Effect of supporting sulphate electrolyte on equilibrium characteristics of Cu(II) and maleic acid solutions

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Titration and spectrophotometric investigations were carried out to reveal the effect of supporting sulphate electrolyte on the equilibrium characteristics of Cu(II) and maleic acid (LH$_2$) solutions. A consideration of ligand protonation and an account for dilution effects makes it possible to perform a rigorous quantitative description of experimental titration curves containing two well-defined jumps of pH. The cumulative stability constants of LH$^-$ and LH$_2$ species (β_1^H and β_2^H, respectively) established in the presence of 0.3 M K$_2$SO$_4$ (log β_1^H = 5.75 ± 0.09, log β_2^H = 7.30 ± 0.08) are lower as compared with solutions containing no supporting electrolyte (log β_1^H = 6.05 ± 0.07, log β_2^H = 7.48 ± 0.07). This effect seems to arise from the higher ionic strength of the former solutions. Very close spectrophotometric data were obtained for Cu(II) sulphate and perchlorate solutions. In both cases, absorption maxima are observed at the same wavelength λ_{max} = 806–808 nm, and they linearly depended on the concentration of Cu^{2+} aqua-ions. The latter results provide no data on the interaction between Cu^{2+} and SO$_4^{2-}$ ions.

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

INTRODUCTION

Various organic ligands, including different organic acids, are widely used in galvanic baths employed for copper electroplating. Because the electroreduction of Cu(II) proceeds via the consecutive transfer of two electrons, the formation of stable intermediate Cu(I) is possible. Its content in ligand-free solutions is usually low and does not exceed 1% of total copper. However, the situation can change radically when a certain ligand is introduced into the system. In this case, the equilibrium concentration of the intermediate should depend essentially on the nature of the ligand.

Most unsaturated organic acids are capable of forming quite stable complexes with Cu$^+$ ions, and maleic (cis-butenedioic) acid HOOC–CH = CH–COOH might be one of the examples. Three species of this ligand are formed in the solutions: neutral LH$_2$, partially protonated anion LH$^-$ and the completely deprotonated form L^{2-}. Successful quantitative analysis of experimental voltammetric data requires exhaustive information on the distribution of system components both in the bulk of solution and at the electrode surface. Such quantities can be computed using material balance equations that involve cumulative stability constants of complex species (β) and similar characteristics of protonated ligands (β^H). The

examination of the available literature has shown that such data are rather exiguous [1–4] and somewhat different, because they depend on the ionic strength of solutions (*I*) and the nature of the supporting electrolyte. For instance, the stability constants of protonated ligands LH$^-$ and LH$_2$ (β_1^H and β_2^H) determined in [2] are ca twofold higher as compared with analogous quantities determined by Peacoc and James [3].

As a rule, perchlorate media have been used in the former experiments, whereas data concerning sulphate solutions are absent at all. At the same time, analysis of the Cu(II)-glycolic acid system has shown [5] that the substitution of sulphates for perchlorates results in a certain diminution of β values. In this connection, it seemed expedient to carry out the experiments offering a clearer view of the equilibrium characteristics of solutions containing maleic acid and a supporting sulphate electrolyte. The spectrophotometry of the solutions and titration methods were chosen for this purpose. At the same time, special efforts were made to improve the quantitative description of acid–basic interactions. In our opinion, the data obtained could promote the further specification of the equilibrium characteristics of the system under discussion.

EXPERIMENTAL

Reakhim (Russia) reagents KOH, K$_2$SO$_4$ (high purity) and Cu-SO$_4 \cdot$ 5 H$_2$O (analytical grade) were used. The latter substance

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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. Pure maleic acid (Fluka) was used as received.

Samples (100 dm³) of maleic acid solutions were taken for titration with 0.1 M KOH. At the same time, some experiments were performed with solutions that additionally contained 0.3 M K$_2$SO$_4$.

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

RESULTS AND DISCUSSION

The equilibrium processes occurring in the system can be described quantitatively using material balance equations that contain concentration terms. Therefore, the processes involving various ligand species,

$$L^{2-} + H^+ \rightleftharpoons LH^-, \tag{1}$$

$$L^{2-} + 2H^+ \rightleftharpoons LH_2, \tag{2}$$
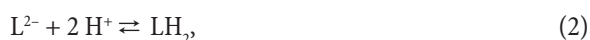
should be also characterized by the respective stability constants expressed in terms of concentration as follows:

$$\beta_1^H = \frac{[LH^-]}{[L^{2-}][H^+]}, \tag{3}$$

$$\beta_2^H = \frac{[LH_2]}{[L^{2-}][H^+]^2}. \tag{4}$$

Both above constants can be determined from titration data when a certain volume V_{alk} of alkali solution with a molar concentration c_{alk} is added to maleic acid solution whose molar concentration is c_{ac} and volume is V_{ac}. Since exactly the pH of solutions is controlled during experiments, the activity coefficient of hydronium ions (γ_{H+}) is required to be defined. As a good approximation, the empiric relationship

$$\log \gamma_{H+} = -Az^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2I \right), \tag{5}$$

proposed by Davies with $A = 0.5115$ [6], seems to be suitable for this purpose. The ionic strength I of the solutions was equal to ca 0.1 M (sulphate-free solutions) or was a little more than 0.9 (solutions containing 0.3 M of supporting K$_2$SO$_4$). In this connection, two γ_{H+} values, 0.77 and 0.70, were selected (see Fig. 1).

Here we consider a more general case when both (acid and alkali) solutions used for titration contain a supporting sulphate electrolyte of the same concentration, which is equal to c_F. A quantitative description of titration processes is performed using material balance equations written for total ligand and total sulphate. The law of charge conservation (the condition of the electrical neutrality of the solutions) is also invoked. Finally, we made corrections accounting for changes
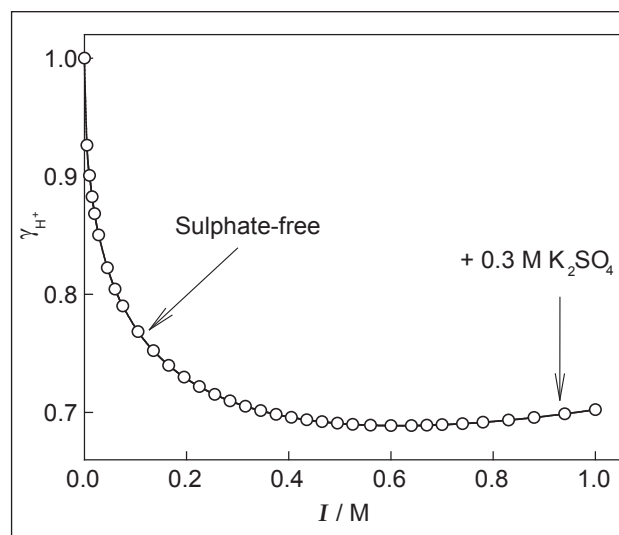

Fig. 1. Activity coefficients of hydronium ions vs ionic strength of solutions depicted according to Eq. (5). Arrows show the position of quantities used in simulations

in concentrations, arising from dilution of interacting solutions.

The quantitative description of the system may be done in the following way. Taking into account Eqns (1)–(4), the material balance for maleic acid may be written as

$$c_{ac} = [L^{2-}] (1 + \beta_1^H [H^+] + \beta_2^H [H^+]^2), \tag{6}$$

where c_{ac} is the total concentration of maleic acid. If this solution contains a certain concentration c_F of the supporting electrolyte (K$_2$SO$_4$), the equilibrium

$$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^- \tag{7}$$
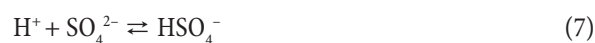
should be accounted for using the equilibrium constant

$$K = \frac{[HSO_4^-]}{[H^+][SO_4^{2-}]}. \tag{8}$$

Then, the material balance for sulphate is given by

$$c_F = [HSO_4^-] + [SO_4^{2-}] = [SO_4^{2-}] (1 + K [H^+]), \tag{9}$$

and the condition of the electrical neutrality of the solution is satisfied when

$$[H^+] + [K^+] = 2 [L^{2-}] + [LH^-] + [OH^-] + {} \\ + [HSO_4^-] + 2 [SO_4^{2-}], \tag{10}$$

where $[K^+] = 2c_F.$ \hfill (11)

It follows from (3), (4), (6) and (8)–(11) that

$$\frac{(2 + \beta_1^H [H^+])c_{ac}}{1 + \beta_1^H [H^+] + \beta_2^H [H^+]^2} = [H^+] - [OH^-] + \frac{K [H^+]c_F}{1 + K [H^+]}. \tag{12}$$

Two unknown quantities, β_1^H and β_2^H, are present in the latter equation, since the concentrations of H$^+$ and OH$^-$ ions may be obtained from the pH measurements with

$$[H^+] = 10^{-pH} / \gamma, \tag{13}$$

$$[H^+][OH^-] = K_w^/ / \gamma^2 \equiv K_w \tag{14}$$

provided that $\gamma_{H^+} = \gamma_{OH^-} = \gamma$ (K_w is the ionic product of water).

Suppose that the solution contains maleic acid (concentration c_{ac}) and sulphate (concentration c_F) at the initial pH equal to pH$_0$. If its volume is V_{ac}, it contains $2c_F V_{ac}$ moles of K$^+$ and $c_F V_{ac}$ moles of total sulphate. Then, the initial concentrations of H$^+$ and OH$^-$ ions are

$$[H^+]_0 = 10^{-pH_0} / \gamma, \tag{15}$$

$$[OH^-]_0 = K_w^/ / [H^+]_0 \tag{16}$$

and their amounts (in moles) are

$$x_0 = [H^+]_0 V_{ac}, \tag{17}$$

$$y_0 = [OH^-]_0 V_{ac}. \tag{18}$$

Let us also assume that the other (alkali) solution contains KOH (concentration c_{alk}) and K$_2$SO$_4$ sulphate with the same concentration c_F as above. When a certain volume of alkali solution (V_{alk}) is added into the acid solution, the amount of OH$^-$ ions increases by $c_2 V_{alk}$. Then the initial equilibrium is destroyed, and a certain amount (z moles) of H$^+$ and OH$^-$ ions should react until a new equilibrium is set and Eq. (14) is obeyed. Then

$$[H^+] = \frac{x_0 - z}{V_{ac} + V_{alk}}, \tag{19}$$

$$[OH^-] = \frac{y_0 + c_{alk} V_{alk} - z}{V_{ac} + V_{alk}}. \tag{20}$$

The mix of acid and alkali solutions results in certain dilution effects as well. Therefore the total concentration of maleic acid decreases, and the material balance equation (6) transforms into

$$(1 - \alpha) c_{ac} = [L^{2-}](1 + \beta_1^H[H^+] + \beta_2^H[H^+]^2), \tag{6a}$$

where $\alpha = \dfrac{V_{alk}}{V_{ac} + V_{alk}}$. $\tag{21}$

The concentration of K$^+$ ions increases up to

$$[K^+] = 2c_F + \alpha c_{alk}, \tag{22}$$

but the total concentration of sulphate remains unchanged and Eq. (9) is still valid. Equation (10) accounting for charge balance remains also unchanged, but it requires an insertion

of new concentrations established for the mix of solutions. The final expression takes the form

$$\frac{(2 + \beta_1^H[H^+])(1-\alpha)c_{ac}}{1 + \beta_1^H[H^+] + \beta_2^H[H^+]^2} =$$
$$= [H^+] - [OH^-] + \frac{K[H^+]c_F}{1 + K[H^+]} + \alpha c_{alk} \tag{23}$$

which can be easily transformed into the following generalized relationship:

$$\frac{V_{alk}}{V_{ac} + V_{alk}} = \frac{Pc_{ac} - Q[H^+] - \left(\dfrac{K_w^/}{[H^+]} + \dfrac{K[H^+]c_F}{1 + K[H^+]} \right)}{Pc_{ac} + Qc_{alk}}, \tag{24}$$

where

$$P = 2 + \beta_1^H[H^+], \tag{25}$$

$$Q = 1 + \beta_1^H[H^+] + \beta_2^H[H^+]^2, \tag{26}$$

K is the stability constant of HSO$_4^-$ ion, and $K_w^/$ is a modified ionic product of water. A special case of $c_F = 0$ can be easily obtained from the above relationships.

Experimental titration curves contain two well-defined jumps of pH (Figs. 2 and 3). Fitting of Eq (4) to experimental data obtained in the absence of supporting electrolyte solutions can be performed with a high correlation coefficient ($R_{sqr} \sim 0.9997$). Addition of 0.3 M K$_2$SO$_4$ into both maleic acid an KOH solutions changes to a certain extent the shape of titration curves (an example is given in Fig. 3). To describe quantitatively such data, more fitting parameters are required, including the protonization constant of sulphate ions (stability constant K of HSO$_4^-$). Digital experiments
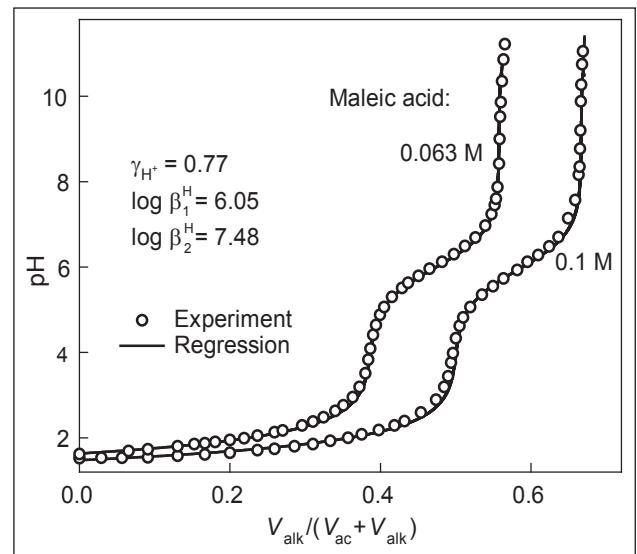

Fig. 2. Experimental titration curves of maleic acid solutions of indicated concentration (symbols). Solid lines represent the results of simulation with listed parameters
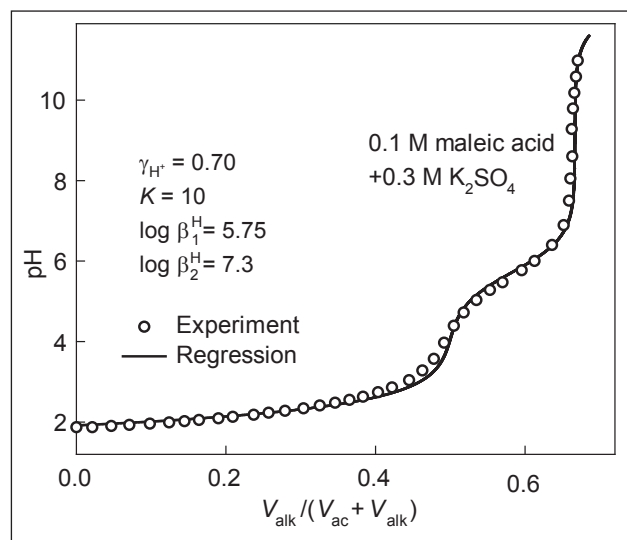
Fig. 3. Experimental titration curve of 0.1 M maleic acid solution containing 0.3 M K$_2$SO$_4$ (symbols). Solid line represents the result of simulation with listed parameters

Fig. 4. Distribution of ligand species in 0.04 M maleic acid solutions containing no (solid lines) and 0.3 M K$_2$SO$_4$ (dashed lines)

have shown that this quantity is the main parameter that determines the titration data in the region before the first pH jump. The best fitting results were obtained with $K = 10$ M^{-1}. This value is not as high as expected, but it falls into the region of data given in the literature [4]. The results obtained are summarized in Table, with the respective literature data also included. The cumulative stability constants established in the presence of 0.3 M K$_2$SO$_4$ are lower. This effect can arise from the higher ionic strength of the solutions (consequently, from the lower activity coefficients of the components). It should be also noted that the protonization constants determined in the present research are expressed in terms of concentration and may be easily introduced into material balance equations.

It is of interest to compare the distribution of ligand species in sulphate-free solutions and in the presence of this supporting electrolyte. Such data were calculated using the material balance equations given above; the results are shown in Fig. 4. In the presence of sulphate, the distribution curves are shifted towards lower pH, and the main difference between the two cases is observed in slightly acid media.

The last problem to be discussed here concerns the interactions between Cu^{2+} and SO$_4^{2-}$ ions. The rather low (<0.1) activity coefficients of Cu^{2+} ions in sulphate solutions imply the existence of such phenomena. Some attempts to treat CuSO$_4$ as a "Cu(II)–sulphate complex" occur in the litera-
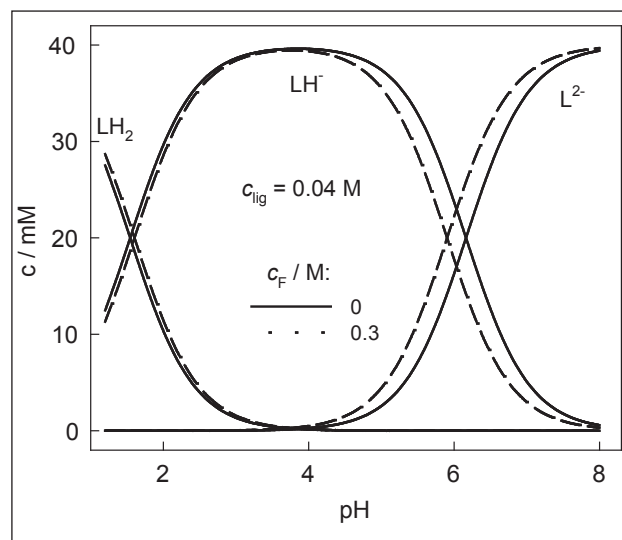
Table. Cumulative stability constants of protonated species of ligand

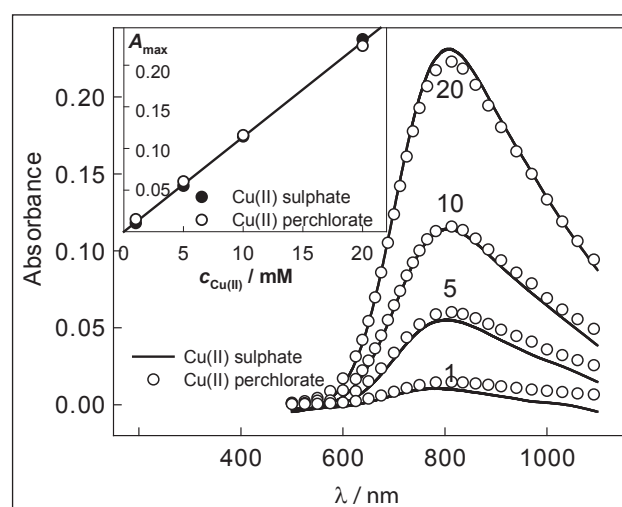| Logarithm of stability constant	Sulphate concentration		Literature data (perchlorate media)
	0	0.3 M	
log β$_1^H$	6.05 ± 0.07	5.75 ± 0.09	5.61 [3]; 5.81 [2]
log β$_2^H$	7.48 ± 0.07	7.30 ± 0.08	7.26 [3]; 7.79 [2]

Fig. 5. Absorption spectra obtained for CuSO$_4$ and Cu(ClO$_4$)$_2$ solutions (concentration, mM, indicated at respective curves). Absorption maxima vs Cu(II) concentration are given in the inset

ture [4], together with stability constants attributed to this product. However, the latter values are rather contradictory and differ ~200 times. In this connection, we turned to spectrophotometric data intending to compare absorption spectra of solutions containing Cu(II) sulphate and perchlorate. The result is demonstrated in Fig. 5. In the case of both systems, absorption maxima (A_{max}) observed at the wavelength $\lambda_{max} = 806$–808 nm linearly depend on the concentration of Cu^{2+} aqua-ions (see inset). It follows from the slope of the general regression line that the extinction coefficient $\varepsilon = 11.4$ M^{-1} cm^{-1}. It should be also noted that the spectra obtained for CuSO$_4$ and Cu(ClO$_4$)$_2$ solutions are very similar, therefore, there is no possibility to elucidate the anticipated interaction between Cu^{2+} and SO$_4^{2-}$ ions. These findings will

be considered in the analysis of the spectrophotometric properties of solutions containing Cu(II)–maleic acid complexes. Analysis of their stability characteristics is scheduled as the subject of our next communication.

CONCLUSIONS

1. Consideration of equilibrium characteristics of maleic acid (LH_2) solutions and accounting for dilution effects makes it possible to perform a rigorous quantitative description of experimental titration curves containing two well-defined jumps of pH.

2. Analysis of titration curves shows that the cumulative stability constants of the protonated species of ligand, LH^- and LH_2, (β_1^H and β_2^H respectively) established in the presence of 0.3 M K_2SO_4 ($\log \beta_1^H = 5.75 \pm 0.09$, $\log \beta_2^H = 7.30 \pm 0.08$) are lower as compared with solutions containing no supporting electrolyte ($\log \beta_1^H = 6.05 \pm 0.07$, $\log \beta_2^H = 7.48 \pm 0.07$). This effect seems to arise from the higher ionic strength of the former solutions.

3. Very close spectrophotometric data were obtained for Cu(II) sulphate and perchlorate solutions. In both cases, absorption maxima are observed at the same wavelength $\lambda_{max} = 806–808$ nm, and they linearly depend on the concentration of Cu^{2+} aqua-ions. The results obtained provide no data on the interaction between Cu^{2+} and SO_4^{2-} ions.

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FONINIO SULFATINIO ELEKTROLITO ĮTAKA CU(II) IR MALEINO RŪGŠTIES TIRPALŲ PUSIAUSVYROSIOMS CHARAKTERISTIKOMS

S a n t r a u k a

Siekiant nustatyti foninio sulfatinio elektrolito įtaką Cu(II) ir maleino rūgšties (LH_2) tirpalų pusiausvyrosioms charakteristikoms, buvo atlikti titravimo ir spektrofotometrijos tyrimai. Įvertinus ligando protonizacijos ir tirpalų prasiskiedimo efektus, galima tiksliai kiekybiškai aprašyti eksperimentines titravimo kreives su dviem ryškiais pH šuoliais. Suminės LH^- ir LH_2 stabilumo konstantos (atitinkamai β_1^H ir β_2^H), nustatytos esant 0,3 M K_2SO_4 ($\log \beta_1^H = 5,75 \pm 0,09$, $\log \beta_2^H = 7,30 \pm 0,08$), yra mažesnės negu tirpaluose be foninio elektrolito ($\log \beta_1^H = 6,05 \pm 0,07$, $\log \beta_2^H = 7,48 \pm 0,07$). Manoma, kad toks efektas atsiranda dėl aukštesnės pirmųjų tirpalų joninės jėgos. Spektrofotometriniai Cu(II) sulfato ir perchlorato tirpalų duomenys yra labai artimi. Abiem atvejais absorbcijos maksimumas atitinka tą patį $\lambda_{max} = 806–808$ nm ir jis yra proporcingas Cu^{2+} akvajonų koncentracijai. Pastarieji rezultatai nesuteikia jokios informacijos apie Cu^{2+} ir SO_4^{2-} jonų sąveiką.