The Hydrolysis of Metal Ions. Part 1. Copper(II)

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The hydrolysis of copper(II) has been investigated by potentiometric titration at 25 °C in 0.10 mol dm^{-3} potassium nitrate. Advanced computing techniques have been used for data treatment. For the species $[Cu(OH)]^+$, $[Cu_2(OH)_2]^{2+}$, and $[Cu_3(OH)_4]^{2+}$, values for $-\log \beta_{pq}$ are found to be 7.71 (0.04), 10.99 (0.02), and 21.62 (0.03), respectively, the estimated standard deviations being in parentheses.

ALTHOUGH the hydrolysis of metal ions has received much attention for many years,[1] an examination of the literature sometimes reveals serious discrepancies between various investigations. These discrepancies go beyond differences in the estimated values of the formation constants; more importantly, the stoicheiometry of the species formed is in dispute. Often, claims are made for a given species, or scheme of species, which are based on inadequate evidence or insufficiently precise data. In addition, important differences between reported results and previously obtained results are sometimes overlooked.

Accordingly, some metal-ion systems have been investigated again in an attempt to remove some of these uncertainties. This initial paper describes the experimental approach adopted and discusses the numerical methods used as illustrated by an investigation of the hydrolysis of copper(II). Reports of other investigations will follow.

EXPERIMENTAL

Reagents.—Unless otherwise stated, all the reagents were Merck G.R. and were used without further purification. The source of copper was spectroscopically pure copper(II) oxide (Johnson, Matthey). The water used was deionised and then distilled; its conductivity was usually *ca.* 0.7 μS cm^{-1}. The primary standard for the preparation of acid and base solutions was disodium tetraborate decahydrate. Sodium hydroxide solution was prepared from a Volucon standard volumetric concentrate (May and Baker Ltd.).

pH *Measurements*.—A Radiometer pHM64 Research pH meter and a Radiometer GK2401C combined glass electrode were used for pH determination. A precision of ±0.001 pH units or better was obtained and no drift in asymmetry potential was detected. The pH scale was defined with 0.05 mol dm^{-3} potassium hydrogenphthalate (Merck DIN 19266) as a standard, this being considered to have a pH of 4.008 at 25.0 °C, which is in accord with the British Standard [2] and has recently been reconfirmed by the National Bureau of Standards.[3]

The measured pH values were considered to be a function of the hydrogen-ion concentration, the proton activity coefficient, the liquid-junction potential, and other uncertainties. The pH meter was calibrated for hydrogen-ion concentration by potentiometric titration according to the method of McBryde [4] (see also ref. 5). It was thus assumed that $[H^+] = 10^{-pH}/\lambda$; the value of λ in 0.10 mol dm^{-3} potassium nitrate was found to be 0.914. This approach assumes that the presence of the hydrolysing copper(II) ion in the metal-ion titrations is unimportant.

A check on the sensitivity of the numerical results of the copper(II) hydrolysis system revealed that the value of λ is not very important. A variation of λ between 0.79 and 0.97 produced insignificant changes in the results and a plot of the error square sum against λ in this range was very nearly a horizontal line. This insensitivity is attributed to the hydrogen-ion concentrations being orders of magnitude smaller than those of the copper concentrations (see Results section).

Base addition. A burette (5 cm^3, Metrohm E457) together with a Teflon ' needle ' (0.01 in bore, Hamilton) as tip were used for base addition. The base solution, nominally 0.01 mol dm^{-3} sodium hydroxide, was stored over nitrogen and accessed by a hypodermic needle. The burette was calibrated gravimetrically with water and found to be precise to ±0.000 1 cm^3. The burette tip was immersed *ca.* 1 cm into the test solution. Diffusion of the titrant into a test solution was undetectable over the period of titration (3—4 h).

Titration procedure. After calibration, the test solution (*ca.* 50 cm^3) was introduced into the titration vessel and *ca.* 2 h were allowed for thermal equilibrium to be achieved, during which time (and throughout the titration) a continuous stream of argon (*ca.* 1 cm^3 s^{-1}) was passed through the solution. The use of a capillary gas-inlet tube rather than a fritted tube largely eliminated any entrainment and/or reflux of the test solution. The solution was stirred slowly and continuously with a magnetic bar. The titration points were obtained on a strict time basis; after base addition, equilibrium was usually reached within ⩽2 min and points were recorded every 5 min.

All the titrations were performed at 25.0 °C in a medium of 0.10 mol dm^{-3} $K[NO_3]$. The stoicheiometric ionic product of water under the conditions employed was derived from the cited value [6] of the activity coefficient of the hydrogen ion; thus $-\log K_w = 13.80$. The titrations are summarised in Table 1; full details are available on request.

RESULTS

The basis of the numerical treatment of the data was provided by the program [7,8] MINIQUAD 75. To conform with this program, the equilibrium constants for the reactions (1) are defined as in (2) where β_{pq} are stoicheiometric

TABLE 1

Details of the potentiometric titrations of copper(II) at 25 °C and 0.1 mol dm^{-3} $K[NO_3]$

Total initial copper concentration (10^{-3} mol dm^{-3})	pH Range	Number of points
2.125	5.638—6.195	20
1.488	5.662—6.313	26
1.062	5.718—6.407	25
0.638	5.857—6.606	30
0.425	5.905—6.724	30
0.212	6.059—7.001	30

constants. Thus, the p and q values are interchanged in meaning when compared with the I.U.P.A.C. convention.[9]

$$p\mathrm{Cu}^{2+} + q\mathrm{H_2O} \rightleftharpoons [\mathrm{Cu}_p(\mathrm{OH})_q]^{(2p-q)+} + q\mathrm{H}^+ \quad (1)$$

$$\beta_{pq} = [\mathrm{Cu}_p(\mathrm{OH})_q{}^{(2p-q)+}][\mathrm{H}^+]^q/[\mathrm{Cu}^{2+}]^p \quad (2)$$

This is also consistent with writing the complexes as $\mathrm{Cu}_p(\mathrm{OH})_q$, that is as hydroxo-complexes of copper rather than copper complexes of hydroxide. The species are also referred to as (p,q) pairs; the hydroxide ion is thus (0,1).

The mass-balance equations appropriate to this system are (3) and (4) where $[\mathrm{Cu}]_\mathrm{T}$ is the total copper concentration and $[\mathrm{H}]_\mathrm{T}$ the analytical proton excess (which can be negative).

$$[\mathrm{Cu}]_\mathrm{T} = [\mathrm{Cu}^{2+}] + \Sigma p\beta_{pq}[\mathrm{Cu}^{2+}]^p[\mathrm{H}^+]^{-q} \quad (3)$$

$$[\mathrm{H}]_\mathrm{T} = [\mathrm{H}^+] - \Sigma q\beta_{pq}[\mathrm{Cu}^{2+}]^p[\mathrm{H}^+]^{-q} \quad (4)$$

$[\mathrm{Cu}]_\mathrm{T}$ can be directly measured whereas $[\mathrm{H}]_\mathrm{T}$ cannot unless the initial extent of hydrolysis is negligibly small. Hydrolysis reactions to the extent of only 1% of the copper(II) introduce significant errors to the proton mass-balance equation. Although for the case of copper this equation is of little importance compared with the metal-ion equation, this is not true in general. For completeness, it was decided to make the *initial* $[\mathrm{H}]_\mathrm{T}$ value for each titration a refinable parameter together with the β_{pq} values and the free copper concentrations. This is the only significant alteration made to MINIQUAD 75 and allows a titration to begin at any pH value irrespective of the presence or absence of free acid or the extent of hydrolysis.

Since the stoicheiometry of the species present cannot be easily predicted, different species $[\mathrm{Cu}_p(\mathrm{OH})_q]^{(2p-q)+}$ were systematically selected for examination subject to the following restrictions: (*a*) the maximum value of p was arbitrarily set at 5; (*b*) the maximum value of q was set at $2p$, which excludes anionic complexes assumed to be absent under the conditions of the experiments; (*c*) the minimum value of q {except for the monomer, $[\mathrm{Cu(OH)}]^+$} was set at $p - 1$, thus limiting the number of copper atoms bonded by any given hydroxide to two.

The choice of the models to be examined (combinations of the above species) is necessarily arbitrary since the total number of all conceivable models, given the p and q values used, was unmanageably large ($2^{24} - 1$ if all the combinations were considered). We therefore adopted the following systematic approach: following Sillén,[10] it was assumed that a ' base model ' could be correctly deduced from the main trends in the data; a new species was added and the model examined using MINIQUAD 75 with all the constants being refined simultaneously. If this model satisfies certain requirements (to be discussed later) the base model can be updated. In general, the initial choice of a base model must be guided by the literature and ' chemical judgement '. In this case, the base model consisted of the single species $[\mathrm{Cu_2(OH)_2}]^{2+}$ since a preliminary calculation (model 1, Table 2) provides reasonable agreement with the data. Following this procedure, all the species from $[\mathrm{Cu(OH)}]^+$ to $[\mathrm{Cu_5(OH)_{10}}]$, subject to the above restrictions, could be tested.

To introduce a new species into a model an estimate of β_{pq} is required. If the new species is not reflected by the data then an excessively large initial estimate may result in the rejection of a species which could genuinely be present. Just how good the initial estimate needs to be for a valid refinement will depend most importantly on how close the current model is to representing the data and how complex the model is.

TABLE 2

Model tests for copper(II) hydrolysis

Model number	Model (p,q) sets	Result	10^{10} × Error square sum
1	(2,2) Base model		9.9
2	(1,1), (2,2)	(1,1) accepted	8.9
3	(1,1), (1,2), (2,2)	(1,2) rejected	
4	(1,1), (2,1), (2,2)	(2,1) rejected	
5	(1,1), (2,2), (2,3)	(2,3) accepted	3.9
6	(1,1), (2,2), (2,3), (2,4)	(2,4) rejected	
7	(1,1), (2,2), (2,3), (3,2)	(3,2) rejected	
8	(1,1), (2,2), (2,3), (3,3)	(3,3) rejected	
9	(1,1), (2,2), (2,3), (3,4)	(2,3) rejected (3,4) accepted	2.9
10	(1,1), (2,2), (3,4), (3,5)	(3,5) rejected	
11	(1,1), (2,2), (3,4), (3,6)	(3,6) rejected	
12	(1,1), (2,2), (3,4), (4,3)	(4,3) rejected	
13	(1,1), (2,2), (3,4), (4,4)	(4,4) rejected	
14	(1,1), (2,2), (3,4), (4,5)	(4,5) accepted	2.6
15—24		All species from (4,6) to (5,10) rejected *	
25	(2,2), (3,4)	Both species accepted	4.8
26	(1,1), (1,2), (2,2), (3,4)	(1,2) rejected	
27	(1,1), (2,1), (2,2), (3,2)	(2,1) and (3,2) rejected	

* Species (5,10) was not reliably rejected because of computer underflow.

From the literature, the approximate values of $-\log \beta_{11}$ and $-\log \beta_{22}$ are taken to be 8 and 11 respectively. If the deprotonation and the condensation steps are considered separately, and provided they each have similar energetics, then the formation of any species, $[\mathrm{Cu}_p(\mathrm{OH})_q]^{(2p-q)+}$, can be considered to involve q deprotonations and $p - 1$ condensations. Consideration of the difference between $[\mathrm{Cu(OH)}]^+$ (one deprotonation) and $[\mathrm{Cu_2(OH)_2}]^{2+}$ (two deprotonations, one condensation) isolates the contribution of the condensation step and, for any species $[\mathrm{Cu}_p(\mathrm{OH})_q]^{(2p-q)+}$, we may write (5). This empirical relation

$$\log \beta_{pq} \sim q \log \beta_{11} - (p - 1)(2 \log \beta_{11} - \log \beta_{22}) \quad (5)$$

generated satisfactory estimates of all the β_{pq} values [except for the (2,1) species values for which are subsequently taken from the literature].

Upon introduction to any given base model, a new species is rejected if it is rejected by MINIQUAD 75 (the value of β_{pq} becomes negative) or if the error square sum is not decreased. Otherwise, the new species is accepted and the base model updated. Alteration of the base model may involve not only the incorporation of the new species but also the removal of an earlier species.

Several ' passes ' through the species list might be necessary in order to examine all the models that can be generated. The criterion for the last pass will be the rejection of all the additional species. Table 2 summarises the results of the first pass, beginning with model 1 (the initial base model) and finishing at model 24. It is noted that since species are either accepted or rejected one at a time, the nature of the earlier models generated will influence the later models. Models 1, 2, and 4 corresponded to those previously postulated,[11-16] whereas models 25—27, although also previously postulated,[17-19] were not generated by our process but are included in Table 2 for completeness. A second pass through the program, with species (1,1), (2,2), (3,4), and (4,5) as base model, rejected all the additional species.

The details provided in Table 3 allow a comparison to be made between the six models accepted by the numerical methods used. The R factor [20] in Table 3 is an agreement factor defined as in (6) where U is the error square sum,

$$R = \{U/\Sigma([\mathrm{Cu}]_\mathrm{T}^2 + [\mathrm{B}]_\mathrm{T}^2)\}^{\frac{1}{2}} \qquad (6)$$

$[\mathrm{Cu}]_\mathrm{T}$ the total copper concentration, $[\mathrm{B}]_\mathrm{T}$ the total base concentration added, and the summation is taken over all the titration points. The R factor is thus a function of the error square sum which is normalised in terms of the total metal concentrations and the amounts of base added during the titrations. This is somewhat different from the R factor originally used in MINIQUAD 75 in which $[\mathrm{H}]_\mathrm{T}$ replaces $[\mathrm{B}]_\mathrm{T}$ in the above definition.

TABLE 3

Comparison of the best models of copper(II) hydrolysis

Model	$-\log \beta_{pq}$	Estimated standard deviation of $-\log \beta_{pq}$	Estimated (relative) standard deviation of β_{qp} (%)	R factor
Model 1				
(2,2)	10.80	0.003	0.8	0.0024
Model 2				
(1,1)	7.88	0.11	24.7	0.0022
(2,2)	10.86	0.02	3.6	
Model 5				
(1,1)	8.13	0.13	29.3	0.0015
(2,2)	10.89	0.01	2.6	
(2,3)	18.41	0.03	7.3	
Model 9				
(1,1)	7.71	0.04	10.0	0.0013
(2,2)	10.99	0.02	3.6	
(3,4)	21.62	0.03	5.9	
Model 14				
(1,1)	7.54	0.05	11.7	
(2,2)	11.08	0.04	8.5	0.0012
(3,4)	21.88	0.12	26.9	
(4,5)	25.20	0.13	30.3	
Model 25				
(2,2)	10.89	0.006	1.4	0.0016
(3,4)	21.76	0.04	8.1	

Now, we can also write expression (7), where $[\mathrm{H}]_\mathrm{T}^0$ is the

$$[\mathrm{H}]_\mathrm{T} = (V_0/V_i)[\mathrm{H}]_\mathrm{T}^0 - [\mathrm{B}]_\mathrm{T} \qquad (7)$$

initial analytical proton excess in a given titration, V_0 the initial volume, and V_i the cumulative volume at the ith titration point. In the present approach $[\mathrm{H}]_\mathrm{T}^0$ is a refinable parameter. The use here of $[\mathrm{B}]_\mathrm{T}$ rather than $[\mathrm{H}]_\mathrm{T}$ ensures that the denominator in the expression for the R factor contains only observed quantities, as is required.[20]

Confronted with a number of models, we have to develop criteria for selection of the ' best ' model. Tests of significance on the agreement factors (the Hamilton ratio test [20]) are not considered appropriate since we believe that the most important errors in precise titration data are of a systematic rather than random origin. Accordingly, the choice of the ' best ' model is unavoidably a subjective one.[21-24]

Our present experience suggests that, for 150—200 titration points, values of R should be *ca.* 0.001 and certainly less than 0.002 if good agreement exists between model and data. However, it is clear from Table 3 that goodness of fit *alone* cannot provide an adequate criterion for model choice when the estimated standard deviations are considered. Similarly, it is possible to have apparently low estimates of the standard deviations in the absence of a good fit. If it is arbitrarily assumed that a species is only acceptable if the estimated standard deviation of β_{pq} is *ca.* $\leqslant 10\%$, then the ' best ' model is clearly 9 since the goodness of fit (R 0.001 3) is excellent. No significance is therefore attached to the (4,5) species; given its high estimated standard deviation and the deleterious effect its inclusion has on the other standard deviations, its ' presence ' could be the combined result of impurities, experimental error, and model error, the latter resulting from inadequately detected species.

TABLE 4

Survey of the results of investigations of the hydrolysis reactions of copper(II)

θ_c/°C	Medium [a]	Total copper concentration (10^{-3} mol dm^{-3})	$-\log \beta_{pq}$ (1,1)	(1,2)	(2,1)	(2,2)	(3,2)	(3,4)	(p,q) [b]	Model number	Ref.
18	0	1.007—999.4	7.97		6.819	10.89				4	16
18	0	As above [c]	8			10.9				2	12
25	3.0 mol dm^{-3} Na[ClO$_4$]	10.0—100.0				10.6				1	12
25	0.1 mol dm^{-3} K[NO$_3$]	0.7—10.1	7.34			10.57				2	13
20	0	0.24—4.8				10.53		21.17	10.2	25	17
Not given [d]	0	0.25—10.0	7.57	14.70		10.84		21.64		26	18
25	0.2 mol fraction dioxan–water 3.0 mol dm^{-3} Li[ClO$_4$]	5.7—34.9	7.60			10.95				2	15
25	3.0 mol dm^{-3} Na[ClO$_4$]	47.6—90.6	7.22			10.75				2	14
25	3 mol dm^{-3} Li[ClO$_4$] 0.1 mol fraction dioxan	15.5—135.6	7.44		6.22	11.35	10.12			27	19
25	3 mol dm^{-3} Li[ClO$_4$] 0.5 mol fraction dioxan	22.6—123.1	7.74		6.40						19
25	3 mol dm^{-3} Li[ClO$_4$]	11.25—71.06	7.54		6.22	11.21	10.36			27	19
37	0.15 mol dm^{-3} K[NO$_3$]	5.0—10.0	7.6			10.49				2	5
25	0.1 mol dm^{-3} K[NO$_3$]	0.212—2.125	7.71			10.99		21.62		9	Present work

[a] Values at zero ionic strength were estimated by the investigators by extrapolation of results obtained at various ionic strengths. [b] This constant refers to the *stepwise* formation of all ' core-plus-links ' $[\mathrm{Cu}_n(\mathrm{OH})_{2n-2}]^{2+}$. [c] Recalculation of Pedersen's results [16] by Berecki-Biedermann.[12] [d] Corrections have been made to the reported constants assuming $-\log K_\mathrm{w} = 14.0$.

DISCUSSION

Table 4 lists the results of some previous investigations together with the present results. Each result is given a model number which corresponds to those used in Tables 2 and 3. In making a comparison of different speciation schemes, the most important thing to consider, assuming adequate pH ranges have been covered, is the range of total metal-ion concentration used. The range used in the present work is, in fact, narrower than in any previous investigation. This was largely influenced by the desire to work at the low ionic strength of 0.10 mol dm^{-3}.

A comparison of the data in Table 4 reveals significant discrepancies in the various speciation schemes which cannot be completely resolved by the differences in total copper(II) concentrations. It is also unlikely that the schemes would have a sufficient medium dependence to explain these discrepancies. Attempts with the present data to accommodate the various models either meet with outright failure or provide an unsatisfactory result, as shown in Tables 2 and 3.

In the present work the inclusion of the (1,1) species seems warranted since it improves the overall fit with only a small increase in the estimated standard deviation of β_{22} and an improvement in that of β_{34}. Perrin,[17] in a careful investigation of this system, was unable to detect $[Cu(OH)]^+$ but it seems likely that in the absence of access to a computer his method of calculation was not adequate to indicate the presence of this minor species.

The existence of the dimer, first postulated by Hagisawa [11] in 1939, has been suggested by all the subsequent studies.[5,11-19] The value of $-\log \beta_{22}$ appears to be remarkably independent of both ionic strength and medium.[17,19] The present data confirm the dimer to be the major hydrolytic species.

The trimer $[Cu_3(OH)_4]^{2+}$ was first postulated by Perrin [17] but could not be detected by Childs [5] or other workers.[11-16,19] Perhaps because of the current disfavour of Sillén's ' core-plus-links ' hypothesis, Baes and Mesmer [1] have also expressed doubt as to its existence. The data in Table 3, however, clearly suggest its presence under the experimental conditions used. Higher members, such as $[Cu_4(OH)_6]^{2+}$, also postulated by Perrin [17] have not been detected. The failure to detect such species, together with $[Cu_2(OH)]^{3+}$ and $[Cu_3(OH)_2]^{4+}$, could be the result of the low total copper(II) concentrations used, but no certain conclusion can be drawn.

The results of the present work strongly suggest that in establishing a speciation scheme for the hydrolysis of a metal ion the use of numerical criteria involving *both* the goodness of fit and the estimated standard deviations are mandatory. The consideration of various species should also be extended as far as is practicable. This approach is essentially the same as that pioneered and developed by Sillén. Previous investigations of the copper(II) and some other systems have failed in this respect, making their conclusions uncertain. It therefore seems likely that some of the more serious discrepancies to be found in Table 4 are the result of these inadequacies. We believe that, unless sufficient care is taken in both data acquisition and data treatment, further investigations of metal-ion hydrolysis reactions can only add to any existing confusion.

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REFERENCES

[1] C. F. Baes, jun., and R. E. Mesmer, ' The Hydrolysis of Cations,' Wiley–Interscience, New York, 1976.

[2] British Standard 1647, British Standards Institution, London, 1961.

[3] H. B. Hetzer, R. A. Durst, R. A. Robinson, and R. G. Bates, *J. Res. Nat. Bur. Stand., Sect. A.*, 1977, **81**, 21.

[4] W. A. E. McBryde, *Analyst*, 1969, **94**, 337.

[5] C. W. Childs, *Inorg. Chem.*, 1970, **9**, 2465.

[6] R. A. Robinson and R. H. Stokes, ' Electrolyte Solutions,' Butterworths, London, 1959.

[7] A. Sabatini, A. Vacca, and P. Gans, *Talanta*, 1974, **21**, 53.

[8] P. Gans, A. Sabatini, and A. Vacca, *Inorg. Chim. Acta*, 1976, **18**, 237.

[9] L. G. Sillén and A. E. Martell, ' Stability Constants of Metal Ion Complexes,' *Special Publ.*, The Chemical Society, London, 1964, no. 17, p. ii.

[10] L. G. Sillén, *Pure Appl. Chem.*, 1968, **17**, 55.

[11] H. Hagisawa, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1939, **18**, 260.

[12] C. Berecki-Biedermann, *Arkiv. Kemi*, 1956, **9**, 175.

[13] F. Achenza, *Ann. Chim. (Italy)*, 1958, **48**, 565.

[14] H. Kakihana, T. Amaya, and M. Maeda, *Bull. Chem. Soc. Japan*, 1970, **43**, 3155.

[15] H. Ohtaki, *Inorg. Chem.*, 1968, **6**, 1205.

[16] K. J. Pedersen, *Kgl. Danske Videnskab Selskab. Mat. Fys. Medd.*, 1943, **20**, 1.

[17] D. D. Perrin, *J. Chem. Soc.*, 1960, 3189.

[18] S. Mahapatra and R. S. Subrahmanya, *Proc. Indian Acad. Sci.*, 1967, **65**, 283.

[19] H. Ohtaki and T. Kawai, *Bull. Chem. Soc. Japan*, 1972, **45**, 1735.

[20] W. C. Hamilton, ' Statistics in Physical Science,' Ronald Press, New York, 1964.

[21] L. G. Sillén, *Acta Chem. Scand.*, 1962, **16**, 159.

[22] A. Sabatini and A. Vacca, *J.C.S. Dalton*, 1972, 1693.

[23] Y. Bard, ' Nonlinear Parameter Estimation,' Academic Press, New York, 1974.

[24] M. R. Davidson and R. N. Sylva, Australian Atomic Energy Commission, unpublished work.