STUDIES IN THE HYDROLYSIS OF METAL IONS

Part I. Copper

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ABSTRACT

The hydrolysis of cupric ion has been studied at various ionic strengths (0·01, 0·05, 0·1 and 0·5 M). The results are analyzed employing 'core + links' theory, log-log plot, normalization plot, and extrapolation method for obtaining the pure mononuclear curve. The stability constants of $Cu_2(OH)_2^{++}$, $Cu_3(OH)_4^{++}$, $Cu(OH)^+$ and $Cu(OH)_2$ have been reported.

INTRODUCTION

THE hydrolysis of cupric ion has been studied by Pederson,[1] Biedermann[2] and Perrin.[3] Pederson has explained his results assuming the formation of $CuOH^+$, Cu_2OH^{3+} and $Cu_2(OH)_2^{2+}$. Biedermann has obtained evidence [10 mM $<$ $(Cu)_t$ $<$ 100 mM] for the formation of only $Cu_2(OH)_2^{++}$ using Sillen's 'core + links' method. Assuming the existence of $Cu_2(OH)_2^{++}$ at low $\bar{n}$ values Perrin obtained constant values for β_{22}. Further, he showed that $Cu_3(OH)_4^{2+}$ is present at higher $\bar{n}$ values. It is therefore clear that there is still obscurity about the nature of complexes. In the present paper an attempt is made to clear up these obscurities by the analysis of $\bar{n}$-pOH curves [$(Cu)_t < 10$ mM] by independent mathematical techniques. Since evidence is obtained for the formation of mononuclear species at low metal concentrations, an extrapolation method has been used to obtain theoretical mononuclear curve.

EXPERIMENTAL

All the chemicals used were either extra pure or analar in quality. Correction is applied for the small quanity of free acid, present in cupric salt solution employing Brosett's method.[4] The pH of the various test solutions is determined with Beckman G pH meter employing the glass electrode, standardized with hydrochloric acid or suitable buffers containing sufficient potassium nitrate to keep the ionic strength same as in the test solution.

Cupric salt solution (100 c.c.) containing known amount of nitric acid (pH = 3) and sufficient potassium nitrate to keep the ionic strength constant (0·01, 0·05, 0·10 and 0·50 M) is titrated with carbonate free sodium hydroxide. After each addition of sodium hydroxide an equal volume of twice the strength of the initial test solution is added to keep the total concentration of cupric copper and ionic strength constant throughout the titration. Equilibrium was attained immediately. However, the pH was read two minutes after each addition. The titration is continued until a faint precipitate appears. Experiments have been conducted with different concentrations of cupric copper. The solution is deaerated with nitrogen and a magnetic stirrer is used to stir the solution. During pH measurements the stirring is stopped.

The value of $\bar{n}$ and pOH is calculated using the following relation[5]:

$$\bar{n} = \frac{B - (C_H - H^+)}{C_M} \; ; \; pOH = pK_w - pH.$$

The value of pK_w in 0·01, 0·05, 0·10 and 0·50 M potassium nitrate solutions determined potentiometrically are 13·72, 13·69, 13·67 and 13·62 respectively.

NOTATIONS

B	Concentration of sodium hydroxide added.
C_H	Total free acid of the initial solution.
$\bar{n}$	Average number of hydroxylion per metal ion.
C_M	Total metal (copper) concentration.
M	Metal (copper) ion.
$[OH^-]$, $[H^+]$, [M]	Concentrations of free hydroxyl, hydrogen and metal ions.
$\beta_{1,1}$, $\beta_{1,2}$, β_{mi}	Stability constants of MOH, $M(OH)_2$ and $M_m(OH)_i$.
$k_{1,1}$, $k_{1,2}$, k_{mi}	Equilibrium constants of the hydrolytic reactions forming MOH, $(M)OH_2$ and $M_m(OH)_i$.
K_w	Ionic product of water.
$k_1, k_2, k_3, \ldots, k_n$	are the constants for the hydrolytic reaction for the complexes containing 1, 2, 3...*n*th links in $Cu((OH)_2Cu)_n^{++}$.

RESULTS

The $\bar{n}$-pOH curves at various metal concentrations in solutions of ionic strength 0·5, 0·1, 0·05 and 0·01 M are given in Figs. 1–4. The maximum value of $\bar{n}$ reached diminishes both with an increase in metal concentration at constant ionic strength and an increase in ionic strength at constant metal concentration.

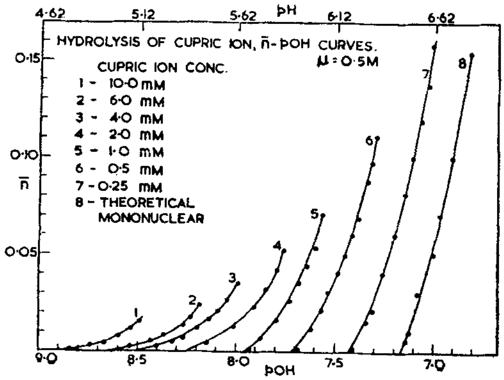

FIG. 1

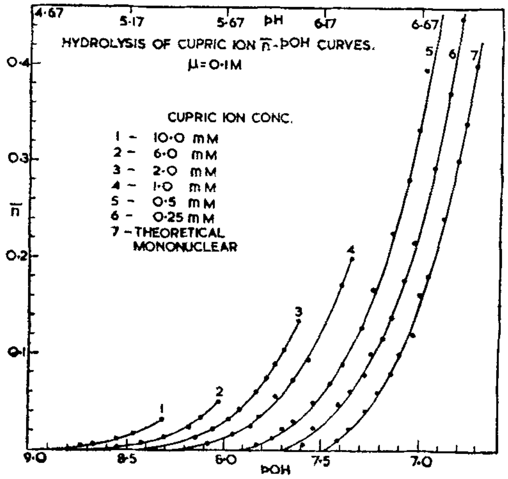

FIG. 2

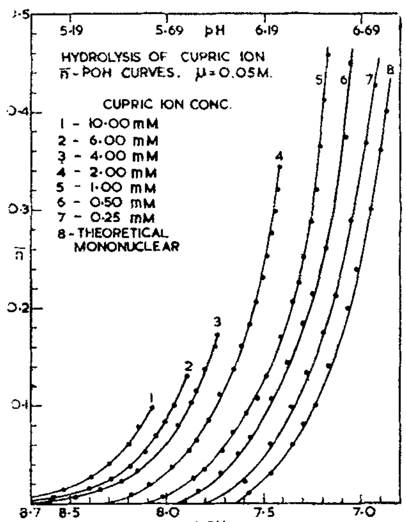

FIG. 3

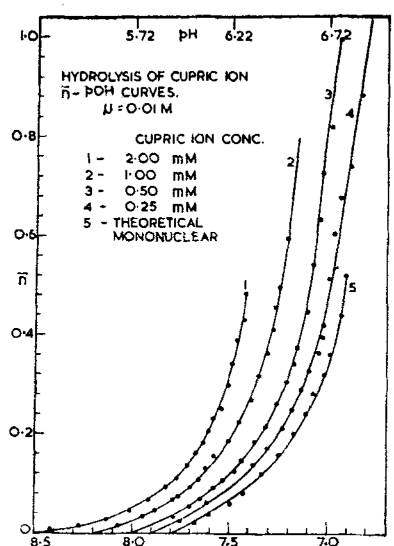

FIG. 4

DISCUSSION

1. *Analysis of $\bar{n}$-pOH Curves for Polynuclear Complex Formation by Sillen's Method*[6]

The spacing of the 11^{el} $\bar{n}$-pH curves indicates that the derivative $(\partial \log C_M / \partial \log [H^+])_{\bar{n}}$ is about 2 and the plots of

$$\text{(i) } \frac{\bar{n}}{2} \ vs. \log \{C_M [OH^-]^2\} \quad \text{or} \quad \text{(ii) } \frac{\bar{n}}{2} \ vs. \log \frac{C_M}{[H^+]^2}$$

[called $y(x)$ curves] coincide indicating that the 'core + links' complexes have the formula $Cu\left(Cu(OH)_2\right)_n^{++}$. A typical $y(x)$ curve is given in Fig. 5. The curve with 0·25 mM copper does not coincide indicating considerable amount of mononuclear species. Direct analysis of plot (i) gives the value of the equilibrium constant for the formation of the complex while that of plot (ii) gives the value for the hydrolytic reaction, the two constants being related by $k_{mi} = \beta_{mi} K_w^{\ i}$. The function $g(v) = f(u) = \Sigma\ k_n u^n$ and u are determined from the area of the $y(x)$ curves using the following equations

$$\log (1 + g) = \int_{-\infty}^{x} y dx + \log (1 - y) + y \log e$$

$$\log u = x - y \log e - \int_{-\infty}^{x} y dx.$$

The plots of the $\log g$ *vs.* $\log u$ are straight lines with the slope near 1·2 at all ionic strengths indicating that the most predominant complex contains one link in the complex. The plots of gu^{-1} *vs.* u (Fig. 6) are straight lines (lowest points very sensitive to small errors in y have been disregarded[7]), the intercept and the slope giving the values of k_1 and k_2 (Table I).

2. *Analysis of $\bar{n}$-pOH Curves by Log-log Plots*[8, 9]

At low values of $\bar{n}$ where one can expect only $CuOH^+$ and the lowest polynuclear species $Cu_q(OH)_p^{(2q-p)+}$, if $CuOH^+$ can be neglected as compared to $Cu_q(OH)_p^{(2q-p)+}$, one can write

$$\bar{n} = \frac{p\,[Cu_q(OH)_p^{(2q-p)+}]}{(Cu)_t}$$

expressing $Cu_q(OH)_p^{(2q-p)+}$ in terms of β_{qp}, etc., noting that $Cu^{++} \cong (Cu)_t$, and taking logarithms one gets

$$\log \bar{n} = \log p + \log \beta_{qp} + (q - 1) \log (Cu)_t + p \log [OH^-].$$

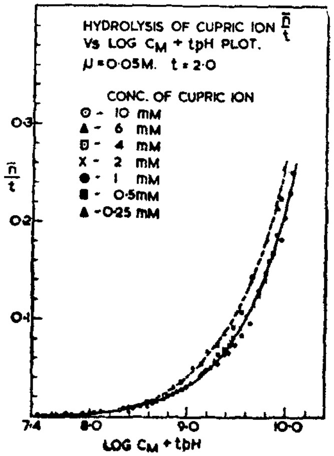

FIG. 5

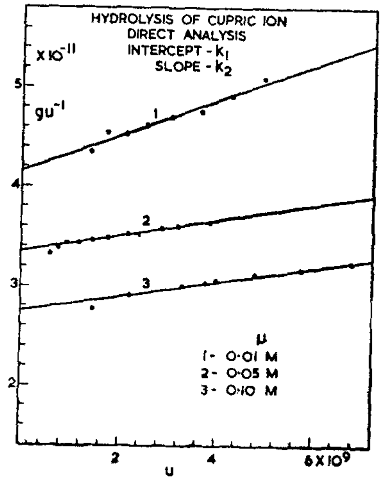

FIG. 6

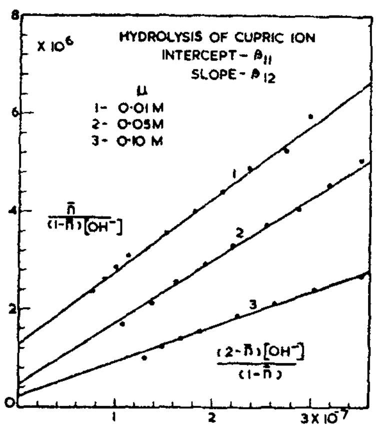

FIG. 7

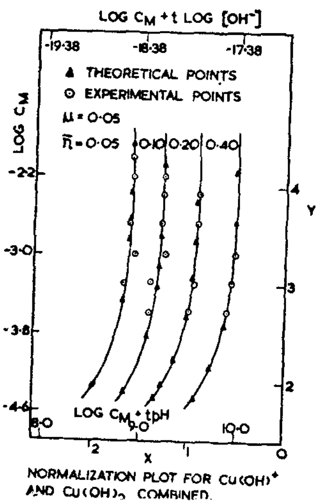

FIG. 8

It follows from the above equation that the plot of log $\bar{n}$ *vs.* log $[OH^-]$ should be a straight line, the slope giving the value of p. The value of q is obtained from the difference in the value of the intercepts. The average values of p and q are $2 \pm 0 \cdot 1$ indicating the most predominant species to be $Cu_2(OH)_2^{++}$ in agreement with Sillen's method. The value of log β_{22} is obtained from the value of the intercept (Table I).

TABLE I

Stability constants of the mono and polynuclear hydrolytic products of cupric copper

Species	Method	Log stability constant at of various ionic strengths (correct to within ± 0·04 except those from Normalization plots where they are correct to ± 0·2)				Thermodynamic constant
		0·50 M	0·10 M	0·05 M	0·01 M	$\mu=0$
$Cu_2(OH)_2^{++}$	Sillen plot	16·41	16·78	16·90	17·05	17·16
$Cu_3(OH)_4^{++}$	do.	..	33·53	33·66	34·11	34·36
$Cu_2(OH)_2^{++}$	Log-log plot	16·38	16·78	16·96	17·19	17·38
$Cu_2(OH)_2^{++}$	Normalization procedure (under all conditions)	..	..	16·9	..	..
$CuOH^+$	Extrapolation method	..	5·38	5·69	6·11	6·43
$Cu(OH)_2$	do.	..	12·85	13·09	13·17	13·30
$CuOH^+$	Normalization procedure ($CuOH^+$ only)	..	..	5·7	..	..
$Cu(OH)^+$	Normalization procedure ($CuOH^+ + Cu(OH)_2$)	..	..	6·3 }	..	..
$Cu(OH)_2$	do.	..	..	12·6 }	..	..
$Cu(OH)_2$	Normalization procedure (only $Cu(OH)_2$)	..	..	13·1	..	..

3. *Analysis of Data for Mononuclear Complexes*

(i) *Extrapolation procedure.*—In the present work it was not possible to obtain sufficient number of points for the mononuclear curve by extrapolating (at constant pOH) the values of $\bar{n}$ at various C_M values to $C_M \to 0$. In a system containing $CuOH^+$, $Cu(OH)_2$, $Cu_2(OH)_2^{++}$, the following equations for C_M, $\bar{n}\,C_M$, $[Cu^{++}]$ and $\bar{n}$ can be written.

$$C_M = [Cu^{++}] + [CuOH^+] + [Cu(OH)_2] + 2\,[Cu_2(OH)_2^{2+}]$$

$$\bar{n}C_M = [CuOH^+] + 2\,[(Cu(OH)_2] + 2\,[Cu_2(OH)_2^{2+}]$$

and

$$[Cu^{++}] = \frac{C_M(1-\bar{n})}{1-\beta_{1,2}[OH^-]^2}$$

$$\bar{n} = \frac{\beta_{11}[OH^-] + 2\beta_{1,2}[OH^-]^2 + 2\beta_{2,2}\dfrac{C_M(1-\bar{n})}{1-\beta_{1,2}[OH^-]^2}[OH^-]^2}{1 + \beta_{1,1}[OH^-] + \beta_{1,2}[OH^-]^2 + 2\beta_{2,2}\dfrac{C_M(1-\bar{n})}{1-\beta_{1,2}[OH^-]^2}[OH^-]^2}.$$

It is therefore obvious that at constant $\bar{n}$, the hydroxyl ion concentration is a function of C_M only. Hence the plot of the hydroxyl ion concentration *vs.* C_M when extrapolated to zero value of C_M would give the value of the hydroxyl ion concentration for the mononuclear cuve for the $\bar{n}$ chosen. The above treatment would be valid even when more than one polynuclear complex is present but the expression for the metal ion would be a higher degree equation. Hence the hydroxyl ion concentration is a function of C_M at constant $\bar{n}$. In Figs. 1–4, the theoretical mononuclear curves obtained as described above are given. The plots of $\bar{n}/\left((1-\bar{n})[OH^-]\right)$ *vs.* $\left((2-\bar{n})[OH^-]\right)/(1-\bar{n})$ are straight lines (Fig. 7) the intercept giving the value of $\beta_{1,1}$ and the slope giving the value of $\beta_{1,2}$ (Table I).

(ii) *Application of the normalization procedure*[10].—The plots of log C_M *vs.* $(\log C_M + t\text{pH})_{\bar{n}}$ have a slight curvature (Fig. 8) indicating the formation of mononuclear complexes. Theoretical plots have been made assuming the presence of (i) $CuOH^+$, (ii) $CuOH^+ + Cu(OH)_2$ and $l = 100$ and (iii) $Cu(OH)_2$. Good fits have been obtained in all cases obviously due to the small amount of the mononuclear species present in the solution. Since the formation of $CuOH^+$ and $Cu(OH)_2$ is indicated in the analysis of the theoretical mononuclear curve only the equations corresponding to this condition are given below.

$$\bar{C}_M = k\beta_{1,1}^{-2} C_M = va^{-2}\left(1 + a + la^2 + \frac{v}{1-v} + \frac{v}{(1-v)^2}\right)$$

$$\log(\bar{C}_M a^2) = \log v + \log\left(1 + a + la^2 + \frac{v}{1-v} + \frac{v}{(1-v)^2}\right)$$

$$= X$$

$$Y = \log \bar{C}_M = X - 2\log a$$

where

$$a = \beta_{1,1}[OH^-] \quad \text{and} \quad l = \beta_{1,2}\beta_{1,1}^{-2}.$$

Also

$$\log \bar{C}_M = \log C_M + \log k - 2\log \beta_{1,1}$$

$$\log(\bar{C}_M a^2) = \log C_M + 2\log[OH^-] + \log k.$$

The values of a at various values of $\bar{n}$ and v are calculated from the equation

$$\frac{l(2-\bar{n})}{(1-\bar{n})}a^2 + a - \left\{\frac{\bar{n}}{1-\bar{n}}\left[1+\frac{v}{1-v}+\frac{v}{(1-v)^2}\right] - \frac{2v}{(1-v)^2(1-\bar{n})}\right\} = 0.$$

Theoretical plots (Y *vs.* X) can now be made for each value of $\bar{n}$ (0·05, 0·1, 0·2 and 0·4) giving suitable values of v, assuming different values for the stability constant ratios (l = 0·1, 1, 10 and 100). In the position of good fit

$$Y - y = \log k - 2\log\beta_{1,1}$$

$$X - x = \log k = \log\beta_{2,2}.$$

The normalization plot (l = 100) is given in Fig. 8 and the stability constants are given in Table I.

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