

On the Hydrolysis of the Copper(II) Ion, Cu^{2+} , in 3 M $(\text{Na})\text{ClO}_4$ Medium at High Copper(II) Ion Concentrations and 25 °C

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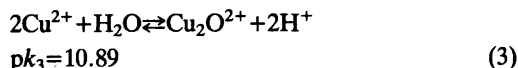
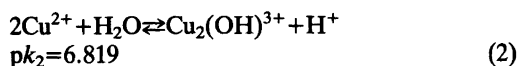
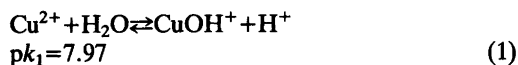
The complex formation equilibria in the system $\text{Cu}^{2+}-\text{H}_2\text{O}$ have been studied by emf measurements. The hydrogen ion concentration at equilibrium, $[\text{H}^+]=h$, was measured with a glass electrode in the concentration ranges $1.9 < -\log h < 3.3$ and $0.3 < [\text{Cu(II)}] \equiv B < 0.895$ M.

The data may be explained by assuming the equilibrium $2\text{Cu}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Cu}_2(\text{OH})^{3+} + \text{H}^+$ $\log \beta_{21} = -5.75 \pm 0.10$. The error quoted is maximum error evaluated graphically. The effects on the constants of medium changes caused by the replacement of a large part of Na^+ with Cu^{2+} were estimated by the specific ion interaction theory (SIT).

The primary object of the present work was the emf studies of the complex formation in the $\text{Cu}^{2+}-\text{H}_2\text{O}-\text{CO}_2(\text{g})$ system. The H^+ -ion concentration range was: $1.9 < -\log h < 3.3$ at the constant total concentration of the copper(II), B ; 0.895, 0.525 M and different carbon dioxide partial pressures (a): 0.959 and 0.297 atm at 25 °C. No formation of soluble copper(II)-carbonate complexes could be detected in the concentration range studied. The data were then extended with titrations at $B=0.656$ M and $B=0.300$ M without the presence of $\text{CO}_2(\text{g})$. Results from titrations at lower B , for example $B=0.100$ M, could not be interpreted with the same accuracy because of the small effect of complex formation. Maximum 1 % of the Cu(II) is present in reaction product. At $B=0.100$ M the expected Z [defined in eqn. (8)] is the same order of magnitude as the experimental error in the pH range studied. The experiments without $\text{CO}_2(\text{g})$ show that the pre-

sence of it in earlier titrations did not effect the pH-range where the precipitate appears. The data could be explained with the formation of a single hydrolysis product $\text{Cu}_2\text{OH}^{3+}$. The existence of this complex has been subject to some controversy.^{1,2}

The hydrolysis of the copper(II) ion has earlier been studied by other investigators.^{1,2,3} Pedersen's studies¹ included investigations at 18 °C using the glass electrode in $\text{Cu}(\text{NO}_3)_2$ solutions of the concentrations: *ca.* 1, 2, 5, 10, 20, 50, 100 and 1000 Mm Cu^{2+} of varying ionic strength. The experimental data could be explained assuming the equilibria:



The values of pK given are valid at infinite dilution. Pedersen determined k_3 and the sum of the constants, $(k_1 + Bk_2)$, accurately. k_1 was then calculated in the total copper(II) concentration range $0.1 \geq B \geq 0.001$ M assuming a rough value for k_2 . On the other hand k_2 was calculated when $1 \geq B \geq 0.01$ M using a rough value for k_1 .

Berecki-Biedermann's² emf studies of the hydrolysis of the copper(II) ion were carried out using glass-electrode measurements at 25 °C at $10 < B < 100$ mM, in the acidity range: $2.5 <$

$-\log h < 5.7$ using a 3 M (Na)ClO₄ ionic medium. The range of Z covered was $0 < Z < 0.1$, where Z is the average bound OH⁻ per one mol copper(II) = $h - H/B$, and H is the total (analytical) concentration of H⁺ ion in excess of H₂O and Cu²⁺. Her results could be explained with the formation of a single "core + links"^{4,5} complex:

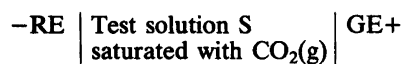


with the equilibrium constant $\log k = -10.6 \pm 0.1$. She recalculated² Pedersen's data using Sillén's systematic approach.^{4,5} The experimental results could again be explained with the presence of the single complex $\text{Cu}((\text{OH})_2\text{Cu})^{2+}$ with an equilibrium constant $\log k = -10.95 \pm 0.10$. Pedersen gave -10.89 for the same constant at infinite dilution.

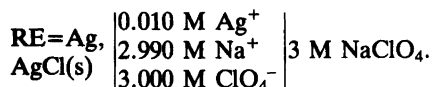
Berecki-Biedermann also considered the possible formation of the complex $\text{Cu}_2\text{OH}^{3+}$. However, the Z -curves in the B , $\log h$ concentration ranges studied were practically the same for the model including $\text{Cu}_2\text{OH}^{3+}$ and that without this complex. Hence, no conclusions about the existence of a complex $\text{Cu}_2\text{OH}^{3+}$ could be drawn from the experimental data.

In Ref. 3 the species $\text{Cu}_2(\text{OH})_2^{2+}$ was found with the equilibrium constant $\log \beta_{22} = -10.75$ and the other doubtful species CuOH^+ with $\log \beta_{11} = -7.22$ in 3 M NaClO₄ medium at 25 °C.

In the present work a series of emf titrations were carried out under different experimental conditions. The hydrogen ion concentration at equilibrium, $[\text{H}^+] = h$, was calculated from the emf of the cell:



where GE denotes a glass electrode and the reference halfcell (RE) had the composition



In order to ensure a reasonable constancy of the activity factors of the reacting species in all the solutions the $[\text{ClO}_4^-]$ was kept at 3 M by addition of NaClO₄ stock solution. The emf in mV of the cell at 25 °C can be written:

$$E = E_0 + 59.16 \log h + E_j \quad (5)$$

where E_0 is constant and E_j is the liquid junction potential between the test solution S and 3 M NaClO₄. The activity factors of the species involved are assumed to be constant. E_j is a function of both h and $[\text{Cu}^{2+}]$. Under the present experimental conditions the concentration of the free copper(II) ions at equilibrium, $[\text{Cu}^{2+}] = b$, can be approximated by B . As B is kept constant during the experiments the term constant $\times B$ of E_j is included in the constant E_0 . Thus E_j can be estimated from the equation⁶

$$E_j = 16.9 h \text{ mV}. \quad (6)$$

The constant E_0 was determined at the end of the titrations, in solutions where the hydrolysis of Cu²⁺ can be neglected: $0.013 < h < 0.030$ M. From these measurements

$$Z = (h - H - [\text{HCO}_3^-])/B$$

was calculated as a function of $\log h$ (Fig. 1). Here H is the total (analytical) concentration of H⁺ ion in excess of H₂O, CO₂ and Cu²⁺, and can be calculated as

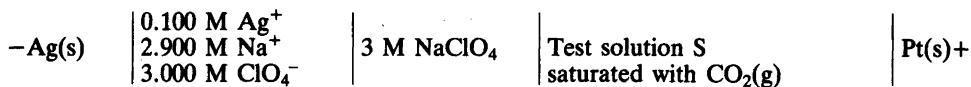
$$H = \frac{V_0 H_0 - V_T C_T + \mu_{\text{H}^+}}{V_0 + V_T + V}, \text{ M} \quad (7)$$

Here V_0 = the initial volume of the cell solution in ml, H_0 its hydrogen ion concentration, V_T = ml ~ 0.1 M NaHCO₃, 3 M NaClO₄ added, C_T = the concentration of NaHCO₃ solution, μ_{H^+} = number of mmoles of H⁺ generated by electrolysis or H⁺ added from a burette (V). All concentrations are expressed as molarities.

EXPERIMENTAL

Reagents and solutions. Sodium perchlorate and dilute perchloric acid solutions were prepared and analyzed as usual in this laboratory.⁷ Analyses were made with an accuracy of $\pm 0.1\%$.

Copper(II) perchlorate solution was prepared by dissolving CuO (Merck *p.a.* product) in a slight excess of hot HClO₄ (Merck *p.a.* 70 %). The solution was filtered through a sintered glass filter G3. The product did not contain any chloride impurities and could be used without further purification. The copper(II) content of



Scheme 1.

the stock solution was analyzed by electro-deposition.⁸ The results of the electrogravimetric determinations of copper agreed to better than $\pm 0.1\%$.

The hydrogen ion content of the copper(II) perchlorate stock solution was determined by adding a weighed amount of the solution to 50.00 ml 3 M NaClO₄ solution and titrated potentiometrically by addition of H⁺ ions generated by a coulometer. The experimental points were evaluated with the help of a GRAN plot.⁹ [H₀⁺]=15.166 10⁻³ M. An attempt to determine the hydrogen ion excess using the ion-exchange method was not successful.

NaHCO₃ solutions used were made of a Merck *p.a.* product. The crystalline substance was tested against standardized HClO₄ solution. The molecular weight found is 84.10. The accuracy is better than $\pm 0.1\%$. The theoretical value is 84.007.

Carbon dioxide or CO₂-N₂ mixture of accurately known composition and nitrogen was taken from a cylinder (AGA Special Gas, Lidingö) and passed through wash bottles of 10% H₂SO₄, H₂O and 3 M NaClO₄ respectively.

The emf measurements. Electrodes. Ag, AgCl(s) electrodes were prepared by

electrolysis.¹⁰ The glass electrodes were Metrohm type EA 109 electrodes.

The coulometric circuit in Scheme 1 was used.

The coulometer was Constant Current Power Supply Model C633 (Electronic Measurements), which was calibrated against a manganin standard resistance type A.C. 1046 (Sullivan and Griffiths).

For the emf measurement a cell arrangement usual in our laboratory¹¹ was employed. The emf of the cell was measured with a Digital Voltmeter type DM 2022 S. Emf values stable to 0.1 mV were reached a few minutes after each addition of reagent solution. The titrations were carried out in such a way that V₀ ml initial solution saturated with CO₂ of the chosen pressure was alkalified first by the addition of V_T from a Metrohm piston Burette until the boundary of precipitation was reached ($-\log h \sim 3.3$). Then the [H⁺] was increased either by coulometrical generation of H⁺ ions (titrations denoted (*) in Figs. 1 and 2) or by burette additions. The E₀ values were determined in solutions at $-\log h < 1.9$ by replacing CO₂(g) by N₂(g).

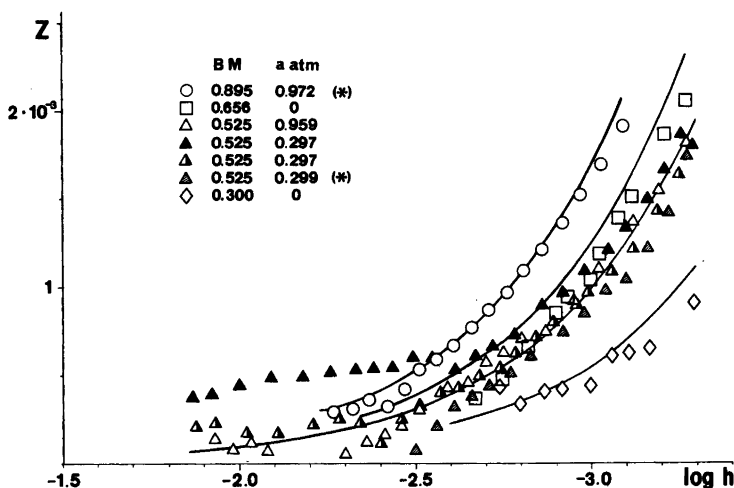


Fig. 1. Z=average number of OH⁻ bound per one mole Cu²⁺ as a function of log h. Points: experimental data. The full drawn curves represent the theoretical Z functions calculated with the constant log K₂₁=-5.72.

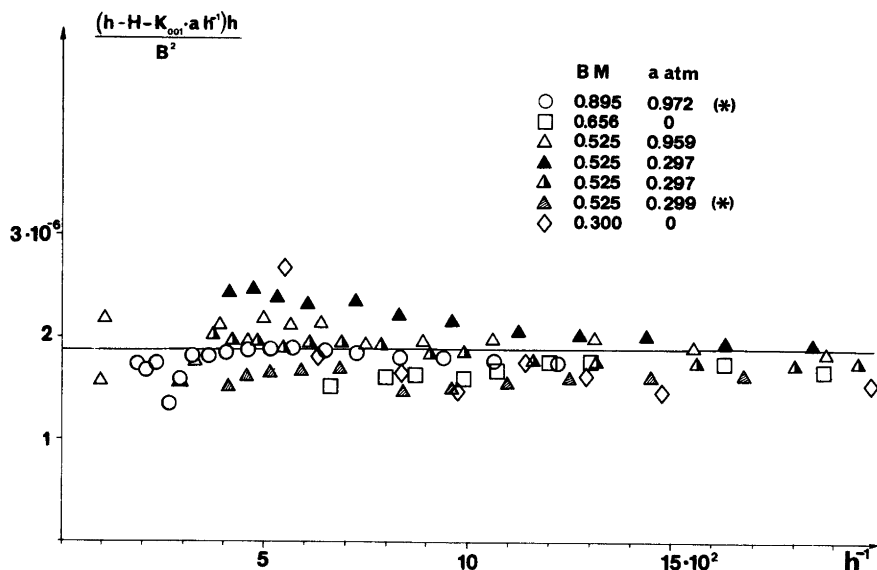


Fig. 2. Graphical determination of K_{21} . $F = (h-H-K_{011}ah^{-1})h/B^2$ as a function of h^{-1} .

TREATMENT OF THE DATA AND RESULTS

The experimental results are presented as functions of $Z = (h-H-K_{011}h^{-1}a)/B$ namely the $[\text{OH}^-]$ bound in Cu^{2+} containing reaction products, against $\log h$ (Fig. 1). Z is defined as

$$Z \equiv \frac{h-H-K_{011}h^{-1}a}{B} =$$

$$\sum_p \sum_q \beta_{pq} b^{p-1} h^{-q} f_p^{-1} f_{\text{Cu}^{2+}}^p f_{\text{H}^+}^{-q} \quad (8)$$

where the different β_{pq} values are the formation constants of the complexes $\text{Cu}_p(\text{OH})_q^{2p-q}$, where p and q are integers. f_i denotes the activity coefficient i on the molar scale. $K_{011} = K_{pqr}$ (where r is the number of CO_2 bound in one mol HCO_3^-) defined as in eqn. (10) and was calculated using the first dissociation constant¹² ($\log \beta_{011} = -7.987 \pm 0.001$) of the $\text{CO}_2(\text{g}) + \text{H}_2\text{O}$ system and the activity coefficients as calculated in the next section.

At each B level studied, less than 1 % of the Cu^{2+} is present as reaction products. Then we can use the approximation $b \approx B$. Moreover, in the general expression (8) the activity coefficients may be considered as constants in the first approximation. Thus eqn. (8) can be written

$$Z = \sum_p \sum_q K_{pq} B^{p-1} h^{-q} \quad (9)$$

where

$$K_{pq} = \beta_{pq} f_p^{-1} f_{\text{Cu}^{2+}}^p f_{\text{H}^+}^{-q} \quad (10)$$

The measurements (presented in Fig. 1) have been made at much lower Z -values ($0 \leq Z \leq 2 \cdot 10^{-3}$) than in the previous investigations. By using high values of B the precision is nevertheless quite good, the reproducibility in Z is within $3 \cdot 10^{-4}$ Z -units. The largest errors are obtained in solutions where $-\log h < 2.5$. The $Z(\log h)_B$ curves are the functions of B which means that the dominating species are polynuclear.

Assuming the presence of the species $\text{Cu}_2(\text{OH})_2^{2+}$, $\text{Cu}_2\text{OH}^{3+}$ and CuOH^+ the function $(h-H-K_{011}h^{-1}a)h/B^2$ was plotted as a function of h^{-1} (Fig. 2):

$$F \equiv (h-H-K_{011}h^{-1}a)h/B^2 =$$

$$2K_{22}h^{-1} + K_{21} + K_{11}/B \quad (11)$$

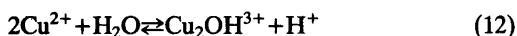
From Fig. 2 it is obvious that the F function is constant within the experimental error, independent of B in the concentration ranges investi-

Table 1. The equilibrium constants obtained graphically and with the SIT.^a

B/M	a/atm	log K ₀₁₁	log K ₂₁	log β ₂₁
0.895	0.972	-8.30	-5.74	-5.76
0.656	0	-8.21	-5.77	-5.79
0.525	0.959	-8.17	-5.70	-5.71
0.525	0.297	-8.17	-5.66	-5.67
0.525	0.297	-8.17	-5.74	-5.75
0.525	0.299	-8.17	-5.79	-5.81
0.300	0	-8.09	-5.79	-5.80
Average			-5.72±0.10	-5.75±0.10

^a The error quoted is maximum deviation from the mean value appearing in Fig. 2.

gated. Hence, only one species Cu₂OH³⁺ is formed. The formal equilibrium constant for the reaction



is presented in Table 1 for the different B levels. The average value of the constant is equal to log K₂₁ = -5.72±0.10. The error quoted is the maximum deviation from the mean value. The most uncertain experimental values corresponding to acidity levels -log h < 2.45 have been excluded from Fig. 2.

The theoretical Z curves (Fig. 1) calculated with the constant K₂₁ = 1.88 · 10⁻⁶ fit to the experimental points within the experimental error. The presence of the species Cu(OH)₂Cu²⁺ is negligible (calculated with the constant of Ref. 2) under the present experimental conditions.

The evaluation of medium effects on the equilibrium constants. The effect on the constants of medium changes caused by the replacement of a large part of Na⁺ with Cu²⁺ were estimated by SIT.¹³⁻¹⁸ The specific ion interaction approach for evaluation of activity factors was outlined by Brønsted¹³ and elaborated by Guggenheim¹⁴ and Scatchard.¹⁵ Examples of applications in the field of equilibrium analysis can be found in Ref. 16-18.

We will calculate the equilibrium constant in 3 M NaClO₄ solvent (β_{p,q}) at trace copper(II) concentrations. This involves evaluation of activity factor changes when part of NaClO₄ is replaced by Cu(ClO₄)₂. We assume that besides Cu²⁺, Na⁺, ClO₄⁻ all other species are present in trace concentrations, so their interactions with species i may not be taken into account.

According to Ref. 17 the molar activity coefficient f_i of the species i, defined so that f_i → 1 as [i] (M) → 0 in the solvent 3 M NaClO₄, may be expressed - in NaClO₄ - Cu(ClO₄)₂ mixtures of ionic strength I mol/l - as

$$\log f_i = -z_i^2[D(I) - D(3)] + \bar{\epsilon}(i, \text{Na}^+)\{[\text{Na}^+] - 3\} + \bar{\epsilon}(i, \text{Cu}^{2+})[\text{Cu}^{2+}] \quad (13)$$

In equation (13) z_i is the charge of i, D is the Debye Hückel term

$$D = \frac{0.5109\sqrt{I}}{1 + 1.5\sqrt{I}} \quad (14)$$

for a solution of ionic strength $I = \frac{1}{2} \sum_i m_i z_i^2$

(m_i is the molality of i). D(I) represents the corresponding function when I expressed in the molar scale. D(3) refers to 3 M NaClO₄ solutions. ε̄(i, x) is the interaction coefficient (liter solvent/mole solute) between the species i and x, in the molar scale.

Using expression (13), the activity coefficients in eqn. (10) will be:

$$\log f_{\text{H}^+} = -[D(I) - D(3)] \quad (15)$$

$$\log f_{\text{Cu}^{2+}} = -4[D(I) - D(3)] \quad (16)$$

$$\log f_{011} = -[D(I) - D(3)] + \bar{\epsilon}(\text{Na}^+, \text{HCO}_3^-)\{[\text{Na}^+] - 3\} + \bar{\epsilon}(\text{Cu}^{2+}, \text{HCO}_3^-)[\text{Cu}^{2+}] \quad (17)$$

$$\log f_{21} = -9[D(I) - D(3)] \quad (18)$$

In eqn. (17) the interaction coefficient $\bar{\epsilon}(\text{Na}^+, \text{HCO}_3^-) = 0.01$ is from Ref. 17. For $\bar{\epsilon}(\text{Cu}^{2+}, \text{HCO}_3^-)$ no experimental value is available. We can assume $\bar{\epsilon}(\text{Cu}^{2+}, \text{HCO}_3^-) \cong \bar{\epsilon}(\text{Cu}^{2+}, \text{ClO}_4^-) = 0.389$ liter solution/mole solute as calculated from $^{18} \alpha(\text{Cu}^{2+}, \text{ClO}_4^-) = 0.32$ kg solvent/mole. Using eqn. (10) and the appropriate function of (15)–(18), K_{011} and the equilibrium constant β_{21} in 3 M NaClO_4 can be calculated for each B level used. The results are presented in Table 1. The average value of the constant is $\log \beta_{21} = -5.75 \pm 0.10$. As seen, only small effects on the constant β_{21} occur when changing a large part of Na^+ with Cu^{2+} . On the other hand the medium effects on the constant β_{011} are quite remarkable. This constant becomes somewhat uncertain because only an approximated $\bar{\epsilon}(\text{Cu}^{2+}, \text{HCO}_3^-)$ value could be used in eqn. (17). The constant found is one order of magnitude larger than the one published in Ref. 1.

Due to the small effect of complex formation definitive conclusions are difficult to make, and further work may be needed, to obtain a better insight into the system $\text{Cu}^{2+} - \text{H}_2\text{O}$, where the pH changes over a wide range.

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REFERENCES

1. Pedersen, K. J. K. *Dan. Vidensk. Selsk., Mat.-Fys. Medd.* 20 (1943) No. 7.
2. Berecki-Biedermann, C. *Ark. Kemi* 9 (1956) 175.
3. Kakihana, H., Amaya, T. and Maeda, M. *Bull. Chem. Soc. Jpn.* 43 (1970) 3155.
4. Sillén, L. G. *Acta Chem. Scand.* 8 (1954) 299.
5. Sillén, L. G. *Acta Chem. Scand.* 8 (1954) 318.
6. Biedermann, G. and Sillén, L. G. *Ark. Kemi* 5 (1953) 425.
7. Biedermann, G. *Ark. Kemi* 9 (1956) 277.
8. Kolthoff, I. M. and Sandell, E. B. *Textbook of Quantitative Inorganic Analysis*, 3rd Ed., Macmillan, New York 1958, p. 407.
9. Gran, G. *Analyst* 77 (1952) 661.
10. Brown, A. S. *J. Am. Chem. Soc.* 56 (1934) 646.
11. Forsling, W., Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* 6 (1952) 901.
12. Ciavatta, L., Ferri, D., Grenthe, I. and Salvatore, F. *Inorg. Chem.* 20 (1981) 463.
13. Brønsted, J. N. *J. Am. Chem. Soc.* 44 (1922) 938 and 877.
14. Guggenheim, E. A. *Applications of Statistical Mechanics*, Clarendon Press, Oxford 1966.
15. Scatchard, G. *Chem. Revs.* 19 (1936) 309.
16. Biedermann, G. In Goldberg, E. D., Ed., *On the Nature of Sea Water*, Dahlem Konferenzen, Berlin 1975, p. 339.
17. Spahiu, K. *Carbonate Complex Formation in Lanthanoid and Actinoid Systems*, Diss., KTH, Stockholm 1983.
18. Ciavatta, L. *Ann. Chim. (Rome)* 70 (1980) 551.

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