Study of the nature of Cu(II) complexes in aqueous ammonium oxalate solutions by ultraviolet-visible spectroscopy

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Abstract: Experimental results of an investigation of aqueous ammonium oxalate solutions containing Cu(II) impurity by ultraviolet–visible spectroscopy are described and discussed from the standpoint of speciation of complexes. The results show that absorption of light by aqueous ammonium oxalate solutions containing Cu(II) impurity in the range $-5 < \ln(c_i/c) < 2.5$ of the ratio of concentrations $c_i$ and $c$ of impurity and solute, respectively, leads to decrease or increase in the intensity of bands of the ultraviolet–visible spectral regions, and these changes may be expressed by full width at half maximum, molar extinction coefficient, peak wavelength and oscillator strength. The changes are caused by the coordination of $C_2O_4^{2-}$ ligand with Cu$(H_2O)_6^{2+}$ aquocomplex, and are related with the impurity–solute concentration ratio $c_i/c$. The coordination of $C_2O_4^{2-}$ ligand with Cu$(H_2O)_6^{2+}$ aquocomplex in the range $0 < \ln(c_i/c) < 2.5$ leads to the formation of Cu$(C_2O_4)_2$ complex, but the coordination of the $C_2O_4^{2-}$ ligand with Cu$(C_2O_4)_2$ complex in the concentration ratio range $-5 < \ln(c_i/c) < 0$ results in the formation of predominantly Cu$(C_2O_4)_2^{2-}$ complex. The effect of successive coordination of the $C_2O_4^{2-}$ ligand is well-defined in the ultraviolet spectral region but poor in the visible region.

1. Introduction
Impurities present in solutions used for growth of crystals have pronounced effect on the their growth kinetics and morphology [1–3]. The effect of ionic impurities on the growth kinetics and morphology of ionic crystals is explained from the standpoint of adsorption of individual ions at kink sites in step ledges or on the surface terrace between neighboring ledges present on the crystal surfaces in contact with the solution [1–3]. Adsorption of ions at kinks and surface terrace of ionic crystals is believed to occur as a result of electrostatic and van der Waals interactions. Although one aspires to have individual ions to adsorb on the growing surface of an ionic crystal, it is difficult to achieve individual ions in real growth systems because of the formation of coordination complexes between impurity cations and solute anions [4–6]. Indeed knowledge of the structure and stability of complexes in growth solutions containing impurities is necessary for understanding the relationship between growth kinetics of crystals and segregation coefficient of impurities in them because both of them are intimately connected with the processes of adsorption of impurity particles at the crystal–medium interface.

Spectroscopic studies are frequently employed to characterize new compounds, to analyze ions, compounds or mixtures, to follow reaction paths and rates, to investigate the constitution and
concentration of species in different media, and to obtain information about the geometry of metal–ligand complexes and the type of coordination of ligands around the metal ions [7–12]. Among several diverse spectroscopic methods, ultraviolet–visible (UV–Vis) spectroscopy finds wide application in quantitative analysis of organic and inorganic compounds using dye reactions and determination of traces of impurities in mixtures of complexes and main components [7–9].

In this paper the experimental results of an investigation of dilute and concentrated aqueous ammonium oxalate solutions containing Cu(II) impurity obtained by ultraviolet-visible spectroscopy are described and discussed. The aim of the present paper is to follow the processes of formation of copper–oxalate complexes in relation to the concentration $c$ of ammonium oxalate and the concentration $c_i$ of Cu(II) and to establish the influence of these parameters on the chemical equilibria in the solutions. This paper is continuation of our earlier works [13,14], where some preliminary results on the investigation of copper–oxalate complexes were reported.

The structure of the paper is as follows: Section 2 briefly describes the experimental procedure used, while Section 3 gives the basic concepts used for the analysis of the experimental results described and discussed in the following sections. Analysis of chemical equilibria occurring in pure aqueous solutions and the results of spectrophotometric investigation in the ultraviolet and visible regions in relation to the structure of complex species present in aqueous solutions are discussed in Section 4. Finally, the main conclusions of the study are enumerated in Section 5.

2. Experimental

For preparing solutions, analytical grade ammonium oxalate monohydrate, (NH$_4$)$_2$C$_2$O$_4$·H$_2$O (with the following impurities: 0.005% SO$_4$, 0.001% Cl, 0.001% Pb and 0.0005% Fe), copper chloride dihydrate, CuCl$_2$·2H$_2$O (with the impurities: 0.005% SO$_4$, 0.001% Fe, 0.0001% As, 0.004% Pb, 0.001% Ni, 0.005% Na and 0.004% nitrogen), and demineralized water were used. (NH$_4$)$_2$C$_2$O$_4$·H$_2$O and CuCl$_2$·2H$_2$O were produced by Polish Chemicals, Lublin (Poland) and BDH Laboratories, Poole (England), respectively.

Ammonium oxalate aqueous solutions containing Cu(II) impurity were investigated at 25°C by using UV–Vis spectroscopy. Optical absorption measurements were made for unsaturated ammonium oxalate (AO) solutions of concentrations $c$ between $3.52 \times 10^{-3}$ and 0.2815 mol/dm$^3$ containing different CuCl$_2$ concentrations $c_i$ between $5 \times 10^{-3}$ and $4 \times 10^{-2}$ mol/dm$^3$. UV–Vis absorption spectra were recorded by employing Shimadzu UV2401 spectrophotometer in conjunction with a computer. The 3.9 version of the UVPC Personal Spectroscopy Software supplied by the manufacturer records the values of absorbance and wavelength $\lambda$ of the peak.

Analysis of speciation of complexes in aqueous AO solutions without and with Cu(II) impurity was carried out by using computer program Hyss [15]. Some preliminary results on these complexes have been reported earlier [13,14]. HySS is a program that can be used to perform two distinct functions: titration simulation and calculation of concentrations of species. Details concerning the algorithm used in the program and its other features are given in ref. [14].

3. Some basic equations and concepts

Appearance of an absorption spectrum is associated with the absorption of photon as a result of excitation of electrons of well-defined types or electrons belonging to small groups of atoms. The energy of transition and the structure and position of bands in the electron spectrum depend on the nature and position of ligands and multiple bonds in the particle as well as their mutual interactions. The problem of the dependence of a spectrum on the constitution of a particle is complicated.

Possible spectral transitions based on the energy difference $\Delta E$ involved during a transition may be arranged in the order [7]: $\sigma \rightarrow \sigma^* > \sigma \rightarrow \pi > \pi \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$. Transitions between orbitals $\sigma \rightarrow \sigma^*$, associated with transitions from binding orbitals in the ground state to unbinding orbitals, require the highest energy, and the bands corresponding to these transitions lie in the ultraviolet region $\lambda \leq 200$ nm. The $n \rightarrow \sigma^*$ transitions are of similar energies and are due to
transition of an electron from unbinding atomic orbital to a molecular orbital of a higher energy ($\lambda \approx 170$–$210$ nm). The lowest energy corresponds to $n \rightarrow \pi^*$ transition and depends on the type of compound. Absorption bands corresponding to this transition lie in the near-ultraviolet or visible region. Intensity of these bands is, as a rule, much lower than the intensity of bands due to other transitions. The $n \rightarrow \pi^*$ transition occurs in molecules in which a heteroatom with a free electron pair is joined with another atom by a multiple bond [7].

Intensity and width of a band in the ultraviolet and visible regions are the main parameters that characterize an absorption spectrum. Contours of the absorption bands are frequently described by Lorentzian- and Gaussian-type functions because the real contours of the bands lie between the contours predicted by these functions. In the case of Gaussian function, absorbance is expressed by [7,9]

$$A = A_{\text{max}} \exp \left\{ -B(v_0 - \nu)^2 \right\}, \quad (1)$$

where $v_0$ is the value of the wavelength $\nu$ at the maximum absorbance $A_{\text{max}}$, and the $B$ parameter is connected with the full width $\Delta\nu_{1/2}$ at half maximum (FWHM; hereafter called half width) of the peak by the relation

$$B = \frac{4\ln 2}{\Delta\nu_{1/2}}. \quad (2)$$

The half width $\Delta\nu_{1/2}$ is measured as the width of the peak of the maximum at its half height.

The electronic band intensity, characterized by the probability of transition of electrons from one state to another, is frequently described by the oscillator strength $f$. The higher the oscillator strength, the higher is the probability of electronic transition. When the band has the shape of a Guassian–type curve, the oscillator strength is given by [7–9]

$$f = 4.60 \cdot 10^{-9} \varepsilon \Delta\nu_{1/2}, \quad (3)$$

where $\varepsilon$ is the molar extinction coefficient at the maximum of the band with $\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ units and $\Delta\nu_{1/2}$ has $\text{cm}^{-1}$ units. The parameter $f$ is close to 1 for allowed electron transitions, while it has relatively small value between $10^{-3}$ and $10^{-4}$ in the case of forbidden transitions.

Molar extinction coefficient $\varepsilon$ of a solution is given by [4,7]

$$\varepsilon = \frac{A}{l c}, \quad (4)$$

where $l$ is the thickness of the cuvette (in our case, $l = 1$ cm), $A$ is the absorbance of the ammonium oxalate solution and $c$ is the ammonium oxalate concentration in the solution.

In the case of multicomponent solutions and mixtures, the resultant (or total) absorbance $A_i$ is given by the additivity rule for absorbance of individual components. The total absorbance $A_i$ is the sum of the absorbances of individual components $1, 2, ..., j$ (i.e. $A_1, A_2, A_3, ..., A_j$), and may be expressed in the form [7]

$$A_i(\lambda)/l = \sum \varepsilon_j(\lambda)c_j = \varepsilon_1(\lambda)c_1 + \varepsilon_2(\lambda)c_2 + \varepsilon_3(\lambda)c_3 + \ldots., \quad (5)$$

where $\varepsilon_j$ and $c_j$ are the molar extinction coefficient and the concentration of component $j$, respectively.

4. Results and Discussion

4.1. Ammonium oxalate solutions in ultraviolet region

Pure ammonium oxalate solutions without Cu(II) impurity reveal characteristic absorption spectra in the ultraviolet region of light. Fig. 1 illustrates the observed $A(\lambda)$ absorption spectra of unsaturated
solutions containing different concentrations of ammonium oxalate. From the observed \( A(\lambda) \) spectra of ammonium oxalate solutions the values of molar extinction coefficient \( \varepsilon \) and half width \( \Delta v_{1/2} \) were obtained. The plots of \( \ln \varepsilon \) against \( \lambda \) are presented in Fig. 2a while the dependence of the values of \( \Delta v_{1/2} \) on \( \ln c \) is shown in Fig. 2b.

**Figure 2.** (a) Plots of \( \ln \varepsilon \) on wavelength \( \lambda \) for unsaturated aqueous AO solutions. Concentration of AO in solutions: (1) 0.00352, (2) 0.00704, (3) 0.01407, (4) 0.02111, (5) 0.03518, (6) 0.04926, (7) 0.05629, (8) 0.07037, (9) 0.14074, (10) 0.2111, and (11) 0.28147 mol/dm\(^3\), (b) Plot of half width \( \Delta v_{1/2} \) on \( \ln c \). Note three distinct slopes of \( \Delta v_{1/2}(\ln c) \) plot.

It may be seen from Fig. 2a that the value of \( \ln \varepsilon \) for 200 nm < \( \lambda \) < 380 nm decreases with an increase in AO concentration \( c \) in the entire interval of wavelength \( \lambda \). However, in this wavelength range, the plot of \( \ln \varepsilon \) against \( \lambda \) reveals three distinct wavelength intervals (i.e. I, II, and III) characterized by linear dependence of \( \ln \varepsilon \) on \( \lambda \) of different slopes. Fig. 2b of the plot of \( \Delta v_{1/2} \) against \( \ln c \) also shows three distinct intervals of AO concentrations \( c \), corresponding to \( -6 < \ln c < -3.4 \), \( -3.4 < \ln c < -2.3 \) and \( -2.3 < \ln c < -1 \), respectively, in which the values of the slope of the linear \( \Delta v_{1/2}(\ln c) \) dependence are different. The transitions in the value of the slopes occur at AO concentration \( c \) of 0.033 mol/dm\(^3\) and 0.1 mol/dm\(^3\), respectively.

It is known [12] that in the UV region dimethyl oxalate and several carboxylic acids and their esters give a characteristic band of low intensity in 210–260 nm region. For example, for the dimethyl oxalate absorption band, \( \lambda_{\text{max}} \) and \( \varepsilon_{\text{max}} \) are 246 nm and 51 dm\(^3\)-mol\(^{-1}\)-cm\(^{-1}\), respectively. It is also known [16] that excitation of electrons in radicals containing carbonyl group C=O results in a band at around 290 nm, but the position of this type of absorption band depends on the nature of other parts of
the radical. Consequently, for this group $\lambda_{\text{max}}$ usually lies between 270 and 290 nm with molar extinction coefficient $\varepsilon_{\text{max}}$ between 10 and 20 dm$^3$-mol$^{-1}$-cm$^{-1}$. In this case, the activity of C=O chromophore is associated with $n \rightarrow \pi^*$ transition and may be attributed to the free electron pair of the oxygen atom. It is also interesting to note [12] that in oxalic acid and 10$^{-2}$ mol/l potassium oxalate solutions low-intensity bands are not observed. However, upon the addition of a strong mineral acid which suppresses the dissociation of oxalic acid, the shape of their absorption band becomes similar to that of dimethyl oxalate [12]. These observations suggest that an increase in the concentration of associated species H$_2$C$_2$O$_4$ in oxalic acid solutions can decrease the band intensity in the 210–260 nm region.

In aqueous AO solutions the following species are formed as a result of dissociation and hydrolysis reactions: C$_2$O$_4^{2-}$, HC$_2$O$_4^-$, H$_2$C$_2$O$_4$, (NH$_4$)$_2$C$_2$O$_4$, NH$_4^+$ and NH$_2$OH. However, the concentrations of the above species depends on the initial AO concentration in the solution. The initial AO concentration and the stability constants $\beta$ of complex species forming in the solutions determine the solution pH. Analysis of speciation of complexes in AO solutions [13] by computer program Hyss [15] revealed that the concentration of species like C$_2$O$_4^{2-}$, HC$_2$O$_4^-$, H$_2$C$_2$O$_4$, NH$_4^+$, NH$_2$OH and (NH$_4$)$_2$C$_2$O$_4$ increases with an increase in AO concentration, but the relative concentrations of the dominating complexes also increase, resulting in an increase in solution pH. Speciation analysis also showed [13] that: (a) in the range of low AO concentration $c < 0.03$ mol/dm$^3$, the dominating species are: C$_2$O$_4^{2-}$, HC$_2$O$_4^-$, H$_2$C$_2$O$_4$, and NH$_4^+$; (b) at relatively high concentrations in the range 0.03 < $c < 0.1$, the main species are: NH$_4^+$, C$_2$O$_4^{2-}$, H$_2$C$_2$O$_4$, HC$_2$O$_4^-$ and (NH$_4$)$_2$C$_2$O$_4$; while (c) in the range of very high concentrations $c > 0.1$, the complex species are: NH$_4^+$, C$_2$O$_4^{2-}$ and (NH$_4$)$_2$C$_2$O$_4$.

From the above discussion it may be concluded that, with an increase in the concentration of ammonium oxalate in the investigated solutions, the concentration of associated species such as H$_2$C$_2$O$_4$ and (NH$_4$)$_2$C$_2$O$_4$ also increases, which results in a decrease in the molar extinction coefficient $\varepsilon_{\text{max}}$ in the 210–260 nm region (Fig. 2a). For ammonium oxalate solutions of concentration 0.004 < $c$ ≤ 0.3 the molar extinction coefficient varies between 750 and 20 dm$^3$-mol$^{-1}$-cm$^{-1}$ (i.e. 6.6 < ln$\varepsilon_{\text{max}}$ < 3; cf. Fig. 2a) and decreases with increasing ammonium oxalate concentration. It should be noted that, irrespective of the ammonium oxalate concentration, practically for all investigated solutions the molar extinction coefficient $\varepsilon_{\text{max}}$ lies between 10 and 20 dm$^3$-mol$^{-1}$-cm$^{-1}$ in the 250–290 nm region and is associated with the activity of the C=O chromophore.

4.2. Aqueous ammonium oxalate solutions containing Cu(II) impurity – Speciation of copper complexes

Fig. 3a illustrates the data on the concentration of different copper complexes in AO aqueous solutions containing different Cu(II) concentrations in the form of the dependences of ln[species] on ln($c$/c). From Fig. 3a it is interesting to note two different trends of the dependences of various complexes in the concentration ratio ranges: −5 < ln($c$/c) < 0, and 0 < ln($c$/c) < 2.5. In the range 0 < ln($c$/c) < 2.5, both ln[Cu(C$_2$O$_4$)$_2^{2-}$] and ln[Cu(C$_2$O$_4$)$_4$] decrease with an increase in ln($c$/c) but the decrease is very pronounced in the case of Cu(C$_2$O$_4$)$_2^{2-}$ complex. In this concentration ratio range, ln[Cu(H$_2$O)$_6^{2+}$] increases with an increase in ln($c$/c). In the concentration ratio range −5 < ln($c$/c) < −1, ln[Cu(H$_2$O)$_6^{2+}$] and ln[Cu(C$_2$O$_4$)$_4$] increase with an increase in ln($c$/c), the increase being more in the case of Cu(H$_2$O)$_6^{2+}$ than in Cu(C$_2$O$_4$)$_4$. However, in this concentration ratio range, ln[Cu(C$_2$O$_4$)$_2^{2-}$] somewhat decreases with an increase in ln($c$/c).

The dependences of ln[species] on ln($c$/c) may be divided into three ln($c$/c) ranges, as illustrated in Fig. 3b. In the concentration ratio ranges C and A, defined by −5 < ln($c$/c) < −3 and 1 < ln($c$/c) < 2.5, respectively, for a given $c$, the values of ln[Cu(H$_2$O)$_6^{2+}$], ln[Cu(C$_2$O$_4$)$_4$] and ln[Cu(C$_2$O$_4$)$_2^{2-}$] change practically linearly with increase in ln($c$/c). However, in the concentration ratio range B, defined by −3 < ln($c$/c) < 1, for a given $c$, the values of ln[Cu(H$_2$O)$_6^{2+}$] and ln[Cu(C$_2$O$_4$)$_4$] suddenly increase while those of ln[Cu(C$_2$O$_4$)$_2^{2-}$] decrease with increase in ln($c$/c). The changes in ln[Cu(H$_2$O)$_6^{2+}$], ln[Cu(C$_2$O$_4$)$_4$] and ln[Cu(C$_2$O$_4$)$_2^{2-}$] are highly pronounced in the range −1.5 < ln($c$/c) < 0.5 i.e. 0.22 <...
The concentration of Cu(H$_2$O)$_6^{2+}$ complexes increase with decrease in $c/c = 1$ corresponds to the preferential formation of the neutral Cu(C$_2$O$_4$) complex.

Figure 3. (a) Dependence of logarithm of concentrations of different complexes (denoted as ln[species]) on ln($c/c$) for unsaturated aqueous AO solutions containing different Cu(II) concentration $c_i$. (b) Data of (a) shown as plots of ln{[Cu(C$_2$O$_4$)$_2$]/[Cu(H$_2$O)$_6^{2+}$]} and ln{[Cu(C$_2$O$_4$)$_2$]/[Cu(H$_2$O)$_6^{2+}$]} against ln($c/c$) for $c_i$. Plots of ln[species] against ln($c/c$) may be divided into three ln($c/c$) ranges A, B and C, as shown in (b).

The dependence of ln[species] on ln($c/c$) in the concentration ratio ranges A and C may be described by the empirical relationship:

$$\text{ln}[\text{species}] = \text{ln}[\text{species}]_0 + Y \cdot \text{ln}(c/c),$$

where ln[species]$_0$ is the extrapolated value of ln[species] when ln($c/c$) = 0 and Y is the slope of the plot of ln[species] against ln($c/c$). The values of ln[species]$_0$ and Y are listed in Table 1. The values of ln[species]$_0$ somewhat depend on the Cu(II) concentration $c_i$, but these were not considered during the analysis of the data. In Fig. 3a, the linear plots are drawn in regions C and A, corresponding to $-5 < \text{ln}(c/c) < -3$ and $1 < \text{ln}(c/c) < 2.5$, for $c_i = 2.93 \times 10^{-3}$ mol/dm$^3$ and $c_i = 3.52 \times 10^{-2}$ mol/dm$^3$, respectively. These concentration ratio ranges correspond to the preferential formation of Cu(C$_2$O$_4$)$_2^{2-}$ and Cu(H$_2$O)$_6^{2+}$ complexes, respectively.

Table 1. Values of ln[species]$_0$ and Y for different complexes

| Complex         | $-5 < \text{ln}(c/c) < -3^*$ | $1 < \text{ln}(c/c) < 2.5^{**}$ |
|-----------------|------------------------------|-------------------------------|
|                 | ln[species]$_0$ | Y | ln[species]$_0$ | Y | ln[species]$_0$ | Y | ln[species]$_0$ | Y |
| Cu(H$_2$O)$_6^{2+}$ | $-19.5$          | $1.35$ | $-4.1$          | $0.3$ | $-0.02$          | $-7.7$ | $-2.2$          |
| Cu(C$_2$O$_4$)]  | $-8$             | $0.66$ | $-3.4$          | $-0.97$ |
| Cu(C$_2$O$_4$)$_2^{2-}$ | $-4$             | $0.02$ | $-7.7$          | $-2.2$ |

For $c_i = 2.93 \times 10^{-3}$ mol/dm$^3$. ** For $c_i = 3.52 \times 10^{-2}$ mol/dm$^3$.

In the concentration ratio range $0 < \text{ln}(c/c) < 2.5$, the concentrations of Cu(C$_2$O$_4$) and Cu(C$_2$O$_4$)$_2^{2-}$ complexes increase with decrease in $c/c$ at the expense of the concentration of Cu(H$_2$O)$_6^{2+}$ complex. The concentration of Cu(H$_2$O)$_6^{2+}$ complex decreases with decrease in $c/c$ (i.e. the slope $Y > 0$). However, in the concentration ratio range $-5 < \text{ln}(c/c) < 0$, the concentration of Cu(C$_2$O$_4$)$_2^{2-}$ complex alone increases with decreasing $c/c$ at the expense of the concentrations of Cu(C$_2$O$_4$) and Cu(H$_2$O)$_6^{2+}$ complexes, which decrease with decrease in $c/c$. These observations are consistent with the fact that,
for a given value of Cu(II) concentration $c_i$, addition of AO leads to the substitution of pairs of water molecules of the Cu(H$_2$O)$_6^{2+}$ complex by C$_2$O$_4^{2-}$ ligands, forming Cu(C$_2$O$_4$) complex first for $c_i/c = 1$ and subsequently Cu(C$_2$O$_4$)$_2^{2-}$ complex for $c_i/c = 0.5$. Therefore, it is better to represent the data on the concentration of different copper complexes as ratio of concentrations of Cu(C$_2$O$_4$) and Cu(C$_2$O$_4$)$_2^{2-}$ complexes to the concentration of Cu(H$_2$O)$_6^{2+}$ complex as a function of $c_i/c$. Fig. 3b shows the plots of $\ln\{[\text{Cu(C}_2\text{O}_4)]/[\text{Cu(H}_2\text{O)}_{6}^{2+}]\}$ and $\ln\{[\text{Cu(C}_2\text{O}_4)]_{2}^{2-}/[\text{Cu(H}_2\text{O)}_{6}^{2+}]\}$ against $\ln(c_i/c)$ for different Cu(II) concentration $c_i$. As seen from the slopes of these plots, the increase in the concentration of Cu(C$_2$O$_4$)$_2^{2-}$ complex with decrease in $\ln(c_i/c)$ is much higher than that of Cu(C$_2$O$_4$) complex.

Cu(H$_2$O)$_6^{2+}$ complex forms deformed octahedral spatial structure with two trans bonds (Fig. 4a) [17,18], while C$_2$O$_4^{2-}$ ligand coordinates with Cu(II) ions at two neighboring sites such that substitution of one pair of water molecules by it forms Cu(C$_2$O$_4$) complex of deformed trigonal structure (Fig. 4b). However, when two C$_2$O$_4^{2-}$ ligands substitute two pairs water molecules, Cu(II) atom is coordinated by four O atoms from two oxalate ligands and two O atoms from water molecules (Fig. 4c) [19,20]. This Cu(C$_2$O$_4$)$_2^{2-}$ complex shows a distorted octahedral coordination geometry, with Cu–O distances showing a typical Jahn–Teller distortion [19,20]. The Cu–O bond length lies between 0.1951 and 0.1914 nm [20]. The symmetry of this complex is close to that of Cu(H$_2$O)$_6^{2+}$ complex. Therefore, it may be argued that the symmetry of complexes decreases in the sequences: Cu(H$_2$O)$_6^{2+}$, Cu(C$_2$O$_4$)$_2^{2-}$ and Cu(C$_2$O$_4$).

![Figure 4](image-url)

**Figure 4.** Schematic illustration of structure of different octahedral complexes formed in aqueous AO solutions containing Cu(II) additive: (a) Cu(H$_2$O)$_6^{2+}$, (b) Cu(C$_2$O$_4$) and (c) Cu(C$_2$O$_4$)$_2^{2-}$; distortion: (a) tetragonal, (b) trigonal and (c) tetrahedral.

### 4.3. Ultraviolet region of absorption spectra

Aqueous AO solutions containing different concentrations (i.e. 5.87 × 10$^{-3}$, 1.17 × 10$^{-2}$, 1.76 × 10$^{-2}$, 2.35 × 10$^{-2}$ and 3.52 × 10$^{-2}$ mol/dm$^3$) of Cu(II) impurity exhibit characteristic bands in the wavelength intervals: 200–300 nm and 650–850 nm, which correspond to ultraviolet and visible regions, respectively. Typical example of the UV–Vis absorption spectrum of AO solution containing 1.17 × 10$^{-2}$ mol/dm$^3$ Cu(II) impurity is presented in Fig. 5.
Assuming that the additive rule is valid for absorption (see Eq. (5)), from the $A_i(\lambda)$ spectra of aqueous solutions of known AO concentrations containing different concentrations of Cu(II) impurity and the $A(\lambda)$ spectra of aqueous solutions of the AO concentrations without the impurity, the difference ($A_i - A$) was determined. Here the difference ($A_i - A$) refers to the absorbance $A$ of Cu(II) impurity and $c$ refers to the concentration $c_i$ of Cu(II) impurity. Then from the difference ($A_i - A$) the values of $\varepsilon_i$ were calculated by using Eq. (4). The results of the difference ($A_i - A$) are presented in Fig. 6 in the form of plots of $\ln \varepsilon_i$ on $\lambda$ for different concentrations of AO and Cu(II) impurity.

Fig. 6a and b shows the change in the values of $\ln \varepsilon_i$ in the wavelength range 200 nm < $\lambda$ < 380 nm as functions of AO concentration $c$ and Cu(II) impurity concentration $c_i$ in the solutions. Fig. 6a illustrates $\ln \varepsilon_i(\lambda)$ curves for aqueous solutions containing Cu(II) impurity alone of three different concentrations (viz. $1.17 \times 10^{-2}$, $2.35 \times 10^{-2}$, and $3.52 \times 10^{-2}$ mol/dm$^3$) as well as $\ln \varepsilon_i(\lambda)$ curves for mixtures of low AO concentrations, while Fig. 6b presents $\ln \varepsilon_i(\lambda)$ curves for mixtures of high AO concentrations.

![Figure 5](image_url)

**Figure 5.** Typical example of the UV-Vis absorption spectrum of AO solution containing $1.173 \times 10^{-2}$ mol/dm$^3$ Cu(II) impurity; AO concentration $c$: (1) 0, (2) $3.52 \times 10^{-3}$, (3) $1.407 \times 10^{-2}$ and (4) $2.815 \times 10^{-2}$ mol/dm$^3$.

![Figure 6](image_url)

**Figure 6.** Plots of $\ln \varepsilon_i$ against wavelength $\lambda$ for different concentrations of Cu(II) impurity: (I) $5.87 \times 10^{-3}$, (II) $1.17 \times 10^{-2}$, (III) $2.35 \times 10^{-2}$, and (IV) $3.52 \times 10^{-2}$ mol/dm$^3$. AO concentration in the solutions: Fig. 6a: (0) 0, (1) 3.52 $\times 10^{-3}$, (2) 1.407 $\times 10^{-2}$ and (3) 2.815 $\times 10^{-2}$ mol/dm$^3$. AO concentration in the solutions: Fig. 6b: (4) 0.070, (5) 0.141, (6) 0.211 and (7) 0.281 mol/dm$^3$.

Pure aqueous solutions containing Cu(II) impurity alone exhibit maximum absorption in the wavelength region between 200 and 240 nm, whereas its molar extinction coefficients have values lying in the range: $4.7 < \ln \varepsilon_i < 5.5$. The value of $\ln \varepsilon_i$ decreases with an increase in impurity concentration $c_i$. In the case of AO solutions containing Cu(II) impurity, three regions of $\lambda$ may be
observed on the \( \ln \varepsilon(\lambda) \) plots in which \( \ln \varepsilon \) takes different values, as shown in Fig. 6b. These regions of \( \lambda \) are: (A) 200 nm < \( \lambda \) < 240 nm, (B) 240 nm < \( \lambda \) < 270 nm, and (C) 270 nm < \( \lambda \) < 320 nm. In region A one observes a decrease in the value \( \ln \varepsilon \) in comparison with pure Cu(II) solutions without AO. In region B there is an increase in \( \ln \varepsilon \) for all impurity and AO concentrations. Shift of the absorption band to the higher wavelengths is a characteristic feature of this region (see Figs. 6a and b). The shift in the band increases with increasing AO concentration. In region C the values of \( \ln \varepsilon \) are practically constant but are higher than those in regions A and B. However, increase in Cu(II) impurity concentration leads to a decrease in the value of \( \ln \varepsilon \) in the entire range of wavelength \( \lambda \) (see Figs. 6a and b).

Pure aqueous copper chloride solutions of concentrations \( 1.17 \times 10^{-2}, 2.35 \times 10^{-2}, \) and \( 3.52 \times 10^{-2} \) mol/dm\(^3\) have their molar extinction coefficient \( \varepsilon \) in the wavelength interval between 200 and 240 nm (see Fig. 6a), and have the values 300, 150 and 110 dm\(^3\)/mol-cm, respectively. Charge-transfer bands for several hydrated metal ions lie in the interval between 200 and 250 nm of the UV region [7,11] and the values of their molar extinction coefficients \( \varepsilon \) are usually greater than 100 dm\(^3\)/mol-cm [7]. Therefore, the bands observed from pure aqueous solutions of Cu(II) impurity of the investigated concentrations \( c \), may be attributed to the formation of Cu(H\( _2 \)O\( _6 \))\(^{2+} \) aquocomplexes involving interactions between individual Cu(II) ions with H\( _2 \)O molecules.

The UV absorption bands for most of the oxalate complexes are similar to the bands of dimethyl oxalate and molecular oxalic acid [12], and appear in the wavelength range between 250–270 nm and the position of their maximum changes with the cation. A characteristic feature of these bands is that the band position shifts to the direction of longer wavelength with increasing Coulomb attractive interaction between metal cation and coordinated oxalate group [12].

It has been observed [7,8,12] that a shift in the absorption band occurs to the higher wavelength region of the spectrum with increasing number of ligands in a given complex, but, in the case of a constant number of ligands, the molar extinction coefficient \( \varepsilon \) attains a constant value in the given wavelength region. The value of the molar extinction coefficient \( \varepsilon \) of a complex containing two ligands is higher than that of the complex with one ligand. This occurs due to the fact that the probability of electronic transitions, and the value of the molar extinction coefficient associated with it, increases with an increase in the number of ligands localized around the cation.

From the above considerations, it may be argued that the shift in adsorption bands to higher wavelengths, observed in Fig. 6, is caused by the entrance of oxalate ions as ligands in the coordination sphere of the Cu(II) ion; the greater the shift in the band, the higher is the concentration of complexes of higher coordination number. This means that, if the dominating complexes are Cu(H\( _2 \)O\( _6 \))\(^{2+} \) and Cu(C\( _2 \)O\( _4 \)) in solutions composed of low AO concentrations, an increase in the AO concentration leads to a shift in the equilibrium of chemical reactions to the formation of complexes such as Cu(C\( _2 \)O\( _4 \)) and Cu(C\( _2 \)O\( _4 \))\(^{2+} \). However, since one also observes that the band shifts are relatively large in solutions of higher AO concentrations, it may be believed that Cu(C\( _2 \)O\( _4 \))\(^{2+} \) complexes dominate in these solutions. A decrease in the values of \( \varepsilon \) with an increase in Cu(II) concentration is due to the opposite situation and is associated with the type and concentration of the complexes formed.

From the dependence of the difference \( (A_i-A) \) on wavelength \( \lambda \) the values of half width \( \Delta \nu_{1/2} \) of the peaks for all Cu(II) and AO concentrations were calculated. The data so obtained are presented as the dependence of \( \Delta \nu_{1/2} \) on \( \nu \) and \( \Delta \nu_{1/2} \) on \( (c/c) \) in Fig. 7a and b, respectively.
It may be seen from Fig. 7a that an increase in the AO concentration \( c \) leads to a decrease in \( \Delta \nu_{1/2} \) in the entire range of concentration \( c \) used, but an increase in the concentration \( c_i \) of Cu(II) impurity leads either to a decrease or increase in the value of \( \Delta \nu_{1/2} \), depending on the range of AO concentration \( c \). In the range of low AO concentration corresponding to \(-5 < \ln(c) < -2.7\), the band FWHM decreases with an increase in impurity concentration \( c_i \). In the high AO concentration interval corresponding to \(-2 < \ln(c) < -1\), an increase in \( c_i \) leads to an increase in \( \Delta \nu_{1/2} \). It is generally accepted that the lower the value of \( \Delta \nu_{1/2} \), the more homogeneous is the solution in terms of the type of complexes [7]. In our case, this means that an increase in AO concentration shifts the reaction equilibrium towards the formation of Cu(C_4O_4^2-) first, followed by Cu(C_4O_4^2-) complex. However, increase in impurity concentration \( c_i \) affects in this way the equilibria of formation of complexes but only in the AO concentration region corresponding to \(-5 < \ln(c) < -2.7\). In the concentration interval \(-2 < \ln(c) < -1\), an increase in impurity concentration \( c_i \) causes the solution to become less homogeneous, implying that Cu(C_4O_4^2-) complexes dissociate and more complexes of Cu(C_4O_4^2-) type are formed.

The results of the values of half width \( \Delta \nu_{1/2} \) as a function of \( \ln(c/c_i) \) may be represented by three characteristic linear plots 1, 2 and 3. These results suggest that each of these linear plots 1, 2 and 3 represents particular types of chemical equilibria between the complexes being formed (i.e. Cu(H_2O)_6^{2+}, Cu(C_4O_4^{2-}), and Cu(C_4O_4^{2-}) and Cu(C_4O_4^{2-})) and also provides information about the dominating complexes in different \( \ln(c/c_i) \) intervals. Thus, it may be concluded that in the three \( \ln(c/c_i) \) regions: (1) \( 0 < \ln(c/c_i) < 2.5 \), (2) \(-3 < \ln(c/c_i) < 0 \), and (3) \(-4 < \ln(c/c_i) < -3 \), the dominating complexes are Cu(H_2O)_6^{2+}, Cu(C_4O_4^{2-}) and Cu(C_4O_4^{2-}) and Cu(C_4O_4^{2-}), respectively. It should be emphasized again that, in the case of solutions of different AO and Cu(II) concentrations and the same value of \( \ln(c/c_i) \) in the region \(-3 < \ln(c/c_i) < 0 \), either Cu(C_4O_4^{2-}) or Cu(C_4O_4^{2-}) complex can be dominant. However, which of these complexes is predominantly formed determines the solution pH. Displacement of peak wavelength \( \lambda_{\text{max}} \) to higher or lower wavelengths is usually associated with structural changes in the complex as a result of entering of different ligands in its coordination sphere [7]. Fig. 8a presents the dependence of \( \lambda_{\text{max}} \) on \( \ln(c/c_i) \). It may be seen from the figure that \( \lambda_{\text{max}} \) increases with a decrease in the value of \( \ln(c/c_i) \) in the entire investigated region of \( c/c_i \). Here as in the case of \( \Delta \nu_{1/2}[^{\ln(c/c_i)}] \) dependence, the \( \lambda_{\text{max}}[^{\ln(c/c_i)}] \) data fit around three linear plots 1, 2 and 3 (see Fig. 6a). It should be noted that the linear plots 1, 2 and 3 describe the results of \( \lambda_{\text{max}} \), the values of which lie in the intervals 250–260, 260–285, 285–290 nm, respectively. This means that the three intervals of \( \lambda_{\text{max}} \) are, respectively, associated with the dominating groups of the following complexes: Cu(H_2O)_6^{2+}, Cu(C_4O_4^{2-}) and Cu(C_4O_4^{2-}), and Cu(C_4O_4^{2-}).
Figure 8. Dependence of (a) peak wavelength $\lambda_{\text{max}}$ and (b) solution pH on $\ln(c_i/c)$ for different concentrations $c_i$ of Cu(II) impurity.

Fig. 8b illustrates the dependence of solution pH on $\ln(c_i/c)$ for different Cu(II) concentrations $c_i$. This figure shows that the trends of the pH[$\ln(c_i/c)$] dependence are similar to those of the plots of $\Delta\nu_{1/2}$ and $\lambda_{\text{max}}$ against $\ln(c_i/c)$, illustrated in Figs. 7b and 8a, respectively. Assuming that linear plots 1, 2 and 3 are due to the dominating complexes in Figs. 7b and 8a, the dominating complexes corresponding to plot 1 in the range $2.5 < \text{pH} < 3.5$, plot 2 in the range $4 < \text{pH} < 6.6$, and plot 3 for pH $> 6.6$ are: Cu(H$_2$O)$_6^{2+}$, Cu(C$_2$O$_4$) and Cu(C$_2$O$_4$)$_2^{2-}$, and Cu(C$_2$O$_4$)$_2^{2-}$, respectively.

4.4. Visible region of absorption spectra

Figs 9a and b show the dependence of half width $\Delta\nu_{1/2}$ and peak wavelength $\lambda_{\text{max}}$, obtained from the spectra in the wavelength region 650–850 nm, on $\ln(c_i/c)$ for unsaturated aqueous AO solutions containing different $c_i/c$ ratios, respectively. Fig. 9a reveals that $\Delta\nu_{1/2}$ increases with decreasing values of $\ln(c_i/c)$ in the concentration ratio defined by $0 < \ln(c_i/c) < 2.5$. At $\ln(c_i/c) = 0$, the value of $\Delta\nu_{1/2}$ abruptly decreases from the highest value of 6000 cm$^{-1}$ to a constant value of about 4400 cm$^{-1}$ for $\ln(c_i/c) < 0$. In the case of the dependence of $\lambda_{\text{max}}$ on $\ln(c_i/c)$ (see Fig. 9b), the value of $\lambda_{\text{max}}$ shifts to lower wavelengths with decreasing $\ln(c_i/c)$ in the concentration ratio given by $0 < \ln(c_i/c) < 2.5$. However, $\lambda_{\text{max}}$ abruptly decreases from a value of about 790 nm at $\ln(c_i/c) = 0$ to a constant value of about 710 nm for $\ln(c_i/c) < 0$.

Figure 9. Dependences of (a) half width $\Delta\nu_{1/2}$ and (b) peak wavelength $\lambda_{\text{max}}$ on $\ln(c_i/c)$ in the visible spectral region for unsaturated aqueous AO solutions containing different impurity concentration $c_i$. 

\[c_i \text{ (mol/kdm$^3$)}: 5.670 \times 10^{-4}, 1.173 \times 10^{-4}, 1.760 \times 10^{-4}, 2.346 \times 10^{-4}, 2.933 \times 10^{-4}, 3.518 \times 10^{-4}\]
As reported earlier [13], the molar extinction coefficient $\varepsilon_{\text{max}}$ for ammonium oxalate solutions containing Cu(II) impurity increase with decreasing value of $\ln(c/c)$, attaining values of 12–16 dm$^3$ mol$^{-1}$ cm$^{-1}$ and 33–37 dm$^3$ mol$^{-1}$ cm$^{-1}$ in $0 < \ln(c/c) < 2.5$ and $\ln(c/c) < 0$, respectively. It is known [12] that Cu(C$_2$O$_4$)$_2^{2-}$ complexes exhibit their band at 700 nm and their molar extinction coefficient $\varepsilon_{\text{max}} = 33.5$ dm$^3$ mol$^{-1}$ cm$^{-1}$. However, Cu(H$_2$O)$_4^{2+}$ aquocomplexes show their band at 794 nm and their molar extinction coefficient $\varepsilon_{\text{max}} = 12$ dm$^3$ mol$^{-1}$ cm$^{-1}$ [7].

From Figs. 9a and b it may be noted that the data of the basic band parameters $\Delta \nu_{1/2}$ and $\lambda_{\text{max}}$ on $\ln(c/c)$ are arranged around two linear plots covering the regions of concentration ratios $-5 < \ln(c/c) < 0$ and $0 < \ln(c/c) < 2.5$. This suggests that the linear plots in the two $\ln(c/c)$ regions are due to two types of chemical equilibria of the forming complexes in the solutions, i.e. Cu(H$_2$O)$_4^{2+}$ and CuC$_2$O$_4$, and CuC$_2$O$_4$ and Cu(C$_2$O$_4$)$_2^{2-}$.

### 4.5. Oscillator strength and structure of complexes

Figs. 10a and b show the plots of oscillator strength $f$, obtained from spectra in the ultraviolet and visible regions of aqueous solutions, against $\ln(c/c)$, respectively. From Fig. 10a it may be noted that the value of oscillator strength $f$, obtained from UV spectra, for copper complexes forming in aqueous AO solutions in the concentration ratio range $-4 < \ln(c/c) < -1$ increases with increasing $\ln(c/c)$ and, depending on the value of $\ln(c/c)$ and impurity concentration $c_i$, $f$ changes from 0.003 to 0.03. However, in this spectral region, the oscillator strength $f$ is practically constant equal to about 0.01 in the range $0 < \ln(c/c) < 2.5$. In contrast to the ultraviolet region, Fig. 10b reveals that the values of $f$ in the visible spectral region lie in the ranges of $2 \times 10^{-4} – 4 \times 10^{-4}$ and $6 \times 10^{-4} – 7 \times 10^{-4}$ for $\ln(c/c) > 0$ and $\ln(c/c) < 0$, respectively. With an increase in $\ln(c/c)$, the value of $f$ in this spectral region somewhat decreases in the range $\ln(c/c) < 0$, while it decreases significantly in the range $\ln(c/c) > 0$.

**Figure** 10. Dependence of oscillator strength $f$ obtained from spectra in (a) ultraviolet and (b) visible regions of aqueous solutions on $\ln(c/c)$ for different Cu(II) concentrations.

The behavior of the plots of oscillator strength $f$ against $\ln(c/c)$ in Figs. 10a and b is similar to that of the plots of $\Delta \nu_{1/2}$ and $\lambda_{\text{max}}$ against $\ln(c/c)$. As before, the dependence of oscillator strength $f$ on $\ln(c/c)$ may be attributed to the formation of metal complexes containing different ligands. However, the complexes formed are of low or high symmetries, depending on the impurity–solute concentration ratio $c_i/c$.

The plots of oscillator strength $f$ against $\ln(c/c)$ are very similar to the plots of $\ln[[\text{Cu(C}_2\text{O}_4)]]/[\text{Cu(H}_2\text{O}_4^{2+}]]$ and $\ln[[\text{Cu(C}_2\text{O}_4)_{2}^{2-}]]/[\text{Cu(H}_2\text{O}_4^{2+}]]$ against $\ln(c/c)$, as shown in Fig. 3b. These observations may be attributed to the formation of increasing concentrations of Cu(C$_2$O$_4$) and Cu(C$_2$O$_4$)$_2^{2-}$ complexes with decrease in $\ln(c/c)$ in the solution as a result of substitution of water.
molecules of the Cu(H₂O)₆²⁺ species by C₂O₄²⁻ ligands. More the reaction shifts to the formation of Cu(C₂O₄) and Cu(C₂O₄)₂²⁻ complexes, the greater is the oscillator strength. This conclusion is consistent with the fact that the probability of electronic transitions, and the oscillator strength associated with it, increases with an increase in the number of ligands around a metal cation [7,8]. The greater the binding force, the greater is the oscillator strength.

From Fig. 10a the following features may be noted:

1. In the range −2 < ln(c/c) < 0, f is practically constant or insignificantly decreases with increasing ln(c/c); see f[ln(c/c)] data for c₁ = 1.17 × 10⁻² and 3.52 × 10⁻² mol/dm³.

2. For −4 < ln(c/c) < −2, the value of f corresponding to a given c₁ linearly decreases with an increase in ln(c/c). The extrapolation of the f[ln(c/c)] plots shows a tendency to intersect at ln(c/c) = −5.

3. For −4 < ln(c/c) < −2, the slope of the f[ln(c/c)] plot decreases with an increase in c₁ such that the slope ∆f/∆[ln(c/c)] approaches zero for the highest value of c₁.

4. Above a certain value of ln(c/c) equal to about −2, the oscillator strength has a constant value f₀. For example, for c₁ = 1.17 × 10⁻² mol/dm³, f₀ ≈ 0.012; but for c₁ = 2.35 × 10⁻² mol/dm³, f₀ ≈ 0.007 but for c₁ = 3.52 × 10⁻² mol/dm³, f₀ ≈ 0.01.

5. Except in the case of the highest impurity concentration c₁ = 3.52 × 10⁻² mol/dm³ used in this study, the products c₁∆f/∆[ln(c/c)] and c₁f₀ are practically constant quantities equal to about 4 × 10⁻⁵ mol/dm³⁻¹ and 1.6 × 10⁻⁵ mol/dm³⁻¹, respectively. However, for c₁ = 3.52 × 10⁻² mol/dm³, c₁∆f/∆[ln(c/c)] ≈ 0 mol/dm³⁻¹ and c₁f₀ ≈ 3.5 × 10⁻⁴ mol/dm³⁻¹.

Feature (1) is associated with the chemical equilibria between Cu(C₂O₄)₂²⁻ and Cu(C₂O₄) complexes forming in this concentration ratio range. Here an increase in c₁ shifts the chemical equilibrium to the formation of Cu(C₂O₄) complex, while an increase in c shifts the equilibrium to the formation of Cu(C₂O₄)₂²⁻ complex. In terms of its absolute value, an increase in f means that the concentration of the Cu(C₂O₄) complex increases with an increase in impurity concentration c₁ and a decrease in AO concentration c. The practically constant value of f in the range −2 < ln(c/c) < 0 suggests that Cu(C₂O₄) complex dominates here. However, in comparison with the f value in −2 < ln(c/c) < 0 range, a somewhat lower value of f for ln(c/c) > 0 implies that Cu(H₂O)₆²⁺ complex is dominant.

Feature (2) of a linear decrease in f and Feature (3) of a decrease in the slope of f[ln(c/c)] with an increase in ln(c/c) is associated with the capability of formation of changing copper-oxalate complexes at a given impurity concentration c₁. Feature (4) of a constant value of f is associated with the constant constitution of the complex formed above the transition value of ln(c/c). Feature (5) of the constant values of the products c₁∆f/∆[ln(c/c)] and c₁f₀ in the regions of ln(c/c) below and above its transition value, respectively, is a consequence of formation of different types of complexes in these regions.

5. Conclusions

1. Changes in the absorption of light by aqueous ammonium oxalate solutions containing Cu(II) impurity in the concentration ratio range −5 < ln(c/c) < 2.5 lead to decrease or increase in the intensity of bands of the UV–vis spectral region. These changes may be expressed by full width at half maximum Δν/Δλ, molar extinction coefficient ε, peak wavelength λmax, and oscillator strength f. The changes are caused by the coordination of C₂O₄²⁻ ligand with Cu(H₂O)₆²⁺ aquocomplex, and are related with the concentration ratio range ln(c/c). The coordination of C₂O₄²⁻ ligand with Cu(H₂O)₆²⁺ aquocomplex in the range 0 < ln(c/c) < 2.5 leads to the formation of Cu(C₂O₄) complexes, but the coordination of the C₂O₄²⁻ ligand with Cu(C₂O₄) complex in the concentration ratio range −5 < ln(c/c) < 0 results in the formation of predominantly Cu(C₂O₄)₂²⁻ complex.

2. The effect of successive coordination of the C₂O₄²⁻ ligand is well—defined in the UV spectral region but poor in the visible region. This difference is associated with nature of overlapping of absorption bands corresponding to different types of complexes. The overlapping effect is pronounced in the case of visible spectral region, but no such effect occurs in the UV region.
(3) Analysis of the UV–vis spectra of aqueous ammonium oxalate solutions containing Cu(II) impurity in the UV region enables to identify two regions of concentration ratios \( \ln(c_i/c) \) in which \( \text{Cu(H}_2\text{O)}_6^{2+}, \text{Cu(C}_2\text{O}_4^- \) and \( \text{Cu(C}_2\text{O}_4)^{2-} \) are dominating complexes. Analysis of the visible region of the spectra, however, enables to establish the two ranges of \( \ln(c_i/c) \) in which the complexes \( \text{Cu(H}_2\text{O)}_6^{2+} \) and \( \text{Cu(C}_2\text{O}_4^- \), and \( \text{Cu(C}_2\text{O}_4)^{2-} \) predominantly coexist in the solutions.

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