Bull. Chem. Soc. Jpn., 58, 2981—2986 (1985)

# Spectrophotometric and Polarimetric Investigations on Complex Formation between Copper(II) and Cyclodextrins in an Alkaline Solution

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(Received May 10, 1985)

Copper(II) forms a 1:1 complex (CuCD), as well as a 2:1 complex ($Cu_2CD$), with cyclodextrin (CD) in an alkaline solution. An equilibrium constant ($K_{dsp}$) for the disproportionation reaction of Cu$\alpha$-CD to $Cu_2\alpha$-CD and $\alpha$-CD was determined by spectrophotometry and polarimetry to be *ca.* 17 in 1.0 mol dm$^{-3}$ NaOH at 25 °C. The $K_{dsp}$ value gradually decreased with increasing NaOH concentration. A ligand-exchange reaction of $Cu_2CD$ with ethylenediaminetetraacetic acid (EDTA) to give Cu(edta)$^{2-}$ and CD was also examined by means of spectrophotometry and polarimetry. The equilibrium constants ($K_{lex}$) for the ligand-exchange reaction was evaluated to be *ca.* 2.1 for an $\alpha$-CD system and *ca.* 1.2 for a $\beta$-CD system in 1.0 mol dm$^{-3}$ NaOH at 25 °C. The $K_{lex}$ value decreased rapidly with increasing NaOH concentration. The role of $OH^-$ in the complexation of Cu(II) with CD is discussed on the basis of these results.

Cyclodextrins (CD) are cyclic oligomers composed of six ($\alpha$-CD), seven ($\beta$-CD), or more $\alpha$-D-glucopyranose units linked 1→4 as in amylose. It has been revealed that copper(II) forms a 2:1 complex ($Cu_2CD$) with CD in an alkaline solution.[1,2] Although the structure of the complex has not fully been elucidated, it has been suggested that the two pairs of C2 and C3′ secondary hydroxyl groups of contiguous glucose units of CD are cross-linked by the $Cu(OH^-)_2Cu$ or $Cu(OH^-)(O^{2-})Cu$ ion bridge.[2] The complex not only binds an organic substrate within the cavity of CD but also markedly affects the reaction rate of the substrate in a similar manner as metalloenzymes.[3]

In the course of a study on $Cu_2CD$, we found that Cu(II) forms a 1:1 complex (CuCD) with CD, as well as a 2:1 complex, especially when the CD concentration is much higher than the Cu(II) concentration. The present work was undertaken to examine the complexation of Cu(II) with CD in more detail by means of spectrophotometry and polarimetry. Furthermore, a ligand-exchange reaction of $Cu_2CD$ with ethylenediaminetetraacetic acid (EDTA) was examined in order to obtain further insight into the thermodynamic stability of $Cu_2CD$.

## Experimental

*Materials.* The $\alpha$- and $\beta$-CD's and copper sulfate were commericially available and were recrystallized from water. The disodium salt of EDTA of a reagent grade was used without further purification.

*Apparatus.* Absorption spectra were recorded using a Hitachi Model 220 spectrophotometer. Polarimetric measurements were carried out with a Union Giken Model PM-101 polarimeter.

*Spectrophotometry and Polarimetry of Complexation between Cu(II) and CD.* Changes in absorbance and optical rotation of an alkaline CD solution with an addition of Cu(II) were followed by means of a spectrophotometer and a polarimeter at 25 °C. A typical run was as follows: Two kinds of aqueous NaOH solutions were prepared, *i.e.*, 100 mmol dm$^{-3}$ CD solutions containing no (Soln A) and 100 mmol dm$^{-3}$ (Soln B) $CuSO_4$. The concentration of NaOH was adjusted to 1.0, 1.5, 2.0, or 2.5 mol dm$^{-3}$. Two cm$^3$ portions of Soln A were pipetted into a pair of 1-cm quartz cells for spectrophotometry. The cells were maintained at 25 °C by means of jackets through which water was circulated from a constant-temperature bath. After the absorption spectrum of the control solution was recorded by scanning from 800 to 370 nm, 0.025 cm$^3$ portions of Soln B were consecutively added to a sample cell. For each addition of Soln B, the absorption spectrum of the resulting solution was recorded. The change of absorbance (*Abs*) at $\lambda$=685 nm, where *Abs* reaches close to a maximum, was used for an analysis of the data. Changes in the optical rotation (*P*) of Soln A upon consecutive additions of Soln B were similarly followed at $\lambda$=405 nm, where the resulting solution showed only a slight absorption of light.

*Determination of Equilibrium Constants for the Disproportionation Reaction of CuCD to $Cu_2CD$ and CD.* The value of *Abs* at 685nm for an alkaline CD solution increased with an increase in the total concentration (*a*) of Cu(II). Then, molar absorbance (*Abs/a*) for Cu(II) was plotted against the ratio (*R*) of *a* to the total concentration (*b*) of CD (Figs. 1 and 2). If Cu(II) forms only a single CD complex such as $Cu_2CD$ as had been suggested previously,[1] the value of *Abs/a* should be constant for any *R* value. However, the observed *Abs/a* value increased with an increasing *R* value. For a Cu–$\alpha$-CD system, all the plots obtained were virtually fitted to a curved line, irrespective of the *b* value. On the other hand, the *Abs/a* value for a Cu–$\beta$-CD system changed not only with a change in *R* but also with a change in *b*. It was postulated that Cu(II) forms a 1:1 complex (CuCD) with CD as well as a 2:1 complex ($Cu_2CD$) at small *R* values. Then, the transformation of CuCD to $Cu_2CD$ with an increase in *R* is represented by a disproportionation reaction as follows:

$$2\mathrm{CuCD} = \mathrm{Cu_2CD} + \mathrm{CD}. \tag{1}$$

The equilibrium constant ($K_{dsp}$) for the disproportionation reaction is represented by

$$K_{\mathrm{dsp}} = yz/x^2, \tag{2}$$

where *x*, *y*, and *z* are the equilibrium concentrations of CuCD, $Cu_2CD$, and CD respectively. The concentration of uncomplexed Cu(II) is neglected, since it may be very low in such an alkaline solution. Then,

$$a = x + 2y \tag{3}$$

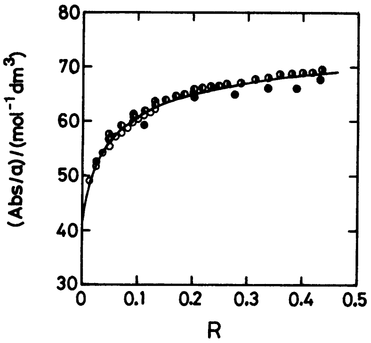

Fig. 1. Plots of *Abs/a* at $\lambda$=685 nm *vs. R* for a Cu-$\alpha$-CD system in 1.5 mol dm$^{-3}$ NaOH at 25 °C. [$\alpha$-CD]=10 (●), 25 (◑), 50 (◐), and 100 (○) mmol dm$^{-3}$.

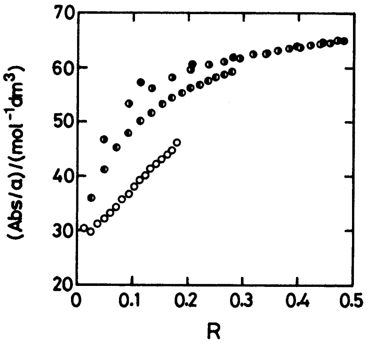

Fig. 2. Plots of *Abs/a* at $\lambda$=685 nm *vs. R* for a Cu-$\beta$-CD system in 1.5 mol dm$^{-3}$ NaOH at 25 °C. [$\beta$-CD]=10 (●), 25 (◑), 50 (◐), and 100 (○) mmol dm$^{-3}$.

and

$$b = x + y + z. \tag{4}$$

Substitution of Eqs. 3 and 4 into Eq. 2 yields

$$x = ad \tag{5}$$

and

$$y = a(1-d)/2, \tag{6}$$

where

$$d = \frac{[R(2-R)(4K_{\mathrm{dsp}}-1)+1]^{1/2}-1}{R(4K_{\mathrm{dsp}}-1)}. \tag{7}$$

The total absorbance due to the Cu(II) complexes is given by

$$Abs = \varepsilon_1 x + \varepsilon_2 y, \tag{8}$$

where $\varepsilon_1$ and $\varepsilon_2$ are the molar absorption coefficients of CuCD and $Cu_2CD$, respectively. Upon introducing Eqs. 5 and 6 to Eq. 8, the following is derived:

$$Abs/a = \varepsilon_1 d + \varepsilon_2(1-d)/2. \tag{9}$$

Since $d$ is only a function of $R$ (Eq. 7), *Abs/a* is also dependent on $R$ alone. This deduction agrees with the observed results for a $\alpha$-CD system as shown in Fig. 1. In a Cu-$\beta$-CD system, the *Abs/a* value at a constant $R$ value decreased with increasing $b$ (Fig. 2). This suggests that some reaction other than the disproportionation of CuCD to $Cu_2CD$ and CD occurs at high CD concentrations. However, no reasonable reaction mechanism can be offered to explain the observation at the present stage of investigation.

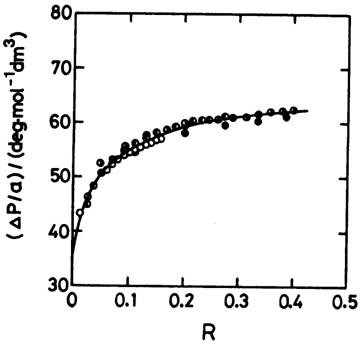

Fig. 3. Plots of $\Delta P/a$ at $\lambda$=405 nm *vs. R* for a Cu-$\alpha$-CD system in 1.5 mol dm$^{-3}$ NaOH at 25 °C. [$\alpha$-CD]=10 (●), 25 (◑), 50 (◐), and 100 (○) mmol dm$^{-3}$.

In the case of polarimetry, the $P$ value for Soln A decreased with an increasing $a$ value. Figure 3 illustrates the plots of $\Delta P/a$ *vs.* $R$ for a Cu-$\alpha$-CD system, where $\Delta P$ is the difference ($P_0-P$) between optical rotations in the absence ($P_0$) and in the presence ($P$) of Cu(II). The plots were also virtually fitted to a curved line, irrespective of $b$. If the molar optical rotations of CD, CuCD, and $Cu_2CD$ are denoted by $f_0$, $f_1$, and $f_2$ respectively, $P_0$ and $P$ are given by

$$P_0 = f_0 b \tag{10}$$

and

$$P = f_0 z + f_1 x + f_2 y. \tag{11}$$

From Eqs. 4, 10, and 11, the following is derived:

$$\Delta P = \Delta f_1 x + \Delta f_2 y, \tag{12}$$

where $\Delta f_1 = f_0 - f_1$ and $\Delta f_2 = f_0 - f_2$. Upon introducing Eqs. 5 and 6 to Eq. 12, we obtain

$$\Delta P/a = \Delta f_1 d + \Delta f_2(1-d)/2. \tag{13}$$

This equation is very similar to Eq. 9, and $\Delta P/a$ is also dependent on $d$ or $R$ alone, as was shown in Fig. 3. The $K_{\mathrm{dsp}}$ values, as well as the values of $\varepsilon_1$ and $\varepsilon_2$ or $\Delta f_1$ and $\Delta f_2$, for Cu-$\alpha$-CD systems at various NaOH concentrations were estimated by analyzing the relationships between *Abs/a* or $\Delta P/a$ and $R$ by the least-squares curve-fitting method with a microcomputer. In a Cu-$\beta$-CD system, the $\Delta P/a$ value was dependent not only on $R$ but also on $b$ in a similar manner as the *Abs/a* value. Thus, no numerical analysis was attempted.

*Spectrophotometry and Polarimetry of Ligand-exchange Reaction between $Cu_2CD$ and EDTA.* Changes in the absorbance and optical rotation of an alkaline $Cu_2CD$ solution upon an addition of EDTA were followed using a spec-

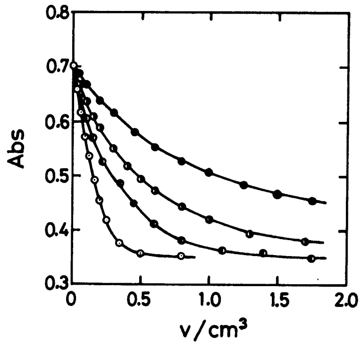

Fig. 4. Plots of *Abs vs. v* for a $Cu_2$ $\alpha$-CD–EDTA system in 0.5 (○), 1.0 (◐), 1.5 (◑), and 2.0 (●) mmol $dm^{-3}$ NaOH at 25 °C.

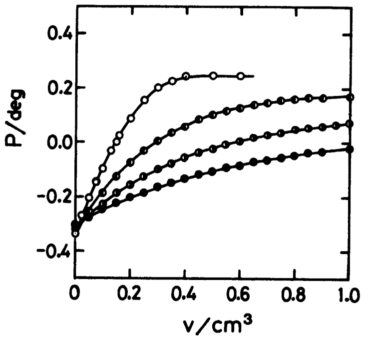

Fig. 5. Plots of $\Delta P$ *vs. v* for a $Cu_2$ $\alpha$-CD–EDTA system in 0.5 (○), 1.0 (◐), 1.5 (◑), and 2.0 (●) mmol $dm^{-3}$ NaOH at 25 °C.

trophotometer and a polarimeter at 25 °C. A typical run was as follows: Two kinds of aqueous solutions of NaOH at a given concentration (0.5, 1.0, 1.5, 2.0, or 2.5 mol $dm^{-3}$ NaOH) were prepared, *i.e.*, (Soln A) an alkaline solution containing 10 mmol $dm^{-3}$ CD and 10 mmol $dm^{-3}$ $CuSO_4$, and (Soln B) an alkaline solution containing 100 mmol $dm^{-3}$ EDTA and 10 mmol $dm^{-3}$ $CuSO_4$. A portion (2.0 $cm^3$) of Soln A was pipetted into a sample cell, and absorption spectrum was recorded. Then, 0.025 to 0.30 $cm^3$ potions Soln B were consecutively added to a sample cell. For each addition of Soln B, the absorption spectrum of the resulting solution was recorded. Changes in absorbance (*Abs*) at 685 nm were used for an analysis of the data. Changes in optical rotation (*P*) of Soln A upon consecutive additions of Soln B were similarly followed at $\lambda$=405 nm.

*Determination of Equilibrium Constant for the Ligand-exchange Reaction of $Cu_2CD$ with EDTA.* The value of *Abs* at 685 nm for Soln A decreased with an addition of Soln B. Figure 4 shows plots of *Abs vs. v*, where *v* is the cumulative volume ($cm^3$) of Soln B added to 2 $cm^3$ of Soln A. On the other hand, the value of *P* at 405 nm for Soln A increased with an addition of Soln B (Fig. 5). It was postulated that $Cu_2CD$ in Soln A reacts with EDTA in Soln B to give $Cu(edta)^{2-}$ and CD (Eq. 14).

$$Cu_2CD + 2edta^{4-} = 2Cu(edta)^{2-} + CD \tag{14}$$

The molar absorbance of $Cu_2CD$ at 685 nm is more than double that of $Cu(edta)^{2-}$; thus, the *Abs* value for Soln A decreases upon an addition of Soln B. Both EDTA and CD are optically inert at 685 nm. The molar optical rotation of $Cu_2CD$ at 405 nm is smaller than that of CD. Therefore, the *P* value for Soln A increases with an addition of Soln B. Both EDTA and $Cu(edta)^{2-}$ are polarimetrically inert at 405 nm.

An equilibrium constant ($K_{lex}$) for a ligand-exchange reaction expressed by Eq. 14 is given by

$$K_{lex} = w^2z/(yu^2), \tag{15}$$

where *u, w, y,* and *z* are the equilibrium concentrations of EDTA, $Cu(edta)^{2-}$, $Cu_2CD$, and CD respectively. Let *a, b,* and *c* be the total concentrations of Cu, CD, and EDTA respectively,

$$a = 2y + w, \tag{16}$$

$$b = y + z, \tag{17}$$

and

$$c = u + w. \tag{18}$$

From Eqs. 15 to 18, we obtain

$$(1+K_{lex})w^3 - [(a+2c)K_{lex}+a-2b]w^2 + cK_{lex}(2a+c)w - ac^2K_{lex} = 0. \tag{19}$$

If the value of $K_{lex}$ is given, it is possible to determine the *w* value by solving Eq. 19 under conditions where *w* is a positive real number and is smaller than *a* and *c*. When *w* is thus determined, the values of *y* and *z* are calculated by $y=(a-w)/2$ and $z=b-y$. Then, the observed *Abs* and *P* values are given by

$$Abs = \varepsilon_1 w + \varepsilon_2 y \tag{20}$$

and

$$P = f_0 z + f_2 y, \tag{21}$$

where $\varepsilon_1$ and $\varepsilon_2$ are the molar absorption coefficients at $\lambda$=685 nm for $Cu(edta)^{2-}$ and $Cu_2CD$ respectively, and $f_0$ and $f_2$, the molar optical rotations at $\lambda$=405 nm for CD and $Cu_2CD$ respectively. Although it is possible to determine directly the values of $\varepsilon_1$, $\varepsilon_2$, $f_0$, and $f_2$ by spectrophotometric and polarimetric measurements of solutions containing individual complexes, these quantities as well as $K_{lex}$ were estimated by analyzing relationships between *Abs* or *P* and *v* (the cumulative volume of Soln B added to 2 $cm^3$ of Soln A) by use of the least-squares curve-fitting method with a FACOM M-140F computer at Shimane University. The values of $\varepsilon_1$ and $\varepsilon_2$, thus estimated, virtually agreed with those directly determined. However, the values of $f_0$ and $f_2$ did not always agree. Therefore, the value of $f_0$ was fixed in the analytical computation to be 32.8 deg $cm^{-1}$ $mol^{-1}$ $dm^3$ for $\alpha$-CD and 41.4 deg $cm^{-1}$ $mol^{-1}$ $dm^3$ for $\beta$-CD, which were experimentally determined. This calculation improvement gave reasonable $f_2$ and $K_{lex}$ values for both $\alpha$- and $\beta$-CD systems.

## Results and Discussion

Table 1 shows the $K_{dsp}$ values as well as the molar

TABLE 1. PARAMETERS FOR THE DISPROPORTIONATION REACTION OF Cu$\alpha$-CD TO $Cu_2$ $\alpha$-CD AND $\alpha$-CD AT 25°C

| [NaOH] | Spectrophotometry | | | Polarimetry | | |
|---|---|---|---|---|---|---|
| | $\varepsilon_1$ | $\varepsilon_2$ | $K_{dsp}$ | $\Delta f_1$ | $\Delta f_2$ | $K_{dsp}$ |
| mol dm$^{-3}$ | cm$^{-1}$ mol$^{-1}$ dm$^3$ | cm$^{-1}$ mol$^{-1}$ dm$^3$ | | deg cm$^{-1}$ mol$^{-1}$ dm$^3$ | deg cm$^{-1}$ mol$^{-1}$ dm$^3$ | |
| 1.0 | 36 | 157 | 17.0 | 34 | 142 | 17.3 |
| 1.5 | 42 | 155 | 11.0 | 36 | 142 | 12.3 |
| 2.0 | 42 | 156 | 10.2 | 36 | 144 | 7.5 |
| 2.5 | 41 | 151 | 7.3 | 33 | 142 | 6.6 |

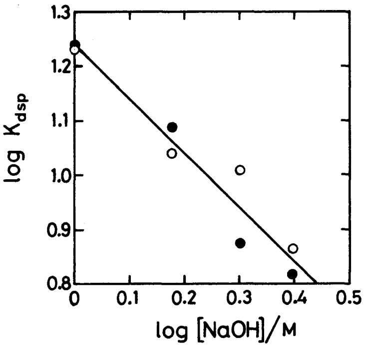

Fig. 6. Plots of log $K_{dsp}$ vs. log [NaOH] for a $Cu_2$-$\alpha$-CD system at 25 °C. The $K_{dsp}$ values were determined by spectrophotometry (○) and polarimetry (●). 1 M = 1 mmol dm$^{-3}$.

absorption coefficients ($\varepsilon_1$ and $\varepsilon_2$) and the differences ($\Delta f_1$ and $\Delta f_2$) in molar optical rotation determined for a Cu-$\alpha$-CD system by a least-squares analysis of the spectrophotometric and polarimetric data in Figs. 1 and 3. The $K_{dsp}$ values estimated by the two methods agreed fairly well with each other at every NaOH concentration, and decreased with increasing NaOH concentration. The $\varepsilon_1$, $\varepsilon_2$, $\Delta f_1$, and $\Delta f_2$ values were virtually constant, irrespective of the NaOH concentration. The average values were $\varepsilon_1=40\pm2$ cm$^{-1}$ mol$^{-1}$ dm$^3$, $\varepsilon_2=154\pm2$ cm$^{-1}$ mol$^{-1}$ dm$^3$, $\Delta f_1=35\pm1$ deg cm$^{-1}$ mol$^{-1}$ dm$^3$, and $\Delta f_2=143\pm1$ deg cm$^{-1}$ mol$^{-1}$ dm$^3$. The molar optical rotation ($f_0$) of $\alpha$-CD at $\lambda=405$ nm was determined to be 32.8 deg cm$^{-1}$ mol$^{-1}$ dm$^3$, so that the molar optical rotations ($f_1$ and $f_2$) of Cu$\alpha$-CD and $Cu_2\alpha$-CD were evaluated to be $-2\pm1$ and $-110$ $\pm1$ deg cm$^{-1}$ mol$^{-1}$ dm$^3$, respectively.

Figure 6 shows a plot of log $K_{dsp}$ vs. log [NaOH]. The plot is virtually linear, and the correlation analysis with the least-squares method gave Eq. 22.

$$\log K_{dsp} = 1.24 - 0.99 \log [\mathrm{NaOH}]; \qquad n = 8, \ r = -0.969 \quad (22)$$

In this equation, $n$ is the number of data and $r$, a correlation coefficient. The slope of the plot is *ca.* $-1.0$, which shows that the disproportionation reaction of Cu$\alpha$-CD to $Cu_2\alpha$-CD and CD is accompanied by the release of 1 mole of $OH^-$. Thus, the stoichiometry for the disproportionation reaction is represented by

$$2[\mathrm{Cu(AH_2)(OH)_2}]^{2-} \rightleftharpoons [\mathrm{Cu_2(A)(OH)_2}]^{2-} + \mathrm{AH_3}^- + \mathrm{OH}^- + \mathrm{H_2O}, \quad (23)$$

where $AH_4$ refers to $\alpha$-CD. It is reasonable to consider that one of the hydroxyl groups of $\alpha$-CD dissociates in such a strongly alkaline solution to give an alkoxide anion ($AH_3^-$), since the p$K_a$ value for $\alpha$-CD is 12.332 at 25 °C.[4)]

Tables 2 and 3 show the $K_{lex}$, $\varepsilon_1$, $\varepsilon_2$, $f_0$, and $f_2$ values determined for the ligand-exchange reactions of $Cu_2\alpha$-CD and $Cu_2\beta$-CD respectively with EDTA by the least-squares analyses of spectrophotometric and polarimetric data. The $K_{lex}$ values estimated by the two methods agreed well with each other at every NaOH concentration, and they decreased rapidly with an increasing concentration of NaOH. The values of $\varepsilon_1$, $\varepsilon_2$, and $f_2$ were virtually constant, irrespective of the NaOH concentration. The average values were $\varepsilon_1=32\pm1$ cm$^{-1}$ mol$^{-1}$ dm$^3$, $\varepsilon_2=135\pm2$ cm$^{-1}$ mol$^{-1}$ dm$^3$, and $f_2=-97\pm2$ deg cm$^{-1}$ mol$^{-1}$ dm$^3$ for a $\alpha$-CD system and $\varepsilon_1=32\pm1$ cm$^{-1}$ mol$^{-1}$ dm$^3$, $\varepsilon_2=132\pm1$ cm$^{-1}$ mol$^{-1}$ dm$^3$, and $f_2=-85\pm2$ deg cm$^{-1}$ mol$^{-1}$ dm$^3$ for a $\beta$-CD system. The $f_2$ value, thus estimated for a $\alpha$-CD system, is in fair agreement with the corresponding value estimated above from the disproportionation reaction.

Figure 7 shows plots of log $K_{lex}$ vs. log [NaOH] for both $\alpha$- and $\beta$-CD systems. The correlation analysis with the least-squares method gave Eq. 24 for a $\alpha$-CD system and Eq. 25 for a $\beta$-CD system.

$$\log K_{lex} = 0.38 - 4.54 \log [\mathrm{NaOH}]; \qquad n = 10, \ r = -0.995 \quad (24)$$

$$\log K_{lex} = 0.08 - 4.17 \log [\mathrm{NaOH}]; \qquad n = 10, \ r = -0.995 \quad (25)$$

The slopes of the plots are *ca.* 4—5. These results suggest that the stoichiometry of the ligand-exchange reaction is mostly expressed by

$$[\mathrm{Cu_2(A)(OH)_2}]^{2-} + 2\mathrm{edta}^{4-} + 3\mathrm{H_2O} \rightleftharpoons 2[\mathrm{Cu(edta)}]^{2-} + \mathrm{AH_3}^- + 5\mathrm{OH}^-. \quad (26)$$

According to Gorelova, *et al.*,[5)] $[Cu(edta)]^{2-}$ reacts with $OH^-$ to afford $[Cu(edta)(OH)]^{3-}$ in an alkaline solution. Then, it is possible that a part of $[Cu(edta)]^{2-}$ in Eq. 26 is converted to $[Cu(edta)(OH)]^{3-}$

TABLE 2. PARAMETERS FOR THE LIGAND-EXCHANGE REACTION OF $Cu_2\alpha$-CD WITH EDTA AT 25 °C

| [NaOH] | Spectrophotometry | | | Polarimetry | | |
|---|---|---|---|---|---|---|
| mol dm$^{-3}$ | $\varepsilon_1$ | $\varepsilon_2$ | $K_{\text{lex}}$ | $f_0$ | $f_2$ | $K_{\text{lex}}$ |
| | cm$^{-1}$ mol$^{-1}$ dm$^3$ | cm$^{-1}$ mol$^{-1}$ dm$^3$ | | deg cm$^{-1}$ mol$^{-1}$ dm$^3$ | deg cm$^{-1}$ mol$^{-1}$ dm$^3$ | |
| 0.5 | 35 | 138 | 72.8 | 32.8 | −100 | 48.0 |
| 1.0 | 34 | 137 | 2.03 | 32.8 | −102 | 2.22 |
| 1.5 | 32 | 138 | 0.368 | 32.8 | −97 | 0.427 |
| 2.0 | 29 | 132 | 0.0616 | 32.8 | −94 | 0.127 |
| 2.5 | 29 | 130 | 0.0322 | 32.8 | −90 | 0.0562 |

TABLE 3. PARAMETERS FOR THE LIGAND-EXCHANGE REACTION OF $Cu_2\beta$-CD WITH EDTA AT 25 °C

| [NaOH] | Spectrophotometry | | | Polarimetry | | |
|---|---|---|---|---|---|---|
| mol dm$^{-3}$ | $\varepsilon_1$ | $\varepsilon_2$ | $K_{\text{lex}}$ | $f_0$ | $f_2$ | $K_{\text{lex}}$ |
| | cm$^{-1}$ mol$^{-1}$ dm$^3$ | cm$^{-1}$ mol$^{-1}$ dm$^3$ | | deg cm$^{-1}$ mol$^{-1}$ dm$^3$ | deg cm$^{-1}$ mol$^{-1}$ dm$^3$ | |
| 0.5 | 34 | 132 | 26.5 | 41.4 | −86 | 21.2 |
| 1.0 | 34 | 133 | 1.26 | 41.4 | −89 | 1.14 |
| 1.5 | 30 | 132 | 0.131 | 41.4 | −86 | 0.226 |
| 2.0 | 31 | 131 | 0.0576 | 41.4 | −84 | 0.0774 |
| 2.5 | 30 | 131 | 0.0257 | 41.4 | −79 | 0.0397 |

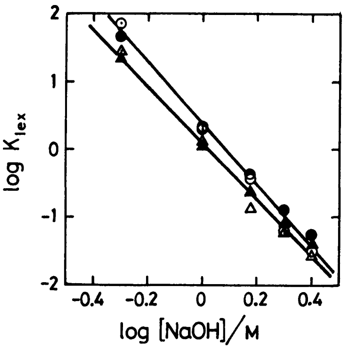

Fig. 7. Plots of log $K_{\text{lex}}$ *vs.* log[NaOH] for $Cu_2$ α-CD-EDTA (○ and ●) and $Cu_2\beta$-CD-EDTA (△ and ▲) systems at 25 °C. The $K_{\text{lex}}$ values were determined by spectrophotometry (○ and △) and polarimetry (● and ▲). 1 M=1 mol dm$^{-3}$.

with the consumption of one mole of $OH^-$. This may be a reason why the slopes of the plots in Fig. 7 are less than 5.

Brunetti, *et al.*[6] have determined the log *K* value for a reaction represented by Eq. 27 to be 18.87.

$$Cu^{2+} + edta^{4-} \rightleftharpoons [Cu(edta)]^{2-} \qquad (27)$$

By combining Eq. 27 with Eq. 26, we obtain

$$2Cu^{2+} + AH_3^- + 5OH^- \rightleftharpoons [Cu_2(A)(OH)_2]^{2-} + 3H_2O. \qquad (28)$$

The log *K* value for this reaction was calculated to be 37.41 for a α-CD system and 37.66 for a β-CD system at [NaOH]=1.0 mol dm$^{-3}$. Furthermore, we obtain from Eqs. 23 and 28

$$Cu^{2+} + AH_3^- + 3OH^- \rightleftharpoons [Cu(AH_2)(OH)_2]^{2-} + H_2O. \qquad (29)$$

The log *K* value for this reaction was calculated to be 18.09 for a α-CD system at [NaOH]=1.0 mol dm$^{-3}$. These results indicate that both of Cuα-CD and $Cu_2\alpha$-CD are very stable in 1.0 mol dm$^{-3}$ NaOH, although they are unstable in a neutral aqueous solution.

It has been suggested in a previous paper[2] that the structure of a $Cu_2\beta$-CD complex is $[Cu_2(A)(OH)(O)]^{3-}$ rather than $[Cu_2(A)(OH)_2]^{2-}$. If this suggestion is valid, the stoichiometry of the ligand-exchange reaction for a β-CD system should be expressed by

$$[Cu_2(A)(OH)(O)]^{3-} + 2edta^{4-} + 4H_2O \rightleftharpoons 2[Cu(edta)]^{2-} + AH_3^- + 6OH^-, \qquad (30)$$

instead of Eq. 26. Then, the slope of the plot of log $K_{\text{lex}}$ *vs.* log [NaOH] should be equal to −6 for a β-CD system. However, the slope experimentally determined was −4.17. It is not clear why this discrepancy was brought about. It is possible to consider that the alkoxide ion ($AH_3^-$) of β-CD dissociates further into a divalent anion ($AH_2^{-2}$) in an solution higher in alkaline concentration than 1 mol dm$^{-3}$. The formation of $AH_2^{2-}$, together with the formation of $[Cu(edta)(OH)]^{3-}$, would consume $OH^-$, resulting in a decrease in the slope of the log $K_{\text{lex}}$ *vs.* log [NaOH] plot. Although this explanation is plausible, there is no clear evidence supporting it at the present time. A more detailed examination is currently under way for a β-CD system.

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