

## Complex Formation Equilibria of Some Aliphatic $\alpha$ -Hydroxycarboxylic Acids. 2. The Study of Copper(II) Complexes

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Complex formation equilibria of copper(II) with five aliphatic  $\alpha$ -hydroxycarboxylic acids, viz. glycolic (HL), lactic (HL), 2-hydroxyisobutyric (HL), L(+)-tartaric (H<sub>2</sub>L) and citric (H<sub>3</sub>L) acids, were studied by means of potentiometric (glass electrode) titrations at 25 °C in an ionic medium of 0.5 M NaClO<sub>4</sub>. In all copper–ligand acid systems studied Cu<sub>q</sub>H<sub>–p</sub>L<sub>r</sub> complexes were found to form at pH > 3–5. The stoichiometry of these complexes were determined by complete *p,q,r* analysis. At the pH < 3–5 the systems with monocarboxylic acids were characterized by mononuclear species CuL<sup>+</sup> and CuL<sub>2</sub>, although with lactic acid only CuL<sup>+</sup> was detected. In the case of tartaric and citric acid systems protonated and dimeric complexes were also found. A separate *p,q,r* analysis was performed for this pH region. The obtained equilibrium models and stability constants are compared with results reported earlier in the literature.

Aliphatic  $\alpha$ -hydroxycarboxylic acids are naturally occurring compounds which are important in many fields of chemistry. The chemistry of natural waters can be studied by investigating the properties of simple hydroxycarboxylic acids. Another example is the mechanism by which plants take up trace metals from the soil. They produce and release citric and tartaric acids from their roots. These form chelates with metal ions, which are then used by the plants. The trace metals that plants need are B, Cu, Mn, Fe, Zn, Co and Mo.

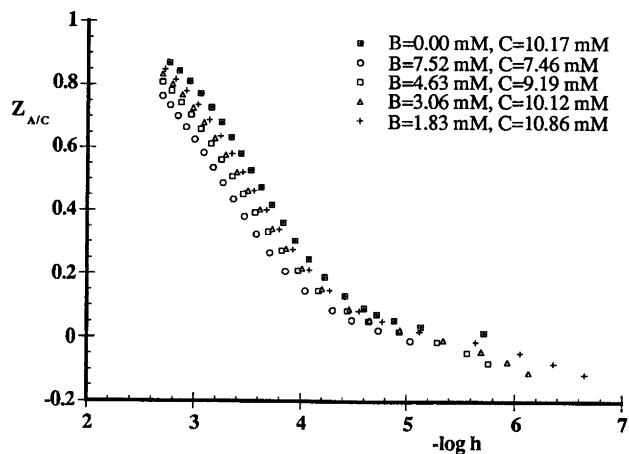
Copper is widely distributed in nature as a metal, and in sulfides, arsenides, chlorides, etc. Its approximate concentration in igneous rocks is 50–90 ppm and in soil (dry) is 20–30 ppm.<sup>1</sup> The tendency of copper to form complexes is involved in many metabolic processes in living organisms. The amount of copper required by different plants varies from about 5 ppm to several hundred ppm.<sup>1</sup> Natural waters contain predominantly alkaline and alkaline earth metals, but they also contain minor quantities of all naturally occurring metals including most transition elements such as copper. Only a very small fraction of the total Cu(II) occurs as the free metal ion. Copper forms both inorganic (carbonato and hydroxo complexes) and organic complexes (e.g. with fulvic and humic acids) in natural waters. In addition, some Cu(II) is adsorbed or bound to the surface of colloids. The investigation of chemical speciation of metals in natural waters is essen-

tial for identifying the mechanisms that control processes in the environment.

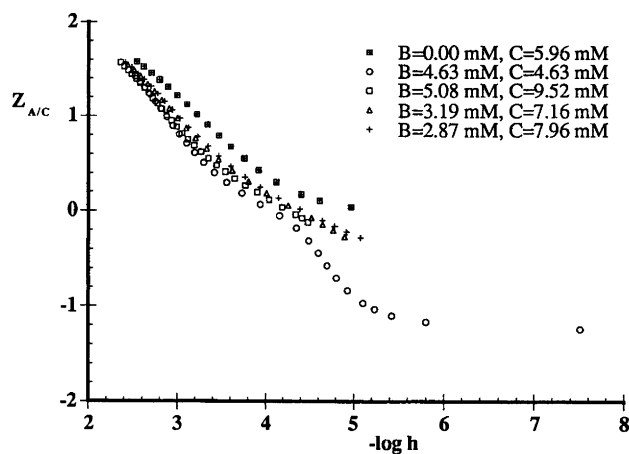
Cu(II) is classified as a 'borderline' acid in Pearson's concept of soft and hard bases (SHAB).<sup>2</sup> The complexation of copper(II) with glycolic, lactic and 2-hydroxyisobutyric acids has not been studied recently. Papers that are available give an inadequate description of the equilibrium models of these systems, because the formation of deprotonated complexes has not been considered.<sup>3–8</sup> Copper(II) tartrate complexes in acid and neutral solutions have been investigated by Bottari and Vicedomini<sup>9</sup> and by Johansson.<sup>10</sup> More alkaline solutions have been studied by Blomqvist and Still.<sup>11</sup> A comparison of these studies did not show an exact agreement concerning the equilibrium models. The copper(II) citrate system has been studied by several investigators. Lefebvre<sup>12</sup> has reported on several Cu(II)–hydroxycarboxylate systems and found for the citrate system that dimeric Cu<sub>2</sub>L<sub>2</sub><sup>2–</sup> was the main species in the acid region. The same species has been confirmed by other investigators.<sup>13,14</sup> Also, equilibrium models without that particular complex have been presented.<sup>15–17</sup> The dominant species in the neutral and alkaline pH region has been considered to be Cu<sub>2</sub>H<sub>–2</sub>L<sub>2</sub><sup>4–</sup>.<sup>12,13,17,18</sup> Also, CuH<sub>–1</sub>L<sub>2</sub><sup>–</sup> has been suggested.<sup>14–16</sup>

The aim of this series of investigations is to study the complexing tendencies of five aliphatic  $\alpha$ -hydroxycarboxylic acids [glycolic, lactic, 2-hydroxyisobutyric, L(+)-tartaric and citric acids] in comparable experimental con-

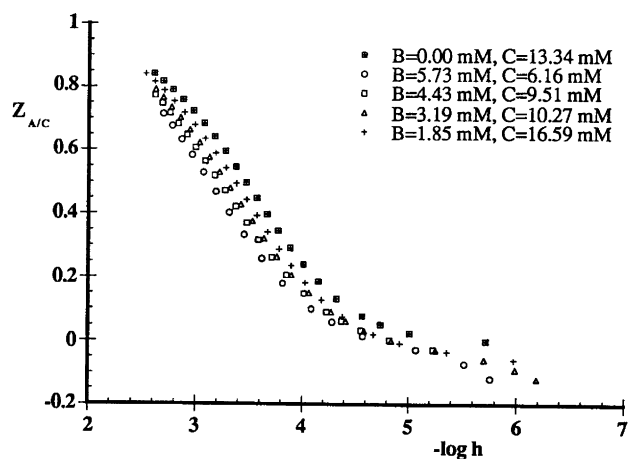
<sup>†</sup> To whom correspondence should be addressed.



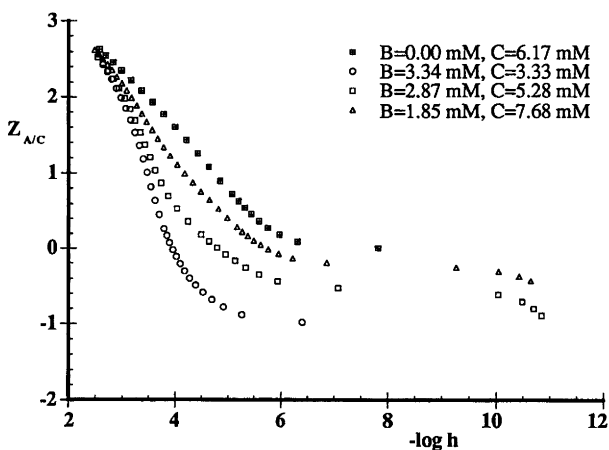
(a)



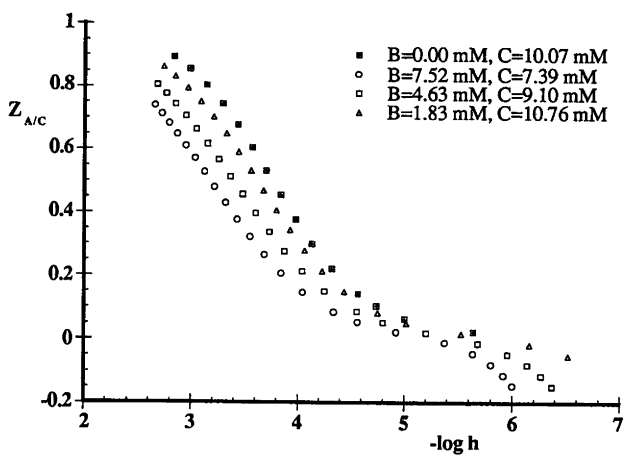
(d)



(b)



(e)



(c)

Fig. 1. Experimental data for copper(II)-ligand acid, viz. glycolic (a), lactic (b), 2-hydroxyisobutyric (c), L(+)-tartaric (d) and citric (e), systems plotted as  $Z_{A/C}$  vs.  $-\log h$ . The concentrations of copper ( $B$ ) and ligand ( $C$ ) in separate titrations are given in the figure.

ditions in order to evaluate their applicability for use in detergents and fertilizers. Also, the chemistry of natural waters is of interest. In the first part in this series we

reported the protonation equilibria and complex formation of calcium(II) and magnesium(II).<sup>19</sup> In this second part the complex formation of copper(II) is studied.

## Experimental

**Chemicals and method.** A stock solution of copper(II) perchlorate was prepared from  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ . The copper concentration was determined by titration with 0.1 M NaOH solution after passage through a cation exchanger. The solution was also analyzed by electrolytical deposition.

The hydroxycarboxylic acids were commercially available and used without further purification [glycolic acid (2-hydroxyethanoic acid,  $\text{C}_2\text{H}_4\text{O}_3$ , HL, Fluka AG), lactic acid (2-hydroxypropanoic acid,  $\text{C}_3\text{H}_6\text{O}_3$ , HL, Merck), 2-hydroxyisobutyric acid (2-hydroxy-2-methylpropanoic acid,  $\text{C}_4\text{H}_8\text{O}_3$ , HL, Riedel-deHaen AG), L(+)-tartaric acid (L(+)-2,3-dihydroxybutanedioic acid,  $\text{C}_4\text{H}_6\text{O}_6$ ,  $\text{H}_2\text{L}$ , Merck) and citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid,  $\text{C}_6\text{H}_8\text{O}_7$ ,  $\text{H}_3\text{L}$ , Merck)]. The concentrations of aqueous solutions of the ligand acids were determined by potentiometric titration with a standard solution of NaOH.

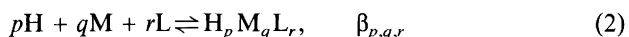
The complex formation equilibria were studied by potentiometric (glass electrode) titrations at  $25.0 \pm 0.1^\circ\text{C}$  in an ionic medium of 0.5 M  $\text{NaClO}_4$ . The preparation of other solutions, apparatus and method used including the procedure to calibrate the glass electrode are fully described in Ref. 19.

Also, combined pH and pCu (copper electrode) measurements have been used to study copper(II) complexes.<sup>10–12,14,18</sup> The free metal concentration can give valuable information for the calculation of complex formation equilibria. A copper electrode was not used in this work, but in some systems the equilibrium models determined by the combined method were tested with our own data. Stability constants calculated in this work were also compared with the constants determined by the two-electrode method.

**Data treatment.** The copper(II) complexes of the hydroxycarboxylic acids were calculated from the potentiometric data with the computer program LETAGROP.<sup>20,21</sup> The analysis of the experimental results was started with a calculation of the experimental  $Z_{A/C}$  for each point of a titration. This value is defined as the average number of protons bound to each ligand:

$$Z_{A/C} = [H - (h - k_w h^{-1})]/C \quad (1)$$

where  $H$  denotes the total concentration of the protons. The curves  $Z_{A/C}$  vs.  $-\log h$  were used to visualize the formation of hydrolyzed complexes. The equilibrium reactions in a three-component system can be described by the general relation (charges are omitted):



In order to find out the pH range where the possible hydrolyzed complexes were formed,  $\bar{n}(\log [\text{L}])$  curves were also plotted. Here  $\bar{n}$  represents the average number of ligands bound to the metal. Searching of the complex model and calculation of the corresponding stability con-

stants were performed by splitting the experimental data. The binary  $\text{Cu}_q\text{L}_r$  complexes and possible protonated complexes were calculated in the pH range where no hydrolyzed complexes existed. Finally, the  $\text{Cu}_q\text{H}_{-p}\text{L}_r$  species were searched by the  $p,q,r$  analysis, assuming the previously calculated values to be known. The aim of the analysis was to find a complex or complexes giving the lowest error-squares sum  $U = \sum (H_{\text{calc}} - H_{\text{exp}})^2$  by testing different  $p,q,r$  combinations. The LETAGROP calculations also gave the standard deviations  $3\sigma(\log \beta_{p,q,r})$ . The program SOLGASWATER<sup>22</sup> was used to calculate distribution diagrams for the equilibrium systems. The hydrolysis of  $\text{Cu}^{2+}$  was taken into account in the calculations by assuming the formation of  $\text{Cu}_2(\text{OH})_2^{2+}$ . The stability constant used for this species in 0.5 M solution is  $\log K = -10.78$ .<sup>23</sup>

## Results and discussion

**Protonation constants.** The protonation constants of the ligand acids were reported recently, and the following constants were used in the calculations:  $\log \beta_{1,0,1} = 3.586$  for glycolic acid,  $\log \beta_{1,0,1} = 3.45$  for lactic acid,  $\log \beta_{1,0,1} = 3.760$  for 2-hydroxyisobutyric acid,  $\log \beta_{1,0,1} = 3.724$  and  $\log \beta_{2,0,1} = 6.471$  for L(+)-tartaric acid, and  $\log \beta_{1,0,1} = 5.317$ ,  $\log \beta_{2,0,1} = 9.464$  and  $\log \beta_{3,0,1} = 12.296$  for citric acid.<sup>19</sup>

**Glycolic, lactic and 2-hydroxyisobutyric acids.** The Cu(II)–glycolic acid system was studied by performing five different titrations with 168 experimental points. The concentrations of ligand ( $C$ ) and metal ( $B$ ) were varied within the ranges  $0.007 < C < 0.011$  M and  $0.002 < B < 0.008$  M, resulting in  $C/B$  ratios of 1–6. These experiments covered the pH range  $2.7 < -\log h < 7$ . The examination of the equilibrium model was started by calculating the curves representing  $Z_{A/C}$  vs.  $-\log h$  (Fig. 1a) and  $\bar{n}$  vs.  $\log [\text{L}]$ , where  $\bar{n}$  corresponds to the average number of ligands bound to Cu. These figures clearly showed the formation of deprotonated species at  $\text{pH} > 4.5$  ( $Z_{A/C} < 0$ ), and the coinciding  $\bar{n}$  curves below this pH are evidence for formation of mononuclear  $\text{CuL}_n$  complexes. Data with pH under 4.5 were used to evaluate the stability of the  $\text{CuL}^+$  and  $\text{CuL}_2$  complexes formed. The following stability constants were obtained:  $\log \beta_{0,1,1} = 2.32 \pm 0.01$  and  $\log \beta_{0,1,2} = 3.73 \pm 0.01$  [the errors given correspond to  $3\sigma(\log \beta_{p,q,r})$ ]. Assuming these values to be constant, the  $p,q,r$  analysis was performed to determine the composition and stability of the remaining species. It was found that the lowest value of  $U$  was obtained for the complex  $\text{CuH}_{-1}\text{L}$  with  $\log \beta_{-1,1,1} = -3.89 \pm 0.03$ .

The Cu(II)–lactic acid system was examined with five different titrations including 177 experimental points. The metal and ligand concentrations were varied within the limits  $0.006 < C < 0.017$  M and  $0.002 < B < 0.006$  M, which gave the  $C/B$  ratios 1–9. The pH of the solutions was varied in the range  $2.5 < -\log h < 6.2$  by the addition

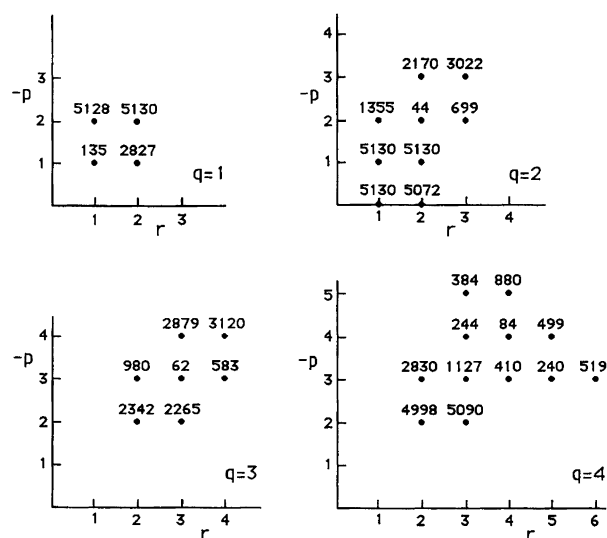


Fig. 2. The LETAGROP search for  $H_pCu_qL_r$  complexes of citric acid. The figures give error square sums  $U(pr)_q \times 10^2$  when one new complex is varied and stability constants for  $CuL^-$  and  $CuH_2L^+$  were assumed to be known.

of NaOH. In the region  $pH < 4.0$  the best fit with the data was obtained by assuming only the  $CuL^+$  complex to exist in the solution. The calculations gave for the stability constant a value  $\log \beta_{0,1,1} = 2.52 \pm 0.01$ . For a search of the deprotonated species the whole data set was used, and the earlier obtained value was kept constant. This  $p,q,r$  analysis was performed with complexes containing up to four copper atoms ( $q = 1-4$ ), giving the fol-

lowing minimum points:  $CuH_{-1}L_2^-$ ,  $Cu_2H_{-1}L_3$ ,  $Cu_3H_{-2}L_5^-$  and  $Cu_4H_{-2}L_6$ . The lowest  $U$ -value was obtained for the  $Cu_2H_{-1}L_3$  species with stability constant  $\log \beta_{-1,2,3} = 4.28 \pm 0.07$ .

The study of the  $Cu(II)$ -2-hydroxyisobutyric acid system was performed with three different titrations including 105 experimental points. The experimental conditions of the solutions were varied within the limits  $0.007 < C < 0.011$  M,  $0.002 < B < 0.008$  M and  $2.7 < -\log h < 6.5$ . The ligand and metal concentrations gave the  $C/B$  ratios 1-6. The complex formation equilibria of this particular system are reminiscent of the corresponding glycolic acid system. The examinations were restricted because of the formation of insoluble precipitate at  $pH > 6.5$ . Data with  $pH$  under 4.0 were used in the calculations of the mononuclear  $CuL^+$  and  $CuL_2$  complexes. By the same methods as mentioned in the case of glycolic acid the following stability constants were obtained:  $\log \beta_{0,1,1} = 2.74 \pm 0.01$ ,  $\log \beta_{0,1,2} = 4.35 \pm 0.02$  and  $\log \beta_{-1,1,1} = -3.96 \pm 0.07$ . The stability constants of copper(II) complexes with glycolic, lactic and 2-hydroxyisobutyric acids are listed in Table 1. The distribution diagrams for these systems showing the amount of different species present in the solution as a function of  $pH$  are presented in Figs. 3a-3c.

As described above, deprotonated complexes (the proton from the  $\alpha$ -OH group of the ligand acid is dissociated) were found to form at  $pH > 4-5$  in all monocarboxylic acid systems studied. This has not been considered in the papers that were available. On the basis of stability constants found (Table 1) it is possible to es-

Table 1. Stability constants of copper(II) complexes of glycolic, lactic and 2-hydroxyisobutyric acids at 25°C.

Ligand	[M]	Formula	$\log(\beta \pm 3\sigma)$	Reference
Glycolic acid	0.5	$CuL^+$	$2.32 \pm 0.01$	This work
	0.5	$CuL_2$	$3.73 \pm 0.01$	This work
	0.5	$CuH_{-1}L$	$-3.89 \pm 0.03$	This work
	1.0	$CuL^+$	$2.31 \pm 0.05$	3
	1.0	$CuL_2$	$3.72 \pm 0.02$	3
	2.0	$CuL^+$	$2.43 \pm 0.03$	3
Lactic acid	0.5	$CuL^+$	$2.52 \pm 0.01$	This work
	0.5	$Cu_2H_{-1}L_3$	$4.28 \pm 0.07$	This work
	0.1	$CuL^+$	2.35	4
	0.1	$CuL_2$	3.90	4
	1.0	$CuL^+$	2.49	5
	1.0	$CuL_2$	3.98	5
	1.0	$CuL^+$	$2.45 \pm 0.05$	6
	1.0	$CuL_2$	$4.08 \pm 0.1$	6
	2.0	$CuL^+$	2.57	7
	2.0	$CuL_2$	4.69	7
2-Hydroxyisobutyric acid	0.5	$CuL^+$	$2.74 \pm 0.01$	This work
	0.5	$CuL_2$	$4.35 \pm 0.02$	This work
	0.5	$CuH_{-1}L$	$-3.96 \pm 0.07$	This work
	0.1	$CuL^+$	2.82	8
	0.1	$CuL_2$	4.62	8
	1.0	$CuL^+$	2.74	5
	1.0	$CuL_2$	4.34	5
	2.0	$CuL^+$	2.35	7
	2.0	$CuL_2$	3.55	7

establish the following direction of changes in stability of  $\text{CuL}^+$  complexes with the three monocarboxylic acids studied: 2-hydroxyisobutyric acid (2.74) > lactic acid (2.52) > glycolic acid (2.32). This order can be attributed to the increased inductive effect of the methyl groups in lactic acid and in 2-hydroxyisobutyric acid. Concerning the first two ligand acids, this order is also confirmed by Thun *et al.*<sup>5</sup> The stability constants they reported are also in good accord with the values determined in this work.

**Tartaric acid.** The  $\text{Cu(II)-L(+)}$ -tartaric acid examinations consisted of six different titrations and 268 experimental points. The experimental conditions were as follows:  $0.005 < C < 0.010$  M,  $0.003 < B < 0.005$  M,  $2.4 < -\log h < 7.5$  and  $1 < C/B < 3$ . The study of this system was started with the calculation of the experimental curves  $Z_{A/C}$  ( $-\log h$ ) (Fig. 1d) and  $\bar{n}$  ( $\log [L]$ ). These figures revealed the formation of polynuclear hydrolyzed complexes at a very low pH. To solve this complicated system the equilibrium models of other works were tested with our own data (Table 2).<sup>9-11</sup> These calculations gave the following complexes and corresponding stability constants that best described our data:  $\log \beta_{0,1,1} = 2.85 \pm 0.01$ ,  $\log \beta_{0,2,2} = 8.77 \pm 0.04$ ,  $\log \beta_{1,1,1} = 5.60 \pm 0.02$ ,  $\log \beta_{-1,2,2} = 4.38 \pm 0.05$ ,  $\log \beta_{-2,2,2} = -0.25 \pm 0.04$ ,  $\log \beta_{-7,6,4} = -5.40 \pm 0.13$  and  $\log \beta_{-10,8,6} = -7.52 \pm 0.08$ . The data with  $C/B = 1$  (three titrations) were used directly as a whole to obtain the results mentioned, but the data with  $C/B = 2-3$  (three titrations) were split into different pH ranges in order to get exact stability constants.

When  $Z_{A/C} > 0$  corresponding to a pH lower than 4 the system is described by mono- and binuclear complexes  $\text{CuHL}^+$ ,  $\text{CuL}$  and  $\text{Cu}_2\text{L}_2$ . The  $\text{CuL}_2^{2-}$  species, proposed by some investigators,<sup>9,10</sup> was not found to form with the concentrations used. The binuclear complex  $\text{Cu}_2\text{L}_2$  begins to be hydrolyzed at pH 3, resulting in  $\text{Cu}_2\text{H}_{-1}\text{L}_2^-$  and  $\text{Cu}_2\text{H}_{-2}\text{L}_2^{2-}$ . Blomqvist and Still<sup>11</sup> also suggested in their study the formation of more hydrolyzed complexes,  $\text{Cu}_2\text{H}_{-3}\text{L}_2^{3-}$  and  $\text{Cu}_2\text{H}_{-4}\text{L}_2^{4-}$ , but in this work the best model was obtained with the first two complexes in this series. When the pH is increased the hydrolysis of the binuclear complexes continues but at the same time the

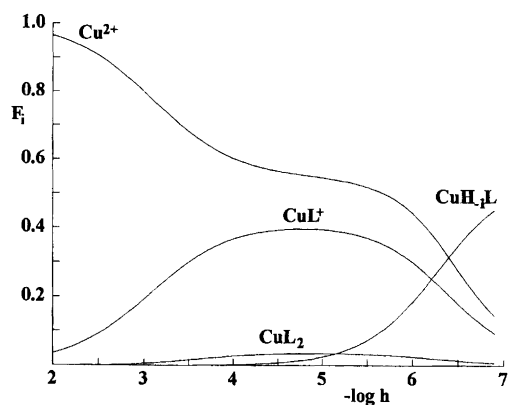
formation of more complicated species becomes predominant. In this pH range the main hydrolysis product was found to have the stoichiometric composition  $\text{Cu:H:L}$  equal to 4:-5:3. This complex is reported as a dimer  $\text{Cu}_8\text{H}_{-10}\text{L}_6^{6-}$ , which is also suggested by other workers.<sup>10,11</sup> The lowest  $U$  was obtained when calculated with an additional complex, namely  $\text{Cu}_6\text{H}_{-7}\text{L}_4^{3-}$ .

The stability constant of the  $\text{CuL}$  complex is slightly higher than the literature values available,<sup>9-11</sup> but also one higher constant was found.<sup>8</sup> Other stability constants are in good agreement with the earlier investigations. When the stability constant of the  $\text{CuL}$  complex is compared with the corresponding constants of the monocarboxylic acids studied, it is found that the tartaric acid complex is slightly more stable than the 2-hydroxyisobutyric acid complex and is therefore well suited to the stability order mentioned above. The distribution diagram for the copper- $\text{L(+)}$ -tartaric acid system is presented in Fig. 3d.

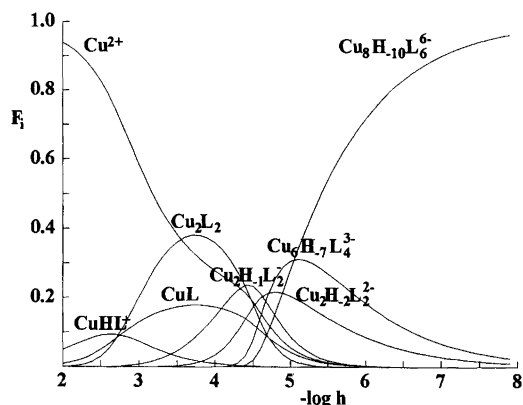
**Citric acid.** The  $\text{Cu(II)-citric acid}$  system was studied by three different titrations and 146 experimental points. The experimental conditions were as follows:  $0.003 < C < 0.008$  M,  $0.002 < B < 0.004$  M,  $2.5 < -\log h < 11$  and  $1 < C/B < 4$ . The steepness of the  $Z_{A/C}$  ( $-\log h$ ) curves (Fig. 1e) indicated a possible formation of protonated complexes, and negative  $Z_{A/C}$  values showed clearly the existence of hydrolyzed complexes. Firstly, separate  $p,q,r$  analysis was performed for the data with  $\text{pH} < 3.5$ . The calculations gave the lowest  $U$  for a two-species system, namely  $\text{CuL}^-$  and  $\text{CuH}_2\text{L}^+$ . Secondly, a complete  $p,q,r$  analysis for the remaining species was done using all the titration data and assuming the earlier determined complexes to be known. Complexes containing up to six copper atoms ( $q = 1-6$ ) were tested, and it was found that the minimum  $U$  with each  $q$ -value was obtained with a species  $[\text{CuH}_{-1}\text{L}]_q$ . The results of these calculations for  $q = 1-4$  are presented in Fig. 2. Also, the combinations of two or more complexes were tested, but the best fit was found with the species  $\text{Cu}_2\text{H}_{-2}\text{L}_2^{4-}$ . When this species was calculated together with the earlier determined ones it was found that the introduction of the  $\text{CuL}_2^{4-}$  gave a

Table 2. Stability constants of copper(II) complexes of (+)-tartaric acid at 25°C [given as  $\log(\beta \pm 3\sigma)$  values].

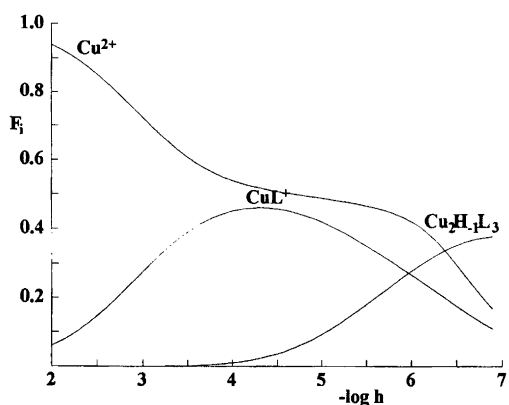
Reference	This work	10	11	9	8
Ionic strength/M	0.5	1.0	0.5	1.0	1.0
Electrolyte	$\text{NaClO}_4$	$\text{NaClO}_4$	$\text{KNO}_3$	$\text{NaClO}_4$	
pH range	2.4-7.5	2-6	4-12	3.7-7	
$\text{CuL}$	$2.85 \pm 0.01$	$2.63 \pm 0.03$	$2.5 \pm 0.1$	$2.70 \pm 0.03$	$2.90 \pm 0.3$
$\text{CuL}_2^{2-}$		$4.38 \pm 0.02$		$4.00 \pm 0.03$	
$\text{Cu}_2\text{L}_2$	$8.77 \pm 0.04$	$8.60 \pm 0.01$	$8.7 \pm 0.1$	$8.58 \pm 0.05$	$8.24 \pm 0.0$
$\text{CuHL}^+$	$5.60 \pm 0.02$	$5.58 \pm 0.01$	$5.5 \pm 0.1$	$5.45 \pm 0.05$	
$\text{CuH}_{-1}\text{L}^-$				$-2.6 \pm 0.3$	
$\text{Cu}_2\text{H}_{-1}\text{L}_2^-$	$4.38 \pm 0.05$	$4.20 \pm 0.02$	$4.5 \pm 0.1$		
$\text{Cu}_2\text{H}_{-2}\text{L}_2^{2-}$	$-0.25 \pm 0.04$	$-0.35 \pm 0.03$	$0.1 \pm 0.1$	$-0.24 \pm 0.20$	
$\text{Cu}_2\text{H}_{-3}\text{L}_2^{3-}$			$-7.0 \pm 0.1$	$-7 \pm 0.5$	
$\text{Cu}_2\text{H}_{-4}\text{L}_2^{4-}$			$-17.3 \pm 0.1$		
$\text{Cu}_6\text{H}_{-7}\text{L}_4^{3-}$	$-5.40 \pm 0.13$	$-5.52 \pm 0.05$			
$\text{Cu}_8\text{H}_{-10}\text{L}_6^{6-}$	$-7.52 \pm 0.08$	$-7.38 \pm 0.05$	$-7.5 \pm 0.2$		



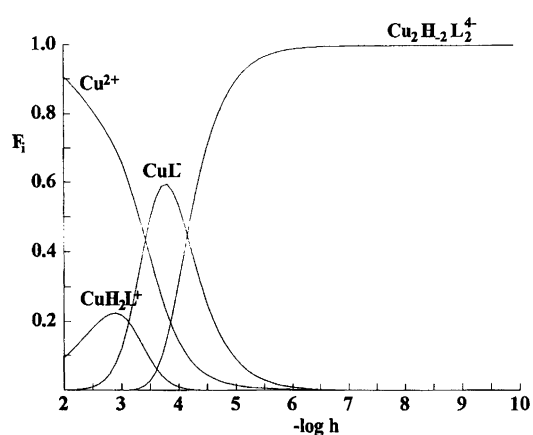
(a)



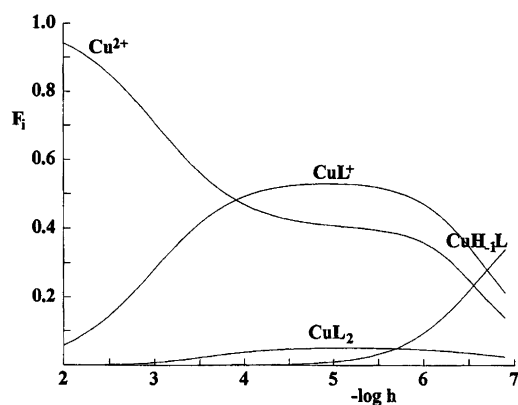
(d)



(b)



(e)



(c)

Fig. 3. Distribution diagrams  $F_i$  [fraction of total copper(II)] vs.  $-\log h$  for copper(II)-ligand acid, viz. glycolic (a), lactic (b), 2-hydroxyisobutyric (c), L(+)-tartaric (d) and citric (e), systems ( $B/C=1$ , 0.003–0.007 M). The calculations have been made using the program SOLGASWATER with constants determined in this work (Tables 1–3).

slightly lower  $U$ . The amount of this species, however, was too small to give a reliable stability constant. Therefore the equilibrium model that best described our experimental data consisted of three complexes with the following stability constants:  $\log \beta_{0,1,1} = 5.67 \pm 0.05$ ,  $\log \beta_{2,1,1} = 11.93 \pm 0.04$  and  $\log \beta_{-2,2,2} = 5.61 \pm 0.10$ . This model is compared with the works of other researchers in Table 3. The distribution diagram for the copper-citric acid system is presented in Fig. 3e.

A comparison of the earlier investigations shows that in the acidic pH region there is some uncertainty where

the existence of dimeric species is concerned. The stability constant of the  $\text{CuL}^-$  complex has been determined at several ionic strengths (0.1–2.0 M).<sup>12,15–17</sup> The constant determined in this work is in good accord with those values. Another disagreement in the acidic pH range is in the composition of the protonated species. Several complexes have been proposed, namely  $\text{CuHL}$ ,<sup>13,14,16</sup>  $\text{CuH}_2\text{L}^+$ ,<sup>15–17</sup>  $\text{CuHL}_2^{3-}$ <sup>17</sup> and  $\text{CuH}_2\text{L}_2^{2-}$ .<sup>2–17</sup> The stability constant of the  $\text{CuH}_2\text{L}^+$  complex determined in this work is slightly higher than that of Petit-Ramel and Khalil<sup>16</sup> determined in 0.5 M solution. In the neutral and

Table 3. Stability constants of copper(II) complexes of citric acid [given as  $\log(\beta \pm 3\sigma)$  values].

Reference	This work	18	13	14	15	16	12	17
Temp./°C	25	25	25	25	30	25	20	25
Ionic strength	0.5	0.1	0.25	0.1	0.1	0.5	1.0	2.0
Electrolyte	NaClO <sub>4</sub>	KNO <sub>3</sub>	Et <sub>4</sub> NBr	KNO <sub>3</sub>	NaNO <sub>3</sub>	NaNO <sub>3</sub>	NaClO <sub>4</sub>	NaClO <sub>4</sub>
pH range	2.5–10.8	4.5–10	3–6.5			2–12.5	1–4.8	
CuL <sup>-</sup>		5.67±0.05			6.5	5.95	5.2	4.40
CuL <sub>2</sub> <sup>4-</sup>						8.09	8.4	7.28
Cu <sub>2</sub> L <sub>2</sub> <sup>2-</sup>			14.77±0.012	14.72±0.10			12.8	
CuHL			9.75±0.05	9.31±0.08		8.68		
CuH <sub>2</sub> L <sup>+</sup>	11.93±0.04				12.5	11.34		11.20
CuHL <sub>2</sub> <sup>3-</sup>								11.78
CuH <sub>2</sub> L <sub>2</sub> <sup>2-</sup>								16.00
CuH <sub>-1</sub> L <sub>2</sub> <sup>2-</sup>				1.61±0.04	2.15	2.16		
CuH <sub>-2</sub> L <sub>2</sub> <sup>3-</sup>								
Cu <sub>2</sub> H <sub>-1</sub> L		5.07±0.02	5.16±0.05					
Cu <sub>2</sub> H <sub>-1</sub> L <sub>2</sub> <sup>3-</sup>		10.82±0.02	11.36±0.05					
Cu <sub>2</sub> H <sub>-2</sub> L <sub>2</sub>								1.90
Cu <sub>2</sub> H <sub>-2</sub> L <sub>2</sub> <sup>4-</sup>	5.61±0.10	5.80±0.07	6.20±0.05				6.0	5.30

alkaline pH region Cu<sub>2</sub>H<sub>-2</sub>L<sub>2</sub><sup>4-</sup> is considered to be the dominant species in the most papers.<sup>12,13,17,18</sup> This was also confirmed in this study. In fact, no other hydrolyzed complexes were found to form.

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