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The Copper(II)-Pyrophosphate Complexes in 1 M $Na^+(ClO_4^-)$ Medium at 25°C

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The equilibria of the copper(II)-pyrophosphate system have been investigated in 1 M *$Na^+(ClO_4^-)$ medium at 25°C by a series of potentiometric titrations using glass and amalgam electrodes. The e.m.f. data can be explained by assuming the formation of $CuH_{p'}P_2O_7^{p'-2}$ and $CuH_{p''}(P_2O_7)_2^{p''-6}$, where $p'=0,1,2$ and $p''=0,1,2,3,4,5$, and by the following equilibrium constants*

$$Cu^{2+}+p'H^++P_2O_7^{4-}\rightleftharpoons CuH_{p'}P_2O_7^{p'-2},\ \beta_{1,p',1}=\frac{[CuH_{p'}P_2O_7^{p'-2}]}{[Cu^{2+}][H^+]^{p'}[P_2O_7^{4-}]} \qquad (1)$$

p'	0	1	2
$\log\beta_{1,p',1}$	7.6±0.2	11.8±0.1	14.71±0.05

$$Cu^{2+}+p''H^++2P_2O_7^{4-}\rightleftharpoons CuH_{p''}(P_2O_7)_2^{p''-6},\ \beta_{1,p'',2}=\frac{[CuH_{p''}(P_2O_7)_2^{p''-6}]}{[Cu^{2+}][H^+]^{p''}[P_2O_7^{4-}]^2} \qquad (2)$$

p''	0	1	2	3	4	5
$\log\beta_{1,p'',2}$	12.45 ±0.05	17.3 ±0.1	22.0 ±0.2	25.7 ±0.1	28.4 ±0.1	30.1 ±0.2

Introduction

The most complete investigation on the equilibria of the Cu^{II}-pyrophosphate system hitherto published is that of O. E. Schupp, P. E. Sturrock, and J. I. Watters[1] who measured at 25°C, using a dropping amalgam electrode the $[Cu^{2+}]$ in solutions where $[Cu^{II}]_{tot}=10^{-3}\,M$, $[P_2O_7^{4-}]_{tot}=0.01$ or $0.05\,M$ and $3\leqslant pH\leqslant 10$. The ionic strength was adjusted to 1 M by adding tetramethylammonium nitrate. The authors find evidence for the presence of the species $CuP_2O_7^{2-}$, $Cu(P_2O_7)_2^{6-}$, $CuHP_2O_7^-$, $CuH_2P_2O_7$, $CuH(P_2O_7)_2^{5-}$, $CuH_2(P_2O_7)_2^{4-}$, $CuH_3(P_2O_7)_2^{3-}$, and $CuH_4(P_2O_7)_2^{2-}$, and calculate the stepwise constants: $10^{9.07}$ and $10^{4.58}$ for $CuP_2O_7^{2-}$ and $Cu(P_2O_7)_2^{6-}$ respecticely, $10^{5.23}$ and $10^{3.31}$ for the successive addition of hydrogen ions to $CuP_2O_7^{2-}$, and $10^{6.76}$, $10^{5.78}$, $10^{4.40}$ and $10^{3.21}$ for the successive addition of H^+ to $Cu(P_2O_7)_2^{6-}$.

Most of the other previous works on the copper(II)-pyrophosphate equilibria has been done either to determine the equilibrium constants for the formation of $CuP_2O_7^{2-}$ and $Cu(P_2O_7)_2^{6-}$, or in a limited concentration range where only one or two predominant species could be detected. Results of these measurements are concisely summarised in reference 2.

The aim of the present work was to study the copper(II) equilibria of pyrophosphate by a titration technique using glass and stationary amalgam electrodes in the range $-1\geqslant\log[H^+]\geqslant -6$, *i.e.* under experimental conditions favorable to the formation of species $CuH_p(P_2O_7)_r^{2+p-4r}$ with a high value of the ratio p/r.

Notation

We shall consider as reagents Cu^{2+}, H^+, and $A^{4-}=P_2O_7^{4-}$. The concentrations of the free reagents are

$$[Cu^{2+}]=b;\quad [H^+]=h;\quad [A^{4-}]=[P_2O_7^{4-}]=a \qquad (1)$$

The equilibrium constant for the formation of a complex $Cu_qH_pA_r$ (charges are often left out) is called $\beta_{q,p,r}$

$$qCu^{2+}+pH^++rA^{4-}\rightleftharpoons Cu_qH_pA_r,\ [Cu_qH_pA_r]=\beta_{q,p,r}b^qh^pa^r \qquad (2)$$

where $q\geqslant 1$, $r\geqslant 1$, and $p\gtreqless 0$. Note that hydrolytic species Cu_qH_p, with $r=0$ and $p<0$, are neglected. This is permissible in the b and h ranges studied as estimated from results by Berecki-Biedermann.[3]

In addition to (2) association occurs between H^+ and A^{4-}

$$H^++H_{n-1}A^{n-5}\rightleftharpoons H_nA^{n-4},\ [H_nA^{n-4}]=k_nh[H_{n-1}A^{n-5}] \qquad (3)$$

If B is the total concentration of Cu^{II}, H the analytical excess of H^+ and A the total $P_2O_7^{4-}$ concentration, then we have from the law of mass action and material balance

$$\eta=\log\frac{B}{b}=\log(1+\sum_q\sum_p\sum_r q\,\beta_{q,p,r}b^{q-1}h^pa^r) \qquad (4)$$

$$H=h+\sum_n nk_1\ldots k_nh^na+\sum_q\sum_r\sum_r p\,\beta_{q,p,1}b^qh^pa^r \qquad (5)$$

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[1] O. E. Schupp, P. E. Sturrock, and J. I. Watters, *Inorg. Chem.*, 2, 106 (1963).

[2] A. E. Martell and L. G. Sillén, "Stability Constants", Special Publication No. 17, The Chemical Society, London (1964).

[3] C. Berecki-Biedermann, *Arkiv Kemi*, 9, 175 (1956).

$$A = a + \sum_n k_1 \ldots k_n h^n a + \sum_q \sum_p \sum_r r\, \beta_{q.p.r} b^q h^p a^r \qquad (6)$$

Method of Measurement

Potentiometric titrations were carried out at 25°C. In each B as well as H were kept constant while A was gradually increased. Both b and h were measured by e.m.f. methods. From these data the functions $\eta(\log h, A)_{B,H}$ were calculated which form the basis of the following treatment.

In order to minimize the variation of activity factors the test solutions were made to contain 1 M Na^+ by adding $NaClO_4$, thus the test solutions had the general analytical composition

$$B\,M\,Cu^{II},\ H\,M\,H^+,\ A\,M\,P_2O_7^{4-},\ 1\,M\,Na^+,$$
$$(1+H+2B-4A)\,M\,ClO_4^- = \text{solution S.}$$

It is assumed in the following that the medium ions do not participate in the equilibria under investigation. This is not quite correct since alkali metal cations are known[2] to form weak complexes with $P_2O_7^{4-}$. The Na^+-complexing does not introduce, however, any significant complication but only the general limitations of a constant ionic medium,[4] *i.e.* no distinction between species containing a different number of solvent salt ions and molecules. Thus the concentration of CuH_3A_2 really represents

$$\sum_x \sum_y \sum_w [CuH_3A_2(Na^+)_x(ClO_4^-)_y(H_2O)_w]$$

with $x \geqslant 0$, $y \geqslant 0$, and $w \geqslant 0$ unknown.

During the course of a titration h and b were determined by means of the cells

$$-\text{RE/solution S/GE}+ \qquad (A)$$

$$-\text{Cu(Hg)(2 phases)/solution S/RE}+ \qquad (B)$$

where GE denotes glass electrode, and RE is the reference half-cell

$$\text{RE} = \text{Ag, AgCl}/0.01M\ Cl^-,\ 0.99M\ ClO_4^-,\ 1M\ Na^+/1M\ NaClO_4$$

Assuming the activity factors remain constant[5] the e.m.f., in mV units, of cells (A) and (B) can be written at 25°C

$$E_A = E_A^\circ + 59.15 \log h + E_j \qquad (7)$$

$$E_B = E_B^\circ - 29.58 \log b - E_j \qquad (8)$$

where E_A° and E_B° are constants and E_j indicates the liquid junction potential between solution S and 1 M $NaClO_4$.

According to G. Biedermann and L. G. Sillén[5] in $NaClO_4$ media E_j is mainly function of h due to the high conductance of H^+ with respect to other ions. By measurements of the e.m.f. of the cell

$$-Cu(Hg)/h\,M\,H^+,\ b\,M\,Cu^{2+},\ 1\,M\,Na^+,$$
$$(1+h+2b)\,M\,ClO_4^-/RE+$$

as a function of h in the interval 0.01 to 0.1 M, at constant $b = 10^{-3}\,M$, we have found that E_j can be expressed in function of h by the linear equation $E_j = -55\,h$ mV.

Before each run E_A° and E_B° were assessed using solutions with $A = 0$, where $B = b$, and $H = h$.

Experimental Section

Chemicals and Analysis. Copper(II) perchlorate, perchloric acid, sodium perchlorate stock solutions were prepared and analysed as described previously.[6]

Sodium pyrophosphate, $Na_4P_2O_7$, was obtained by heating up to 1000°C in a platinum crucible a Schering-Kahlbaum $Na_4P_2O_7 \cdot 10H_2O$ product which was crystallised twice from water. The dry salt was stored in vacuum desiccator over conc. H_2SO_4.

The $Na_4P_2O_7$ preparations were analysed for P^V as $Mg_2P_2O_7$ according to B. Schmitz,[7] after transformation of the P^V to phosphate in boiling 1:1 HNO_3. It is concluded on the basis of these analyses that the solid had a purity better than 99.9 per cent.

Copper amalgam 2 per cent (two phases) was made by bringing into contact electrolytic copper with bidistilled mercury in a nitrogen atmosphere. The amalgam was stored under 0.01 M $HClO_4$.

Nitrogen from cylinders was freed from O_2 by activated copper, and purified by passing it through 10% H_2SO_4, 10% NaOH, water and finally 1 M $NaClO_4$.

Apparatus. The e.m.f. measurements were carried out at 25.00±0.05°C in a paraffin-oil thermostat. The cell arrangement was similar to that described by W. Forsling, S. Hietanen and L. G. Sillén.[8] Ag, AgCl electrodes were prepared according to A. S. Brown.[9]

Beckman glass electrodes of type NO 1190-80 were employed. They came to equilibrium in few minutes and gave reproducible $E_A - E_A^\circ$ values within ±0.2 mV. E_A was measured with a valve Radiometer PHM4 potentiometer.

E_B was measured with a Leeds & Northrup type K3 compensator. The amalgam electrode functioned satisfactorily in our solutions and gave $E_B - E_B^\circ$ values reproducible within ±0.1 mV.

Data and Calculations

Table I gives the primary data $\eta(\log h, A)_{B,H}$. The H values ranged from 0.025 to 0.1 M. For each H comparatively small values of B, $\leqslant 0.02\,H$, have been investigated. Under these experimental conditions, $B \ll H$, the last term of equation (5) is negligible with respect to H, hence

$$H \cong h + \sum_n n k_1 \ldots k_n h^n a \qquad (9)$$

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(4) L. G. Sillén, *J. Nucl. Inorg. Chem.*, *8*, 176 (1958).
(5) G. Biedermann and L. G. Sillén, *Arkiv Kemi*, *5*, 425 (1953).
(6) L. Ciavatta and M. Villafiorita, *Gazzetta*, *95*, 1247 (1965).
(7) B. Schmitz, *Z. anal. Chem.*, *45*, 513 (1906).
(8) W. Forsling, S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, *6*, 901 (1952).
(9) A. S. Brown, *J. Am. Chem. Soc.*, *56*, 646 (1934).

which enables us to express a in function of H and h only. By combining (9) with (4) we obtain an expression of $\eta = \eta(b,h)_H$ which is more convenient than (4) to find the composition of the reaction products.

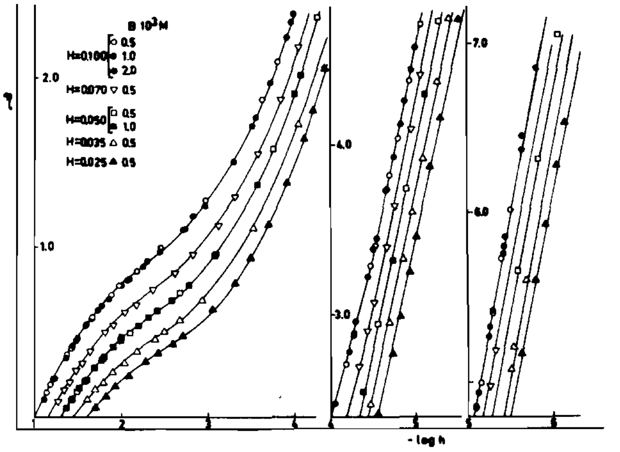

Figure 1. $\eta = \log([Cu^{II}]/[Cu^{2+}])$ as a function of $-\log h$ at different B and H values. The curves, calculated with the equilibrium constants of Table IV, correspond to $B = 5\times10^{-4}M$. Curves for higher B practically coincide with those of $B = 5\times10^{-4}M$.

It is seen from the graph $\eta(\log h)_{B,H}$, illustrated in Figure 1, that the $\eta(h)$ points at constant H fall on the same curve, within the limits of experimental uncertainty, as B ranges from 5×10^{-4} to 2×10^{-3} M. Thus species mononuclear in Cu^{II}, CuH_pA_r, may predominate.

The correctness of our conclusions is demonstrated by a special series of experiments performed with solutions where $B = 0.02$ M, $H = 0.1$ M and $\log h \geqslant -2$. These data could be explained with equilibrium constants $\beta_{1,p,r}$ determined at lower B by assuming only mononuclear complexes, indicating further that in solutions with $\log h \geqslant -2$ a can be expressed with good approximation as a function of h and H, equation (9). Although the measurements at $B = 0.02$ M could not be extended to $\log h < -2$ because of the formation of solid Cu^{II} pyrophosphates, the independence on B of
a should be still valid at lower acidities. As a matter of fact species containing a minor number of H^+, p, are favored at decreasing acidities, therefore the last term of (5) becomes more and more negligible.

The calculations will be divided into two parts. First values of a are calculated from the primary data, then the prevailing p and r values in the formula CuH_pA_r as well as the corresponding values of $\beta_{1,p,r}$ are found from the set $\eta(h,a)_{B,H}$ by following the approach proposed by L. G. Sillén.[10] This consists in deriving from three variable data, such as $\eta(h,a)$, relationships between two of the concentration variables at a constant value of the third, which are conveniently analysed by two-variable methods.[11]

Calculation of the free $P_2O_7^{4-}$ concentration, a. From the experimental data $\eta(\log h,A)_{B,H}$, given in Table I, we wished to calculate the actual $P_2O_7^{4-}$ concentration, a. Since complexes mononuclear in Cu^{II} predominate, and moreover the hydrogen ion excess, H, is high compared to B, accurate values of a can be obtained by successive approximations employing equations (9), (6) and

$$B\left(\frac{d\eta}{d\log a}\right)_h = \sum\sum r\,\beta_{1,p,r}bh^pa^r \qquad (10)$$

which is easily derived from (4). Preliminary values a' of a are deduced from (9) and the derivative of (10) is estimated from the plot $\eta(\log a')_h$. Then better values of a are obtained from (6). The couple a, $(d\eta/d\log a)_h$ is refined by successive approximation until convergence is obtained.

Table I. Survey of measurements

$H = 0.100\,M$

$B = 0.5\times10^{-3}\,M$

series a: $\eta(-\log h, A\times10^3)$: 0.406 (1.423, 24.25); 0.588 (1.664, 32.68); 0.722 (1.884, 38.30); 0.866 (2.175, 43.40); 1.104 (2.706, 48.06); 2.096 (3.805, 50.94); 2.878 (4.278, 52.32); 3.410 (4.532, 53.67); 3.823 (4.702, 54.98); 4.386 (4.931, 57.49); 4.998 (5.156, 61.01); 5.729 (5.397, 66.33).

series b: $\eta(-\log h, A\times10^3)$: 0.146 (1.142, 9.06); 0.368 (1.375, 21.94); 0.549 (1.600, 30.67); 0.777 (1.965, 40.04); 0.998 (2.447, 46.54); 1.278 (2.983, 49.51); 1.875 (3.620, 50.93); 2.322 (3.955, 51.62); 2.712 (4.192, 53.31); 3.291 (4.481, 53.65); 4.041 (4.800, 56.23); 4.756 (5.071, 59.87); 5.407 (5.301, 64.27); 6.017 (5.505, 69.21).

$B = 1.00\times10^{-3}\,M$

series a: $\eta(-\log h, A\times10^3)$: 0.109 (1.112, 8.11); 0.229 (1.232, 15.39); 0.349 (1.358, 21.95); 0.464 (1.502, 27.91); 0.581 (1.661, 33.33); 0.697 (1.855, 38.30); 0.817 (2.094, 42.86); 0.888 (2.251, 45.00); 0.970 (2.442, 47.06); 1.109 (2.729, 49.04); 1.244 (2.965, 50.00); 1.506 (3.296, 50.94); 1.717 (3.506, 51.41); 1.971 (3.717, 51.87); 2.237 (3.911, 52.33); 2.481 (4.063, 52.78); 2.893 (4.287, 53.67); 3.227 (4.445, 54.54); 3.743 (4.675, 56.25); 4.126 (4.829, 57.89); 4.579 (5.005, 60.26); 4.940 (5.132, 62.50); 5.329 (5.267, 65.32); 5.801 (5.433, 69.23).

series b: $\eta(-\log h, A\times10^3)$: 0.189 (1.184, 11.84); 0.418 (1.441, 25.00); 0.538 (1.597, 30.68); 0.657 (1.776, 35.87); 0.777 (1.999, 40.63); 0.917 (2.295, 45.00); 1.186 (2.853, 49.04); 52.78); 3.451 (4.549, 54.55); 3.932 (4.758, 56.25); 4.448 (4.954, 58.70); 4.853 (5.105, 61.02); 5.266 (5.254, 63.93); 5.756 (5.424, 67.97); 6.373 (5.642, 73.91); 6.855 (5.811, 79.10).

$B = 2.00\times10^{-3}\,M$

$\eta(-\log h, A\times10^3)$: 0.224 (1.218, 14.51); 0.446 (1.478, 26.47); 0.631 (1.732, 34.61); 0.811 (2.065, 41.75); 2.389 (3.984, 52.32); 2.961 (4.302, 53.67); 3.390 (4.506, 54.97); 3.737 (4.658, 56.25); 4.265 (4.873, 58.69); 4.861 (5.096, 62.13); 5.426 (5.294, 66.33); 5.858 (5.445, 70.15); 6.456 (5.646, 76.05).

$H = 0.070\,M$

$B = 0.50\times10^{-3}\,M$

series a: $\eta(-\log h, A\times10^3)$: 0.096 (1.276, 6.45); 0.208 (1.407, 12.25); 0.319 (1.551, 17.47); 0.541 (1.913, 26.53); 0.660 (2.173, 30.48); 0.845 (2.614, 34.11); 1.130 (3.118, 35.82); 1.554 (3.580, 36.65); 2.183 (4.052, 37.46); 2.700 (4.339, 38.25); 3.077 (4.525, 39.03); 3.645 (4.767, 40.55); 4.417 (5.064, 43.41); 5.187 (5.331, 47.35).

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(10) L. G. Sillén, *Acta Chem. Scand.*, *10*, 803 (1956).
(11) L. G. Sillén, *Acta Chem. Scand.*, *10*, 186 (1956).

series b: $\eta(-\log h, A\times 10^3)$: 0.165 (1.341, 9.43); 0.278 (1.477, 14.92); 0.390 (1.636, 19.90); 0.504 (1.813, 24.42); 0.621 (2.041, 28.55); 0.754 (2.366, 32.34); 0.960 (2.823, 34.98); 1.301 (3.315, 36.24); 1.875 (3.838, 37.06); 2.905 (4.444, 38.65); 3.399 (4.669, 39.80); 4.095 (4.956, 42.01); 4.980 (5.269, 46.08).

$H = 0.050\ M$

$B = 0.50\times 10^{-3}\ M$

$\eta(-\log h, A\times 10^3)$: 0.156 (1.484, 6.42); 0.358 (1.803, 14.63); 0.497 (2.102, 19.35); 0.734 (2.674, 23.58); 1.580 (3.758, 25.59); 2.358 (4.275, 26.47); 2.947 (4.565, 27.38); 3.743 (4.899, 29.15); 4.736 (5.265, 32.43); 5.661 (5.590, 36.82); 6.314 (5.832, 40.68); 7.049 (6.170, 46.15).

$B = 1.00\times 10^{-3}\ M$

series a: $\eta(-\log h, A\times 10^3)$: 0.055 (1.369, 2.78); 0.111 (1.437, 5.41); 0.173 (1.516, 7.90); 0.232 (1.600, 10.26); 0.291 (1.688, 12.50); 0.348 (1.793, 14.63); 0.411 (1.905, 16.67); 0.475 (2.038, 18.61); 0.541 (2.202, 20.45); 0.627 (2.415, 22.22); 0.780 (2.787, 23.91); 0.952 (3.081, 24.73); 1.372 (3.573, 25.53); 2.019 (4.074, 26.32); 2.548 (4.379, 27.08); 3.324 (4.735, 28.57); 4.303 (5.112, 31.37).

series b: $\eta(-\log h, A\times 10^3)$: 0.110 (1.428, 5.41); 0.219 (1.578, 10.26); 0.336 (1.768, 14.63); 0.451 (2.006, 18.64); 0.588 (2.314, 22.22); 0.690 (2.581, 23.91); 0.966 (3.096, 25.61); 1.911 (3.999, 27.08).

$H = 0.035\ M$

$B = 0.50\times 10^{-3}\ M$

series a: $\eta(-\log h, A\times 10^3)$: 0.104 (1.607, 4.32); 0.202 (1.789, 8.21); 0.314 (2.028, 11.71); 0.452 (2.391, 14.88); 1.110 (3.527, 17.78); 2.474 (4.475, 19.13); 2.952 (4.702, 19.78); 3.333 (4.861, 20.43); 3.921 (5.091, 21.67); 4.375 (5.252, 22.86); 4.756 (5.390, 24.00); 5.079 (5.504, 25.10).

series b: $\eta(-\log h, A\times 10^3)$: 0.164 (1.693, 6.32); 0.265 (1.894, 10.00); 0.387 (2.175, 13.33); 0.501 (2.500, 15.63); 0.568 (2.677, 16.36); 0.685 (2.937, 17.08); 1.723 (4.043, 18.46); 3.605 (4.961, 21.05); 5.208 (5.538, 25.63); 5.609 (5.685, 27.17).

$H = 0.025\ M$

$B = 0.50\times 10^{-3}\ M$

series a: $\eta(-\log h, A\times 10^3)$: 0.059 (1.700, 2.08); 0.185 (1.930, 5.92); 0.321 (2.276, 9.37); 0.426 (2.593, 10.98); 0.791 (3.309, 12.50); 1.132 (3.696, 12.87); 1.638 (4.109, 13.23); 2.053 (4.364, 13.60); 2.416 (4.562, 13.95); 2.992 (4.824, 14.65); 3.462 (5.010, 15.34); 4.163 (5.274, 16.67); 5.169 (5.629, 19.14); 5.926 (5.913, 21.43); 6.529 (6.153, 23.53).

series b: $\eta(-\log h, A\times 10^3)$: 0.123 (1.822, 4.05); 0.241 (2.084, 7.69); 0.371 (2.418, 10.19); 0.477 (2.708, 11.36); 0.634 (3.051, 12.13); 0.938 (3.489, 12.65); 1.377 (3.910, 13.02); 1.804 (4.221, 13.38); 2.772 (4.729, 14.31); 3.257 (4.932, 15.00); 3.871 (5.169, 16.01); 4.749 (5.482, 17.93); 5.602 (5.793, 20.31); 6.279 (6.050, 22.50).

Special series of measurements

$B = 0.020\ M$; $H = 0.100\ M$

$\eta(-\log h, A\times 10^3)$: 0.045 (1.052, 4.17); 0.086 (1.110, 8.11); 0.131 (1.164, 11.84); 0.173 (1.222, 15.38); 0.213 (1.272, 18.75); 0.255 (1.333, 21.95); 0.303 (1.396, 25.00); 0.366 (1.460, 27.91); 0.388 (1.529, 30.68); 0.438 1.600, 33.33); 0.484 (1.680, 35.87); 0.533 (1.764, 38.30); 0.616 (1.859, 40.62).

For the calculations we used the values of k_n: $k_1 = (2.3\pm0.3)10,^7$ $k_1k_2 = (5.25\pm0.25)10,^{12}$ $k_3 = 25\pm5$, $k_3k_4 = 141\pm15$. These were determined by the procedure illustrated later. On the basis of the uncertainties with which the k_n values are known we have estimated that the values of $\log a$ are accurate within ±0.02.

The values of p and r in the formula CuH_pA_r.

Approach I. By rearranging (4) we have

$$\varphi = (10^{\eta}-1)a^{-1} = \sum_r \sum_p \beta_{1,p,r} h^p a^{r-1} = \sum_r \gamma_r a^{r-1} = \sum_p \delta_p h^p \qquad (11)$$

where the functions

$$\gamma_r = \sum_p \beta_{1,p,r} h^p \qquad (12)$$

are constant at a given hydrogen ion concentration, and the functions

$$\delta_p = \sum_r \beta_{1,p,r} a^{r-1} \qquad (13)$$

are constant at a given a. Analysis of the $\varphi(a)_h$ functions gives values of r and of the parameters γ_r. Examination of the dependence on h of γ_r yields the predominating values of p and the equilibrium constants $\beta_{1,p,r}$. Alternatively inspection of $\varphi(h)_a$ gives p and δ_p, then r and $\beta_{1,p,r}$.

The functions $\varphi(a)_h$ and $\varphi(h)_a$ were calculated by linear interpolation from the set $\eta(h,a)_{B,H}$. No significant loss of accuracy was involved in the interpolation since for each H a considerable number of points was available and the $\eta(\log h)_H$ as well as $\eta(\log a)_H$ plots have a small curvature.

The plots of $\varphi(a)_h$ *versus* a showed that $(\varphi)_h$ can be expressed with good approximation as a linear function of a in the whole h range investigating the predominance of $CuH_{p'}A$ and $CuH_{p''}A_2$ species. From the slope and intercept of the best line passing through the $\varphi(a)_h$ points the values of γ_1 and γ_2, given in Table II, were calculated.

Table II. Survey of γ_1 and γ_2 values

$-\log h$	$\log \gamma_1$	$\log \gamma_2$
1.75	11.25 ± 0.02	21.66 ± 0.05
1.85	11.06 ± 0.02	21.21 ± 0.05
2.00	10.78 ± 0.02	20.55 ± 0.03
2.25	10.31 ± 0.02	19.57 ± 0.05
2.75	9.44 ± 0.02	17.75 ± 0.04
3.25	8.74 ± 0.02	16.18 ± 0.03
3.75	8.20 ± 0.02	14.80 ± 0.03
4.50	7.85 ± 0.02	13.26 ± 0.03
5.00	7.65 ± 0.02	12.76 ± 0.03
5.50	7.60 ± 0.02	12.58 ± 0.03
6.00	—	12.46 ± 0.03

Analysis of the $\varphi(h)_a$ functions gave no reliable results because more than 3 values of p are represented in a rather limited h range. In the following we must therefore content ourselves with discussing only the γ_1 and γ_2 functions.

Table III. Survey of K_t values

H M	0.100	0.070	0.050	0.035	0.025
$-\log(h^2a)$	14.05	14.19	14.35	14.52	14.65
$\log K_o$	0.81 ± 0.02	0.64 ± 0.03	0.44 ± 0.02	0.24 ± 0.02	0.10 ± 0.02
$-\log K_{-1}$	2.01 ± 0.02	2.24 ± 0.02	2.44 ± 0.02	2.64 ± 0.02	2.80 ± 0.02
$-\log K_{-2}$	5.87 ± 0.05	6.12 ± 0.05	6.38 ± 0.05	6.67 ± 0.05	6.85 ± 0.05

The number of hydrogen ions, p, bound in the $CuH_{p'}A$ and $CuH_{p''}A_2$ complexes was established from the dependence on h of γ_1 and γ_2. According to (12) each of these quantities equals a power series in h where each term is multiplied with the corresponding equilibrium formation constant $\beta_{1,p,r}$.

Since the derivative $d\log\gamma_1/d\log h \cong p'$ was found to have limiting values 0 ($-\log h=6$) and 2 ($-\log h=1.75$), species with $r=1$ are CuA, CuHA and CuH_2A. The values of $\beta_{1,p',1}$ for their formation were calculated by comparing the $\log\gamma_1(\log h)$ plot with the normalised[11] function

$$\Gamma = \log(1+\alpha u+u^2) \qquad (14)$$

where $u^2 = \beta_{1,2,1}\beta_{1,0,1}{}^{-1}h^2$, $\Gamma = \log\gamma_1 - \log\beta_{1,0,1}$, $\alpha = \beta_{1,1,1}\times(\beta_{1,2,1}\beta_{1,0,1})^{-1/2}$. In the position of best fit we have obtained the $\beta_{1,p',1}$ values given in Table IV.

Table IV. Survey of $\beta_{1,p,r}$ equilibrium constants

	Approach I	Approach II	Proposed value
$\log\beta_{1,0,1}$	7.5_6 ± 0.2	7.6 ± 0.2	7.6 ± 0.2
$\log\beta_{1,1,1}$	11.8_4 ± 0.1	11.78 ± 0.05	11.8 ± 0.1
$\log\beta_{1,2,1}$	14.72 ± 0.05	14.70 ± 0.05	14.71 ± 0.05
$\log\beta_{1,0,2}$	12.45 ± 0.05	—	12.45 ± 0.05
$\log\beta_{1,1,2}$	17.3 ± 0.1	—	17.3 ± 0.1
$\log\beta_{1,2,2}$	21.9_5 ± 0.1	22.1 ± 0.2	22.0 ± 0.2
$\log\beta_{1,3,2}$	25.7_4 ± 0.1	25.7 ± 0.1	25.7 ± 0.1
$\log\beta_{1,4,2}$	28.3 ± 0.1	28.4 ± 0.1	28.4 ± 0.1
$\log\beta_{1,5,2}$	30.1 ± 0.2	—	30.1 ± 0.2

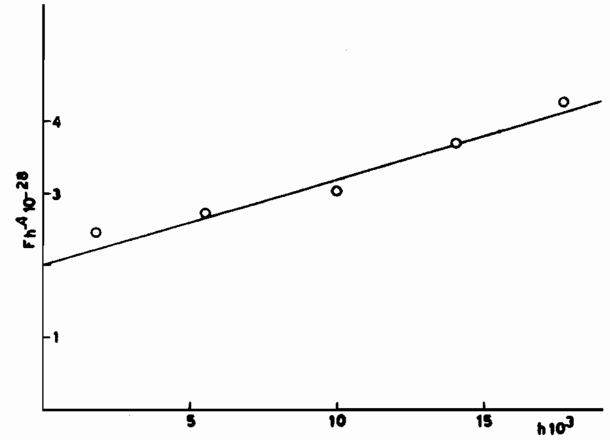

Figure 2. $Fh^{-4}=(\gamma_2-\sum_0^4\beta_{1,p'',2}h^{p''})h^{-4}$ as a function of h. The line represents $Fh^{-4}=2\times10^{28}+1.2\times10^{30}\times h$.

The plot of $\log\gamma_2$ *versus* $\log h$ was found to have slopes ranging from 0 ($-\log h=6$) to 4.5 ($-\log h=1.75$) indicating the formation of species $CuH_{p''}A_2$ with $p''>4$ in addition to CuA_2, $CuHA_2$, CuH_2A_2, CuH_3A_2, CuH_4A_2. In order to obtain the values of $\beta_{1,p'',2}$ as well as the composition of species with $p''>4$ the data were treated by Leden's[12] method. The results of calculations are given in Table IV and in Figure 2. It is seen that the plot of $Fh^{-4}=(\gamma_2-\sum_0^4\beta_{1,p'',2}h^{p''})h^{-4}$ against h can be approximated, within the limits of estimated uncertainty, by a straight line indicating the formation of CuH_5A_2 in the most acidic solutions.

Approach II. By inspection of the ($\log h$, $\log a$) data it was found that for H constant the quantity $2\log h+\log a$ remains constant, within ±0.02, in the $-\log h$ interval from 2.5 to 4.5. Setting $t=p-2r$ and

$$K_t = \sum_r \beta_{1,p,r}(h^2a)^r \qquad (15)$$

equation (4) is transformed to

$$10^{\eta}-1 = \sum_t K_t h^t \qquad (16)$$

which at h^2a constant can provide values of t and K_t. Examination of the dependence of h^2a on K_t gives the required p, r and $\beta_{1,p,r}$ values. Even if this approach gives informations only on complexes predominant in the $\log h$ range from -2.5 to -4.5, it offers however the advantage of employing directly the experimental data and not interpolated values.

We found that the plot of $\log(\frac{B}{b}-1)h$ *versus* $-\log h$ could be fitted to normalised curves $Y(\log\nu)_l$ of the function

$$Y = \log(\nu+1+l\nu^{-1}) \qquad (17)$$

indicating the predominance of species with $t=0$, -1 and -2. Since

$$Y = \log(\frac{B}{b}-1)h-\log K_{-1},$$

$$\log\nu = \log K_oK_{-1}{}^{-1}h, \quad l = K_{-2}K_oK_{-1}{}^{-2} \qquad (18)$$

we obtained in the position of best fit from $Y=0$ and $\log\nu=0$ the values of K_t, given in Table III.

The plots of $K_o\,(h^2a)^{-1}$, $K_{-1}\,(h^2a)^{-1}$ and $K_{-2}\,(h^2a)^{-1}$ *versus* h^2a were all found to be well approximated by straight lines, consequently the data can be explained with the presence of CuH_2A, CuH_4A_2, CuHA, CuH_3A_2, CuA and CuH_2A_2. In Table IV are given the corresponding $\beta_{1,p,r}$ values, obtained as slope and intercept

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[12] I. Leden, Thesis, Lund (1943).

of the best lines passing through the $K_t(h^2a)^{-1}$ *versus* h^2a points. That the species CuH_5A_2, CuA_2 and $CuHA_2$ could not be detected in the range $-2.5 \geq \log h \geq -4.5$ is understandable on the basis of the $\beta_{1,0,2}$, $\beta_{1,1,2}$ and $\beta_{1,5,2}$ constants evaluated under Approach I.

From the equilibrium constants of Table IV theoretical $\eta(\log h)_{B,H}$ curves were calculated for all B and H. The fit between experimental points $\eta(\log h)_{H,5\times10^{-4}}$ and calculated curves is shown in Figure 1. Curves for higher B practically coincide within 0.01 η units.

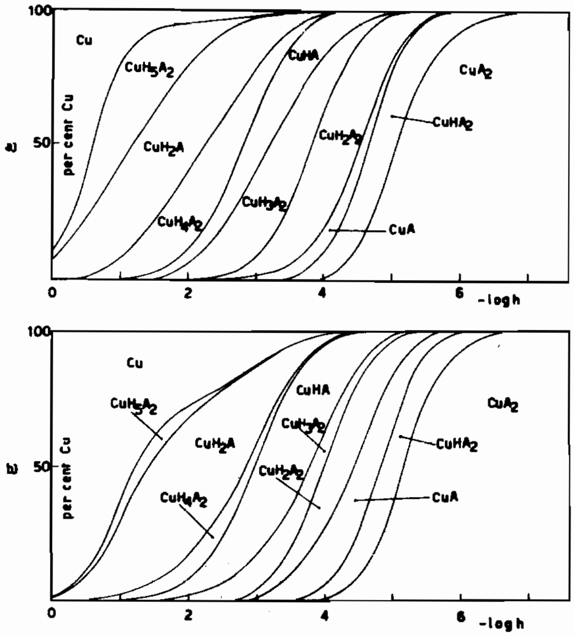

Figure 3. Distribution of complexes as a function of $\log h$. $B = 5\times10^{-4}\,M$. (a) $A = 0.10\,M$; (b) $A = 0.025\,M$.

Figure 3 shows the distribution of the total copper over the various complexes as a function of $\log h$, for $B = 5\times10^{-4}\,M$ at two different A values.

The determination of k_n, the equilibrium constant for: $H^+ + H_{n-1}A^{n-5} \rightleftharpoons H_nA^{n-4}$. The e.m.f. of the cell

$$-H_2(Pt)/H\,M\,H^+,\ A\,M\,P_2O_7^{4-},\ 1\,M\,Na^+,$$
$$(1+H-4A)\,M\,ClO_4^-/RE+ \qquad (H)$$

was measured as a function of H and A in the ranges: $0 \leq H \leq 0.1\,M$, and $0.02 \geq A \geq 0.01\,M$. From these data we have calculated the function $Z = (H-h)A^{-1}$ *versus* $-\log h$, which is illustrated by Figure 4.

It is seen that association between H^+ and A^{4-} occurs in two separate acidity ranges. For $\log h < -3$ the species A^{4-}, HA^{3-}, and H_2A^{2-} predominate. The data indicate the presence of H_2A^{2-}, H_3A^-, and H_4A in the most acidic solutions.

Assuming $k_2 \geq k_3 10^4$ the values of k_1 and k_2 can be obtained independently of those of k_3 and k_4, the former from data at $Z < 2$, the latter at $Z > 2$.

Data at $Z < 2$. Z can be expressed as a function of h by means of

$$Z = (k_1h + 2k_1k_2h^2)(1 + k_1h + k_1k_2h^2)^{-1} \qquad (19)$$

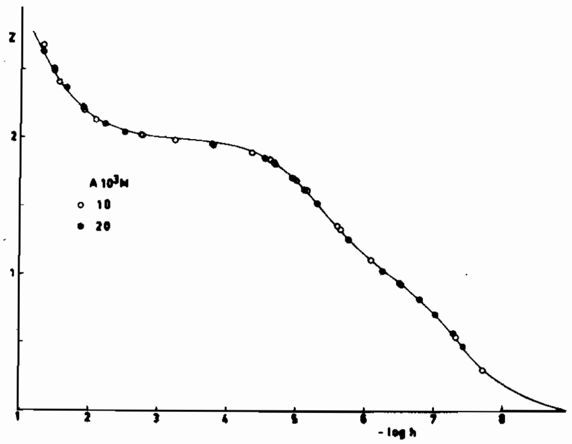

Figure 4. The association of $P_2O_7^{-4}$ with H^+. Z, the average number of H^+ per $P_2O_7^{4-}$, as a function of $\log h$. The curve has been calculated with: $\log k_1 = 7.36$, $\log k_1k_2 = 12.72$, $\log k_3 = 1.4$ and $\log k_3k_4 = 2.15$.

Comparison of the experimental points $Z(\log h)$ with the normalised[11] form of (19) gave in position of best fit

$$\log k_1 = 7.36 \pm 0.05,\quad \log k_1k_2 = 12.72 \pm 0.02$$

Data at $Z > 2$. Z can be expressed as a function of h by

$$Z-2 = (k_3h + 2k_3k_4h^2)(1 + k_3h + k_3k_4h^2)^{-1} \qquad (20)$$

When the graph $(Z-2)$ against $\log h$ was superimposed to the normalised form of (20) we read off in position of best fit

$$\log k_3 = 1.4 \pm 0.1,\quad \log k_3k_4 = 2.15 \pm 0.05$$

The values of the constants are in good agreement with those determined by other authors under experimental conditions very similar to ours. R. Näsänen[13] found $\log k_3 = 1.50$, $\log k_1k_2 = 12.95$, $\log k_1 = 7.49$. R. A. Simonaitis[14] determined $\log k_1 = 7.48$ and $k_1k_2 = 12.98$.

Discussion

The main conclusions of the present work are that Cu^{II} and pyrophosphate ions form the complexes CuA and CuA_2, as well as a series of mixed $Cu^{II}-H^+-A$ species. From the values of the constants, given in Table IV, some qualitative informations concerning the nature of the complexes can be obtained.

The Cu^{II} ion is known[2] to form weak complexes with oxygen-donor ligands, however the complexes may attain high stability when 5- or 6-membered chelate rings are formed ("chelation effect"). Thus the high stability of CuA and CuA_2, $10^{7.6}$ and $10^{12.5}$ respectively, suggests the formation of 6-membered chelate rings with $P_2O_7^{4-}$, two PO_4 tetrahedra sharing a corner

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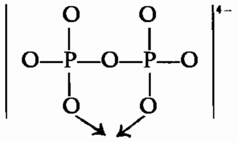
(13) R. Näsänen, *Suom. Kem.*, *33B*, 47 (1960).
(14) R. A. Simonaitis, *Diss. Abstr.*, *23*, 3101 (1963).



These configurations indicate that the complexing oxygen atoms for H^+ are placed at equivalent sites, and are consistent with the small differences found between the stepwise formation constants for the addition of H^+ to CuA and CuA_2. From the $\beta_{1,p,r}$ values of Table IV we estimate the constants $10^{4.2}$ and $10^{2.9}$ for the successive addition of H^+ to CuA, and the constants $10^{4.8}$, $10^{4.7}$, $10^{3.7}$, $10^{2.7}$, $10^{1.7}$ for the successive addition of H^+ to CuA_2. The small differences may be explained by supposing that protons are bound to oxygen atoms of different tetrahedra placed so far away from each other that electrostatic effects due to decreasing negative charge have only limited influence on the introduction of a new proton. The value of the constant for $CuH_4A_2 + H^+ \rightleftharpoons CuH_5A_2$, $10^{1.7}$, is of the same order of magnitude as that for $H_2A + H^+ = H_3A$, $10^{1.4}$, which suggests that two protons in CuH_5A_2 are bound to oxygen atoms in the same tetrahedron.

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