

# Spectrophotometric investigation of the formation of Cu(II)–maleic acid complexes

Julija Uljanionok\*,

Aldona Jagminienė,

Arvydas Survila

*Institute of Chemistry,  
A. Goštauto 9,  
LT-01108 Vilnius,  
Lithuania*

Spectrophotometric investigations of Cu(II) and maleic acid solutions containing 0.3 M  $K_2SO_4$  as a supporting electrolyte were carried out over the pH range from 2 to 6. Addition of maleic acid ( $LH_2$ ) into Cu(II) solutions results in a significant rise of the absorption maximum and its shift from 806 to 722 nm. Similar effects were also observed when the pH of the solutions was increased at a constant ligand concentration.

Experimental absorption spectra can be described quantitatively on the assumption that two species, viz.  $Cu^{2+}$  and  $CuL$ , are responsible for absorption in the region of visible light. Then, a modified Lorentz distribution, which follows from the description of a driven harmonic oscillator, is applicable to each partial spectrum.

The stability constant ( $\beta_1$ ) of  $CuL$  species, expressed in terms of concentration, was determined. Using the recently obtained cumulative stability constants of protonated ligands  $LH^-$  and  $LH_2$  ( $10^{5.75}$  and  $10^{7.3}$ , respectively), we found that  $\log \beta_1 = 2.2 \pm 0.07$ .

**Key words:** copper, maleic acid, stability constants, spectrophotometry

## INTRODUCTION

Systems containing ligands capable of forming complexes with both  $Cu^{2+}$  and  $Cu^+$  ions are interesting objects for investigation. Cis-butenedioic or maleic acid,  $HOOC-CH=CH-COOH$ , symbolized further as  $LH_2$ , exhibits such properties. Three species of ligand ( $LH_2$ ,  $LH^-$  and  $L^{2-}$ ), which can be produced in solutions, show quite a different chemical affinity to  $Cu^+$  and  $Cu^{2+}$  ions. Generally, an interaction between  $Cu^{2+}$  and common organic acids is possible when H is removed from the carboxylic group [1]. Then, the coordination bond may be formed between  $Cu^{2+}$  and the oxygen atom in  $-COO^-$  group. Since Cu(II) chelates are usually formed, the anion  $L^{2-}$  should be considered in this case as the most active form of ligand. Its concentration and, as a consequence, the complexation degree of Cu(II) should strongly depend on solution pH. In contrast,  $\pi$ -orbitals in the double bond  $-HC=CH-$  are responsible for coordination between  $Cu^+$  and maleic acid [2]. It is unlikely that the dissociation of carboxylic group could noticeably change the electronic characteristics of this bond. Thus, no substantial effect of pH on Cu(I) complexation degree should be expected.

Quantitative data concerning the distribution of system components in the solution can be simulated using material balance equations (see, e. g., [3]) that involve cumulative stability constants of complex species ( $\beta$ ). Unfortunately,

the literature concerning formation and stability of copper maleates is very slender [1, 4, 5]. Polarography has been used [4] for the investigation of slightly acidic (pH 4–7) Cu(II) solutions containing perchlorate as a supporting electrolyte at the ionic strength  $I = 0.2$  M. Reversible two-electron waves have been observed and  $\beta$  values have been reported for three complex species, viz.  $CuL$ ,  $CuL_2^{2-}$  and  $CuL_3^{4-}$ . However, Peacoc and James [5] who have analysed pH changes resulting from the addition of  $CuCl_2$  into sodium maleate solutions, found only one monoligand complex,  $CuL$ .

Considering such discrepancies, we carried out some preliminary polarographic experiments with Cu(II)–maleic acid solutions containing  $K_2SO_4$  as a supporting electrolyte. Unfortunately, the obtained polarograms did not show any evidence of reversibility, and the shift of half-wave potential was rather weak. In this connection, we turned to spectrophotometry which is often used for the determination of stability constants. In this study, we made an attempt to perform an analysis of absorption maxima in combination with a quantitative description of the entire experimental spectra. The data reported here are necessary for the further investigation of the electrochemical characteristics of the system.

## EXPERIMENTAL

The preparation of solutions and spectrophotometric investigations were the same as in our previous investigation [6].

\* Corresponding author. E-mail: uljanionok@mail.ru

KOH,  $K_2SO_4$  (high purity) and  $CuSO_4 \cdot 5 H_2O$  (analytical grade, Reakhim (Russia)) were used. The latter substance was recrystallized from thrice-distilled water which was also used for the preparation of solutions. Cu(II) concentration in the stock solution was controlled by complexometric titration. Maleic acid (>99%, Fluka) was used as received. Besides, the study solutions contained 0.3 M  $K_2SO_4$  as a background electrolyte.

UV-visible spectra were recorded in 1.0 cm path length quartz cells using a Perkin–Elmer Lambda 35 UV / VIS spectrophotometer. The reference cell contained pure water. All experiments were carried out at 20 °C.

## RESULTS AND DISCUSSION

According to our previous communication [6], absorption spectra obtained for  $CuSO_4$  and  $Cu(ClO_4)_2$  solutions are very similar. In both cases, the absorption maxima are observed at  $\lambda_{max} = 806–808$  nm, and their height ( $A_{max}$ ) linearly depends on the concentration of  $Cu^{2+}$  aqua-ions. The extinction coefficient  $\epsilon = 11.4 M^{-1} cm^{-1}$  was determined in this case. Although maleic acid does not absorb in the visible region of the spectrum, addition of this substance into Cu(II) solutions considerably changes their spectrum characteristics. Some typical examples of spectrophotometric data obtained for ligand-containing solutions are shown in Fig. 1. An increase in ligand concentration results in a gradual rise of the characteristic maximum and its shift towards shorter wavelengths (the upper part of Fig. 1). Similar tendencies were also observed when the solution pH increased (bottom of Fig. 1), i. e. when more favourable conditions appeared for complex formation.

More regularity can be revealed from the data presented in Fig. 2. It should be noted that a rise of  $A_{max}$  with maleic acid concentration ( $c_{mal.ac.}$ ) slackens and tends to some limiting value. A similar feature is also characteristic of the sigmoidal dependence of  $A_{max}$  on pH obtained at a constant ligand concentration. It is particularly remarkable that  $A_{max}$  and  $\lambda_{max}$  are interrelated by a single-valued function that does not depend on solution composition (Fig. 3). These features give grounds to suppose that monoligand complexes predominate at  $pH < 6$ . Therefore, only two species, viz.  $Cu^{2+}$  aqua-complexes and  $CuL$ , should be responsible for the absorbance in the visible part of the spectrum. Unfortunately, individual spectra of the above complexes overlap, and this circumstance hinders the analysis of experimental data. In this case, quantitative methods allowing to separate the components of spectra are needed.

Individual absorption characteristics of  $Cu^{2+}$  aqua-complexes can be obtained in the simplest way since such solutions can be easily prepared and investigated. The problem under discussion becomes simpler due to the fact that the shape of the spectra does not actually depend on Cu(II) concentration. This can be seen from Fig. 4 (part A) where normalized absorbances are plotted against the quantum energy. The transformed data lie very close and can be approximated

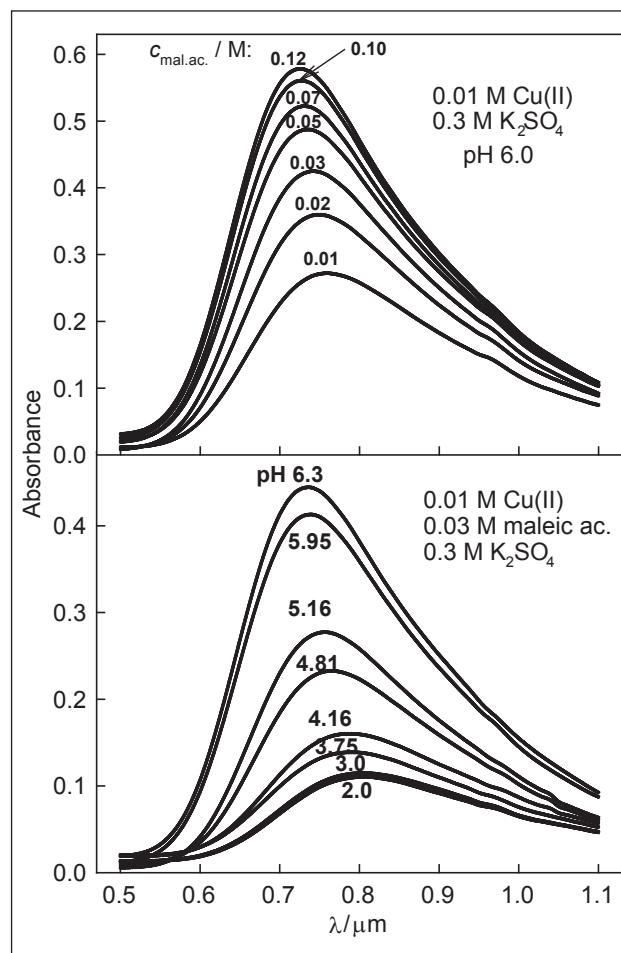


Fig. 1. Absorption spectra of 0.01 M Cu(II) solutions containing indicated amounts of maleic acid at pH 6 (top), or 0.03 M of maleic acid at indicated pH (bottom)

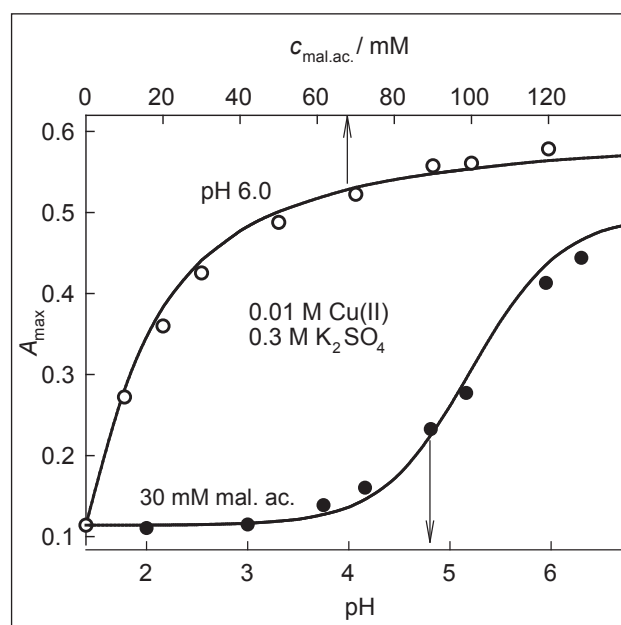


Fig. 2. Absorption maxima of 0.01 M Cu(II) solutions vs maleic acid concentration at pH 6 (white circles) and vs pH of the solutions containing 0.03 M of maleic acid (black circles). Solid lines represent results of simulation (see text)

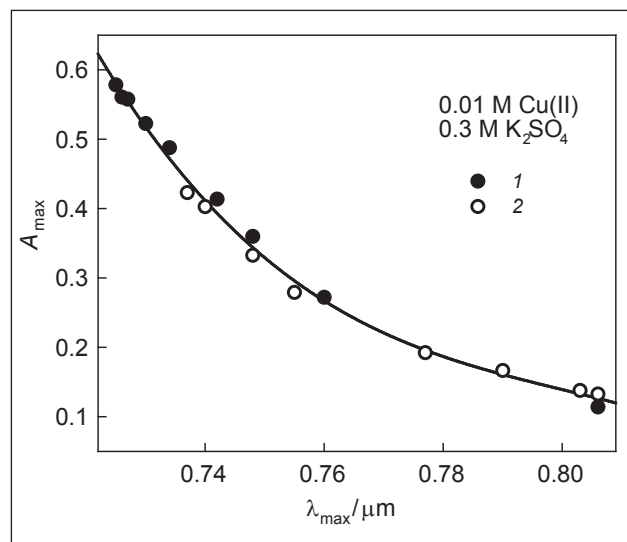


Fig. 3. Coordinates of absorption peaks obtained for 0.01 M Cu(II) solutions at pH 6 and different concentrations of maleic acid (1) and at constant concentration (0.03 M) of maleic acid and different pH (2)

by a single curve. Since the spectrum maxima are asymmetric, we used for this purpose the modified Lorentz distribution that follows from the description of a driven harmonic oscillator. It was established that the relationship

$$y \equiv \frac{A}{A_{\max}} = \frac{a}{(x^2 - x_0^2)^2 + 4x^2g^2} + g_0 \quad (1)$$

fits experimental data quite well; here  $x$  is a frequency or other adequacy term,  $x_0$ ,  $a$ ,  $g$  and  $g_0$  are fitting parameters. The maximum value of this function,

$$y_{\max} = \frac{a}{4g^2(x_0^2 - g^2)} + g_0, \quad (2)$$

corresponds to

$$x_{\max} = \sqrt{x_0^2 - 2g^2}. \quad (3)$$

The regression line presented in Fig. 1 for ligand-free solutions was obtained with  $x = hv$ ,  $a = 1.37$ ,  $x_0 = 1.60$ ,  $g = 0.338$  and  $g_0 = -0.225$ .

Similar properties are shown also by the spectra obtained for 0.01 M Cu(II) solutions with a high excess of ligand at pH 6 (Fig. 4, part B). When the ratio  $c_{\text{mal.ac.}} / c_{\text{Cu(II)}}$  exceeds 15, the spectra approach some limit and cease to depend on ligand concentration. It might be assumed that the maximum complexation degree is reached, and the Cu(II) complex (presumably CuL) predominates in these conditions. In this case, the fitting parameters acquire somewhat different values:  $a = 2.316$ ,  $x_0 = 1.763$ ,  $g = 0.379$  and  $g_0 = -0.332$ . At  $\lambda > 450$  nm, the absorbance of Cu(II)-free maleic acid solutions is less than 0.01. Then, the extinction coefficient, following from the  $A_{\max}$  value (at  $\lambda_{\max} = 722$  nm), can be determined. We have found by extrapolation procedures that

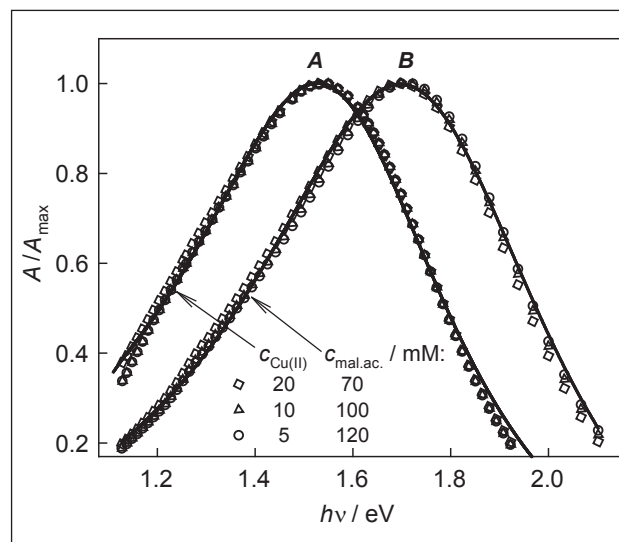


Fig. 4. Normalized absorption spectra obtained for ligand-free Cu(II) solutions (A) and for 0.01 M Cu(II) solutions with high excess of ligand (B)

$\epsilon = 59 \text{ M}^{-1} \text{ cm}^{-1}$  is ca fivefold higher than that obtained for  $\text{Cu}^{2+}$  aqua-ions in ligand-free solutions (vide supra).

Using the above assumptions and established parameters, absorption spectra were simulated, provided that they might be obtained by a simple addition of two spectra related to  $\text{Cu}^{2+}$  and CuL. In this case, the condition  $[\text{Cu}^{2+}] + [\text{CuL}] = 0.01 \text{ M}$  was also fulfilled. Simulated and experimental spectra were found to show the same regularities. At the same time, functions representing a correlation between  $A_{\max}$  (or  $\lambda_{\max}$ ) and  $[\text{Cu}^{2+}]$  were obtained (Fig. 5). The dependence of  $A_{\max}$  on  $[\text{Cu}^{2+}]$  is very close to linear, but this is not valid for  $\lambda_{\max}$  plots. The first correlation was used to assign a certain concentration of free  $\text{Cu}^{2+}$  ions and CuL complexes to any solution under study. Further,

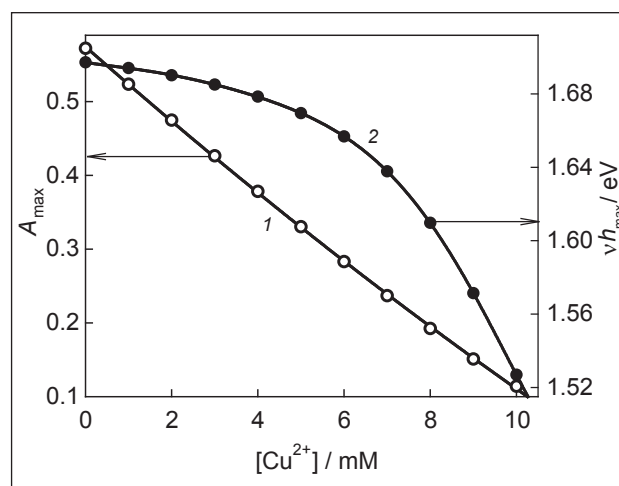


Fig. 5. Plots correlating  $A_{\max}$  (1, ordinate to the left) and  $hv_{\max}$  (2, ordinate to the right) with  $\text{Cu}^{2+}$  concentration

the concentration of the free ligand,  $[L^{2-}]$ , was obtained using the material balance equation written for the total ligand concentration:

$$c_{\text{mal.ac.}} = [\text{CuL}] + [L^{2-}] (1 + \beta_1^{\text{H}} [\text{H}^+] + \beta_2^{\text{H}} [\text{H}^+]^2). \quad (4)$$

The stability constants of the protonated ligands  $\text{LH}^-$  and  $\text{LH}_2$  ( $\log \beta_1^{\text{H}} = 5.75$ ,  $\log \beta_2^{\text{H}} = 7.30$ ) and the activity coefficient of hydronium anions  $\gamma_{\text{H}} = 0.7$  were taken from [6]. Finally, using the definition

$$\beta_1 = [\text{CuL}] / [\text{Cu}^{2+}] [L^{2-}], \quad (5)$$

it was found that  $\log \beta_1 = 2.2 \pm 0.07$ .

To check the reliability of this value, absorption spectra were simulated and compared with experimental data. For this purpose, the distribution of Cu(II)-containing species was calculated firstly using material balance equations. Then, partial spectra were obtained on the basis of Eq. (1) and, finally, total absorption spectra were synthesized. The results are shown in Fig. 2 by solid lines. Quite a good agreement between simulated and experimental values of  $A_{\text{max}}$  is observed.

Peacoc and James [5] reported the value  $10^{3.9}$  for  $\beta_1$  expressed in activity terms; according to polarographic data [4],  $\log \beta_1 = 3.4$ . The concentration constant obtained in the present investigation is significantly lower. However, the activity-corrected quantity  $\beta_1^{\text{T}}$  could be estimated for 0.3 M sulphate solutions, provided that the activity coefficients ( $\gamma$ ) of CuL and  $L^{2-}$  are similar and  $\gamma$  for  $\text{Cu}^{2+}$  is rather low ( $\sim 0.07$ ) [7, 8]. Then, the substitution of activities for concentrations in Eq. (5) yields  $\log \beta_1^{\text{T}} \approx 3.35$ .

## CONCLUSIONS

1. Addition of maleic acid ( $\text{LH}_2$ ) into Cu(II) solutions results in a significant rise of the absorption maximum and its shift towards shorter wavelengths from 806 to 722 nm. Similar effects are also observed when the pH of the solutions is increased at a constant ligand concentration.

2. Experimental absorption spectra can be described quantitatively on the assumption that two species, viz.  $\text{Cu}^{2+}$  and CuL, are responsible for absorption in the region of visible light. Then, the modified Lorentz distribution, which follows from the description of a driven harmonic oscillator, is applicable to each partial spectrum.

3. The stability constant ( $\beta_1$ ) of CuL species, expressed in concentration terms, was determined for Cu(II)-maleic acid solutions containing  $\text{K}_2\text{SO}_4$  as a supporting electrolyte. It has been found that  $\log \beta_1 = 2.2 \pm 0.07$  when the cumulative stability constants of protonated ligands  $\text{LH}^-$  and  $\text{LH}_2$  are  $10^{5.75}$  and  $10^{7.3}$ , respectively.

## References

1. L. G. Sillen, A. E. Martel (eds.), *Stability Constants of Metal-Ion Complexes, Special Publications N 17 and N 25*, Chemical Society, London, **1** (1964), **2** (1971).
2. R. M. Keefer, L. J. Andrews, *J. Amer. Chem. Soc.*, **71**, 2379 (1949).
3. A. Survila, *Electrode processes in systems of labile complexes of metals* (in Russian). Vilnius: Moksas (1989).
4. T. Nozaki, T. Mise, K. Higaki, *Nippon Kagaku Zasshi*, **88**, 1168 (1967).
5. J. M. Peacoc, J. C. James, *J. Chem. Soc.*, 2233 (1951).
6. J. Uljanionok, A. Survila, *Chemija*, **20**(2), **84** (2009).
7. *Spravochnik Khimika*, t. 3, B. P. Nikol'sky, O. N. Pirogov, M. E. Pozin ir dr. (red.), Moskva, Leningrad: Khimiya, 1964 (Chemist's reference book).
8. *Kratkij spravochnik fiziko-khimicheskikh velichin*, K. P. Mishchenko, A. A. Ravel' (red.), Moskva, Leningrad: Khimiya, 1965 (Concise reference book of physico-chemical quantities).

Julija Uljanionok, Aldona Jagminienė, Arvydas Survila

## Cu(II) IR MALEINO RŪGŠTIES KOMPLEKSŲ SUSIDARYMO SPEKTROFOTOMETRINIS TYRIMAS

### Santrauka

Cu(II) ir maleino rūgšties tirpalų su foniniu 0,3 M  $\text{K}_2\text{SO}_4$  elektrolitu spektrofotometriniai tyrimai buvo atlikti pH intervale nuo 2 iki 6. Maleino rūgšties priedai Cu(II) tirpaluose gerokai padidina absorbcijos maksimumą ir pastumia jį nuo 806 iki 722 nm. Analogiški reiškiniai vyksta ir tada, kai, palaikant pastovią ligando koncentraciją, yra didinamas tirpalų pH.

Eksperimentinius absorbcijos spektrus galima aprašyti kiekybiškai, priimant, kad dviejų rūšių dalelės,  $\text{Cu}^{2+}$  ir CuL, absorbuoja šviesą matomoje spektro srityje. Tada kiekvienam daliniam spektrui galima pritaikyti Lorencio susiskirstymo dėsnį, kuris seka iš valdomo harmoninio osciliatoriaus teorijos.

Atlikus spektrų analizę, buvo nustatyta koncentracinė CuL stabilumo konstanta  $\beta_1$ . Pasinaudojus anksčiau gautomis protonizuotų ligandų  $\text{LH}^-$  ir  $\text{LH}_2$  kumuliatyvinių stabilumo konstantų reikšmėmis (atitinkamai  $10^{5.75}$  ir  $10^{7.3}$ ), buvo gauta, kad  $\log \beta_1 = 2,2 \pm 0,07$ .