClO$_4$.

2) In a system of a 0.5 mole fraction dioxane-water mixture, hydrogen ions were generated coulometrically, because solubility of copper hydroxo complexes was so low that a fairly small amount of hydrogen ions had to be added for carrying out measurements and the solution was so viscous that addition of a titrant from a buret gave rise to erroneous results. The electric circuit for coulometry was as follows.

(−) Pt	0.10 M AgClO$_4$ 2.90 M LiClO$_4$ in water	3 M LiClO$_4$ in water	3 M LiClO$_4$ in mixture	Test soln	Pt (+)

Neither precipitation nor turbidity was observed during the course of experiments. A constant emf was obtained within 10 min after addition of a titrant, and remained unchanged for at least 5 hours within the accuracy 0.1 mV.

---

[1] H. Ohtaki, *Inorg. Chem.*, **6**, 808 (1967).

[2] H. Ohtaki and H. Kato, *ibid.*, **6**, 1935 (1967).

[3] T. Shedrovsky and R. L. Kay, *J. Phys. Chem.*, **60**, 151 (1956).

[4] H. S. Dunsmore and J. C. Speakmann, *Trans. Faraday Soc.*, **50**, 236 (1954).

[5] A. K. Covington and M. J. Tait, *Disscuss. Faraday Soc.*, **39**, 176 (1956).

[6] M. H. Miles and E. M. Eyring, *J. Phys. Chem.*, **69**, 467 (1965).

[7] F. J. Welcher, "Organic Anayltical Reagents," Vol. III. 2nd ed. D. Van Nostrand C., Inc., New York, N. Y. (1947), p. 262.

The hydrogen ion concentration was determined by means of the cell

Ref | Test Solution | GE, (A)

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

3.000 M $LiClO_4$ in mixture	2.990 M $LiClO_4$ 0.010 M $AgClO_4$ in water	AgCl-Ag

(B)

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

$$E = E_0' + 59.15 \log h + 59.15 \log f_H + E_j(h, B), \qquad (2)$$

where E_0' is a constant and f_H represents the activity coefficient of hydrogen ion. The standard state is so defined that f_H as well as the activity coefficients of the reacting species tends to unity as the composition approaches 3 M $LiClO_4$ in a given solvent. $E_j(h, B)$ denotes the liquid junction potential at the junction, test solution | 3 M $LiClO_4$ aqueous solution. The liquid junction potential at the other junction, 3 M $LiClO_4$ in the aqueous or mixed solvent | 2.99 M $LiClO_4$, 0.01 M $AgClO_4$ aqueous solution, can be assumed to be constant throughout the course of titration.

In such a case where the total ionic concentration B, and the solvent composition are kept constant, constancy of f_H can be assumed in the course of a series of potentiometric measurements. When h is small and the total copper ion concentration is kept $E_j(h, B)$ can be a constant and Eq. (2) may be written as follows[2].

$$E = E_0 + 59.15 \log h \qquad (3)$$

where

$$E_0 = E_0' + 59.15 \log f_H + E_j(h, B)$$

This was used to determine the hydrogen ion concentration from emf data.

Experimental

Reagents and Analysis. *Copper(II) perchlorate*: Reagent grade copper(II) nitrate recrystallized twice from water was heated under an infrared lamp until no evolution of NO_2 gas could be recognized, and then in an electric oven for 1 day at 800°C. The copper(II) oxide thus prepared was dissolved in a hot perchloric acid solution and then filtered. Copper(II) perchlorate crystals were obtained by recrystallization. The stock solution of copper perchlorate was prepared by dissolving the crystals in water. pH of the solution was about 2. The acid concentration in the stock solution was determined in the following way. An aliquot (about 50 m*l*) of aqueous 3 M $LiClO_4$ solution containing about 10^{-3} M $HClO_4$ was gradually neutralized coulometrically. As the volume change is negligible during the course of coulometric titration, the end point was located by plotting $10^{E/59.15}$ against microfaradays passed (Gran plot[8]). A small and known amount of the stock solution of copper(II) perchlorate was then added to the vessel from a weighing buret and the solution was gradually acidified by means of a coulometric generation of hydrogen ions. The amount of acid present in the solution could be estimated from a similar plot of $10^{E/59.15}$ *vs.* microfaradays.

The total perchloric acid concentration determined by the ion exchange method agreed satisfactorily with the sum of equivalent concentrations of copper(II) and hydrogen ions in the solution.

Lithium perchlorate was prepared by the method described by Biedermann and Ciavatta.[9]

Dioxane was purified by the method described elsewhere.[1]

Apparatus. *Glass electrode and pH meter*: Beckman No. 40498 glass electrodes were used in combination with Radiometer PHM-4d pH meter (Copenhagen).

The Wilhelm-type of the half-cell described by Forsling, Hietanen, and Sillén[10] was used for emf measurements.

A coulometric analyzer (Leeds & Northrup Co., Philadelphia, Pa.) was employed as a current power source. Constant currents of 0.643 and 6.43 mA were used; the currents were held constant within ±0.05 and ±0.1%, respectively. Emf measurements were carried out at 25.00±0.01°C in a paraffin oil thermostat in a room thermostated at 25±1°C.

Results

Values of Z and $-\log h$ in each series of B calculated from the emf data are represented graphically in Figs. 1, 2, and 3. The compositions and the formation constants of the species were evaluated on the basis of the data.

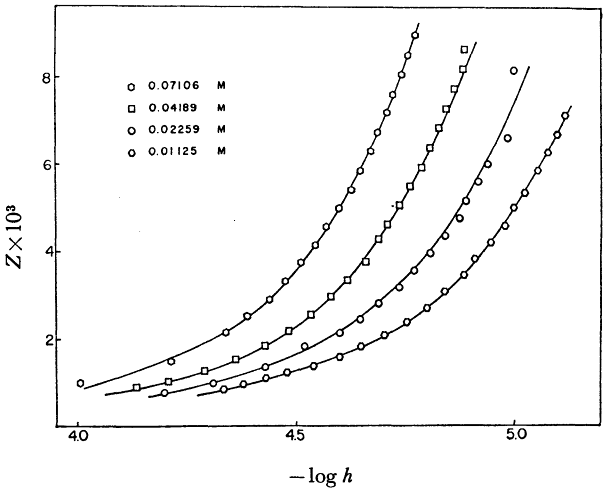

Fig. 1. Values of Z *vs.* $-\log h$ in the aqueous solution. Solid lines show calculated curves of Z with formation constants of $\log {}^*\beta_{1,1} = -7.54$, $\log {}^*\beta_{1,2} = -6.22$, $\log {}^*\beta_{2,2} = -11.12$ and $\log {}^*\beta_{2,3} = -10.36$.

The concentration of hydrogen ion set free by hydrolysis BZ is given by the general formula

$$BZ = \sum_p \sum_q p[Cu_q(OH)_p] = \sum_p \sum_q p {}^*\beta_{p,q} b^q h^{-p} \qquad (4)$$

In the case where maximum value of Z is very low, we can, without introducing any appreciable error, simplify the preliminary calculations by employing the approximation

$$[Cu^{2+}] = b \approx B \qquad (5)$$

Applying the approximation to Eq. (4) and rearrang-

---

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

[9] C. Berecki-Biedermann, *Ark. Kemi*, **9**, 175 (1955).

[10] W. Forsling, S. Hietanen, and G. Sillén, *Acta Chem. Scand.*, **6**, 901 (1952).

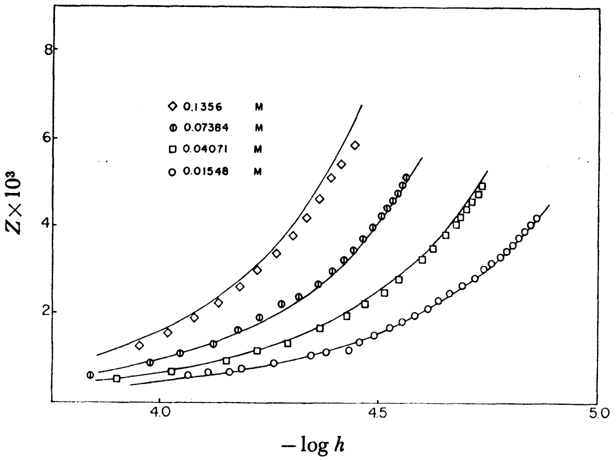

Fig. 2. Values of Z *vs.* $-\log h$ in the solution of a 0.1 mole fraction dioxane-water mixture. Solid lines show calculated curves of Z with formation constants of $\log {}^*\beta_{1,1}=-7.44$, $\log {}^*\beta_{1,2}=-6.22$, $\log {}^*\beta_{2,2}=-11.35$, and $\log {}^*\beta_{2,3}=-10.12$.

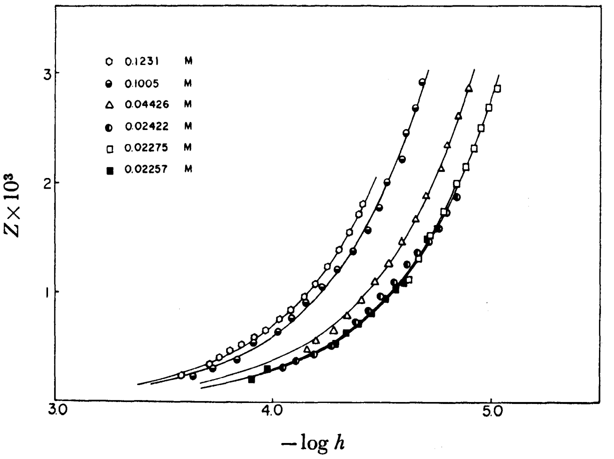

Fig. 3. Values of Z *vs.* $-\log h$ in the solution of a 0.5 mole fraction dioxane-water mixture. Solid lines show calculated curves of Z with formation constants of $\log {}^*\beta_{1,1}=-7.74$ and $\log {}^*\beta_{1,2}=-6.40$.

ing it, we have

$$Zh = \sum_p pK_p h^{-(p-1)} \tag{6}$$

where

$$K_p = \sum_q {}^*\beta_{p,q} B^{q-1} \tag{7}$$

By plotting Zh against h^{-1} we obtain sets of straight lines with various slopes in the system of water and a 0.1 mole fraction dioxane-water mixture, and a set of horizontal lines in the system of the 0.5 mole fraction dioxane-water mixture. We see that there are homoligandic complexes with one and two hydroxo groups in water and in the 0.1 mole fraction dioxane-water mixture, whereas homoligandic complexes with one hydroxo group are formed in the 0.5 mole fraction dioxane water mixture. Plots of $K_1=\sum_q {}^*\beta_{1,q}B^{q-1}$ *vs.* B gave a straight line in each solvent system, which showed that q is equal to 1 and 2 at $p=1$; thus, CuOH and Cu_2OH are present in all solvent compositions examined. The formation constants of the CuOH and Cu_2OH complexes can be obtained from the intercept and the slope of the plot in each solvent system.

The values of the slope ($K_2=2\sum_q {}^*\beta_{2,q}B^{q-1}$) are plotted against B in the case of water and a 0.1 mole fraction dioxane-water mixture. The plot gave a smooth curve with zero intercept. If values of K_2 divided by B were plotted against B, a straight line was obtained in both solvent systems. The result indicates that q is equal to 2 and 3 at $p=2$; the $Cu_2(OH)_2$ and $Cu_3(OH)_2$ complexes exist as dihydroxo complexes. From the intercepts and slopes of these plots the formation constants of the $Cu_2(OH)_2$ and $Cu_3(OH)_2$ complexes are obtained. No other complexes have been detected.

The species formed by hydrolysis of copper(II) ion are found to be CuOH, Cu_2OH, $Cu_2(OH)_2$, and $Cu_3(OH)_2$ in water and in the 0.1 mole fraction dioxane-water mixture, and CuOH and Cu_2OH in the 0.5 mole fraction dioxane-water mixture. Thus, Eq. (4) can be written as

$$BZ = {}^*\beta_{1,1}h^{-1}b + {}^*\beta_{1,2}h^{-1}b^2 + 2{}^*\beta_{2,2}h^{-2}b^2 + 2{}^*\beta_{2,3}h^{-2}b^3 \tag{8}$$

for the systems of water and 0.1 mole fraction dioxane-water mixture and,

$$BZ = {}^*\beta_{1,1}h^{-1}b + {}^*\beta_{1,2}h^{-1}b^2 \tag{8'}$$

for the system of 0.5 mole fraction dioxane-water mixture.

The data were treated by a generalized least-squares method with an electronic computer, HITAC 5020E, in order to make the error square sum $U=\sum(Z-Z_{\text{calcd}})^2$ a minimum for the set of formation constants ${}^*\beta_{p,q}$.

The final values of the constants obtained by computer calculation and their uncertainties estimated are collected in Table 1.

Discussion

Several workers[9,11,12] proposed the formation of $CuOH^+$ and $Cu_2(OH)_2{}^{2+}$ complexes in aqueous 3 M (Li or Na) ClO_4 solution. Pedersen[13] reported formation of the $CuOH^+$, Cu_2OH^{3+}, and $Cu_2(OH)_2{}^{2+}$ complexes. Mahapatra[14] confirmed the formation of higher polynuclear complexes.

In the present study we have found the formation of the $Cu_3(OH)_2{}^{4+}$ complex as well as complexes found by previous workers.[9,11–13] Addition of dioxane, however, prevents the formation of higher complexes.

The difference between $\log {}^*\beta_{1,1}$ and $\log {}^*\beta_{1,2}$ is close to that between $\log {}^*\beta_{2,2}$ and $\log {}^*\beta_{2,3}$. This shows that the stabilization of the Cu_2OH^{3+} complex formed by the combination of a copper ion with an OH^- group in the $CuOH^+$ complex is similar to that of the $Cu_3(OH)_2{}^{4+}$ complex formed by the combination of a copper ion with the $Cu_2(OH)_2{}^{2+}$ complex. This

---

11) H. Ohtaki, *Inorg. Chem.*, **7**, 1205 (1958).

12) H. Kakihana, T. Amaya, and M. Maeda, This Bulletin, **43**, 3155 (1970).

13) K. J. Pedersen, *Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd.*, **20**, 1 (1939).

14) S. Mahapatra and R. S. Subrahmanya, *Proc. Indian Acad. Sci., Sect. A.*,. **65**, 283 (1967).

TABLE 1. FORMATION CONSTANTS (log $^{*}\beta_{q,p}$)

Solvent	CuOH	Cu_2OH	$Cu_2(OH)_2$	$Cu_3(OH)_2$
water	−7.54 ±0.02	−6.22 ±0.02	−11.12 ±0.05	−10.36 ±0.05
0.1 m.f. dioxane-H_2O	−7.44 ±0.02	−6.22 ±0.02	−11.35 ±0.05	−10.12 ±0.08
0.2 m.f. dioxane-H_2O[11]	−7.60 ±0.05	<−7.4	−10.98 ±0.05	
0.5 m.f. dioxane-H_2O	−7.74 ±0.02	−6.40 ±0.02	—	—

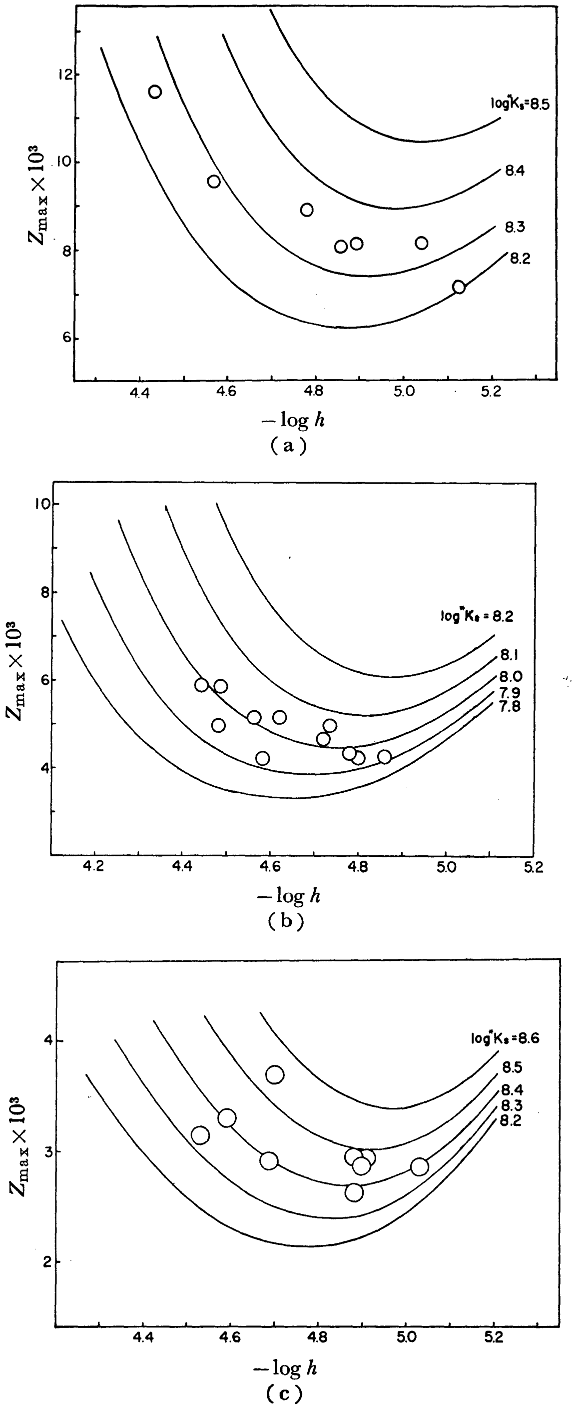

Fig. 4. Z_{max} plotted against −log h. Solid lines are calculated curves of Z_{max} at various values of K_s. a) Water, b) the 0.1 mole fraction dioxane-water mixture, c) the 0.5 mole fraction dioxane-water mixture.

suggests that in the latter reaction the copper ion makes a bond with one OH^- group which is connected with only one copper atom, as in the case of a copper atom combining with one OH^- group in the Cu_2OH^{3+} complex in the former reaction. Thus, the $Cu_2(OH)_2^{2+}$ complex can take a linear form but not a ring form and the $Cu_3(OH)_2^{4+}$ complex can have two single OH^- bridges in the molecule.

In the range of concentration of dioxane up to 0.2 mole fraction, the composition of species produced and their formation constants were scarcely affected by solvent compositions. However, in the 0.5 mole fraction (83.5 wt%) dioxane-water mixture, dihydroxo complexes disappeared while monohydroxo complexes existed without appreciable change in formation constants.

The maximum value of Z, *i,e.*, Z_{max}, at a given B depends on the solubility product of copper hydroxide as well as the formation constants of the complexes in the solution, provided that the solution is equilibrated with copper hydroxide precipitates. If the solubility product $^{*}K_s$ is defined by

$$^{*}K_s = [Cu^{2+}][H^+]^{-2} = bh^{-2} \simeq Bh^{-2} \tag{9}$$

we get the following equations by substituting this relation into Eqs. (8) and (8′), respectively;

$$Z_{max} \simeq {}^{*}\beta_{1,1}h_{max}^{-1} + {}^{*}\beta_{1,2}{}^{*}K_s h_{max} + 2{}^{*}\beta_{2,2}{}^{*}K_s + 2{}^{*}\beta_{2,3}{}^{*}K_s^2 h^2_{max} \tag{10}$$

for systems of water and 0.1 mole fraction dioxane-water mixture, and

$$Z_{max} \simeq {}^{*}\beta_{1,1}h_{max}^{-1} + {}^{*}\beta_{1,2}{}^{*}K_s h_{max} \tag{10'}$$

for the system of 0.5 mole fraction dioxane-water mixture.

Some supplementary experiments have been achieved to determine Z_{max} at various values of B in these solvents. Since no appreciable increase in Z_{max} was observed when agitation of a solution with copper hydroxide precipitates was continued for 3—7 days, we regarded the solution as a saturated solution with copper hydroxide. Values of Z_{max} thus found are plotted against −log h in Fig. 4. They are compared with values of Z_{max} calculated by Eqs. (10) and (10′) with various values of $^{*}K_s$. From these plots the most probable values of log $^{*}K_s$ were estimated to be 8.3±0.2 in the aqueous solution, 8.0±0.2 in the 0.1 mole fraction dioxane-water mixture and 8.4±0.2 in the 0.5 mole fraction dioxane-water mixture containing 3M $LiClO_4$ as an ionic medium. From these results it is seen that the solubility product of $Cu(OH)_2$ given in terms of $^{*}K_s$ is practically independent of solvent composition as is so the formation constant of the $Cu_q(OH)_p^{(2p-q)+}$ complex described in terms of $^{*}\beta_{p,q}$.

The authors thank Prof. M. Tanaka, Nagoya University, for his advice. They are indebted to Dr. M. Maeda for valuable discussions.