Copper(II) Ion Hydrolysis in Aqueous Solution

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A copper(II) ion-selective-electrode potentiometric method was used to determine the first and second hydrolysis constants of Cu^{2+}. Special techniques prevented copper(II) hydroxide precipitation, and copper(II) carbonate and copper(II) organic complexation during the titration of the experimental solution over the pH range 6.8–8.4. The large change in the total copper concentration during the titration due to adsorption of copper onto the vessel walls was accounted for by measuring the total copper concentration at each pH by atomic absorption spectrophotometry. The two hydrolysis constants were determined at 25°C in 0.7 and 0.05 m $NaClO_4$ media. The measured stability constants are independent of the copper concentration and yield similar zero ionic strength values. Also, the stepwise equilibrium constants decrease as the ligand number increases.

1. INTRODUCTION

The hydrolysis of Cu^{2+} plays an important role in the chemistry of copper in many aqueous systems. In solutions with total copper concentrations less than 10^{-5} m and with pH less than 8.5, the hydrolysis of copper(II) ions can be characterized by the following reaction:

$$Cu^{2+} + nH_2O \rightleftarrows Cu(OH)_n^{2-n} + nH^+$$

$$^*\beta_n = \frac{[Cu(OH)_n^{2-n}][H^+]^n}{[Cu^{2+}]} \tag{1}$$
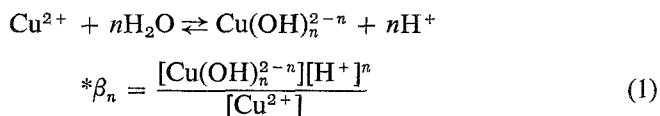
where $n = 1$ or 2 and the square brackets designate molality.

The stability constant $^*\beta_1$ has been calculated from the uptake of the hydroxide ion using pH measurements.[1-5] The calculation of $^*\beta_2$ was based

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on the equilibration of the solid phase, $Cu(OH)_2(s)$, with the solution.[6,7] The two hydrolysis constants were determined by measuring $[Cu^{2+}]$ using the copper(II) ion-selective electrode (ISE)[8-10] in $NaClO_4$ solutions at 25°C and at two ionic strengths (0.05 and 0.7 m).

2. EXPERIMENTAL

2.1. Method

$NaClO_4$ (Fisher "Purified") was dissolved in deionized distilled water to the appropriate ionic strength, filtered through 0.4 and 0.1 μm Nuclepore filters, UV oxidized to destroy organic matter, and adjusted to pH 4 with $HClO_4$. The solution was purged of CO_2 with purified N_2 and the pH was adjusted to 8.5 with carbonate-free NaOH. Experimental solutions of 1, 2, or 4×10^{-6} m total copper concentration, T(Cu), and pH $\approx$ 8.3 were prepared by slow addition of a 3×10^{-3} m solution of Fisher $CuCl_2$ in $NaClO_4$ which had been adjusted to pH 4 with $HClO_4$. This procedure of adding an acidic copper solution to an alkaline $NaClO_4$ medium prevented local supersaturation of $Cu(OH)_2(s)$. To verify the absence of a copper precipitate, copper retained on a 0.1 μm Nuclepore filter was analyzed by atomic absorption spectrophotometry (AAS). The emf of the copper(II) ISE-reference electrode couple, E_{Cu}, and the glass electrode-reference electrode couple, E_H, were monitored sequentially at one minute intervals for one hour with a digital pH meter with a 0.1 mV resolution. Aliquots of the solution were then withdrawn and acidified for subsequent analysis of T(Cu) by AAS. The experimental solution was titrated with $HClO_4$ to lower the pH and the emf of the electrode couples was monitored for one hour and another aliquot was withdrawn for T(Cu) analysis. This procedure of electrode monitoring and aliquot withdrawal was repeated to give 8–10 data points with equal spacing of pH from the original pH to pH 7. For the last point the pH was lowered to 4. At the end of the experiment, samples were analyzed for total organic carbon to verify the absence of competing organic ligands. The solutions were blanketed by a positive pressure of N_2 during the titration to exclude CO_2. The experimental system was thermostated at 25°C for all measurements.

2.2. Data Analysis

In an aqueous solution containing no complexing anions other than hydroxide ions, the copper will be either in the free copper(II) form, Cu^{2+}, or in a hydrolyzed form, $CuOH^+$ and $Cu(OH)_2$ (if the pH is less than 8.5):

$$T(Cu) = [Cu^{2+}] + [CuOH^+] + [Cu(OH)_2] \qquad (2)$$

The degree of hydrolysis will control the portion of the total copper which is in the free form provided there is no solid phase present. Equation (1) may be substituted for $CuOH^+$ and $Cu(OH)_2$ in Eq. (2) to yield

$$T(Cu) = [Cu^{2+}](1 + {}^*\beta_1/[H^+] + {}^*\beta_2/[H^+]^2) \qquad (3)$$

The experimental method was designed to minimize the presence of copper(II) hydroxide precipitates and copper(II) complexation with anions other than hydroxide. The analysis of copper retained on a $0.1 \ \mu m$ filter revealed that less than 1% of the total copper was in the particulate form. The organic carbon content of the solution ranged from 0.2–0.6 mg/liter with a reagent blank of 0.3 mg/liter. The precautions to exclude CO_2 in the handling of the reagents and the experimental apparatus were designed to avoid copper(II) carbonate complexation. Polynuclear copper(II) hydroxide complexes were negligible due to the low total copper concentration.

Sets of $T(Cu)$, $[Cu^{2+}]$, and $[H^+]$ from each experiment were used in a nonlinear regression based on Eq. (3) which yielded the coefficients ${}^*\beta_1$ and ${}^*\beta_2$ and their corresponding uncertainties. The E_H and E_{Cu} were converted to $[H^+]$ and $[Cu^{2+}]$ respectively using a modification of the Nernst equation

$$E_M = E_{M'} + S \log [M] \qquad (4)$$

where the liquid-junction potential and activity coefficient terms are grouped into $E_{M'}$. The electrode potentials were calibrated by adding known amounts of H^+ or Cu^{2+} to a $NaClO_4$ solution at the same ionic strength solution as the experimental solutions. A linear regression was performed on sets of E_M and $[M]$ according to Eq. (4) to yield $E_{M'}$ and S. For the glass electrode couple at 25°C, S was 59.5 ± 0.5 while that of the copper(II) ISE couple was 29.6 ± 1.0. To account for the day-to-day drift of $E_{H'}$, the E_H of a $0.005 \ M$ potassium hydrogen phthalate solution was measured at the end of the calibration and at the beginning of an experiment. By assuming that $[Cu^{2+}] = T(Cu)$ in the final experimental solution which is at a pH of 4, $E_{Cu'}$ can be determined by substituting $[Cu^{2+}]$ and E_{Cu} of this data point into Eq. (4). Further details of the experimental design and analysis of the data are provided by Paulson.[11]

3. RESULTS

One of the important findings of this study was that the total copper concentration changed with pH during the titration due to adsorption within the apparatus. In a typical experiment, $T(Cu)$ changed with pH due to adsorption while $[Cu^{2+}]$ changed due to both adsorption and hydrolysis (Fig. 1). The difference between these curves is due to hydrolysis alone (Fig. 2). Eight
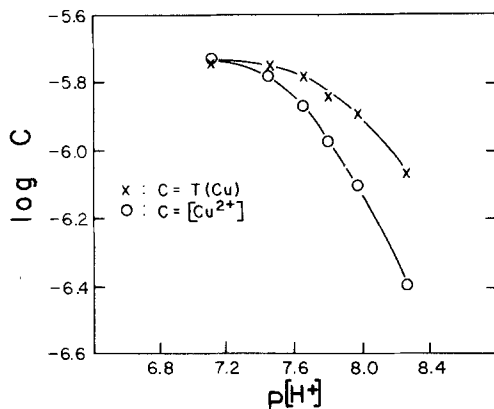
Fig. 1. Primary data for one experiment at a total copper concentration of 2×10^{-6} m: ×, T(Cu) measured by AAS; ○, $[Cu^{2+}]$ measured by ISE.

experiments were performed to obtain the stability constants at two ionic strengths (Table I).

In the absence of polynuclear species, the complexation of the copper(II) ion should be independent of the total copper concentration. This condition was tested by determining the stability constants from experiments at different T(Cu): 1, 2, and 4×10^{-6} m. There was no systematic difference in the stability constants with copper concentration.[11]
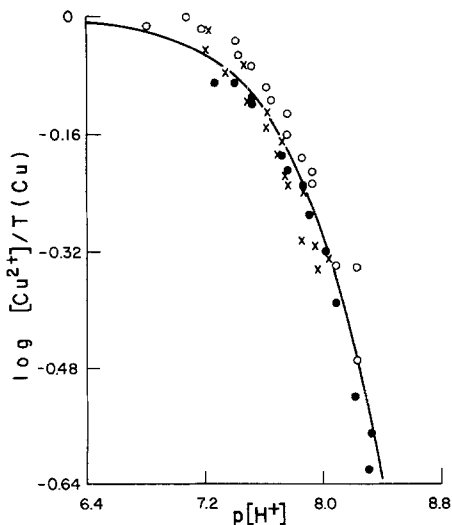

Fig. 2. Processed data at 0.7 m ionic strength for three total copper concentrations: ●, T(Cu) = 1×10^{-6}; ○, T(Cu) = 2×10^{-6}; ×, T(Cu) = 4×10^{-6}. The solid curve is calculated using $*\beta_1 = 7.7 \times 10^{-9}$ and $*\beta_2 = 2.1 \times 10^{-17}$.

Table I. Copper(II) Hydroxide Stability Constants at 25°C

Ionic strength (m)	$T(Cu) \times 10^6$ (m)	$*\beta_1 \times 10^9$	$*\beta_2 \times 10^{17}$
0.05	2	7.5 ± 0.9^a	3.9 ± 1.1^a
0.7	1, 2, and 4	7.7 ± 0.7	2.1 ± 0.5

^{a} One standard error yielded by the regression program.

The experiments at two ionic strengths provide independent estimates of the infinite-dilution constants based on the following:

$$*\beta_n(0 \text{ corr}) = \frac{\gamma_{Cu(OH)_n^{2-n}}(\gamma_{H^+})^n}{\gamma_{Cu^{2+}}} *\beta_n(I) \tag{5}$$

In one estimate, the stability constants at 0.7 m ionic strength were corrected to infinite dilution using the "rule of thumb" coefficients of Kester[12]: $\gamma_{Cu^{2+}} = 0.25$, $\gamma_{CuOH^+} = 0.4$, $\gamma_{Cu(OH)_2} = 0.8$, and $\gamma_{H^+} = 0.95$. The results at 0.05 m ionic strength were corrected to infinite dilution using the modified Debye–Hückel formula of Kielland.[13] An ion size parameter of 6 was used for both Cu^{2+} and $CuOH^+$ while a value of 9 was used for H^+. The activity coefficient of $Cu(OH)_2$ was assumed to be unity. The experimental results and the estimates of the thermodynamic constants are shown in Fig. 3.

Although $*\beta_1$ is the same at 0.05 and 0.7 m ionic strength, the estimates of $*\beta_1(0 \text{ corr})$ are also very similar ($10^{-7.99}$ for 0.05 m and $10^{-7.93}$ for 0.7 m) because the ratio of $\gamma_{Cu^{2+}}/\gamma_{CuOH^+}$ is nearly the same at the two ionic strengths. The estimates of $*\beta_2(0 \text{ corr})$ are $10^{-16.26}$ and $10^{-16.21}$ from the results at 0.05 and 0.7 m ionic strength, respectively. This work suggests that $*\beta_2$ varies with ionic strength essentially according to $\gamma_{Cu^{2+}}$ because $\gamma_{Cu(OH)_2}$ and γ_{H^+} remain close to unity for $I < 0.7 m$.

The results of this work can be summarized as follows: for $I \leqslant 0.05 m$, $\log *\beta_1 = -7.96 - 0.88[\sqrt{I}/(1 + \sqrt{I})]$; for $0.05 m \leqslant I \leqslant 0.7 m$, $\log *\beta_1 = -8.12$; for $I \leqslant 0.7 m$, $\log *\beta_2 = -16.24 - 0.94[\sqrt{I}/(1 + \sqrt{I})]$.

Baes and Mesmer[14] have shown that the $*\beta_1$ of numerous cations varies with the charge:size ratio. If this concept is applied to the hydrolysis series of a single cation, one would expect that the stepwise constants (K_1, K_2, etc.) would decrease as the number of OH^- ligands increases due to the reduced charge. In this study, K_2 is less than K_1 at both ionic strengths and at infinite dilution. The estimated stepwise constants at $I = 0$ from this study are $pK_1 = 7.93$ and $pK_2 = 8.37$.
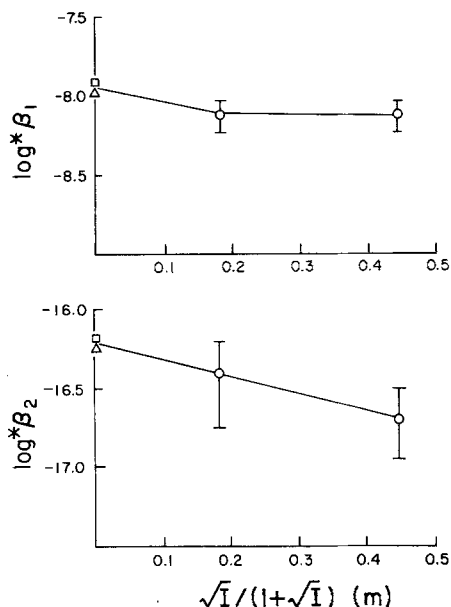
Fig. 3. The variation of the stability constants with ionic strength: $\ominus$, statistically derived constant and its 95% confidence interval; $\triangle$, estimates of the constants at $I = 0$ based on the results at 0.05 m; $\square$, estimates at $I = 0$ based on the results at 0.7 m.

4. DISCUSSION

The results of the investigation yield stability constants which are smaller than those of previous investigations using the copper(II) ISE (Table II). The different total copper concentration used in the copper(II) ISE studies may result in systematic errors when determining the hydrolysis of the copper(II) ion. Hittinger[8] studied copper(II) hydroxide complexation with T(Cu) = 2–8 $\times$ 10^{-5} m. Experiments by us under these conditions indicated the presence of copper-containing particles, in which case the decrease of $[Cu^{2+}]$ with pH could be controlled by copper(II) hydroxide precipitation rather than copper(II) hydroxide complexation. The semiquantitative study of Vuceta and Morgan[10] with T(Cu) < 10^{-7} m did not consider the adsorption of Cu^{2+} onto the container surfaces which was found to be significant in this study. Although Sunda[9] studied copper(II) hydroxide complexation with copper concentrations similar to those of this investigation, he reported a greater degree of hydrolysis than that found in this study. The cause of this difference could not be ascertained due to the lack of detail in the description of his experimental method.

In the hydrogen ion electrode method,[1–5] the results at high copper concentrations must be extrapolated to low copper concentrations providing

Table II. Comparison of Our Results to Previous Investigations[a]

Medium	p*β_1	p*β_2	log *K_{so}	Method	Source
3 M LiClO$_4$	7.6			H	1
3 M NaClO$_4$	7.2			H	2
0 corr	8			H	3
0.1 M KNO$_3$	7.3			H	4
0.1 M NaClO$_4$	7.7			H	5
1.0 m NaClO$_4$		15	8.9	S	6
0 corr		14.8	8.1	S	7
0.7 m NaClO	7.4	14.6	10.7	ISE	8
0.02 M NaNO$_3$	7.4			ISE	9
0.001 M NaCl		closer to 13.7 than to 17.3		ISE	10
0.001 M Cu(NO$_3$)$_2$			10.7	ISE	15
0.7 m NaClO$_4$	8.1	16.7		ISE	This study
0.05 m NaClO$_4$	8.1	16.4		ISE	This study

[a] Abbreviations: p$X = -\log X$; H, hydrogen ion electrode; S, solubility; ISE, ion-selective electrode.

an insensitive determination of *β_1. Some of the solutions used in investigations employing this method were supersaturated with respect to Cu(OH)$_2$(s).[11]

The values of *β_2 obtained by both investigations using the Cu(OH)$_2$(s) solubility method[6,7] are two orders of magnitude greater than the values determined in this study. In the solubility method T(Cu) is measured in the pH range where Cu(OH)$_2$ complexation dominates (pH 8–10) and *β_2 is calculated from the following equation:

$$*\beta_2 = T(Cu)/*K_{so} \qquad (6)$$

where *K_{so} is the solubility product. The *K_{so} was measured in a pH region where the copper(II) ion is unhydrolyzed (less than a pH of 4.5). Measurements of *K_{so} by the copper(II) ion-selective electrode at a higher pH (8–10) yield a much higher *K_{so}[8,15] (Table II). The solubility product of Cu(OH)$_2$(s) has been shown to be dependent on its molar surface area[16] and on time due to the conversion to tenorite (CuO).[7,8] Since it is not unreasonable to expect that these parameters are pH dependent, *K_{so} should be measured in solutions which are at the pH similar to those for which *β_2 is determined. When an average value of *K_{so}, as determined by the copper(II) ISE, is used to calculate *β_2, the solubility data of Spivakovskii and Makovskaya[7] and Gubeli et al.[6] yield a *β_2 of 10^{-17}(0 corr) and $10^{-17.1}$ (1 M ionic strength) respectively. Thus it appears that most of the difference between *β_2 determined by the

Table III. Percentage of the Total Dissolved Copper in Each Form at Various pH's and the Total Dissolved Copper, T(Cu), at Equilibrium with $Cu(OH)_2(s)$ Having a $*K_{so} = 2 \times 10^{10}$ in Dilute Solutions

Form of copper	pH			
	6.0	7.0	8.0	9.0
Cu^{2+}	99	90	37	1.5
$CuOH^+$	1	9.8	41	16
$Cu(OH)_2$	0.006	0.5	21	83
T(Cu)	2×10^{-2}	2.23×10^{-4}	5.34×10^{-6}	1.39×10^{-6}

copper(II) ISE and by the $Cu(OH)_2(s)$ solubility method is due to the characteristics of the solid-phase equilibration ($*K_{so}$) rather than due to the solution-phase hydrolysis.

A number of experimental factors are important when determining $*\beta_1$ and $*\beta_2$: (a) selection of a technique and set of conditions which avoid poly-nuclear complexes, (b) supplemental measurements to assure that solid phases do not control the solution equilibria and that adsorption is accounted for, and (c) control of additional ligands such as carbonate and organic substances which may complex with copper. This investigation provides the first consistent set of measurements for $*\beta_1$ and $*\beta_2$; previous studies considered only one of these stability constants or used information from other sources to estimate one of the two constants.

Two ionic strengths were used which gave consistent values for the stability constants corrected to zero ionic strength. The $0.7\ m$ ionic strength medium provides a stability constant which may be applied to the chemistry of copper in marine systems without having to estimate activity coefficients.

The relative importance of the three forms of copper in aqueous solution considered in this study is illustrated in Table III. Also included in this table is an estimate of the total dissolved copper in equilibrium with a $Cu(OH)_2(s)$ phase having a $*K_{so} = 2 \times 10^{10}$. This illustration is based on the infinite-dilution values of $*\beta_1 = 1.10 \times 10^{-8}$ and $*\beta_2 = 5.75 \times 10^{-17}$.

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