
Determination of the stability constant of the dinuclear Cu(II)– β -cyclodextrin complex by the ligand displacement method

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Cu(II) ions form (pH > 12.5) a dinuclear complex with the anion of β -cyclodextrin (CD) in alkaline solutions under conditions of metal ion excess. The spectrophotometric method of ligand displacement was applied for determination of the stability constant of this complex, using EDTA and OH⁻ ions as competitive ligands. The results obtained are in agreement with the 2:1 stoichiometry of the complex, namely Cu₂CD; the stability constant logarithm is 39.2 ± 0.2 . This complex predominates in the solutions within the pH range from 12.5 to 14.3 (3M NaOH solution), transforming with an increase in alkalinity to Cu(OH)₄²⁻.

Key words: β -cyclodextrin, copper(II), complex formation, stability constant

INTRODUCTION

β -cyclodextrin (β -CD) is an important representative of cyclic polyhydroxylic carbohydrates. Metallo-cyclodextrins are potential metallo enzyme models having a range of applications in catalysis and molecular recognition [1]. Cyclodextrin (CD) inclusion complex formation with different compounds is well known and widely investigated [2–5], whereas data on cyclodextrin interaction with metal ions in aqueous solutions are not numerous.

CDs show a relatively poor coordination ability in acidic and neutral solutions. For example, circular dichroism measurements confirmed that there is no direct complexation of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) at non-basic pH [6]. However, the chelating properties of β -CD can be enhanced in alkaline solutions due to deprotonation of OH-groups. The acid behaviour of β -CD had been already investigated, showing that unsubstituted β -CD is a rather weak acid ($pK_a = 12.201$ [7]).

Several authors have reported on Cu(II) complexes with β -CD. For the first time the possibility

of Cu(II) ion complexation by β -CD in alkaline solutions was documented by Messmer [8], and further investigations were made by Matsui and coworkers [9–12].

The latter authors first reported the preparation of Cu(II) complexes with β -CD, which were analysed for a Cu: β -CD ratio of 2:1 in 0.1–1.0 M NaOH solutions, and the light absorption spectra were characterized by a maximum at 668 nm and the molar extinction coefficient 128 ± 1 in 0.1 M NaOH solution [9]. Cu₂– β -CD complex was investigated by means of pH-metric and conductometric titrations and polarimetric measurements [10]. The authors found that one mole of β -CD in the presence of two moles Cu(OH)₂ consumes three moles of hydroxide ion. Based on observations, they determined the Cu₂(OH)(O) β -CD³⁻ formula of the complex, β -CD being fourfold deprotonated. Using molecular models it was suggested that the two pairs of deprotonated C₂ and C₃ secondary OH-groups of adjacent glucopyranose units are cross-linked by the =Cu(OH)(O)Cu= ion bridge [10], whereas the bridge of =Cu(OH)₂Cu= was shown also to be possible [9, 11]. In the course of later study the possibility of 1:1 Cu(II)– β -CD complex formation was shown in alkaline solutions. The suggested formula

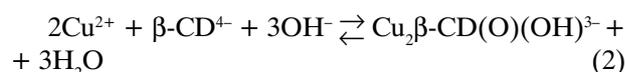
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of this complex was $\text{Cu}\beta\text{-CD}(\text{OH})_2^{2-}$, $\beta\text{-CD}$ being in form of double-deprotonated anion [12]. In the same work the equilibrium constant of the reaction,



was determined in 1M NaOH solution. The obtained logarithm value was found to be 37.66 [12].

The determination of the formation constant of 2:1 Cu(II)- $\beta\text{-CD}$ complex was carried out by spectrophotometric titration with EDTA, using optical window factor analysis [13]. The equilibrium relationship was written as



and the formation constant as

$$K = \frac{[\text{Cu}_2\beta\text{-CD}(\text{O})(\text{OH})^{3-}]}{[\text{Cu}^{2+}]^2[\text{OH}^-]^3[\beta\text{-CD}^{4-}]} \quad (3)$$

In the authors' opinion, the high value of the formation ($\log K = 35.78 \pm 0.38$) suggests that the complex is highly stable in alkaline solutions [13].

The $\text{Cu}_2\text{-}\beta\text{-CD}$ complex was synthesized and characterized by means of electronic spectroscopy, magnetic susceptibility, FTIR and Raman spectroscopic studies [14]. The structure of this complex was assigned as $\text{Na}_2[\text{Cu}_2\beta\text{-CD}(\text{OH})_2 \cdot 2\text{H}_2\text{O}]$. According to the authors, the data presented are consistent with the proposal of a dinuclear hydroxy-bridged complex and the presence of simultaneous first and second sphere interaction [14].

Other authors obtained similar FTIR results, however, their interpretation did not involve a hydroxy-bridged structure [15]. The results supported the assumption that the $\text{Cu}_2\text{-}\beta\text{-CD}$ complex is formed by linkages between secondary OH-groups of $\beta\text{-CD}$ and Cu(II) ions. The spectral data discussed are consistent with those reported in [14] and lend support of the proposal of the existence of simultaneous first and second sphere interaction. However, evidences not for a dinuclear hydroxy-bridged system but, rather for a structure containing two aquo-Cu(II) ions for one molecule of $\beta\text{-CD}$ were found. Cu(II) ions react with the secondary OH-groups of $\beta\text{-CD}$, and water molecules coordinated to Cu(II) ions are directed partly into and partly out of the $\beta\text{-CD}$ cavity [15].

The evidence of covalent binding between Cu(II) ions and $\beta\text{-CD}$ was shown on the basis of circular dichroism study, as significant changes observed in spectra of Cu(II)- $\beta\text{-CD}$ complexes suggest that the covalent binding of Cu(II) ions to the OH-groups of $\beta\text{-CD}$ is involved [16].

Klüfers and coworkers [17] isolated from solution blue crystals formulated as $\text{Li}_4[\text{Li}_7\text{Cu}_4(\beta\text{-CDH}_{11.5})_2] \cdot x\text{H}_2\text{O}$ (where $\beta\text{-CDH}_{21}$ is undeprotonated $\beta\text{-CD}$, and $x \sim 40$). The stoichiometry of 2:1 for Cu(II): $\beta\text{-CD}$ was obtained, and the X-ray data were interpreted in terms of a $\beta\text{-CD}$ double torus with bridges formed between four Cu(II) ions. No hydroxy-bridges were found [17].

Summarizing the literature data it can be noted that most of the results obtained are only qualitative and do not provide information on stability constants of the complexes formed in alkaline Cu(II)- $\beta\text{-CD}$ solutions.

This paper presents a spectrophotometric study of complex formation with the aim to determine the stability constant of the dinuclear $\text{Cu}_2\text{-}\beta\text{-CD}$ complex formed in alkaline solutions.

EXPERIMENTAL

Materials

Analytical grade chemicals were used, and $\beta\text{-cyclo-dextrin}$ ($M_r = 1135$) was "purum" from Fluka. NaNO_3 and NaOH solutions were used to keep ionic strength (J) of the solutions constant and equal to 1 M.

Spectrophotometry

Light absorption spectra were recorded using a Perkin Elmer *Lambda 35* UV/VIS spectrometer at 20 °C in 1 cm-thick quartz cells. The optical blank solution was pure water.

pH-metric measurements

Measurements of the solution pH were carried out using a Toledo Mettler *MP 220* pH-meter. At higher NaOH concentrations when pH exceeded 13.5, it was not measured directly but calculated as:

$$\text{pH} = \text{p}K_w - \text{pOH} \quad (1)$$

using the activity of OH^- ions and $\text{p}K_w$ given in [18].

RESULTS AND DISCUSSION

Copper(II) forms no complexes with $\beta\text{-CD}$ at $\text{pH} < 12.5$ in alkaline solutions, when the molar ratio of Cu(II) : $\beta\text{-CD}$ is 2:1. Formation of the $\text{Cu}(\text{OH})_2$ precipitate is visually observed in the solution. At higher pH no precipitate is formed and the solution becomes blue in color, which is indicative of Cu(II) complex formation. Since copper(II) complexation begins at pH over 12.5, and $\text{Cu}(\text{OH})_2$ precipitate is

formed when Cu(II) : β -CD ratio exceeds 2:1, the results obtained can be accounted for by the dinuclear Cu(II)- β -CD complex formation with the deprotonated form of β -CD.

Light absorption spectra of the dinuclear Cu(II)- β -CD complex almost coincide in the pH range from 12.5 to 13.9. The constancy of absorbance in a rather wide range of alkalinity (from 0.05 to 1.0 M NaOH) suggests formation of one kind of complex, *e. g.* solely-dinuclear Cu(II)- β -CD complex Cu_2CD (CD^{4-} is anion of fourfold deprotonated β -CD), and support earlier obtained data, that no hydroxy-bridges are formed in the complex [15, 17]. Curve 1 in Fig. 1 represents the spectrum of Cu_2CD at pH 13.0, showing the light absorption maximum at $\lambda = 675$ nm, the molar extinction coefficient (ϵ) being $120 \text{ mol}^{-1} \text{ l cm}^{-1}$. It can be noted that our results are in good agreement with that presented in ref. [9].

The method of ligand displacement was used for the determination of the stability constant of the complex formed. In accordance with this method, the competitive ligand is supposed to form a Cu(II) complex compound with different optical properties, *e. g.*, its light absorption maximum and/or molar extinction coefficient should differ quite a little from that of Cu_2CD . We selected as a competitive ligand EDTA (ethylenediaminetetraacetic acid), since it is known that at higher pH values ($\text{pH} \geq 13.0$) to form only one complex, namely the hydroxy-complex $\text{CuY}(\text{OH})^{3-}$ (Y^{4-} is the fourfold deprotonated

anion of EDTA), light absorption maximum of which is at $\lambda = 750$ nm, the stability constant logarithm $\log \beta_{\text{CuY}(\text{OH})^{3-}}$ being 21.1 [19]. Curve 7 in Fig. 1 represents the spectrum of $\text{CuY}(\text{OH})^{3-}$ at pH 13.0, showing the light absorption maximum at $\lambda = 750$ nm, ϵ being $42 \text{ mol}^{-1} \text{ l cm}^{-1}$.

It is worth noting that the shape of the spectra obtained in our experiments differs to a certain degree from those given in [13]. The spectrum of the dinuclear Cu(II)- β -CD complex is comparable, whereas spectra of the Cu(II)-EDTA system differ. The difference can be attributed to the pH of solutions used by authors of ref. [13]. The data presented in [13] are obtained at pH 12, at this pH, CuY^{2-} and $\text{CuY}(\text{OH})^{3-}$, two complexes known to be in equilibrium in the Cu(II)-EDTA system [19]. Therefore, in our opinion, the data of ref. 13 were not given an exhaustive analysis.

Addition of EDTA into alkaline Cu(II)- β -CD solution changes light absorption spectra so that light absorbance decreases and light absorption maximum shifts to longer wavelengths with an increase in EDTA concentration (Fig. 1). The isobestic point at *ca.* 770 nm indicates that at least two complex compounds are in equilibrium. Thus, the spectra obtained demonstrate conversion of the dinuclear Cu(II)- β -CD complex into a complex of $\text{CuY}(\text{OH})^{3-}$ (Fig. 1).

When two complex compounds (in our case dinuclear Cu_2CD and $\text{CuY}(\text{OH})^{3-}$) exist in equilibrium in the solution and their spectra differ, the concentrations of the complexes could be calculated from the experimental data obtained at different wavelengths by solving the system of equations:

$$\begin{cases} 2c_{\text{Cu}_2\text{CD}} + c_{\text{CuY}(\text{OH})^{3-}} = [\text{Cu}(\text{II})]_0 \\ c_{\text{Cu}_2\text{CD}} \epsilon_{\lambda_{\text{Cu}_2\text{CD}}} + c_{\text{CuY}(\text{OH})^{3-}} \epsilon_{\lambda_{\text{CuY}(\text{OH})^{3-}}} = A_{\lambda_i} / l \end{cases} \quad (2)$$

where c stands for the concentrations (M) of the corresponding complexes, $[\text{Cu}(\text{II})]_0$ is the total Cu(II) concentration (mol/l), A_{λ_i} is the light absorbance at the wavelength λ_i , l is the cell width (cm), ϵ_{λ_i} is the molar extinction coefficient values of the corresponding complexes at the wavelength λ_i calculated according to

$$\epsilon_{\lambda_i} = A_{\lambda_i} / cl \quad (1 \text{ mol}^{-1} \text{ cm}^{-1}). \quad (3)$$

It should be noted that equations (1) and (2) are valid when a linear dependence of light absorbance on complex concentration is observed, *i. e.* under conditions of the Beer law validity. Therefore, before the calculations, a series of spectra of solutions with different Cu(II) concentrations but a constant metal-to-ligand ratio were recorded. The

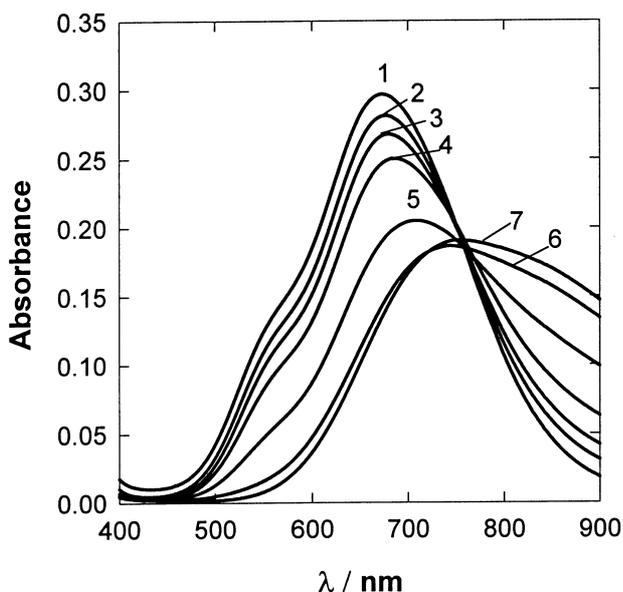


Fig. 1. Cu(II) light absorption spectra in alkaline solutions of β -cyclodextrin (1), EDTA (7) and their mixture (2-6). Solution composition (M): $[\text{Cu}(\text{II})]_0 = 0.005$; $[\beta\text{-cyclodextrin}]_0 = 0.0025$; $[\text{EDTA}]_0$: 1 - 0, 2 - 0.0005, 3 - 0.001, 4 - 0.002, 5 - 0.004, 6 - 0.008, 7 - 0.01. Solution pH - 13.0; 20 °C; $l = 1$

results obtained show a linear dependence of absorbance on the concentration of complexes, the plots going through the origin of coordinates (Fig. 2). The plots obtained demonstrate the validity of the Beer law for the system under investigation.

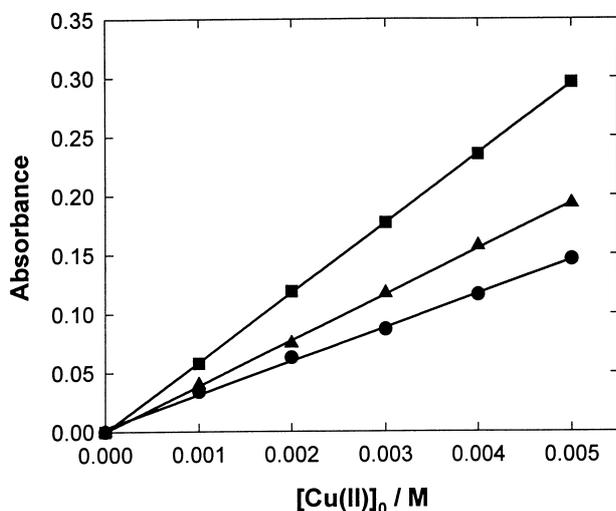


Fig. 2. Dependence of light absorbance on Cu(II) concentration. Solution composition: (●) – Cu(II) and 5 M NaOH; (▲) – Cu(II) and EDTA (molar ratio 1:2), pH – 13.0, $\lambda = 750$ nm, $I = 1$; (■) – Cu(II) and β -cyclodextrin (molar ratio 2:1), pH – 13.0, $\lambda = 675$ nm, $I = 1$. 20 °C

The results obtained show that the quantities of Cu_2CD and $\text{CuY}(\text{OH})^{3-}$ complexes are comparable only at approximately equal concentrations of Cu(II) ligands. With a further increase in EDTA concentration the amount of $\text{CuY}(\text{OH})^{3-}$ complex increases, and this complex predominates at a higher excess of EDTA (Table 1).

Knowing the concentrations of Cu(II) complexes present in the solution under investigation, the equilibrium concentrations of deprotonated ligand forms as well as the concentration of free copper(II) ions can be calculated. We assumed that EDTA is completely fourfold deprotonated ($\text{p}K_{\text{a}4} \sim 10.3$ [18, 20] and that in the case of dinuclear Cu(II)– β -CD

complex the fourfold deprotonated β -CD (CD^{4-}) is involved in complex formation, since only deprotonated OH-groups can form sufficiently strong complexes in alkaline solutions [20–22].

With regard to the deprotonation of β -CD, according to our data, there is only one original reference on the $\text{p}K_{\text{a}}$ value of β -CD [7]. Further papers or reviews cite this work and indicate the same $\text{p}K_{\text{a}1}$ value equal to 12.20 [2–5]. On the one hand, this value seems to be too low, because a comparison of our results with that obtained when investigating Cu(II) complex formation with saccharose [23, 24], which has a rather similar $\text{p}K_{\text{a}1}$ value ($\text{p}K_{\text{a}1} = 12.43$ [25]), revealed differences: the formation of soluble Cu(II)–saccharose complexes begins at pH over 11 (*i. e.* at pH values much lower than $\text{p}K_{\text{a}}$), whereas the complexation of Cu(II) ions in the Cu(II)– β -CD system occurs only at pH over 12.5 (*i. e.* at pH values higher than $\text{p}K_{\text{a}}$). In general, formation of soluble Cu(II) complexes with polyhydroxylic compounds, such as tartrate [26], glycerol [24, 27], dextran [28], D-mannitol [29], D-sorbitol [30], begins in solutions at pH values lower (*ca.* by 1–3 units) than the $\text{p}K_{\text{a}}$ values of corresponding polyhydroxylic ligands. On the other hand, if a fourfold deprotonated anion of β -CD is involved in complex formation, to calculate the equilibria we need to know the $\text{p}K_{\text{a}1}$ – $\text{p}K_{\text{a}4}$ values of β -CD. Therefore, an additional investigation of β -CD deprotonation should be carried out. According to recent ^{13}C and ^1H NMR results [31], the $\text{p}K_{\text{a}1}$ – $\text{p}K_{\text{a}4}$ values of β -CD deprotonation are of the same order, and the $\text{p}K_{\text{a}1,2,3,4}$ values, highly approximately equal to 13.5 [31], were used to calculate the equilibrium concentration of the fourfold deprotonated β -CD anion.

The stability constant of Cu_2CD complex,

$$\beta = [\text{Cu}_2\text{CD}] / [\text{Cu}(\text{II})]^2 \cdot [\text{CD}^{4-}], \quad (4)$$

was calculated using spectrophotometric data on Cu(II) distribution among the complexes (Table 1), whereas the concentration of free Cu(II) ions was taken from

Table 1. Data on equilibria in the system Cu(II)– β -cyclodextrin(CD)–EDTA calculated from the spectrophotometric data of Figs. 1, 3 and 4

[Cu(II)] ₀ , M	[CD] ₀ , M	pH M	[EDTA (H ₄ Y)] ₀ , M	*[CuY(OH) ³⁻], M	*[Cu ₂ CD], M	[Y ⁴⁻], M	[CD] ₀ – [Cu ₂ CD], M	[CD ⁴⁻], M	log[Cu(II)]	log $\beta_{\text{Cu}_2\text{CD}}$
1	2	3	4	5	6	7	8	9	10	11
0.005	0.0025	13.0	0.0005	0.00048	0.00260	0.00002	0.00024	0.000058	–18.3	38.9
			0.001	0.00093	0.00204	0.00007	0.00047	0.00011	–18.9	39.1
			0.002	0.00170	0.00165	0.00030	0.00085	0.00020	–19.3	39.5
			0.004	0.00320	0.00090	0.00080	0.00160	0.00038	–19.4	39.2
			0.008	0.00460	0.00020	0.00340	0.00230	0.00055	–19.9	39.4
Mean:										39.2 ± 0.2

Table 1 (continued)

1	2	3	4	5	6	7	8	9	10	11
0.01	0.005	13.0	0.001	0.00091	0.0045	0.00009	0.0005	0.000012	-19.0	39.6
			0.002	0.00190	0.0041	0.00010	0.0009	0.00022	-18.7	38.7
			0.004	0.00340	0.0033	0.00060	0.0017	0.00041	-19.3	39.6
			0.008	0.00710	0.0015	0.00090	0.0035	0.00084	-19.1	38.6
			0.016	0.00960	0.0002	0.00640	0.0048	0.00115	-19.8	38.9
Mean: 39.1 \pm 0.6										
0.005	0.0025	13.5	0.0005	0.00043	0.00229	0.00007	0.00021	0.000105	-19.8	40.9
			0.001	0.00096	0.00202	0.00004	0.00048	0.00024	-19.1	39.2
			0.002	0.00190	0.00155	0.00010	0.00095	0.000475	-19.2	39.0
			0.004	0.00385	0.00058	0.00015	0.00192	0.00096	-19.1	38.0
			0.008	0.00494	0.00003	0.00306	0.00247	0.001235	-20.3	39.0
Mean: 39.2 \pm 1.3										

*Averages of the values calculated at 600, 650, 700, 800, 850 and 900 nm wavelengths.

$$[\text{Cu(II)}] = [\text{CuY(OH)}^{3-}] / \beta_{\text{CuY(OH)}^{3-}} \cdot [\text{Y}^{4-}] \cdot a_{\text{OH}^-} \quad (5)$$

where a_{OH^-} is activity of OH^- ions calculated from pH and $\text{p}K_w$ value was taken from [18] according equation (1).

The results obtained at different EDTA concentrations correlate well, the mean value of $\log \beta_{\text{Cu}_2\text{CD}}$ being 39.2 ± 0.2 (Table 1).

The other experiments were performed at the same Cu(II) : β -CD molar ratio (2:1), but at twice as high concentrations of Cu(II) and β -CD (Fig. 3)

or at a higher pH using the same concentrations (Fig. 4). The calculated value of $\log \beta_{\text{Cu}_2\text{CD}}$ coincides in margins of error (Table 1), the mean value of $\log \beta_{\text{Cu}_2\text{CD}}$ being 39.2. The results obtained are in agreement with the existence of a dinuclear Cu(II)- β -CD complex of the mentioned composition under study conditions. It is worth noting that our experiments show no evidence of formation of Cu(II)- β -CD polymeric or hydroxy-complexes, since the $\log \beta_{\text{Cu}_2\text{CD}}$ value obtained with different solution compositions is the same.

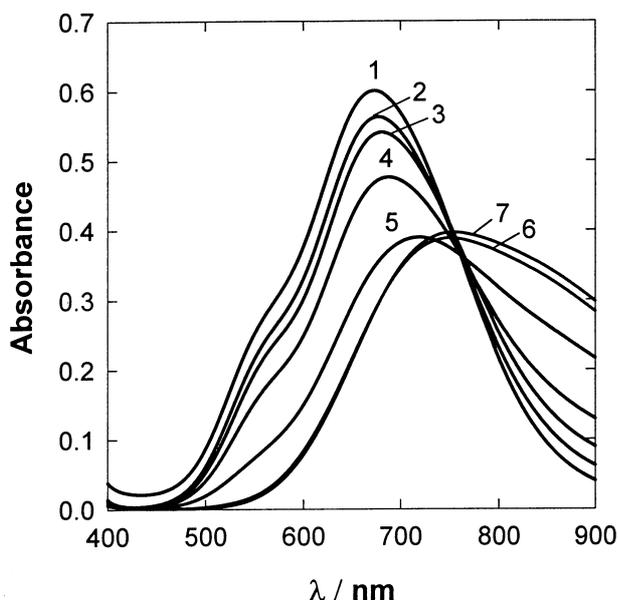


Fig. 3. Cu(II) light absorption spectra in alkaline solutions of β -cyclodextrin (1), EDTA (7) and their mixture (2-6). Solution composition (M): $[\text{Cu(II)}]_0 = 0.005$; $[\beta\text{-cyclodextrin}]_0 = 0.0025$; $[\text{EDTA}]_0$: 1 - 0, 2 - 0.001, 3 - 0.002, 4 - 0.004, 5 - 0.008, 6 - 0.016, 7 - 0.02. Solution pH - 13.0; 20 °C; $I = 1$

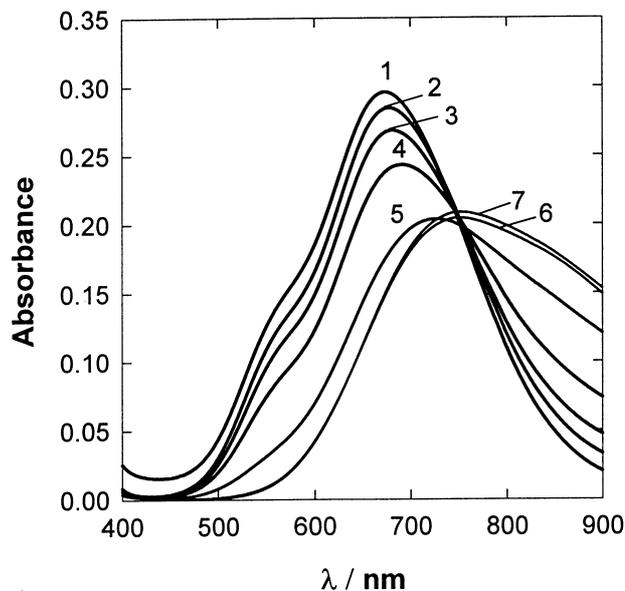


Fig. 4. Cu(II) light absorption spectra in alkaline solutions of β -cyclodextrin (1), EDTA (7) and their mixture (2-6). Solution composition (M): $[\text{Cu(II)}]_0 = 0.005$; $[\beta\text{-cyclodextrin}]_0 = 0.0025$; $[\text{EDTA}]_0$: 1 - 0, 2 - 0.0005, 3 - 0.001, 4 - 0.002, 5 - 0.004, 6 - 0.008, 7 - 0.01. Solution pH - 13.5; 20 °C; $I = 1$

Additional experiments were carried out using OH⁻ ions as a competitive ligand, since it is documented that Cu(II) ions form a tetrahydroxycuprate(II) (Cu(OH)₄²⁻) complex in concentrated solutions of sodium hydroxide [32–37]. The stability constant of this complex compound is known and equals 15.5 ± 0.1 [37].

As stated above, no changes in the spectrum of Cu₂CD complex are observed in the pH range from 12.5 to 13.9 (1M NaOH solution). With a further increase in sodium hydroxide concentration the light absorption maximum decreases, shifts towards shorter wavelengths and approaches the spectrum of Cu(OH)₄²⁻, which is defined with the light absorption maximum at $\lambda = 640$ nm, ϵ being $30 \text{ mol}^{-1} \text{ l cm}^{-1}$ (Fig. 5). The results obtained provide a clear evidence of Cu₂CD complex transformation into tetrahydroxycuprate(II).

Since the Beer law is valid for the system under investigation (Fig. 2), the procedure analogous to that described for the Cu(II)– β -CD–EDTA system was used for determination of the stability of Cu₂CD complex. The following system of equations was solved:

$$\begin{cases} 2c_{\text{Cu}_2\text{CD}} + c_{\text{Cu(OH)}_4^{2-}} = [\text{Cu(II)}]_0 \\ c_{\text{Cu}_2\text{CD}} \epsilon_{\lambda_{\text{Cu}_2\text{CD}}} + c_{\text{Cu(OH)}_4^{2-}} \epsilon_{\lambda_{\text{Cu(OH)}_4^{2-}}} = A_{\lambda_i} / l \end{cases} \quad (6)$$

The stability constant of Cu₂CD complex (Equation (4)) was calculated using spectrophotometric data on Cu(II) distribution among the complexes (Table 2), whereas the concentration of free Cu(II) ions was taken from

$$[\text{Cu(II)}] = [\text{Cu(OH)}_4^{2-}] / \beta_{\text{Cu(OH)}_4^{2-}} \cdot a_{\text{OH}^-}^4 \quad (7)$$

The stability constant value obtained ($\log \beta_{\text{Cu}_2\text{CD}} = 38.4$) is slightly lower (0.8 unit) than that determined when investigating the Cu(II)– β -CD–EDTA system. The inconsiderable discrepancy can be as-

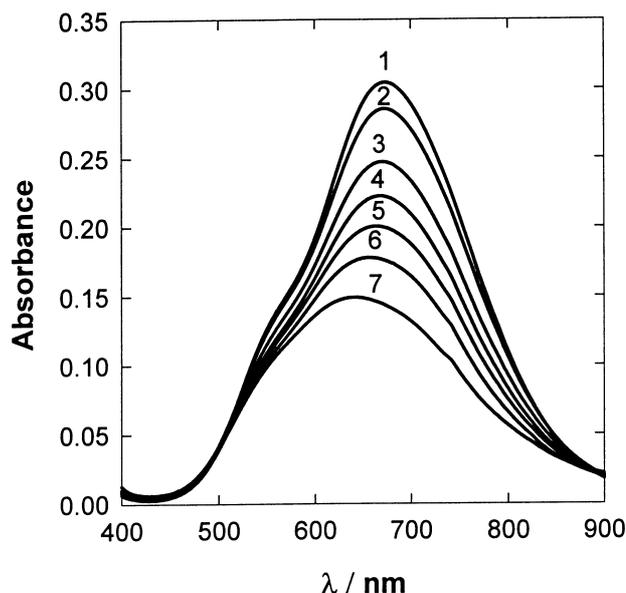


Fig. 5. Cu(II) light absorption spectra in alkaline β -cyclodextrin solutions. 1 – Cu₂CD, 7 – Cu(OH)₄²⁻. Solution composition (M): [Cu(II)]₀ – 0.005; [β -cyclodextrin]₀: 1–6 – 0.0025, 7 – 0; [NaOH]₀: 1 – 1.0, 2 – 2.0, 3 – 3.0, 4 – 3.6, 5 – 4.2, 6 – 5.0, 7 – 5.0. 20 °C

cribed to changes in ionic strength (it was not maintained constant) as well as to inaccuracies while estimating the activity of OH⁻ ions in concentrated NaOH solutions, *i. e.* calculations from data of the reference book.

The close values of the $\log \beta_{\text{Cu}_2\text{CD}}$ obtained using two different systems, Cu(II)– β -CD–EDTA and Cu(II)– β -CD–OH⁻, are in agreement with the model of the formation of a dinuclear Cu(II)– β -CD complex of the mentioned composition under study conditions, and with conclusions of other authors about composition of this dinuclear complex [14, 15]. It can be noted that the stability constant of this Cu₂CD complex is determined for the first time, whereas the data presented in [12] and [13] concern equilibria models of formation of dinuclear

Table 2. Data on equilibria in the system Cu(II)– β -cyclodextrin(CD)–OH⁻ ions calculated from the spectrophotometric data of Fig. 5. [Cu(II)]₀ – 0.005 M, [CD]₀ – 0.0025 M

[NaOH] ₀ , M	pH M	*[Cu(OH) ₄ ²⁻], M	*[Cu ₂ CD], M	[OH ⁻] M	[CD] ₀ – [Cu ₂ CD], M	[CD ⁺], M	log[Cu(II)]	log $\beta_{\text{Cu}_2\text{CD}}$
2.0	14.20	0.0005	0.0023	1.9995	0.0002	0.00017	–19.2	39.6
3.0	14.30	0.0017	0.0017	2.9983	0.0008	0.00069	–19.0	38.4
3.6	14.40	0.0025	0.0013	3.5975	0.0012	0.00107	–19.0	38.1
4.2	14.55	0.0032	0.0009	4.1968	0.0016	0.00147	–19.1	37.9
5.0	14.75	0.0040	0.0005	4.9960	0.0020	0.00189	–19.3	38.0
Mean:								38.4 ± 0.8

*Averages of the values calculated at 600, 650, 700, 750 and 800 nm wavelengths.

Cu(II)- β -CD complexes of different composition (Eqns. (1) and (2)).

The results of the present study show β -CD to be a strong chelating agent for binding Cu(II) ions in alkaline and strongly alkaline solutions.

CONCLUSION

Under conditions of metal ion excess, Cu(II) ions in alkaline solutions (pH > 12.5) form a polynuclear complex with the anion of β -cyclodextrin. The results of employing the spectrophotometric method of ligand displacement are in agreement with the existence of dinuclear complexes Cu_2CD , the stability constant logarithm being 39.2 ± 0.2 . This complex predominates in solutions within the pH range from 12.5 to 14.3 (3M NaOH solution), transforming with an increase in alkalinity to $\text{Cu}(\text{OH})_4^{2-}$.

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DIBRANDUOLINIO CU(II)- β -CIKLODEKSTRINO KOMPLEKSO PATVARUMO KONSTANTOS NUSTATYMAS LIGANDO PAKEITIMO METODU

S a n t r a u k a

Šarminiuose tirpaluose (pH > 12.5), esant metalo jonų pertekliui, Cu(II) jonai sudaro su β -ciklodekstrino (CD) anijonu dibranduolinį kompleksą. Šio komplekso patvarumo konstantai nustatyti buvo pritaikytas spektrofotometrinis ligando pakeitimo metodas, panaudojus konkuruojančius ligandus – EDTA ir OH^- jonus. Eksperimentiniai duomenys gali būti prašyti dibranduolinio komplekso Cu_2CD susidarymu $\log\beta_{\text{Cu}^2\text{CD}} = 39,2 \pm 0,20$. Pastarasis kompleksas vyrauja tirpaluose, kai pH yra 12,5–14,3, o toliau didinant šarmingumą pereina į $\text{Cu}(\text{OH})_4^{2-}$.