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Stability of a Dinuclear Cu(II)–β-Cyclodextrin Complex

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Cu(II) ions form a dinuclear complex with the tetraanion of β-cyclodextrin (CD^{4-}) in alkaline solutions ($pH > 12.5$) under conditions of metal ion excess. The spectrophotometric method of ligand displacement was used for the 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 Cu_2CD, the logarithm of the stability constant being 39.2 ± 0.2. This complex predominates in the pH range from 12.5 to 14.3 (3 M NaOH solution), transforming with the increase in alkalinity to $Cu(OH)_4^{2-}$.

Keywords: Copper(II); β-Cyclodextrin; Stability constant; Spectrophotometry

INTRODUCTION

Inclusion complexes of cyclodextrins have been widely investigated and documented [1–4], whereas data on the interaction of cyclodextrins (CDs) with metal ions in aqueous solutions are not numerous, in spite of the fact that metallocyclodextrins have potential as metalloenzyme models with a range of applications in catalysis and molecular recognition [5].

The coordination ability of β-CD, consisting of seven glucopyranose units, is relatively weak in acidic and neutral solutions [6], but the chelating properties of β-CD are enhanced in alkaline solutions due to the deprotonation of the OH groups. The pK_a value of unsubstituted β-CD was determined to be 12.201 [7].

Complexation of Cu(II) ions by β-CD in alkaline solutions for the first time was documented by Messmer [8], and further investigations were made by Matsui and co-workers [9–12]. The latter authors first reported the preparation of the Cu(II) complex with β-CD which corresponds to a Cu:β-CD ratio of 2:1 in 0.1–1.0 M NaOH solutions; the absorption spectra were characterized by a maximum at 668 nm and molar absorption coefficient 128 ± 1 in 0.1 M NaOH solution [9]. The Cu_2–β-CD complex was investigated by means of pH 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 these observations they determined $Cu_2(OH)(O)\beta\text{-}CD^{3-}$ as the formula of the complex, β-CD being fourfold deprotonated. Using molecular models it was suggested that the two pairs of deprotonated secondary OH groups at C_2 and C_3 on adjacent glucopyranose units are cross-linked by the $=Cu(OH)(O)Cu=$ ion bridge [10], whereas the bridge of $=Cu(OH)_2Cu=$ was also shown to be possible [9,11]. In the course of a later study the possibility of a 1:1 Cu(II)–β-CD complex formation was shown in alkaline solutions. The suggested formula of this complex is $Cu\text{-}\beta\text{-}CD(OH)_2^{2-}$, i.e. the β-CD being in the form of a double-deprotonated anion [12]. In the same work the equilibrium constant of the reaction:

$$2Cu^{2+} + \beta\text{-}CD^- + 5OH^- \rightleftarrows Cu_2\beta\text{-}CD(OH)_2^{2-} + 3H_2O \qquad (1)$$

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

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

$$2\mathrm{Cu}^{2+} + \beta\text{-}\mathrm{CD}^{4-} + 3\mathrm{OH}^- \rightleftarrows \mathrm{Cu}_2\beta\text{-}\mathrm{CD(O)(OH)}^{3-} + \mathrm{H_2O} \tag{2}$$

and the formation constant as follows:

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

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

The Cu_2–β-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 $Na_2[Cu_2\beta\text{-}CD(OH)_2\cdot 2H_2O]$. 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 Cu_2–β-CD complex is formed by linkages between secondary OH groups of β-CD and Cu(II) ions. The spectral data discussed are consistent with those reported in [14] and provide support of the suggestion of the simultaneous existence of the first and second interaction spheres. However, the evidence indicated the presence of a structure containing two aqua-Cu(II) ions for one molecule of β-CD rather than a dinuclear hydroxy-bridged system, which was not present. Cu(II) ions react with the secondary OH groups of β-CD, and water molecules coordinated to the Cu(II) ions are directed partly into and partly out of the β-CD cavity [15].

The evidence for covalent binding between Cu(II) ions and β-CD was proved on the basis of a circular dichroism study. Significant changes observed in the spectra of the Cu(II)–β-CD complexes suggest that the covalent binding of Cu(II) ions to the OH groups of β-CD is involved [16].

Klüfers and co-workers [17] isolated blue crystals from solution, formulated as $Li_4[Li_7Cu_4(\beta\text{-}CDH_{11.5})_2]\cdot x\,H_2O$, where β-$CDH_{21}$ is protonated β-CD and $x \sim 40$. A stoichiometry of 2:1 for Cu(II):β-CD was obtained, and the X-ray data were interpreted in terms of a β-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 results obtained are only qualitative or describe the equilibria which do not provide information about the actual stability constants of the complexes formed in alkaline Cu(II)–β-CD solutions.

Therefore this paper deals with a spectrophotometric study of complex formation with the aim of determining the stability constant of the dinuclear Cu_2–β-CD complex formed in alkaline solutions.

MATERIALS AND METHODS

Analytical grade chemicals were used, and β-cyclodextrin ($M_r = 1135$) was "purum" from Fluka. $NaNO_3$ and NaOH solutions were used to keep the ionic strength (J) of the solutions constant and equal to 1 M.

The 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.

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

$$\mathrm{pH} = \mathrm{p}K_w - \mathrm{pOH} \tag{4}$$

using the activity of OH^- ions and pK_w given in [18].

RESULTS AND DISCUSSION

Copper(II) forms no complexes with β-CD at pH < 12.5 in alkaline solutions at the molar ratio Cu(II): β-CD 2:1. Formation of the $Cu(OH)_2$ 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 $Cu(OH)_2$ precipitate is formed when the 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.

Absorption spectra of the dinuclear Cu(II)-β-CD complex almost coincide in the pH range 12.5 to 13.9. The constant absorbance over a rather wide range of alkalinity, i.e. from 0.05 to 1.0 M NaOH suggest formation of one kind complex, e.g. the solely dinuclear Cu(II)–β-CD complex Cu_2CD (CD^{4-} is the 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 absorption maximum at $\lambda = 675$ nm,

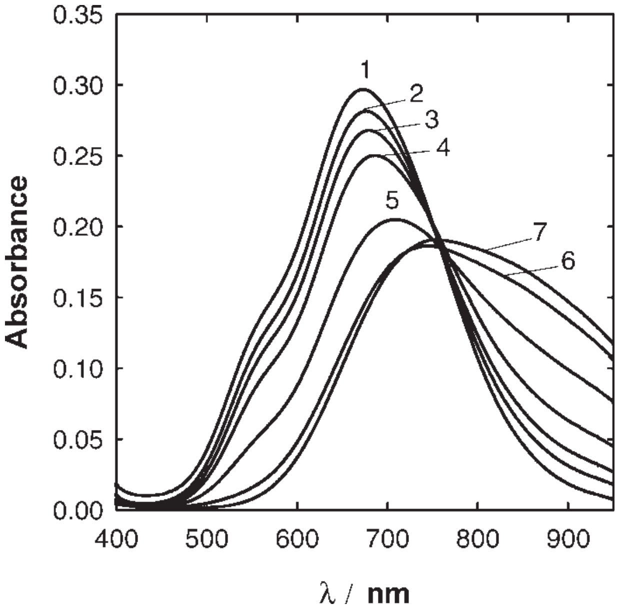

FIGURE 1 Cu(II) absorption spectra in alkaline solutions of β-cyclodextrin (1), EDTA (7) and their mixture (2–6). Solution composition (M): $[\mathrm{Cu(II)}]_0$–0.005; $[\beta\text{-cyclodextrin}]_0$–0.0025; $[\mathrm{EDTA}]_0$: 1–0, 2–0.0005, 3–0.001, 4–0.002, 5–0.004, 6–0.008, 7–0.01. Solution pH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

the molar absorption coefficient (ε) being $120\,\mathrm{l\,mol^{-1}\,cm^{-1}}$. It can be noted that our results are in good agreement with those 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 the Cu(II) complex compound with different optical properties, e.g. its absorption maximum and/or molar absorption coefficient should differ quite considerably from that of $\mathrm{Cu_2CD}$. We selected EDTA (ethylenediaminetetraacetic acid) as the competitive ligand, since it is known that at higher pH values (pH $\geq$ 13.0) EDTA forms entirely the hydroxy-complex $\mathrm{Cu}Y(\mathrm{OH})^{3-}$ (Y^{4-} is the fourfold deprotonated anion of EDTA), the absorption maximum of which is at $\lambda = 750\,\mathrm{nm}$ and the stability constant logarithm $\log\beta_{\mathrm{Cu}Y(\mathrm{OH})^{3-}}$ being 21.1 [19]. Curve 7 in Fig. 1 represents the spectrum of $\mathrm{Cu}Y(\mathrm{OH})^{3-}$ at pH = 13.0 showing the absorption maximum at $\lambda = 750\,\mathrm{nm}$, ε being $42\,\mathrm{l\,mol^{-1}\,cm^{-1}}$.

It is noteworthy that the shape of the spectra obtained in our experiments differ to a certain degree from those given in [13]. The spectra of the dinuclear Cu(II)–β-CD complex are comparable, whereas the spectra of the Cu(II)–EDTA system differ. The difference can be attributed to solution pH. The data presented in [13] are obtained at pH 12 and it is known that at this pH the two complexes are in equilibrium in the Cu(II)–EDTA system, i.e. $\mathrm{Cu}Y^{2-}$ and $\mathrm{Cu}Y(\mathrm{OH})^{3-}$ [19].

Addition of EDTA into the alkaline Cu(II)–β-CD solution changes the absorption spectra, i.e. absorbance decreases and the absorption maximum shifts to longer wavelengths with an increase in EDTA concentration (Fig. 1). The isosbestic point at ca. 770 nm indicates that the two complexes are in equilibrium. Thus, the spectra obtained demonstrate the conversion of the dinuclear Cu(II)–β-CD complex into $\mathrm{Cu}Y(\mathrm{OH})^{3-}$ complex (Fig. 1).

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

$$\begin{cases} 2c_{\mathrm{Cu_2CD}} + c_{\mathrm{CuY(OH)^{3-}}} = [\mathrm{Cu(II)}]_0 \\ c_{\mathrm{Cu_2CD}}\varepsilon_{\lambda_{i\mathrm{Cu_2CD}}} + c_{\mathrm{Cu}Y(\mathrm{OH})^{3-}}\varepsilon_{\lambda_{i\mathrm{CuY(OH)^{3-}}}} = A_{\lambda_i}/l \end{cases} \tag{5}$$

where c is the concentration (M) of the corresponding complexes, $[\mathrm{Cu(II)}]_0$ is the total Cu(II) concentration (M), A_{λ_i} is the absorbance at wavelength λ_i, l is the cell width (cm), ε_{λ_i} is the molar absorption coefficient values of the individual corresponding complexes at wavelength λ_i calculated according to Eq. (6):

$$\varepsilon_{\lambda_i} = A_{\lambda_i}/cl\,(\mathrm{l\,mol^{-1}\,cm^{-1}}) \tag{6}$$

It should be noted that Eqs. (5) and (6) are valid when the linear dependence of the 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 constant metal-to-ligand ratio were recorded. The results obtained show linear dependence of absorbance on concentration of the 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.

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

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

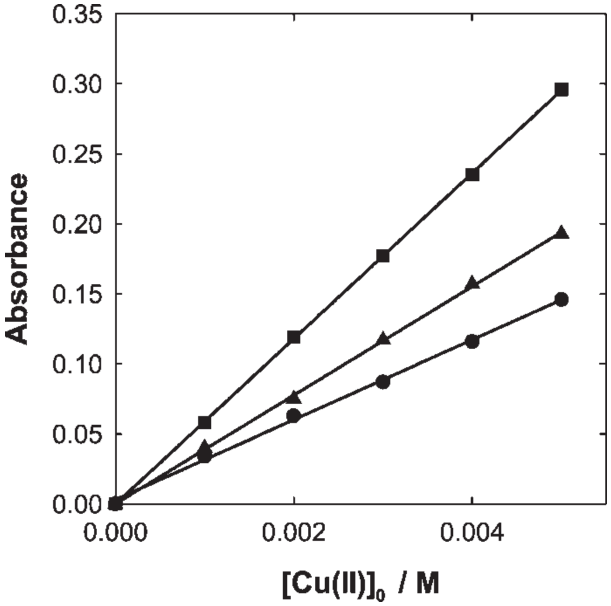

FIGURE 2 Dependence of absorbance on concentration of Cu(II). Solution composition: (●)–Cu(II) and 5 M NaOH; (▲)–Cu(II) and EDTA (molar ratio 1:2), pH 13.0, λ = 750 nm, $I = 1$; (■)–Cu(II) and β-cyclodextrin (molar ratio 2:1), pH 13.0, $\lambda = 675$ nm, $I = 1$, 20°C.

With regard to the deprotonation of β-CD, according to our data, there is only one original reference regarding the pK_a value of β-CD [7]. Further papers or reviews cite this work and indicate the same pK_{a1} value equal to 12.20 [2–5]. On one hand this value seems to be too low, because comparison of our results with those obtained when investigating the Cu(II) complex formation with saccharose [23,24], which has rather similar pK_{a1} value (p$K_{a1} = 12.43$ [25]), shows differences: the formation of soluble Cu(II)-complexation begins at pH over 11 (i.e. at pH values much lower than the pK_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 a pH value higher than the pK_a). In general, formation of soluble Cu(II) complexes with polyhydroxylic compounds, e.g. tartrate [26], glycerol [24,27], dextran [28], D-mannitol [29], D-sorbitol [30], begins in solutions at pH values, which are lower (ca. 1–3 units) than the pK_a values of corresponding polyhydroxylic ligands. On the other hand, if the fourfold deprotonated anion of β-CD is involved in complex formation, for calculation of the equilibrium we need to know the pK_a values of β-CD. Therefore, an additional investigation of the deprotonation of β-CD should be carried out. According to recent ^{13}C and ^{1}H NMR results [31], the pK_{a1} and pK_{a2} values of β-CD deprotonation determined from NMR titration curves coincide in the margins of experimental error and are ca. 13.5. The determination of accurate pK_{a3} and pK_{a4} values was difficult due to the rather marginal shifts in NMR spectra [31]. In this case we assumed that deprotonation of the first two OH groups of β-CD is crucial for complex formation, and further deprotonation is promoted by Cu(II) ions, because metal ion-promoted deprotonation of the alcoholic hydroxy groups is documented [20,32]. Thus the pK value equal to 13.5 [31] was used for calculations of equilibrium concentration of the fourfold deprotonated anion of β-CD.

The stability constant of the Cu_2CD complex:

$$\beta = [Cu_2CD]/[Cu(II)]^2 \cdot [CD^{4-}] \qquad (7)$$

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

$$[Cu(II)] = [CuY(OH)^{3-}]/\beta_{CuY(OH)^{3-}} \cdot [Y^{4-}]a_{OH^-} \qquad (8)$$

TABLE I 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	[EDTA (H_4Y)]$_0$/M	$[CuY(OH)^{3-}]^*$/M	$[Cu_2CD]^*$/M	$\log \beta_{Cu_2CD}$
0.005	0.0025	13.0	0.0005	0.00048	0.00260	38.9
			0.001	0.00093	0.00204	39.1
			0.002	0.00170	0.00165	39.5
			0.004	0.00320	0.00090	39.2
			0.008	0.00460	0.00020	39.4
						Mean: 39.2 ± 0.2
0.01	0.005	13.0	0.001	0.00091	0.0045	39.6
			0.002	0.00190	0.0041	38.7
			0.004	0.00340	0.0033	39.6
			0.008	0.00710	0.0015	38.6
			0.016	0.00960	0.0002	38.9
						Mean: 39.1 ± 0.6
0.005	0.0025	13.5	0.0005	0.00043	0.00229	40.9
			0.001	0.00096	0.00202	39.2
			0.002	0.00190	0.00155	39.0
			0.004	0.00385	0.00058	38.0
			0.008	0.00494	0.00003	39.0
						Mean: 39.2 ± 1.3

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

where a_{OH^-} is the activity of OH^- ions calculated from the pH and the pK_w value was taken from [18] according to Eq. (1).

The results obtained at different EDTA concentrations correlate well, the mean value of $\log \beta_{\mathrm{Cu_2CD}}$ being 39.2 ± 0.2 (Table I).

The other experiments were performed at the same Cu(II):β-CD molar ratio (2:1), but at two times higher concentrations of Cu(II) and β-CD (Fig. 3) or at higher pH using the same concentrations (Fig. 4). The obtained calculated values of $\log \beta_{\mathrm{Cu_2CD}}$ coincide within the margins of error (Table I), the mean value of $\log \beta_{\mathrm{Cu_2CD}}$ being 39.2. The results obtained are in agreement with the existence of the dinuclear Cu(II)–β-CD complex with the above-mentioned composition under the conditions investigated. It is noteworthy that our experiments show no evidence of the formation of the Cu(II)–β-CD polymeric or hydroxy-complexes, since the $\log \beta_{\mathrm{Cu_2CD}}$ value obtained under different solution compositions is the same.

Additional experiments were carried out using OH^- ions as the competitive ligand, since it is documented that Cu(II) ions form the tetrahydroxycuprate(II) $[\mathrm{Cu(OH)}_4^{2-}]$ complex in concentrated solutions of sodium hydroxide [33–38]. The stability constant of this complex compound is known and equal to 15.5 ± 0.1 [37].

As stated above, no changes in the spectrum of the $\mathrm{Cu_2CD}$ complex are observed in the pH range from 12.5 to 13.9 (1 M NaOH solution). With further increase in sodium hydroxide concentration the absorption intensity decreases and the maximum shifts towards shorter wavelengths, and approaches to the spectrum of $\mathrm{Cu(OH)}_4^{2-}$, which is defined with the absorption maximum at $\lambda = 640\,\mathrm{nm}$, ε being $30\,\mathrm{l\,mol^{-1}\,cm^{-1}}$ (Fig. 5). The results obtained show clear evidence of the transformation of the $\mathrm{Cu_2CD}$ complex into the tetrahydroxycuprate(II).

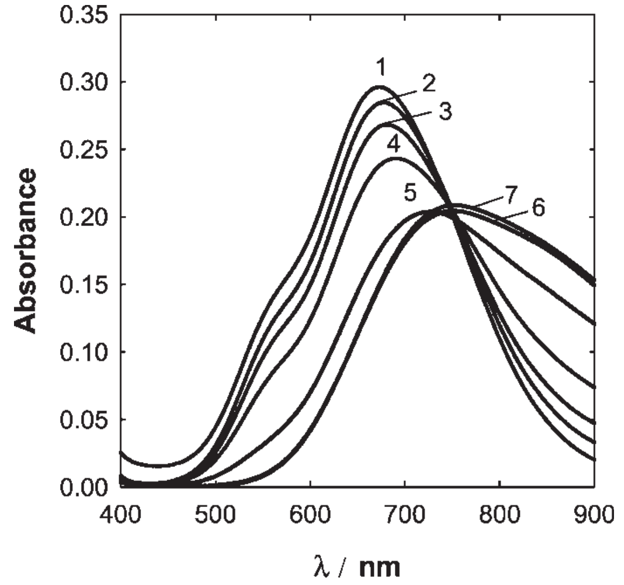

FIGURE 4 Cu(II) absorption spectra in alkaline solutions of β-cyclodextrin (1), EDTA (7) and their mixture (2–6). Solution composition (M): $[\mathrm{Cu(II)}]_0$–0.005; $[\beta\text{-cyclodextrin}]_0$–0.0025; $[\mathrm{EDTA}]_0$: 1–0, 2–0.0005, 3–0.001, 4–0.002, 5–0.004, 6–0.008, 7–0.01. Solution pH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

Since the Beer law is valid for the system under investigation (Fig. 2), the analogous procedure described for the Cu(II)–β-CD–EDTA system was

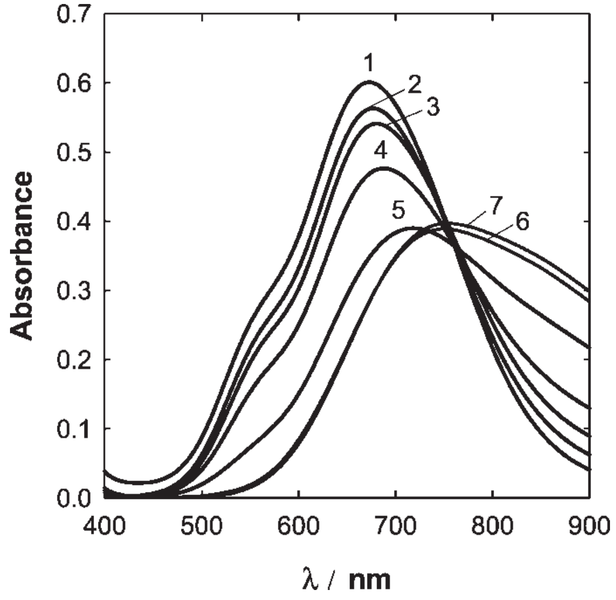

FIGURE 3 Cu(II) absorption spectra in alkaline solutions of β-cyclodextrin (1), EDTA (7) and their mixture (2–6). Solution composition (M): $[\mathrm{Cu(II)}]_0$–0.01; $[\beta\text{-cyclodextrin}]_0$–0.005; $[\mathrm{EDTA}]_0$: 1–0, 2–0.001, 3–0.002, 4–0.004, 5–0.008, 6–0.016, 7–0.02. Solution pH 13.0; 20°C; $I = 1$.

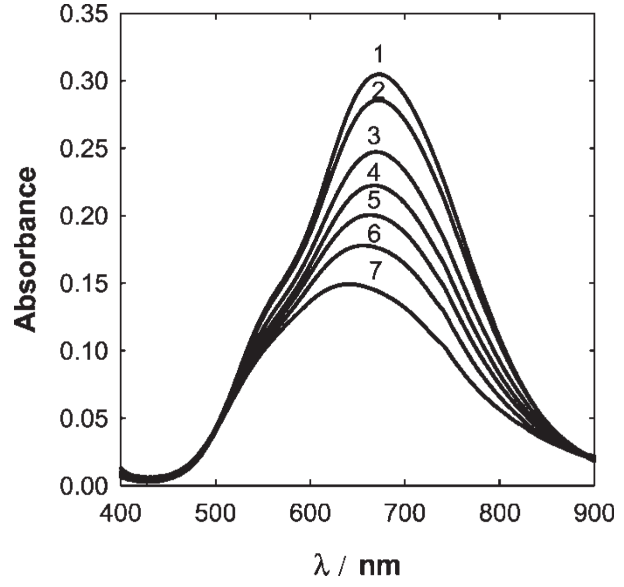

FIGURE 5 Cu(II) absorption spectra in alkaline β-cyclodextrin solutions. 1–$\mathrm{Cu_2CD}$, 7–$\mathrm{Cu(OH)}_4^{2-}$. Solution composition (M): $[\mathrm{Cu(II)}]_0$–0.005; $[\beta\text{-cyclodextrin}]_0$: 1–6–0.0025, 7–0; $[\mathrm{NaOH}]_0$: 1–1.0, 2–2.0, 3–3.0, 4–3.6, 5–4.2, 6–5.0, 7–5.0; 20°C.

TABLE II 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	$[Cu(OH)_4^{2-}]$*/M	$[Cu_2CD]$*/M	$\log \beta_{Cu_2CD}$
2.0	14.20	0.0005	0.0023	39.6
3.0	14.30	0.0017	0.0017	38.4
3.6	14.40	0.0025	0.0013	38.1
4.2	14.55	0.0032	0.0009	37.9
5.0	14.75	0.0040	0.0005	38.0
				Mean: 38.4 ± 0.8

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

used for the determination of the stability of the Cu_2CD complex. The following system of equations was solved:

$$\begin{cases} 2c_{Cu_2CD} + c_{Cu(OH)_4^{2-}} = [Cu(II)]_0 \\ c_{Cu_2CD}\varepsilon_{\lambda_{i_{Cu_2CD}}} + c_{Cu(OH)_4^{2-}}\varepsilon_{\lambda_{Cu(OH)_4^{2-}}} = A_{\lambda_i}/l \end{cases} \qquad (9)$$

The stability constant of the Cu_2CD complex [Eq. (7)] was calculated using spectrophotometric data on Cu(II) distribution among the complexes (Table II), whereas the concentration of free Cu(II) ions was taken from:

$$[Cu(II)] = [Cu(OH)_4^{2-}]/\beta_{Cu(OH)_4^{2-}} \cdot a_{OH^-}^4 \qquad (10)$$

The stability constant value obtained ($\log \beta_{Cu_2CD} = 38.4$) (Table II) is slightly lower (0.8 unit) than that determined when investigating the Cu(II)–β-CD–EDTA system. Small discrepancies can be ascribed to changes in ionic strength (it was not maintained at a constant value) as well as to inaccuracies in the estimation of the activity of OH^- ions in concentrated solutions of NaOH, i.e. calculations from data from reference books.

The near values of the $\log \beta_{Cu_2CD}$ obtained using two different systems, i.e. Cu(II)–β-CD–EDTA and Cu(II)–β-CD–OH^-, are in agreement with the model of dinuclear Cu_2CD complex formation under the conditions investigated, and with the conclusions of other authors about composition of this dinuclear complex without hydroxy bridges [15,17]. It can be noted, that the stability constant of this Cu_2CD complex is determined for the first time.

The results of this investigation show β-CD being a strong chelating agent for the binding of Cu(II) ions in alkaline and strongly alkaline solutions under the conditions of metal ion excess. For example, the addition of 0.0025 M β-CD to 0.005 M solution of Cu(II) after adjusting the pH to 13 diminishes the concentration of free (uncomplexed) Cu(II) ions by ca. 16–17 orders of magnitude compared with that of the initial Cu(II) solution.

CONCLUSIONS

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

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