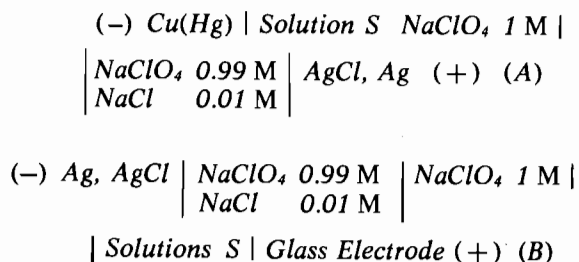


On the Formation of Cu^{II}-Tartrate Complexes in Acid Solution*

E. Bottari, A. Liberti, and A. Rufolo

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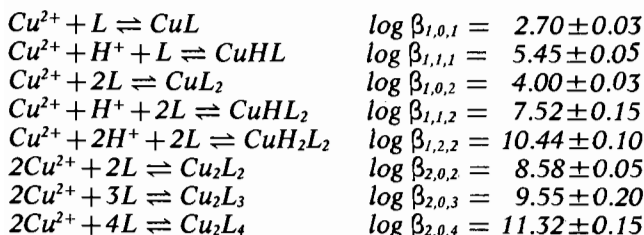
The formation of complexes between Cu²⁺ and tartrate ions (L) was studied (25°C, 1M Na⁺(ClO₄⁻)) by measuring the e.m.f. of the cells:



The solutions had the general composition: BM in

Cu^{II}, HM in H⁺, [Na⁺] = 1.00 M [ClO₄⁻] = (1+H+2B-2A) M and L = AM.

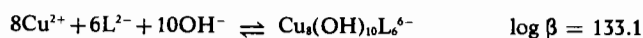
The experimental data can be explained according to the following equilibria:



Introduction

Several investigations have been made on the system Cu²⁺ tartrate ions (L) but very few quantitative results are available. S. Froneaus,¹ by means of electrometric measurements at 20°C and in 1 M NaClO₄, found no evidence for mixed or polynuclear complexes, and explained the experimental data by assuming the existence of the species CuL; CuL₂; CuL₃; CuL₄; with formation constants, log k₁ = 3.00; log k₂ = 2.11; log k₃ = 0.65; log k₄ = 0.44, respectively, L being the racemic form of the tartrate ion. J. Lefebvre,² under the same experimental conditions, reported the formation of Cu₈(OH)₁₀L₆,

according to the following equilibrium:



Recently Martell and Rajan³ have measured (25°C, 1 M KNO₃) the activity of H⁺, using of a glass electrode in solutions of copper (II) and tartrate ions. They explained their data by assuming the existence of CuL (log k = 2.6) and Cu₂L₂ (log β_{2,0,2} = 8.2) and claimed that at pH > 4 the complex Cu₂L₂ undergoes a further polymerization.

The aim of the present research is to investigate, the behaviour of solutions which contain copper(II) and tartrate ions over a wide concentration range, using an amalgam and a glass electrode. The potentiometric measurements were carried out in a range where the formation of species Cu_qH_pL_r with high ratios q/r and p/r is favoured.

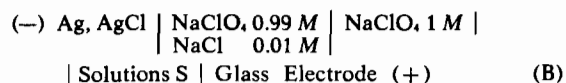
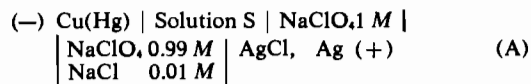
Symbols.

B = total concentration of Cu²⁺; b = free concentration of Cu²⁺; H = total concentration of H⁺; h = free concentration of H⁺; A = total concentration of tartrate; a = free concentration of tartrate; η = log(B/b); β_{q,p,r} = stability constant of a species Cu_qH_pL_r^{2q+p-2r}, defined by the following:

$$[\text{Cu}_q\text{H}_p\text{L}_r^{2q+p-2r}] = \beta_{q,p,r} b^q h^p a^r$$

k_n = stability constants of the species [H_nLⁿ⁻²] = k_nh · [H_{n-1}Lⁿ⁻³]. Charges are generally omitted; the tartrate ion is indicated by L.

Method of investigation. The activity of copper(II) and H⁺ ions was determined by measuring, by means of potentiometric titrations, the electromotive force (e.m.f.) of the cells,



In order to keep the activity coefficients constant the solution S was always prepared by adding an

(*) This paper was presented at the X Congresso Società Chimica Italiana - Padova - June 1968.

(1) S. Froneaus, Thesis - Lund 1948.

(2) J. Lefebvre, *J. Chim. Phys.*, 601 (1957).

(3) K. S. Rajan and A. E. Martell, *J. Inorg. Nuclear Chem.*, 29, 465 (1967).

excess of an inert salt (NaClO_4) so that in all solutions $[\text{Na}^+] = 1 M$, constant; thus the general composition of the solution S was as follows: BM in Cu^{II} ; HM in H^+ ; AM in L ; $1 M$ in Na^+ ; $(1+H+2B-2A)M$ in $\text{ClO}_4^- =$ solution S.

Under these experimental conditions, according to Biedermann and Sillén,⁴ the activity coefficients can be assumed to be constant and concentrations can replace activities in all calculations.

The potentiometric titrations were carried out at 25°C by adding a solution of tartrate ion to an initial solution, where B and H were known and $A=0$. In each titration B and H were kept constant as A was gradually increased.

The e.m.f. of the cells (A) and (B) can be written at 25° as follows:

$$E_A = E_A^\circ - 29.58 \log b - E_j$$

$$E_B = E_B^\circ + 59.15 \log h + E_j$$

The e.m.f. are expressed in mV units; E_A° and E_B° are constants, determined in the first part of each titration in solutions where $B=b$ and $H=h$, i.e. in absence of tartrate, and E_j is a function of h . We have found, following the procedure of Biedermann and Sillén,⁴ that under our experimental conditions $E_j = -50 h$ mV in the range $2 > -\log h > 1$.

Experimental Section

Copper(II) perchlorate, perchloric acid, sodium perchlorate were prepared and analyzed as described previously.⁵

Sodium tartrate racemic. A Riedel-de Hæen product, $\text{Na}_2\text{L} \cdot 2\text{H}_2\text{O}$, was used without further purification.

Copper amalgam 2% (two phases) was prepared as previously described.⁶

Nitrogen. The gas was passed through two activated copper columns, to remove O_2 and further purified by bubbling in 10% H_2SO_4 , 10% NaOH , distilled water, and 1 M NaClO_4 .

Apparatus. The cells and the salt-bridge arrangement were similar to those described by W. Forsling, S. Hietanen, and L. G. Sillén.⁷ All measurements were carried out in a paraffin oil thermostat at $25.00 \pm 0.05^\circ\text{C}$.

Ag, AgCl electrodes were prepared according to A. S. Brown.⁸

The e.m.f. of the cell (A) was measured with a Leeds and Northrup K3 potentiometer.

The behaviour of the amalgam in the solutions was very satisfactory. The e.m.f. values became constant within 15-30 minutes and remained constant for several hours.

The $E_A - E_A^\circ$ were reproducible within ± 0.1 mV. E_B values were measured with a Beckman glass electrode (No 1190-80) by using a valve Radiometer PHM4 potentiometer.

The value of E_B was constant within a few minutes and $E_B - E_B^\circ$ was reproducible within ± 0.2 mV.

Results and Discussion

Experimental data. The experimental data $\eta(-\log h)_{B,H}$ are collected in Table I and plotted in Figure 1. Since titrations were carried out at constant H , constant B , at a known concentration the following general equation may be written

$$B = b + \sum_q \sum_p \sum_r q \beta_{q,p,r} b^q h^p a^r \quad (1)$$

and from (1) the following expression is derived:

$$\eta = \log(B/b) = \log(1 + \sum_q \sum_p \sum_r q \beta_{q,p,r} b^{q-1} h^p a^r) \quad (2)$$

and for the total acidity, H :

$$H = h + \sum_n k_n h^n a + \sum_q \sum_p \sum_r p \beta_{q,p,r} b^q h^{p-1} a^r \quad (3)$$

The values $k_1 \dots k_n$ were determined earlier under the same experimental conditions:⁹

$$k_1 = 4.90 \times 10^3 \text{ and } k_1 k_2 = 2.77 \times 10^6$$

In equations (1) and (3) hydrolytic species of copper(II) were not considered because, according to Berecki-Biedermann,¹⁰ they are negligible under the selected experimental conditions.

The quantity $\sum_q \sum_p \sum_r p \beta_{q,p,r} b^q h^{p-1} a^r$ depends on B , H , and A . This means that when $B \ll H$ the last term of the (3) is negligible as compared to H and the a value may be calculated as follows:

$$a = \frac{H-h}{\sum_n k_n h^n} \quad (4)$$

This approximation is correct, as the range of H and B investigated was 10^{-1} to $25 \times 10^{-3} M$ for the former and 2×10^{-3} to $0.5 \times 10^{-3} M$ for the latter. The value of $\sum_q \sum_p \sum_r p \beta_{q,p,r} b^q h^{p-1} a^r$ decreases on increasing $-\log h$, and has therefore the highest value at a very low pH. From calculations made at very low pH, where $B \approx b$, the concentration of mixed complexes should be negligible with respect to H . The value of a is therefore calculated from equation (4) without any loss of accuracy.

Figure 1 shows clearly that species such as $\text{Cu}_q\text{H}_p\text{L}_r$ should be present since the experimental points do not fit the same curve, but rather different curves for each value of H and B . η is then a function of H , B and A .

(4) G. Biedermann and L. G. Sillén, *Arkiv Kem.*, 5, 425 (1955).
 (5) E. Bottari, A. Liberti, A. Rufolo, *J. Inorg. Nuclear Chem.*, 30, 2175 (1968).
 (6) E. Bottari and L. Ciavatta, *Inorg. Chim. Acta*, 2, 74 (1968).
 (7) W. Forsling, S. Hietanen, L. G. Sillén, *Acta Chem. Scand.*, 6, 901 (1952).
 (8) A. S. Brown, *J. Am. Chem. Soc.*, 56, 646 (1934).

(9) E. Bottari and A. Rufolo, *Mh. Chem.*, 99, 2383 (1968).
 (10) C. Berecki, Biedermann, *Arkiv. Kem.*, 9, 175 (1956).

Table I. Survey of measurements

$H = 0.0998 M$ $B = 0.5 \times 10^{-3} M$ Series a: η_p - $\log h$: 0.017, 1.179; 0.060, 1.539; 0.126, 1.798; 0.278, 2.121; 0.607, 2.508; 1.120, 2.909; 1.688, 3.279.
Series b: η_p - $\log h$: 0.031, 1.348; 0.115, 1.742; 0.412, 2.307; 0.857, 2.719; 1.440, 3.123.
$B = 1.0 \times 10^{-3} M$ Series a: η_p - $\log h$: 0.024, 1.352; 0.135, 1.850; 0.403, 2.293; 0.877, 2.713; 1.137, 2.888; 1.326, 3.022; 1.540, 3.161; 1.781, 3.313; 2.107, 3.516.
Series b: η_p - $\log h$: 0.011, 1.156; 0.027, 1.353; 0.077, 1.643; 0.257, 2.087; 0.602, 2.483; 1.040, 2.821; 1.250, 2.965; 1.586, 3.193; 1.930, 3.389; 2.161, 3.531.
$B = 1.4 \times 10^{-3} M$ Series a: η_p - $\log h$: 0.032, 1.211; 0.074, 1.604; 0.210, 1.984; 0.500, 2.368; 0.871, 2.679; 1.510, 3.110; 2.072, 3.457.
Series b: η_p - $\log h$: 0.037, 1.404; 0.124, 1.783; 0.335, 2.185; 0.656, 2.513; 1.221, 2.914; 1.825, 3.308.
$B = 2.0 \times 10^{-3} M$ Series a: η_p - $\log h$: 0.007, 1.243; 0.187, 1.950; 0.685, 2.525; 1.204, 2.890; 1.694, 3.203; 2.191, 3.507.
Series b: η_p - $\log h$: 0.075, 1.641; 0.408, 2.268; 0.925, 2.703; 1.439, 3.042; 1.936, 3.355.
$H = 0.0698 M$ $B = 0.5 \times 10^{-3} M$ Series a: η_p - $\log h$: 0.013, 1.418; 0.087, 1.886; 0.463, 2.517; 0.913, 2.904; 1.528, 3.321; 2.239, 3.749.
Series b: η_p - $\log h$: 0.035, 1.609; 0.236, 2.207; 0.701, 2.738; 1.238, 3.127; 1.847, 3.522.
$B = 1.0 \times 10^{-3} M$ Series a: η_p - $\log h$: 0.032, 1.523; 0.128, 1.950; 0.482, 2.498; 0.691, 2.684; 1.032, 2.946; 1.278, 3.112; 1.508, 3.267; 1.735, 3.414; 2.023, 3.593; 2.280, 3.749.
Series b: η_p - $\log h$: 0.007, 1.304; 0.025, 1.497; 0.052, 1.681; 0.098, 1.866; 0.169, 2.065; 0.332, 2.339; 0.446, 2.474; 0.653, 2.664; 0.843, 2.816; 1.076, 2.983; 1.317, 3.149; 1.537, 3.289; 1.783, 3.445; 1.989, 3.575; 2.287, 3.749.
$B = 1.4 \times 10^{-3} M$ Series a: η_p - $\log h$: 0.013, 1.321; 0.037, 1.555; 0.065, 1.729; 0.132, 1.972; 0.378, 2.388; 0.739, 2.719; 1.258, 3.083; 1.932, 3.521.
Series b: η_p - $\log h$: 0.022, 1.430; 0.049, 1.639; 0.086, 1.827; 0.222, 2.170; 0.969, 2.887; 1.574, 3.292; 2.190, 3.676.
$B = 2.0 \times 10^{-3} M$ Series a: η_p - $\log h$: 0.014, 1.411; 0.145, 2.011; 0.610, 2.591; 1.154, 2.987; 1.941, 3.505.
Series b: η_p - $\log h$: 0.055, 1.710; 0.346, 2.341; 0.859, 2.784; 1.532, 3.240; 2.196, 3.664.
$H = 0.0398 M$ $B = 0.5 \times 10^{-3} M$ Series a: η_p - $\log h$: 0.013, 1.571; 0.087, 2.043; 0.261, 2.464; 0.505, 2.760; 0.819, 3.036; 1.318, 3.399; 1.950, 3.815.
Series b: η_p - $\log h$: 0.039, 1.812; 0.161, 2.261; 0.346, 2.588; 0.651, 2.897; 1.008, 3.179; 1.638, 3.615; 2.188, 3.955.
$B = 1.4 \times 10^{-3} M$ Series a: η_p - $\log h$: 0.012, 1.583; 0.082, 2.038; 0.236, 2.403; 0.451, 2.664; 0.779, 2.943; 1.376, 3.372; 1.845, 3.690.
Series b: η_p - $\log h$: 0.044, 1.857; 0.161, 2.261; 0.320, 2.522; 0.617, 2.812; 1.135, 3.201; 1.609, 3.529; 2.065, 3.827.
$B = 2.0 \times 10^{-3} M$ Series a: η_p - $\log h$: 0.009, 1.548; 0.049, 1.881; 0.137, 2.195; 0.345, 2.535; 0.768, 2.905; 1.249, 3.250; 1.708, 3.565; 2.262, 3.923.

Table I. (Continued)

Series b: η_p - $\log h$: 0.028, 1.746; 0.080, 2.021; 0.222, 2.368; 0.487, 2.675; 0.986, 3.064; 1.493, 3.419; 1.995, 3.754.
$H = 0.0390 M$ $B = 1.0 \times 10^{-3} M$ Series a: η_p - $\log h$: 0.046, 1.945; 0.580, 2.812; 1.130, 3.233; 1.749, 3.658.
Series b: η_p - $\log h$: 0.226, 2.422; 0.893, 3.063; 1.450, 3.458; 2.051, 3.849.
$H = 0.0248 M$ $B = 0.5 \times 10^{-3} M$ Series a: η_p - $\log h$: 0.007, 1.776; 0.095, 2.287; 0.325, 2.738; 0.770, 3.171; 1.195, 3.502; 1.705, 3.854; 2.161, 4.138.
Series b: η_p - $\log h$: 0.035, 2.019; 0.193, 2.530; 0.569, 2.983; 0.998, 3.353; 1.466, 3.693; 1.947, 4.009.
$B = 1.0 \times 10^{-3} M$ Series a: η_p - $\log h$: 0.012, 1.795; 0.175, 2.478; 0.715, 3.076; 1.182, 3.483; 1.535, 3.685; 1.882, 3.913.
Series b: η_p - $\log h$: 0.051, 2.087; 0.436, 2.828; 0.954, 3.264; 1.380, 3.573; 1.709, 3.803; 2.126, 4.069.
$B = 1.4 \times 10^{-3} M$ Series a: η_p - $\log h$: 0.008, 1.784; 0.132, 2.380; 0.616, 2.968; 0.974, 3.245; 1.486, 3.617; 1.922, 3.913.
Series b: η_p - $\log h$: 0.038, 2.035; 0.315, 2.681; 0.811, 3.122; 1.231, 3.433; 1.670, 3.746; 2.191, 4.085.
$B = 2.0 \times 10^{-3} M$ Series a: η_p - $\log h$: 0.017, 1.842; 0.087, 2.239; 0.129, 2.359; 0.172, 2.452; 0.296, 2.631; 0.437, 2.784; 0.660, 2.973; 0.796, 3.078; 1.021, 3.247; 1.230, 3.401; 1.394, 3.519; 1.583, 3.653; 1.808, 3.808; 1.995, 3.933.
Series b: η_p - $\log h$: 0.020, 1.861; 0.101, 2.273; 0.728, 3.027; 1.524, 3.612; 1.719, 3.746; 1.990, 3.930.

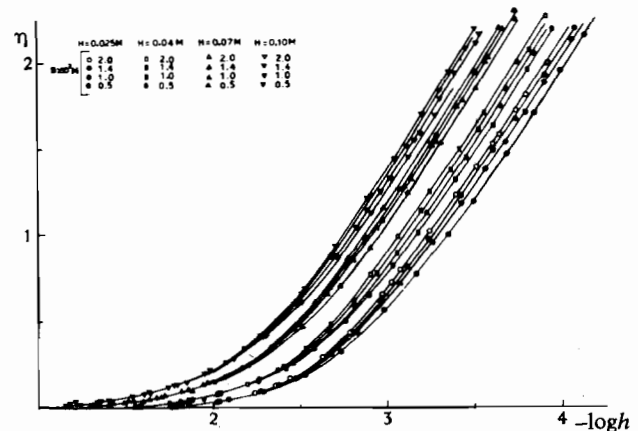


Figure 1. Experimental data ($\eta = \log([Cu^{II}]/[Cu^{II+}])$) as a function of $-\log h$ at different B and H values. The curves were drawn using the equilibrium constants of Table IV.

2) Calculation of constants in first approximation. From equation (4), for each H ($-\log h$ constant), a does not vary and can easily be calculated. Equation (2) can now be written:

$$\eta' = \eta_{H,h} = \log(1 + \sum q \gamma_a b^{q-1})_{H,h} \quad (5)$$

and from it the following expression is obtained:

$$\varphi = 10^{\eta'} - 1 = \sum q \gamma_a b^{q-1} \quad (6)$$

Table II. γ_1 and γ_2 values

$-\log h = 2.70$			$-\log h = 2.85$		
H	γ_1	γ_2	H	γ_1	γ_2
0.0998	4.92	5.35×10^3	0.0998	7.65	2.10×10^4
0.0698	3.21	1.85	0.0698	5.06	6.00×10^{-3}
0.0398	1.61	5.40×10^2	0.0398	2.48	1.73
0.0248	0.85	2.47	0.0248	1.30	8.00×10^3
$-\log h = 3.00$			$-\log h = 3.17$		
H	γ_1	γ_2	H	γ_1	γ_2
0.0998	13.80	5.35×10^4	0.0998	25.40	2.12×10^5
0.0698	8.30	2.07	0.0698	14.70	8.50×10^4
0.0398	4.00	5.85×10^3	0.0398	6.80	2.20
0.0248	2.05	2.37	0.0248	3.43	8.30×10^3
$-\log h = 3.35$			$-\log h = 3.50$		
H	γ_1	γ_2	H	γ_1	γ_2
0.0998	48.00	7.80×10^5	0.0998	79.67	2.52×10^6
0.0698	28.30	2.94	0.0698	52.10	8.15×10^5
0.0398	12.50	7.00×10^4	0.0398	21.50	1.95
0.0248	6.20	2.65	0.0248	10.05	7.70×10^4

η' is thus obtained by a graphic interpolation and from it b is calculated. No significant loss of accuracy was involved in the graphical interpolation since for each set of titrations a large number of experimental points was available.

In Figure 2 φ is plotted versus b and it is shown that, to a good approximation throughout the a and h range investigated, a linear relationship exists, indicating the presence of monuclear and binuclear complexes of the form CuH_pL_r and $\text{Cu}_2\text{H}_p\text{L}_r$. For each H and h , γ_1 is the intercept and $2\gamma_2$ is the slope. In Table II, γ_1 and γ_2 values thus calculated have been collected.

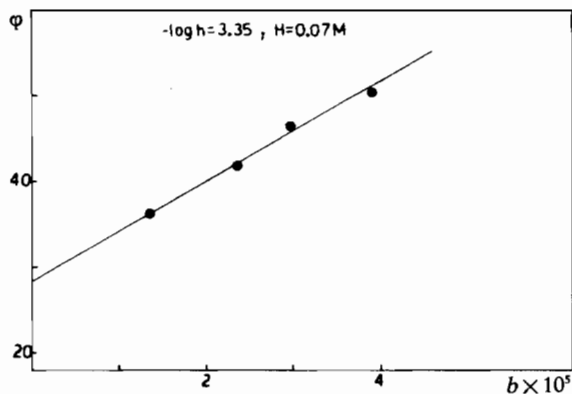


Figure 2. $\varphi = \gamma_1 + \gamma_2 b$ as a function of b . The straight line represents: $28.30 + 2 \times 2.94 \times 10^3 b$.

From (5) it is evident that γ_1 and γ_2 are functions of H and h and consequently of a and h . Therefore, the following equations can be written:

$$\gamma_1 = \sum_p \sum_r \beta_{1,p,r} h^p a^r = \sum_r \delta_{1,r} a^r \quad (7)$$

and

$$\gamma_2 = \sum_{p,r} \sum_{p',r'} \beta_{2,p',r'} h^{p'} a^{r'} = \sum_{r'} \delta_{2,r'} a^{r'} \quad (8)$$

For the mononuclear complexes, it follows from (7):

$$\gamma_1 a^{-1} = \sum_r \delta_{1,r} a^{r-1} \quad (9)$$

By plotting the values $\gamma_1 a^{-1}$ versus a , a straight line is obtained. This indicates that r assumes only the values 1 and 2. From the intercept and the slope respectively, $\delta_{1,1}$ and $\delta_{1,2}$ values are obtained, which are function only of h .

Therefore, one obtains from (7):

$$\delta_{1,1} = \sum_p \beta_{1,p,1} h^p \quad (10)$$

and the plot of $\delta_{1,1}$ versus h yields a straight line from which the values for the constants $\beta_{1,0,1}$ and $\beta_{1,1,1}$ can be calculated. In a similar way when $r = 2$:

$$\log \delta_{1,2} = \log (\sum_p \beta_{1,p,2} h^p) \quad (11)$$

The plot of $\log \delta_{1,2}$ versus $-\log h$ was examined by fitting to it the normalized curves¹¹ of equation:

$$y = \log(1 + \alpha u + u^2) \quad (12)$$

where $\log \delta_{1,2} - y = \log \beta_{1,0,2}$; $u = (\beta_{1,2,2}/\beta_{1,0,2})^{1/2} h$; $\alpha = \beta_{1,1,1}(\beta_{1,0,2}\beta_{1,2,2})^{-1/2}$. From the best fit, $\beta_{1,0,2}$, $\beta_{1,1,2}$ and $\beta_{1,2,2}$ values have been calculated.

In the case of the binuclear complexes, from equation (8) the following relationship may be obtained:

$$\log(\gamma_2 a^{-2}) = \log(\sum_{r'} \delta_{2,r'} a^{r'-2}) \quad (13)$$

This equation was compared with the normalized form of the equation

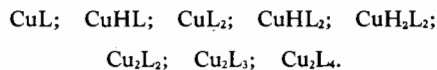
$$y = \log(1 + \alpha u + u^2) \quad (14)$$

where $u = (\delta_{2,4}/\delta_{2,2})^{1/2} a$ and $\alpha = \delta_{2,3}(\delta_{2,2}\delta_{2,4})^{-1/2}$. The position of the best fit provides the values for $\log \delta_{2,2} = \log(\gamma_2 a^{-2}) - y$, $\log \delta_{2,3}$ and $\log \delta_{2,4}$.

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

In this case $\delta_{2,2}$, $\delta_{2,3}$ and $\delta_{2,4}$ satisfactorily agree for the different $-\log h$ values, and lead us to conclude that these values are not a function of h .

The $\delta_{2,2}$, $\delta_{2,3}$ and $\delta_{2,4}$ values, therefore, correspond to $\beta_{2,0,2}$, $\beta_{2,0,3}$ and $\beta_{2,0,4}$ values. This approach provides evidence for the existence of the following species:



The values of the first approximation constants for these complexes are collected in Table III.

Table III. Values of first-approximation constants

$\log \beta_{1,0,1} = 2.70$	$\log \beta_{2,0,2} = 8.36$
$\log \beta_{1,1,1} = 5.50$	$\log \beta_{2,0,3} = 10.12$
$\log \beta_{1,0,2} = 4.04$	$\log \beta_{2,0,4} = 11.40$
$\log \beta_{1,1,2} = 7.44$	
$\log \beta_{1,2,2} = 10.50$	

3) *Improvement of the equilibrium constants.* It might be thought that, because of these operations, a significant loss of accuracy might be involved for the calculation of the above constants and the values obtained are only approximations of the real values.

The presence of the species proposed above has been considered in further calculations and they are accounted for in the following procedure. Should the assumption be incorrect a significant deviation would be anticipated in the successive calculations. The figures of Table III indicate that in the range $1 < -\log h < 2.5$ only two complexes predominate, CuL and CuHL, and, by correcting the experimental values of η for those complexes which are present only in minor concentration, an error not greater than 1% is introduced, which corresponds to the reliability of the reported stability constants. To obtain improved equilibrium constants the following relationship is set:

$$\eta'' = \log \frac{B - \beta_{1,0,1}ba^2 - \beta_{1,1,1}bha^2 - \beta_{1,2,1}bh^2a^2 - 2\beta_{2,0,2}b^2a^2 - 2\beta_{2,0,3}b^2a^3 - 2\beta_{2,0,4}b^2a^4}{b} = \log(1 + \beta_{1,0,1}a + \beta_{1,1,1}ha) \quad (15)$$

which is rearranged to the expression:

$$\psi = \log(10^{\eta''} - 1)a^{-1} = \log(\beta_{1,0,1} + \beta_{1,1,1}h) \quad (16)$$

The corresponding data are superimposed on the normalized curve obtained from the following equation:

$$y = \log(1 + u) \quad (17)$$

where $\psi - y = \log \beta_{1,0,1}$ and $u = h \beta_{1,1,1} \beta_{1,0,1}^{-1}$.

From the best fit the values of $\log \beta_{1,0,1}$ and $\log \beta_{1,1,1}$ are calculated. The values of the constants $\beta_{1,0,2}$, $\beta_{1,1,2}$ and $\beta_{1,2,2}$ were obtained by a similar treatment of the experimental data.

From a similar elaboration of (2), the following relationship is obtained:

$$\eta''' = \log \frac{B - \beta_{1,0,1}ba - \beta_{1,1,1}bha - 2\beta_{2,0,2}b^2a^2 - 2\beta_{2,0,3}b^2a^3 - 2\beta_{2,0,4}b^2a^4}{b} = \log(1 + \beta_{1,0,2}a^2 + \beta_{1,1,2}ha^2 + \beta_{1,2,2}h^2a^2) \quad (18)$$

and also

$$\psi' = \log(10^{\eta'''} - 1)a^{-2} = \log(\beta_{1,0,2} + \beta_{1,1,2}h + \beta_{1,2,2}h^2) \quad (19)$$

When ψ' is plotted versus $-\log h$ (Figure 3) the points fall on a curve which is fitted by a normalized curve of the type:

$$y = \log(1 + \alpha u + u^2) \quad (20)$$

where $\psi' - y = \log \beta_{1,0,2}$; $u = h(\beta_{1,2,2}/\beta_{1,0,2})^{1/2}$; $\alpha = \beta_{1,1,2}(\beta_{1,0,2}\beta_{1,2,2})^{-1/2}$. Since the values of the constants for all the mononuclear species present are now known, the concentrations of these complexes, calculated by refined constants, are subtracted from B .

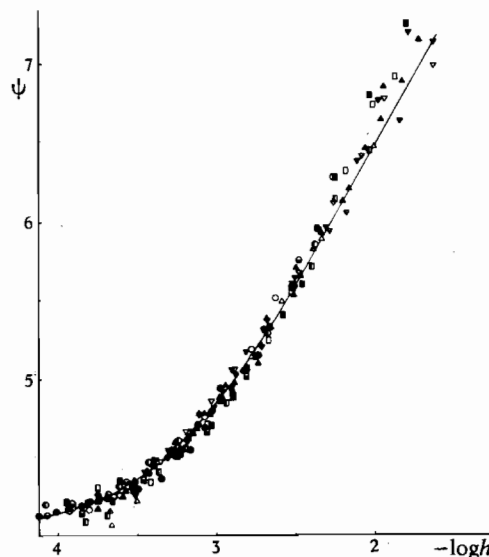


Figure 3. $\psi = \log(\beta_{1,0,2} + \beta_{1,1,2}h + \beta_{1,2,2}h^2)$ as a function of $-\log h$. The curve is calculated from the values of the mixed complex constants of Table IV.

The concentration of the polynuclear complexes present in the solution can now be calculated by setting:

$$\eta^{IV} = \log \frac{B - \beta_{1,0,1}ba - \beta_{1,1,1}bha - \beta_{1,0,2}ba^2 - \beta_{1,1,2}bh^2a^2 - \beta_{1,2,2}bh^2a^2}{b} = \log(1 + 2\beta_{2,0,2}ba^2 + 2\beta_{2,0,3}ba^3 + 2\beta_{2,0,4}ba^4) \quad (21)$$

and the following expression is obtained:

$$\Gamma = \log(10^{\eta^{IV}} - 1)b^{-1}a^{-2} = \log(2\beta_{2,0,2} + 2\beta_{2,0,3}a + \beta_{2,0,4}a^2) \quad (22)$$

By comparing, as in Figure 4, the plot of Γ versus $-\log a$ with the normalized function:

$$\Gamma' = \log(1 + \alpha u + u^2) \quad (23)$$

where $\Gamma - \Gamma' = \log 2\beta_{2,0,2}$; $u = a(\beta_{2,0,4}/\beta_{2,0,2})^{1/2}$ and $\alpha = \beta_{2,0,3}(\beta_{2,0,2}\beta_{2,0,4})^{-1/2}$ the improved constants for the polynuclear species are calculated.

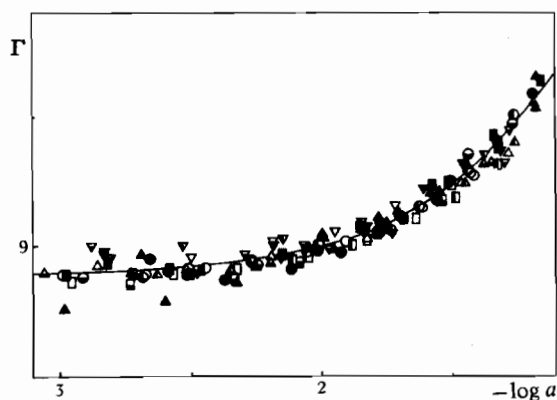


Figure 4. $\Gamma = \log(2\beta_{2,0,2} + 2\beta_{2,0,3}a + 2\beta_{2,0,4}a^2)$ as a function of $-\log a$. The curve is calculated from the values of the polynuclear complex constants of Table IV.

By means of equations (16) and (18) better values for the mixed-complex constants can now be obtained. In Table IV the values of the constants obtained by means of the revised procedure are collected. The good agreement between these data and the figures of Table III is good support for the assumptions made in carrying out these calculations.

Table IV. Refined values for the formation constants

$\log \beta_{1,0,1} = 2.70 \pm 0.03$	$\log \beta_{2,0,2} = 8.58 \pm 0.05$
$\log \beta_{1,1,1} = 5.45 \pm 0.05$	$\log \beta_{2,0,3} = 9.95 \pm 0.20$
$\log \beta_{1,0,2} = 4.00 \pm 0.03$	$\log \beta_{2,0,4} = 11.32 \pm 0.15$
$\log \beta_{1,1,2} = 7.52 \pm 0.15$	
$\log \beta_{1,2,2} = 10.44 \pm 0.10$	

The theoretical curves $\eta(-\log h)_{B,H}$ of Figure 1 have been calculated for all B and H values by using the

values of Table IV and the experimental data fit these curves quite well. However, in the region $\eta > 2.2$ the data cannot be explained by assuming only the presence of the species found in this investigation. It seems likely that other complexes are present at $\eta > 2.2$ and in more basic solutions and the subject needs further investigation.

Discussion

Copper(II) and tartrate ions in acidic solution yield mixed and polynuclear complexes. At low $-\log h$ the mixed complexes predominate and it appears from Figure 1 that the concentration of polynuclear complexes is quite low. Since the formation of a 7-membered ring is very unusual an alternative explanation is that formation of complexes between copper and tartrate ions occurs by means of only one $-\text{COO}^-$. One might expect that the second $-\text{COO}^-$ of the tartrate ion should be preferentially protonated instead of bonding to the copper ion. As the concentration of free tartrate increases a further tartrate ion becomes bonded to the copper ion and, as in the previous case, one unprotonated complex and two mixed complexes are found. The formation of the polynuclear species Cu_2L_2 , Cu_2L_3 and Cu_2L_4 may be justified since it is known that 14-membered ring compounds have a high stability and these rings should be present in the above species.

From the above data we conclude that there is no evidence for a complex of the type Cu_2L . Its existence is, in fact, very unlikely, since the measurements carried out in the $-\log h$ range investigated indicate that only the carboxylate groups are able to bond to copper ions. Thus the existence of a complex with two copper-ion bonds to one tartrate ion, with no possible stabilization by ring formation, is very improbable.

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