Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **27:** 57–67, 1997.

Inclusion Behavior of α-Cyclodextrin with 2-Methylnaphthalene in Aqueous Solutions

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(Received: 26 March 1996; in final form: 21 May 1996)

Abstract. By means of absorption and fluorescence spectroscopy, 2-methylnaphthalene (2MN) was found to be incorporated into the cavity of α-cyclodextrin (α-CD) to form a 1 : 1 inclusion complex. The 1 : 1 inclusion complex further associated with another α-CD molecule, resulting in the formation of a 2 : 1 α-CD–2MN inclusion complex. The equilibrium constants for the formation of the 1 : 1 and 2 : 1 inclusion complexes were estimated to be 44.6 and 376 mol^{-1} dm^3, respectively, on the basis of a simulation of the observed 2MN fluorescence intensities. The induced circular dichroism spectra suggested that 2MN, buried within the α-CD inclusion complexes, resided in a different orientation relative to the CD symmetry axis, as compared to 2MN within a β-CD inclusion complex.

Key words. α-Cyclodextrin, 2-methylnaphthalene, 2 : 1 inclusion complex, fluorescence, induced circular dichroism.

1. Introduction

α-, β- and γ-Cyclodextrins (CDs) are oligosaccharides composed of six, seven, and eight D-glucose residues, respectively, in a toroidal arrangement that gives rise to a hydrophobic cavity [1]. CDs form inclusion complexes, in which a guest substrate is incorporated into the CD cavity. For long-chain substrates such as heptane, or bulky substrates such as l-adamantanecarboxylic acid, a 2 : 1 α-CD-substrate inclusion complex is formed [2–4]. α-CD is believed to best accommodate a benzene ring; this means that the α-CD cavity size is most appropriate for encapsulating a molecule having dimensions similar to the benzene ring, to form an inclusion complex. The β-CD cavity, which has a diameter greater than α-CD, snugly fits a naphthalene nucleus [5–8]. Consequently, there have been few studies concerning interactions between α-CD and naphthalene derivatives.

Recently, however, 2 : 1 α-CD–naphthalene derivative inclusion complexes have been reported [9–12]. A 2 : 1 α-CD–2-acetylnaphthalene inclusion complex has been suggested from an analysis of the fluorescence quenching of the guest at high concentrations of α-CD [9]. For 2-naphthol, the equilibrium constants (K_1) for the formation of 1 : 1 inclusion complexes with α-CD and β-CD have been determined to be 250 ± 50 and 590 ± 50 mol^{-1} dm^3, respectively [10]. The K_1 value for α-CD is about half of that for β-CD. The equilibrium constant (K_2) for the formation of a 2 : 1 α-CD–2-naphthol inclusion complex from α-CD and a 1 : 1 inclusion complex

has been estimated to be 35 ± 5 mol^{-1} dm^3, which is one order of magnitude less than K_1 for α-CD [10]. 6-Bromo-2-naphthol also associates with α-CD to form a 1 : 1 inclusion complex with $K_1 = 560$ mol^{-1} dm^3 [11, 12]. The K_2 value for 6-bromo-2-naphthol has been evaluated to be 530 mol^{-1} dm^3, which is nearly the same as K_1 for 6-bromo-2-naphthol and is one order of magnitude greater than K_2 for 2-naphthol. ^{1}H-NMR spectral analyses have shown that the first α-CD molecule binds to 6-bromo-2-naphthol from the Br-substituted side of 6-bromo-2-naphthol. The second α-CD molecule accommodates the guest molecule in the 1 : 1 α-CD–6-bromo-2-naphthol inclusion complex from the hydroxy group-substituted side of the guest, since the Br-substituted side of the guest is already encapsulated to form the 1 : 1 inclusion complex. In aerated aqueous solutions, the 2 : 1 α-CD–6-bromo-2-naphthol inclusion complex emits room-temperature phosphorescence, whereas the 1 : 1 inclusion complex does not. The formation of a 2 : 1 α-CD–6-bromo-2-naphthol inclusion complex, therefore, can alter the emission behavior of a guest molecule incorporated into the α-CD cavity.

No investigations have been done to discover whether or not a hydroxy group affects the magnitude of the equilibrium constant for the formation of a 2 : 1 α-CD–guest inclusion complex. There is a possibility that the association, particularly the second association, of α-CD with 6-bromo-2-naphthol takes place through hydrogen bonding between α-CD and the hydroxy group of 6-bromo-2-naphthol. In order to understand the interactions between α-CD and a hydroxy group of a guest, inclusion complexation between α-CD and a guest having no hydroxy group must be investigated as a reference. Under these circumstances, we have been interested in the formation of a 2 : 1 inclusion complex of α-CD, which contains a guest having no hydroxy (or acetyl) group capable of forming a hydrogen bond. Although Fujiki *et al.* have suggested the formation of 2 : 1 inclusion complexes of α-CD and alkylnaphthalenes by means of a volatilization method [13], the formation of 2 : 1 inclusion complexes of α-CD has not been spectroscopically examined. Thus, 2-methylnaphthalene (2MN) was selected as a guest, and its electronic absorption, fluorescence, and induced circular dichroism spectra in aqueous solutions were examined in the absence and presence of α-CD. In this paper, we report the formation of a 2 : 1 α-CD–2MN inclusion complex as well as a 1 : 1 inclusion complex, and the estimation of equilibrium constants for the formation of these inclusion complexes.

2. Experimental

α-Cyclodextrin (α-CD) was purchased from Nacalai Tesque, Inc. and was used as received. β-CD (Nacalai Tesque, Inc.) was recrystallized twice from water. 2-Methylnaphthalene (2MN) (Tokyo Kasei Kogyo Co., Ltd.) was purified by silica-gel column chromatography. The concentrations of 2MN for the measurements of absorption spectra and induced circular dichroism (icd) spectra were around

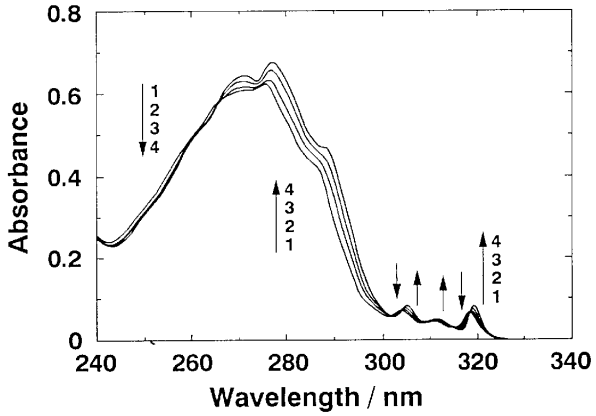

Figure 1. Absorption spectra of 2MN (1.3×10^{-4} mol dm^{-3}) in aqueous solutions containing α-CD of various concentrations. Concentration of α-CD: (1) 0, (2) 5.0×10^{-3}, (3) 1.0×10^{-2}, and (4) 2.0×10^{-2} mol dm^{-3}.

1.3×10^{-4} mol dm^{-3}, while those for fluorescence spectra were around 2.6×10^{-5} mol dm^{-3}.

Absorption and fluorescence spectra were recorded on a Shimadzu UV-260 spectrophotometer and a Shimadzu RF-501 spectrofluorometer equipped with a cooled Hamamatsu R-943 photomultiplier. Fluorescence spectra were corrected for the spectral response of the fluorometer. ICD spectra were run on a JASCO J-600 spectropolarimeter. Spectroscopic measurements were performed at 25.0 ± 0.1 °C, except for measurements of ICD spectra which were taken at room temperature.

3. Results and Discussion

Figure 1 shows the absorption spectra of 2-methylnaphthalene (2MN) in aqueous solutions containing α-cyclodextrin (α-CD) of various concentrations. Upon increasing the α-CD concentration, the absorption maxima shifted to longer wavelengths, accompanied by the appearance of isosbestic points at 265.5, 302, 304, 315.5, and 318 nm. In addition, the vibronic bands of the 2MN absorption spectra were sharpened upon the addition of α-CD. These findings indicate the formation of at least a 1 : 1 α-CD–2MN inclusion complex (α-CD·2MN):

$$\alpha\text{-CD} + 2\text{MN} \overset{K_1}{\rightleftharpoons} \alpha\text{-CD}\cdot 2\text{MN} \tag{1}$$

Here, K_1 is the equilibrium constant for the formation of the 1 : 1 α-CD–2MN inclusion complex.

When only one equilibrium in the aqueous solutions of 2MN containing α-CD is established between free, uncomplexed 2MN and a 1 : 1 α-CD–2MN inclusion complex, a Benesi–Hildebrand type relation should hold [7, 14]:

$$1/(A - A_0) = 1/a + 1/(aK_1[\alpha\text{-CD}]_0) \tag{2}$$

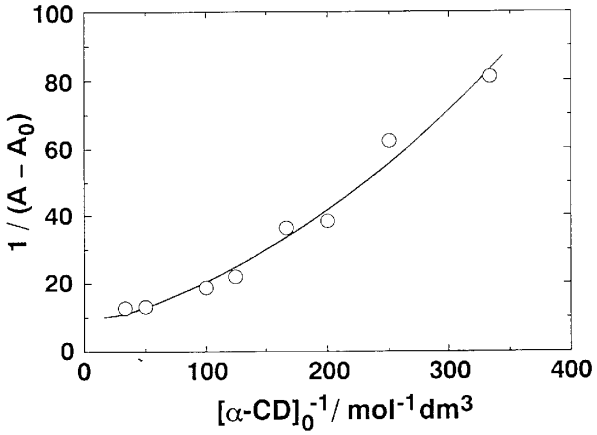

Figure 2. Plot of $1/(A - A_0)$ against $1/[\alpha\text{-CD}]_0$. $[2MN]_0 = 1.3 \times 10^{-4}$ mol dm^{-3}. $\lambda_{obs} = 277$ nm.

where A, A_0, and a are the absorbance of 2MN in the presence of α-CD, that in the absence of α-CD, and a constant, respectively. The subscript 0 in the concentration term represents the initial concentration.

A double reciprocal plot of $1/(A - A_0)$ against $1/[\alpha\text{-CD}]_0$ is shown in Figure 2. The plot exhibits an upward concave curvature, evidently indicating that an inclusion complex other than the 1 : 1 α-CD–2MN inclusion complex is present in aqueous 2MN solutions with α-CD, although the isosbestic points are observed in the absorption spectra. Since the α-CD cavity is not large enough to wholly accommodate a 2MN molecule, part of the 2MN molecule is most likely to extrude from the α-CD cavity. Consequently, an additional α-CD molecule can associate with a 1 : 1 inclusion complex, resulting in the formation of a 2 : 1 α-CD–2MN inclusion complex ((α-CD)$_2$·2MN):

$$\alpha\text{-CD}\cdot 2MN + \alpha\text{-CD} \overset{K_2}{\rightleftharpoons} (\alpha\text{-CD})_2\cdot 2MN \tag{3}$$

where K_2 is the equilibrium constant for the formation of the 2 : 1 α-CD–2MN inclusion complex.

Figure 3a illustrates induced circular dichroism (ICD) spectra of 2MN in aqueous solutions containing α-CD of 3.0×10^{-3} and 1.0×10^{-2} mol dm^{-3}. At an α-CD concentration of 3.0×10^{-3} mol dm^{-3}, the ICD spectrum of 2MN showed a positive band in the wavelength range of 265–320 nm with a maximum wavelength of 294 nm, possessed no intensity in the wavelength range of 245–265 nm, and showed negative signals at wavelengths below 245 nm. For a 2MN solution containing α-CD of 1.0×10^{-2} mol dm^{-3}, the ICD spectrum exhibited a maximum wavelength of 290 nm in the positive-signal region, which was shorter than that observed in the ICD spectrum for an α-CD concentration of 3.0×10^{-3} mol dm^{-3}, although the intensity of the ICD spectrum was enhanced in the 265–320

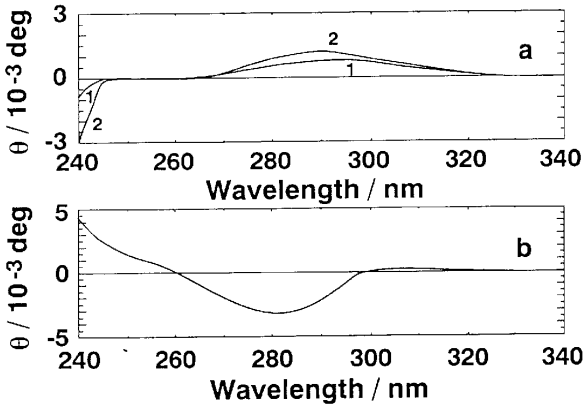

Figure 3. (a) Induced circular dichroism spectra of 2MN (1.3×10^{-4} mol dm^{-3}) in aqueous solutions in the presence of α-CD. Concentration of α-CD: (1) 3.0×10^{-3} and (2) 1.0×10^{-2} mol dm^{-3}; (b) induced circular dichroism spectrum of 2MN (1.3×10^{-4} mol dm^{-3}) in an aqueous solution containing β-CD (1.0×10^{-2} mol dm^{-3}).

nm region. This finding provides additional evidence for the existence of a 2 : 1 α-CD–2MN inclusion complex. As in the cases of 2-naphthol and 2-naphthylamine, the 315-nm, 270-nm, and 240-nm bands of 2MN can be assigned to the ^1L_b, ^1L_a, and ^1B_b bands, respectively [15]. Since 2MN does not possess a hydroxy group, hydrogen bonding between α-CD and a guest is not essential to form a 2 : 1 α-CD–naphthalene derivative inclusion complex, although there may be hydrogen bonding between two α-CD molecules constituting a 2 : 1 inclusion complex.

In the case of β-CD, 2MN in neutral aqueous solutions forms a 2 : 2 inclusion complex as well as a 1 : 1 inclusion complex [16]. It has been suggested that the disposition of a 2MN molecule in the 2 : 2 inclusion complex relative to the β-CD molecule is nearly the same as that in the 1 : 1 inclusion complex [16]. Figure 3b (Figure 12a in Ref. 16) illustrates the ICD spectrum of 2MN in a neutral aqueous solution of β-CD (1.0×10^{-2} mol dm^{-3}), which gives very slightly positive, negative, and positive signals for the ^1L_b, ^1L_a, and ^1B_b bands, respectively. This spectrum indicates that the directions of transition moments of the ^1L_b and ^1B_b bands for naphthalene are parallel to the longitudinal axis of naphthalene, while that of the ^1L_a band is perpendicular to the longitudinal axis. Because the axial inclusion of a naphthalene nucleus by β-CD is revealed for 2-substituted naphthalenes [17], 2MN would be most likely included by β-CD with a naphthalene nucleus being almost parallel to the symmetry axis of β-CD.

When, inside the CD cavity, the angle between the direction of an electronic transition moment of a guest molecule and the symmetry axis of CD is between $-54.44°$ and 54.44°, a positive signal is expected for the ICD spectrum [18]. The angle between the direction of the ^1L_b transition moment for 2MN and the symmetry axis of β-CD should be close to and less than 54.44° since a considerably small, positive signal for the ^1L_b transition is observed as shown in Figure 3b.

Consequently, the direction of the ^1L_b transition moment for 2MN is rotated by approximately 54° from the longitudinal axis of the naphthalene nucleus. In Figure 3b, negative and positive signals are observed for the ^1L_a and ^1B_b bands, respectively. Therefore, the angle between the direction of the ^1L_a transition moment for 2MN and the β-CD symmetry axis is in the range of 54.44–125.56°, whereas that between the direction of the ^1B_b transition and the β-CD symmetry axis is in the range of -54.44 to 54.44°.

The ICD spectra for α-CD and β-CD solutions are different from each other (Figure 3), indicating that the dispositions of 2MN in the α-CD and β-CD inclusion complexes are different with respect to the CD symmetry axis. In order to effectively accommodate the methyl group in 2MN, the α-CD symmetry axis is most likely tilted 30° from the longitudinal axis of a naphthalene nucleus. Assuming an angle of 30° for the α-CD orientation, the angle between the direction of the ^1L_b transition moment and the α-CD symmetry axis is approximately 24°, leading to a definitely positive signal, which is consistent with the observed ICD spectra (315-nm band) shown in Figure 3a. For the ^1L_a and ^1B_b bands, the angles between the transition moment and the longitudinal axis are similarly deduced to be in the range of -24.44 to 84.44° and -95.56 to -24.44°, respectively.

From the results on the α-CD and β-CD solutions, the directions of the ^1L_a and ^1B_b transition moments of 2MN are estimated to be tilted by 54.44–84.44° and -24.44 to -54.44° from the 2MN longitudinal axis, respectively. The direction of the transition moment of the ^1L_a band of 2MN on the basis of the longitudinal axis of the naphthalene ring is similar to that of 6-bromo-2-naphthol whereas those of the ^1L_b and ^1B_b bands of 2MN are dissimilar to those of 6-bromo-2-naphthol [12]. Consequently, these results indicate that the perturbation effect of a methyl group on the direction of a transition moment is different from those of a hydroxy group and/or a Br substituent. The approach employing both α-CD and β-CD inclusion complexes is useful in evaluating the directions of the electronic transition moments of a guest molecule, although a method employing an inclusion complex of only one kind (e.g., a β-CD inclusion complex) has been used to roughly estimate the directions of transition moments [19]. Our method offers an advantage of allowing the directions of transition moments on the basis of the molecular axis to be estimated more definitely than the method using one kind of inclusion complex.

Figure 4 exhibits fluorescence spectra of 2MN in aqueous solutions containing various amounts of α-CD. As the α-CD concentration increased, the fluorescence intensity was considerably enhanced with a sharpening of vibronic bands, indicating the formation of an inclusion complex(es). The sharpening of the vibronic bands implies the greater hydrophobicity of the α-CD cavity compared to the bulk water environment. When a 1 : 1 inclusion complex alone exists as an inclusion complex, a Benesi–Hildebrand type plot for the fluorescence intensity change as well as the absorbance change should be linear [7]:

$$1/(I_f - I_f^0) = 1/a' + 1/(a' K_1[\alpha\text{-CD}]_0) \tag{4}$$

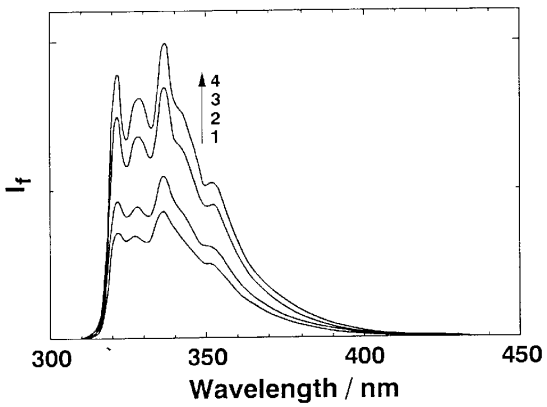

Figure 4. Fluorescence spectra of 2MN (2.6×10^{-5} mol dm^{-3}) in aqueous solutions containing α-CD of various concentrations. Concentration of α-CD: (1) 0, (2) 3.0×10^{-3}, (3) 1.0×10^{-2}, and (4) 2.0×10^{-2} mol dm^{-3}. $\lambda_{ex} = 290$ nm.

where I_f, I_f^0, and a' are the fluorescence intensity in the presence of α-CD, and that in the absence of α-CD, and a is a constant, respectively. A plot based on Equation (4) exhibited an upward concave curvature (not shown), suggesting the existence of a 2 : 1 α-CD–2MN inclusion complex.

As a consequence, the observed fluorescence intensity, I_f, is represented as the sum of the fluorescence intensity of free 2MN, that of the 1 : 1 inclusion complex (α-CD·2MN), and that of the 2 : 1 inclusion complex ((α-CD)$_2$·2MN):

$$I_f = b[\text{2MN}] + c[\alpha\text{-CD}\cdot\text{2MN}] + d[(\alpha\text{-CD})_2\cdot\text{2MN}] \quad (5)$$

where [2MN] is the concentration of free 2MN, and b, c, and d are constants, which depend on the magnitudes of the molar absorption coefficient and the fluorescence quantum yield of each species.

The concentrations of the above three species are respectively expressed as follows:

$$[\text{2MN}] = [\text{2MN}]_0/(1 + K_1[\alpha\text{-CD}]_0 + K_1K_2[\alpha\text{-CD}]_0^2) \quad (6)$$

$$[\alpha\text{-CD}\cdot\text{2MN}] = K_1[\text{2MN}]_0[\alpha\text{-CD}]_0/(1 + K_1[\alpha\text{-CD}]_0 + K_1K_2[\alpha\text{-CD}]_0^2) \quad (7)$$

and

$$[(\alpha\text{-CD})_2\cdot\text{2MN}] = K_1K_2[\text{2MN}]_0[\alpha\text{-CD}]_0^2/(1+K_1[\alpha\text{-CD}]_0+K_1K_2[\alpha\text{-CD}]_0^2) \quad (8)$$

We have thus simulated the fluorescence intensity observed at 336 nm using K_1, K_2, b, c, and d as parameters. Figure 5 shows the best fit curve for the observed fluorescence intensity as a function of the α-CD concentration, in which K_1, K_2, b, c, and d are assumed to be 44.6, 376, 0.411, 1.76, and 2.57 mol^{-1} dm^3, respectively.

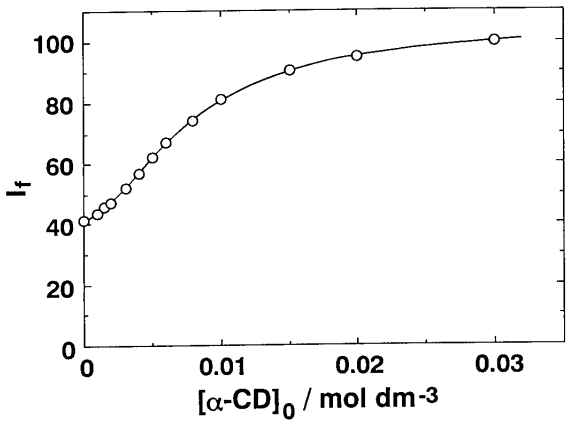

Figure 5. α-CD concentration dependence of the 2MN fluorescence intensity observed at 336 nm. The fluorescence intensity at an α-CD concentration of 3.0×10^{-2} mol dm^{-3} is normalized to 100. Circles represent experimental points. The best fit curve was obtained by use of assumed parameters; $K_1 = 44.6$ mol^{-1} dm^3, $K_2 = 376$ mol^{-1} dm^3, $b = 0.411$ mol^{-1} dm^3, $c = 1.76$ mol^{-1} dm^3, and $d = 2.57$ mol^{-1} dm^3.

The values of b, c, and d are proportional to the fluorescence quantum yield of each species, although the absorption coefficient of each species is included in these parameters. Consequently, the order $b < c < d$ is consistent with the enhancement of the 2MN fluorescence intensity with the increase in the α-CD concentration. The K_1 value for 2MN is about one-fifth of that for 2-naphthol, and is one order of magnitude less than that for 6-bromo-2-naphthol. On the other hand, the K_2 value for 2MN is one order of magnitude greater than that for 2-naphthol, and is slightly less than that for 6-bromo-2-naphthol.

As in the case of the fluorescence intensity, the absorbance, A, of a 2MN solution containing α-CD is expressed by

$$A = \epsilon_o[\text{2MN}]l + \epsilon_1[\alpha\text{-CD}\cdot\text{2MN}]l + \epsilon_2[(\alpha\text{-CD})_2\cdot\text{2MN}]l \tag{9}$$

where ϵ_0, ϵ_1, and ϵ_2 are the molar absorption coefficients of free 2MN, α-CD·2MN, and $(\alpha\text{-CD})_2$·2MN, respectively, and l is the path length (1 cm).

The concentrations of three species in Equation (9) are represented by Equations (6), (7), and (8). In order to check the reliability of the K_1 and K_2 values, which were obtained from an analysis employing the fluorescence intensity change, we tried to simulate the absorbance change of 2MN upon changing the α-CD concentration, using the previously evaluated K_1 and K_2 values, an ϵ_0 value, and parameters ϵ_1 and ϵ_2. If the evaluated K_1 and K_2 values are unreasonable, it would not be expected that a simulation curve would reproduce the observed absorbance data shown in Figure 1 well. In this simulation, the ϵ_0 value at 277 nm for an aqueous 2MN solution was assumed to be equal to that (4930 mol^{-1} dm^3 cm^{-1}) for an ethanol solution of 2MN. Figure 6 illustrates the best fit curve for the absorbance

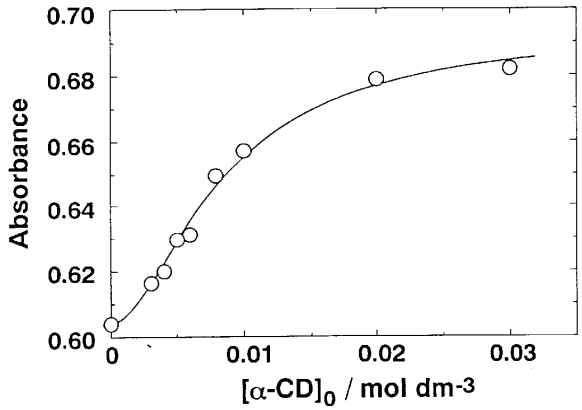

Figure 6. α-CD concentration dependence of the 2MN absorbance observed at 277 nm. Circles represent experimental points. The best fit curve was obtained by use of the evaluated K_1 (44.6 mol^{-1} dm^3) and K_2 (376 mol^{-1} dm^3) values, the ϵ_0 value (4930 mol^{-1} dm^3 cm^{-1}), and assumed ϵ_1 (5030 mol^{-1} dm^3 cm^{-1}) and ϵ_2 (5680 mol^{-1} dm^3 cm^{-1}) values. $[2MN]_0 = 1.3 \times 10^{-4}$ mol dm^{-3}.

change, which was calculated using the assumed ϵ_1 (5030 mol^{-1} dm^3 cm^{-1}) and ϵ_2 (5680 mol^{-1} dm^3 cm^{-1}) values, together with the absorbance data observed at 277 nm. The quality of the fit to the observed data is good. These ϵ_1 and ϵ_2 values are greater than the ϵ_0 value, and the ϵ_2 value is greater than the ϵ_1 value. The relationship among the absorption coefficients is consistent with the experimental result that the absorbance at 277 nm, shown in Figure 1, successively increased with the increase in the α-CD concentration, indicating that the K_1 (44.6 mol^{-1} dm^3) and K_2 (376 mol^{-1} dm^3) values determined in this work are reasonable. The finding that K_1 is less than K_2 may imply that the second association of α-CD with 2MN is accelerated by the presence of another α-CD molecule constituting a 1 : 1 inclusion complex. Hydrogen bonding between the two α-CD molecules in a 2 : 1 α-CD–2MN inclusion complex may play an important role in the acceleration of the formation of the 2 : 1 inclusion complex. It has been reported that K_1 and K_2 for 2MN are 22 ± 5 and 12 ± 4 mol^{-1} dm^3, respectively [13]. Although the K_2 value reported in the literature is considerably less than the K_2 value which we obtained, the reported K_1 value is the same order of magnitude as the K_1 value obtained by us.

Due to the hydrophobic nature of the CD cavity, CD favorably binds to a hydrophobic moiety of a guest. Because the hydroxy group of 2-naphthol is hydrophilic, the first α-CD molecule in a 2 : 1 α-CD–2-naphthol inclusion complex seems to bind to a benzene ring, in the naphthalene nucleus, having no hydroxy group. The incorporation by α-CD of a naphthalene nucleus having no substituent probably brings about an equilibrium constant of the order of 100, taking account of K_1 for 2-naphthol being 250 ± 50 mol^{-1} dm^3. In the case of 2MN, the first α-CD molecule may associate with the methyl substituent on the naphthalene nucleus of

2MN, resulting in the very small K_1 value compared to 2-naphthol. If so, however, there remains a question why the first α-CD molecule does not accommodate 2MN from the naphthalene-nucleus side having no methyl group.

In Figure 1, the absorption spectra of 2MN exhibit isosbestic points, although two kinds of inclusion complexes, α-CD·2MN and (α-CD)$_2$·2MN, coexist in the solutions. Since K_1 is significantly less than K_2, the concentration of α-CD·2MN at α-CD concentrations higher than around 5×10^{-3} mol dm^{-3} is much lower than that of (α-CD)$_2$·2MN. Therefore, α-CD·2MN makes a considerably small contribution to the observed absorption spectra compared to (α-CD)$_2$·2MN. This seems to cause the appearance of the apparent isosbestic points in the 2MN absorption spectra.

4. Conclusion

In aqueous solutions, α-CD forms a 1 : 1 inclusion complex with 2MN, which further associates with α-CD to form a 2 : 1 α-CD–2MN inclusion complex. The existence of the 2 : 1 inclusion complex of 2MN possessing no hydroxy group indicates that hydrogen bonding between α-CD and a guest is not essential as the driving force for the formation of the 2 : 1 inclusion complex of α-CD. From an analysis of the fluorescence intensity change upon changing the α-CD concentration, the equilibrium constants for the formation of 1 : 1 and 2 : 1 inclusion complexes have been estimated to be 44.6 and 376 mol^{-1} dm^3, respectively. Induced circular dichroism spectra of 2MN suggest that the longitudinal axis of 2MN within the α-CD cavity is tilted by about 30° from the α-CD symmetry axis, and that the relative orientation of 2MN within the α-CD cavity is different from that within the β-CD cavity.

Acknowledgment

I thank Professor Akihiko Ueno of the Department of Bioengineering, Faculty of Bioscience and Biotechnology, Tokyo Institute of Technology for measurements of induced circular dichroism spectra.

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