



Cu(II) Ion Complexation by Excess of β -cyclodextrin in Aqueous Alkaline Solutions

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Abstract

Polarographic investigations of Cu(II) complexation in aqueous alkaline solutions containing an excess of β -cyclodextrin (β -CD) show that the complex formation begins at pH > 11, the concentration of free (uncomplexed) Cu(II) ions being in the range from ca. 10^{-12} to ca. 10^{-19} M, depending on β -CD concentration and pH. The formation of copper(II) 1:1 hydroxy-complex with β -cyclodextrin anion (CD^{2-}) was observed at pH 11–14. The logarithm of the stability constant of $CuCD(OH)_2^{2-}$ complex is 19.7 ± 0.2 (20 °C, ionic strength 1.0), the values of the molar extinction coefficient and of the diffusion coefficient of this complex are $50 \text{ M}^{-1} \text{ cm}^{-1}$ ($\lambda_{\text{max}} = 660 \text{ nm}$) and $1.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively.

Introduction

β -cyclodextrin (β -CD) is an important representative of cyclic polyhydroxylic carbohydrates. Cyclodextrin complexes with metal ions have a range of applications in catalysis and molecular recognition [1]. Formation of cyclodextrins (CDs) inclusion complexes with different compounds is well known and widely investigated [2–5], whereas the data about cyclodextrin interaction with metal ions in aqueous solutions are not numerous.

CDs have relatively poor coordination ability in acidic and neutral solutions, e.g. 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) in non-basic solutions [6]. However, chelating properties of β -CD can be enhanced in alkaline solutions due to the deprotonation of hydroxyl-groups. The acid behaviour of β -CD has 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 [8–12]. Most investigations on Cu(II)– β -CD system were carried out under conditions of metal ion excess. Dinuclear Cu_2 – β -CD complexes were characterized in solutions as well as in the solid state [9–17]. The stability constant of this complex has been determined recently, showing the complex to be highly stable in alkaline solutions ($\log \beta_{Cu_2CD} = 39.2$) [17].

There are only few publications on the study of Cu(II)– β -CD system under the conditions of ligand excess. The

evidence of covalent binding between Cu(II) ions and β -CD was shown on the basis of circular dichroism study – significant changes observed in the spectra of Cu(II)– β -CD complexes suggest that the covalent binding of Cu(II) ions to the OH-groups of β -CD is involved [18]. The possibility of 1:1 Cu(II)– β -CD complex formation was shown in alkaline solutions. The suggested formula of this complex is $Cu\beta\text{-CD}(\text{OH})_2^{2-}$, i.e. β -CD being in the form of double-deprotonated anion [12].

Since the results obtained under conditions of ligand excess are only qualitative and do not provide information about stability constants and other characteristics of the complexes formed in alkaline Cu(II)– β -CD solutions, the aim of this paper was the determination of the characteristics of Cu– β -CD complex formed at the excess of β -CD, as well as the evaluation of β -CD complexing ability in alkaline solutions. The main method used was polarography, since it is a sensitive method for the determination of the concentration of uncomplexed (“free”) heavy metal ions as well as other characteristics of complex compounds formed, i.e. stability constants and diffusion coefficients.

Experimental

Analytical grade chemicals were used, and β -cyclodextrin ($M_r = 1135$) was “purum” from Fluka. $NaNO_3$ and $NaOH$ solutions were used to keep ionic strength (I) of the solutions constant and equal to 1 M. The main investigations were carried out at 20 °C.

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The polarographic curves were recorded by a *PU* – 1 polarograph using a dropping mercury electrode in a thermostated three-electrode cell.

The UV-visible spectra were recorded with a Perkin Elmer *Lambda 35* UV/VIS spectrometer in 1.0 cm path length quartz cells. The optical blank solution was pure water.

Measurements of the solutions pH were carried out by means of a Mettler Toledo MP 220 pH-meter using Mettler Toledo InLab 410 glass electrode. At higher NaOH concentrations when pH exceeded 13.5, it was not measured directly but calculated by:

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

using the activity of OH^- ions and $\text{p}K_w$ given in Ref. [19].

The methods used are described in details previously [17, 20–22].

Results and discussion

No $\text{Cu(II)}-\beta\text{-CD}$ complex formation is observed at $\text{pH} < 10$, even if there is an excess $\beta\text{-CD}$ in the solution. Formation of the Cu(OH)_2 precipitate is visually observed in the solution at $\text{pH} 8-10$, and there is actually no polarographic wave of Cu(II) reduction. At pH over 11.0 the precipitate of Cu(OH)_2 disappears and the solution becomes blue, which is indicative of formation of a Cu(II) complex.

The quasi-reversible Cu(II) reduction waves (definition of the quasi-reversibility and methods of analysis of the quasi-reversible polarograms are given in [23, 24]) are observed at $\text{pH} > 11$. Before the interpretation of the results the analysis of polarographic waves obtained was performed. It was evaluated that the limiting currents of Cu(II) reduction in alkaline solutions of $\beta\text{-CD}$ are diffusion controlled. This was demonstrated by measurements at different heights of mercury column and at different temperatures – the limiting current dependence on the square root of the mercury column height is almost linear and the temperature coefficient of the limiting current is rather small and equal to ca. 1.3% per 1 °C, showing prevailing of the diffusion in the reduction process of Cu(II) ions.

In the pH range from 11 to ca. 14 the polarographic waves of the Cu(II) reduction in alkaline solutions of $\beta\text{-CD}$ shift to more negative potentials (Figure 1). This fact can be attributed to above-mentioned deprotonation of $\beta\text{-CD}$ in alkaline solutions and herewith to strengthening of $\beta\text{-CD}$ chelating ability and complex formation with Cu(II) ions. Thus it can be concluded that undissociated $\beta\text{-CD}$ does not interact with Cu(II) ions, but the deprotonated $\beta\text{-CD}$ forms complexes with Cu(II) ions. The same tendency of complex formation only in alkaline solutions was observed when investigating interaction of $\beta\text{-CD}$ with Pb(II) [25], Cd(II) [26] or, e.g., when studying Cu(II) complex formation with the related polyhydroxylic compounds, such as saccharose [27, 28], glycerol [28, 29], D-mannitol [30], D-sorbitol [31] and dextran [32].

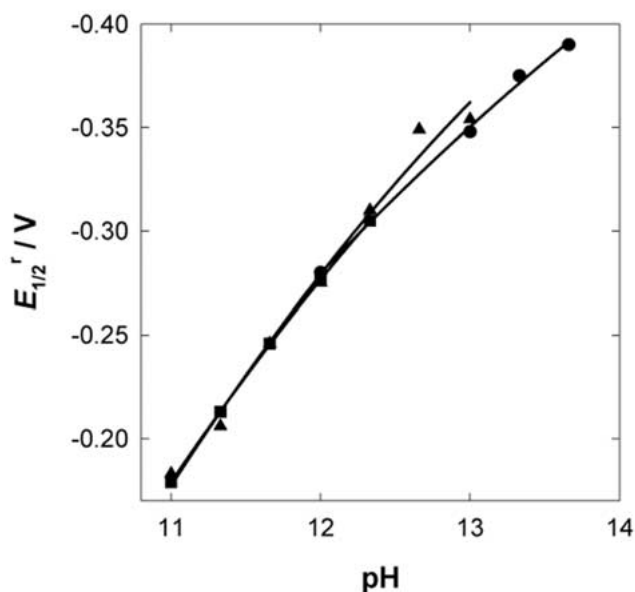


Figure 1. Dependence of the reversible Cu(II) reduction half-wave potential ($E'_{1/2}$) on pH of the solution. Solution composition (mM): $[\text{Cu(II)}]_0 - 0.5$; $[\beta\text{-cyclodextrin}]_0$: ● – 4.4, ▲ – 22.0, ■ – 35.2; $I = 1$; 20 °C.

As was stated above, knowing the initial total concentration of metal ion in the solution and the shift of the reversible half-wave potential ($\Delta E'_{1/2}$), polarography can be used for determination of the concentration of uncomplexed (free) metal ions in the solutions without knowing exact complex formation equilibria. The following equation is used:

$$\text{pCu} = nF/2.303RT(-\Delta E'_{1/2}) - \log[\text{Cu(II)}]_0, \quad (2)$$

where $[\text{Cu(II)}]_0$ is the total Cu(II) concentration.

The concentration of free (uncomplexed) Cu(II) ions obtained from the polarographic data (Figure 2, curves 1–3) in all the cases is lower than that calculated from the solubility product (SP) of Cu(OH)_2 (Figure 2, curve 4). The difference between pCu values obtained and pCu calculated according to the solubility product of Cu(OH)_2 ($\text{SP}_{\text{Cu(OH)}_2} \sim 10^{-18}$ [33–35]) reaches ca. 0.5 unit at $\text{pH} 11.0$, whereas it increases up to ca. 2–3 units at pH over 13.0, showing significant complexation of Cu(II) ions in strongly alkaline solutions of $\beta\text{-CD}$ (Figure 2).

The slope of the half-wave potential shift of Cu(II) reduction depends on pH of the solution and on the concentration of $\beta\text{-CD}$. At constant concentrations of $\beta\text{-CD}$ the slope of the $\Delta E'_{1/2}$ dependences is equal to ca. 80–100 mV per pH unit, which for the single-stage two electron reduction of Cu(II) indicates coordination of Cu(II) with 3 ligand particles (presumably with the anion of $\beta\text{-CD}$ and the OH^- ions). Since with an increase in the solution pH the activity of OH^- ions rises as well as the equilibrium concentration of deprotonated form of $\beta\text{-CD}$, the number of deprotonated $\beta\text{-CD}$ particles involved in complex formation can be determined from the slope of $\Delta E'_{1/2}$ on $\beta\text{-CD}$ concentration at constant pH values. The slopes obtained and calculated for the tenfold increase in the concentration of $\beta\text{-CD}$ do not

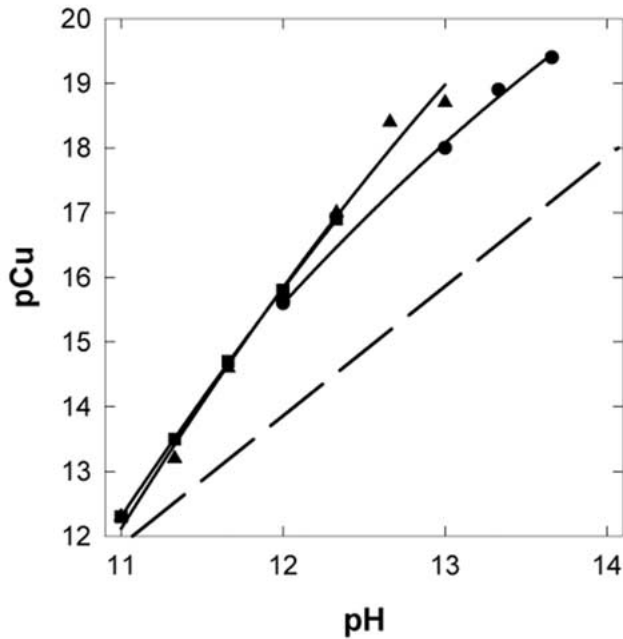
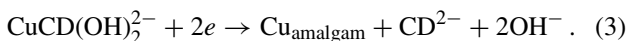


Figure 2. Dependence of pCu on the solution pH, calculated from the polarographic data. Solution composition (mM): $[\text{Cu(II)}]_0 - 0.5$; $[\beta\text{-cyclodextrin}]_0$: ● – 4.4, ▲ – 22.0, ■ – 35.2; $I = 1$; 20 °C. The dashed line represents pCu calculated from the Cu(OH)_2 solubility product value [31–33].

exceed -29 mV, showing one anion of $\beta\text{-CD}$ taking part in complex formation.

The results obtained showed the possibility of existence of Cu(II) complex with two ligands – one anion of $\beta\text{-CD}$ (according to ^{13}C and ^1H NMR results [36] in the case of excess of the ligand we suggest participation of doubly deprotonated anion $\beta\text{-CD}^{2-}$, $\text{p}K_{a1,2}$ value being 13.5 [36] and two OH^- groups – with the formula CuCD(OH)_2^{2-} . The composition of the complex is in agreement with that obtained earlier [12].

Knowing composition of the Cu(II) complex formed in alkaline solutions of $\beta\text{-CD}$, the equation which describes the reduction of Cu(II) on a dropping mercury electrode can be written:



Since the polarographic waves of Cu(II) reduction in the system under the investigation are quasi-reversible the characteristics of Cu(II) complex formation can be calculated.

The values of the actual half-wave potential $E_{1/2}$ were determined from a plot of $\log(\bar{i}/\bar{i}_{\text{lim}} - \bar{i})$ against E . The values of the transition coefficient α and the reversible half-wave potential $E'_{1/2}$ were calculated using Equations (4) and (5) [23, 24], where $E'_{1/2}$ is the half-wave potential determined by extrapolation of the linear part of the graph $\log(\bar{i}/\bar{i}_{\text{lim}} - \bar{i})$ against E at sufficiently negative potentials, and $E_{1/11}$ is the potential where the current exceeds the value equal to 1/11 of the limiting current value. The corrections for a decrease in \bar{i}_{lim} were made in calculation of $\Delta E'_{1/2}$ for the case of complex formation as shown in Equation (6) [24].

$$\alpha = 2.303 \frac{RT}{nF} \left\{ \frac{\Delta \log(\bar{i}/\bar{i}_{\text{lim}} - \bar{i})}{\Delta(-E)} \right\}_{E \rightarrow -\infty} \quad (4)$$

$$E'_{1/2} = E_{1/11} - 2.303 \frac{RT}{nF} \times \left\{ \log \left[10 - \exp \frac{\alpha nF}{RT} (E_{1/11} - E'_{1/2}) \right] \right\} \quad (5)$$

$$\Delta E'_{1/2} = (E'_{1/2})_{\text{compl}} - (E'_{1/2})_{\text{free}} - 2.303 \times \frac{RT}{nF} \log \sqrt{\frac{\bar{i}_{\text{lim free}}}{\bar{i}_{\text{lim compl}}}} \quad (6)$$

The values of $\Delta E'_{1/2}$ were used for the calculations of parameters of copper(II)– $\beta\text{-CD}$ complex according to Equation (7):

$$\sum_{x_i, y_i=0}^N \beta_{x_i, y_i} [L^{n-}]^{x_i} a_{\text{OH}^-}^{y_i} = \exp[(nF/RT)(-\Delta E'_{1/2})] - 1 \quad (7)$$

where $[L^{n-}]$ is an equilibrium concentration of the deprotonized form of $\beta\text{-cyclodextrin}$, and a stands for the activity of OH^- ions.

Logarithm of the stability constant of the CuCD(OH)_2^{2-} complex, calculated from polarographic data in the pH range from 11.0 to 13.7 is equal to 19.7 ± 0.2 . The results of the complex stability constant calculation correlate well with the experimental results – the difference between experimental and calculated values of $\Delta E'_{1/2}$ do not exceed 8 mV.

It should be noted, that formation of tetrahydroxycuprate(II) – Cu(OH)_4^{2-} ($\log \beta_{\text{Cu(OH)}_4^{2-}} = 15.5$ [37]) – was also considered in the calculations, but no evidence of this complex formation under conditions investigated was obtained.

Formation of one kind of Cu(II)– $\beta\text{-CD}$ complex species under conditions of ligand excess was confirmed by spectrophotometry. The spectra of alkaline Cu(II)– $\beta\text{-CD}$ solutions (the molar ratio of Cu(II): $\beta\text{-CD}$ was from 1:2 to 1:5) practically coincide in the pH region 11.0–14.0. CuCD(OH)_2^{2-} complex compound has a distinct absorption maximum at 660 nm with the molar extinction coefficient (ϵ) value equal to $50 \text{ M}^{-1} \text{ cm}^{-1}$.

The values of the diffusion coefficient (D) were determined using the Ilkovič equation:

$$D^{1/2} = \frac{\bar{i}_{\text{dif}}}{607ncm^{2/3}t^{1/6}} \quad (8)$$

where \bar{i}_{dif} is the limiting diffusion current (μA), n is the number of electrons involved in electrochemical reaction, c is the total concentration of Cu(II) ions (mM), m is the flow rate of Hg (mg s^{-1}), and t is the time of the drop formation (s).

The value of diffusion coefficient of CuCD(OH)_2^{2-} complex was calculated from limiting current values obtained in the solutions with the lowest concentration of $\beta\text{-CD}$ (4.4 mM). The mean value obtained ($D = 1.0 \times 10^{-6} \text{ cm}^2$

s⁻¹) shows formation of large size Cu(II) complex species in alkaline solutions containing β -CD. It can be noted, that diffusion coefficient of $\text{CuCD}(\text{OH})_2^{2-}$ coincides with the diffusion coefficient of $\text{Cd}(\text{II})$ - β -CD complex [26] and is very close to that of calculated for $\text{Pb}(\text{II})$ - β -CD complex ($D = 1.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) [25].

With respect to the possible structure of the $\text{CuCD}(\text{OH})_2^{2-}$ complex, we presume that the partly hydrated Cu(II) ion is bound to two deprotonated secondary OH-groups (adjacent to C-2 and C-3 carbon atoms of β -CD glucopyranose unit), which are located in the larger rim of β -CD torus and are more acidic than the primary one, and two additional hydroxide OH^- groups are coordinated with Cu(II) ion.

Since the experimental data obtained (values of the limiting current and of half-wave potential) correlate well with the model of $\text{CuCD}(\text{OH})_2^{2-}$ complex formation, we believe that there is no additional complexation of Cu(II) or Cu(II) hydroxy-species in the β -CD cavity.

The comparison of the $\text{CuCD}(\text{OH})_2^{2-}$ complex with other Cu(II) complexes with polyhydroxylic or hydroxypolycarboxylic and polyaminopolycarboxylic ligands shows that the stability of Cu(II) complex with the β -CD is in the same range as that of Cu(II) complexes with EDTA, DTPA, L- and DL-tartrate, and saccharose [38].

The results obtained might be useful for understanding of heavy metal ion interaction with polyhydroxylic compounds in alkaline solutions, what is very important, e.g. when investigating peculiarities of pulping process. The knowledge of the structure and of the stability of complex of Cu(II) with β -CD helps in understanding why the traces of Cu(II) are so strongly bound on cellulose pulps [39]. This knowledge would be applied for the development of new more efficient ways to purify the pulps from Cu(II) that catalyses decomposition of hydrogen peroxide during their bleaching. Determination of composition and stability of $\text{CuCD}(\text{OH})_2^{2-}$ complex could give also support for creating of different enzyme-mimetic complexes.

Conclusions

Copper(II) reacts with the β -cyclodextrin anion ($\beta\text{-CD}^{2-}$) in alkaline solutions ($11 < \text{pH} < 14$) forming $\text{CuCD}(\text{OH})_2^{2-}$ hydroxy-complex with the stability constant value equal to $10^{19.7}$, the molar extinction coefficient value equal to 50 M^{-1} ($\lambda_{\text{max}} = 660 \text{ nm}$) and diffusion coefficient value equal to $1.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

The difference between pCu values obtained (the concentration of free – uncomplexed – Cu(II) ions are in the range from ca. 10^{-12} to ca. 10^{-19} M , depending on β -CD concentration and pH) and pCu calculated from the solubility product of $\text{Cu}(\text{OH})_2$ reaches ca. 0.5 unit at pH 11.0, whereas it increases up to ca. 2–3 units at pH over 13.0, showing significant complexation of Cu(II) ions in strongly alkaline solutions of β -CD.

No evidence of Cu(II) ions or Cu(II) hydroxy-species encapsulation into the β -CD cavity (host-guest complex formation) was found.

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