Excimer Formation in Inclusion Complexes of β-Cyclodextrin with 1-Alkylnaphthalenes in Aqueous Solutions

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In aqueous solutions, β-cyclodextrin (β-CD) has been found to form inclusion complexes with 1-methylnaphthalene, 1-ethylnaphthalene, 1-(chloromethyl)naphthalene, and 2-ethylnaphthalene. Addition of β-CD to aqueous solutions of 1-methylnaphthalene and 2-ethylnaphthalene has resulted in the observation of the excimer fluorescence of each compound. From simulations of the observed excimer fluorescence intensities of 1-methylnaphthalene and 2-ethylnaphthalene, the excimer fluorescence is concluded to be due to a 2 : 2 β-CD–alkylnaphthalene inclusion complex. In the cases of 1-ethylnaphthalene and 1-(chloromethyl)naphthalene, the excimer formation within the β-CD cavities seems to be prohibited due to the steric hindrance caused by a substituent, although the 2 : 2 β-CD–alkylnaphthalene inclusion complex is likely to be formed. Equilibrium constants for the formation of these 1 : 1 and 2 : 2 inclusion complexes have been evaluated from the monomer and excimer fluorescence intensity changes with β-CD concentration.

α-, β-, and γ-cyclodextrins (α-, β-, and γ-CDs) are naturally occurring cyclic oligosaccharides composed of six, seven, and eight D-glucose units, respectively. Because CDs are shaped like a truncated cone with a cavity in center, they accommodate a substrate molecule in their cavities to form an inclusion complex. Usually, a single guest molecule is incorporated into the CD cavity, forming a 1 : 1 host–guest inclusion complex.[1,2] However, naphthalene excimer fluorescence is observed in naphthalene solutions containing β-CD.[3] In aqueous solutions, β-CD forms a 1 : 1 inclusion complex with naphthalene, followed by the self-association of the 1 : 1 inclusion complexes to form a 2 : 2 β-CD–naphthalene inclusion complex. The excimer fluorescence is attributed to a naphthalene excimer, which is formed from two naphthalene molecules within the 2 : 2 inclusion complex. Afterwards, the self-association of 1 : 1 inclusion complexes to a 2 : 2 inclusion complex has also been found for the systems of β-CD–sodium 2-anthracenesulfonate,[4,5] β-CD–sodium 2-anthracenecarboxylate,[5] β-CD–sodium 2-naphthalenesulfonate,[5] β-CD–1-cyanonaphthalene,[6] β-CD–2-chloronaphthalene,[7] β-CD–2-methylnaphthalene,[8] γ-CD–sodium 1-pyrenebutyrate,[9,10] γ-CD–pyrene,[11] γ-CD–2-methylnaphthalene,[8] and 6-*O*-α-D-glucosyl-β-CD–4-(dimethylamino)benzonitrile.[12] In the solid state as well as in aqueous solutions, two β-CD molecules are often coupled by intermolecular hydrogen bonds between secondary hydroxy groups to form a β-CD dimer, which accommodates two guest molecules.[13—16]

Because the cavity diameter of β-CD is smaller than that of γ-CD, naphthalene derivatives, particularly 1-substituted naphthalenes, having a bulky substituent may not form the excimer within the relatively narrow β-CD cavities in a 2 : 2 inclusion complex even when a 2 : 2 inclusion complex is produced. Hence, we have been interested in whether or not 1-alkylnaphthalene forms a 2 : 2 inclusion complex with β-CD, and whether or not the excimer of 1-alkylnaphthalene is formed within the 2 : 2 inclusion complex if the 2 : 2 inclusion complex is generated. With sodium anthracenesulfonates and sodium naphthalenesulfonates, 2-substituted compounds form a 2 : 2 inclusion complex with β-CD but 1-substituted ones do not.[5] Due to the hydrophilic property, the sulfonato group seems to protrude from the β-CD cavity into the bulk water environment when anthracenesulfonates and naphthalenesulfonates form inclusion complexes with β-CD. On the other hand, a hydrophobic alkyl group can be encapsulated by β-CD. Consequently, the position effects of an alkyl substituent on the self-association of 1 : 1 inclusion complexes may be different from those of a sulfonato substituent. We, thus, investigated the emission behavior of 1-methylnaphthalene, 1-ethylnaphthalene, and 1-(chloromethyl)naphthalene in aqueous β-CD solutions, comparing with that of 2-ethylnaphthalene. Among these naphthalene derivatives, 1-methylnaphthalene and 2-ethylnaphthalene were found to exhibit the excimer emission in aqueous solutions containing β-CD. In this article, we report the formation of a 2 : 2 inclusion complex between β-CD and 1-methylnaphthalene (or 2-ethylnaphthalene), which is responsible for the excimer emission.

Experimental

β-Cyclodextrin purchased from Nacalai Tesque, Inc. was recrystallized twice from water. 1-Methylnaphthalene (Tokyo Kasei Kogyo, Co., Ltd.), 1-ethylnaphthalene (Tokyo Kasei Kogyo, Co., Ltd.), and 2-ethylnaphthalene (Aldrich) were purified through a silica-gel column. 1-(Chloromethyl)naphthalene (Tokyo Kasei Kogyo, Co., Ltd.) was recrystallized twice from cyclohexane. In preparation of aqueous solutions of alkylnaphthalenes, purified naphthalene derivatives were plunged into water for several days in

the dark.

Absorption and fluorescence spectra were recorded on a Shimadzu UV-260 spectrophotometer and a Shimadzu RF-540 spectrofluorometer, respectively. Fluorescence spectra were corrected for the spectral response of the fluorometer. Spectroscopic measurements were made at 25.0±0.1°C.

Results and Discussion

Inclusion of 1-Methylnaphthalene by β-Cyclodextrin. Figure 1 shows absorption spectra of 1-methylnaphthalene (1.0×10^{-4} mol dm^{-3}) in aqueous solutions containing various concentrations of β-cyclodextrin (β-CD). When the β-CD concentration is increased, absorption peaks are shifted to longer wavelengths, accompanied by isosbestic points of 258, 274, and 282 nm. In addition, the absorption bands are slightly broadened with the increase in the β-CD concentration. These findings suggest the formation of a β-CD–1-methylnaphthalene inclusion complex. Figure 2 illustrates fluorescence spectra of 1-methylnaphthalene (1.0×10^{-4} mol dm^{-3}) in aqueous solutions containing various amounts of β-CD. As the β-CD concentration is increased, below about 1.0×10^{-3} mol dm^{-3}, the monomer fluorescence intensity of 1-methylnaphthalene is enhanced. With a further increase in the β-CD concentration, the monomer fluorescence is conversely reduced in intensity. Upon the addition of β-CD, a broad, structureless emission emerges at longer wavelengths of around 400 nm. This broad emission can be assigned to the excimer fluorescence of 1-methylnaphthalene. Such emission behavior of 1-methylnaphthalene upon adding β-CD indicates that at least two kinds of inclusion complexes exist in aqueous solutions containing β-CD; one inclusion complex (1 : 1 inclusion complex) emits the monomer fluorescence more strongly than free 1-methylnaphthalene does, and the other inclusion complex emits the excimer fluorescence of 1-methylnaphthalene. At high β-CD concentrations, the concentration of the second inclusion complex is increased, so that it predominantly contributes to the fluorescence spectra of 1-methylnaphthalene; the excimer fluorescence is enhanced in intensity at the expense of the monomer fluorescence intensity. As shown in Fig. 2, at β-CD concentrations higher than approximately 3.0×10^{-3} mol dm^{-3}, the excimer fluorescence intensity is increased while the monomer fluorescence intensity is rather decreased compared to that in the absence of β-CD.

When the 1-methylnaphthalene concentration is diluted to about 1/30 (3.3×10^{-6} mol dm^{-3}), no excimer fluorescence is observed in spite of the presence of β-CD (Fig. 3). In addition, as the β-CD concentration is increased in the dilute solutions of 1-methylnaphthalene, the monomer fluo-

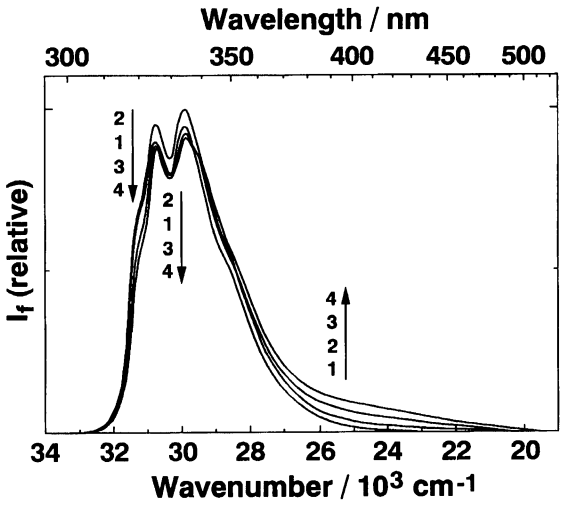

Fig. 2. Fluorescence spectra of 1-methylnaphthalene (1.0×10^{-4} mol dm^{-3}) in aqueous solutions containing various concentrations of β-CD. Concentration of β-CD: (1) 0, (2) 1.0×10^{-3}, (3) 3.0×10^{-3}, and (4) 1.0×10^{-2} mol dm^{-3}. λ_{ex} = 273 nm.

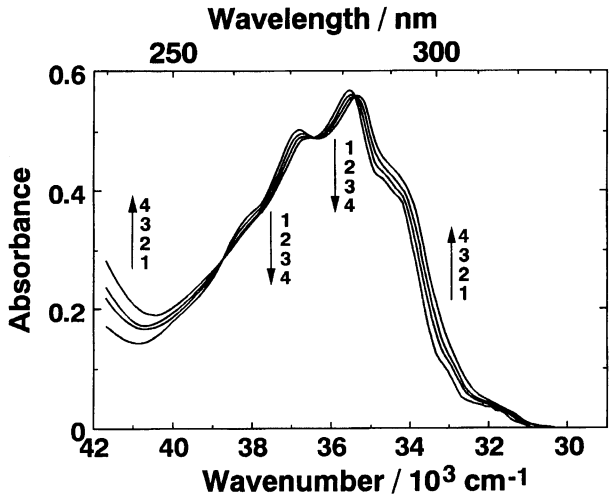

Fig. 1. Absorption spectra of 1-methylnaphthalene (1.0×10^{-4} mol dm^{-3}) in aqueous solutions containing various concentrations of β-CD. Concentration of β-CD: (1) 0, (2) 1.2×10^{-3}, (3) 3.0×10^{-3}, and (4) 1.0×10^{-2} mol dm^{-3}.

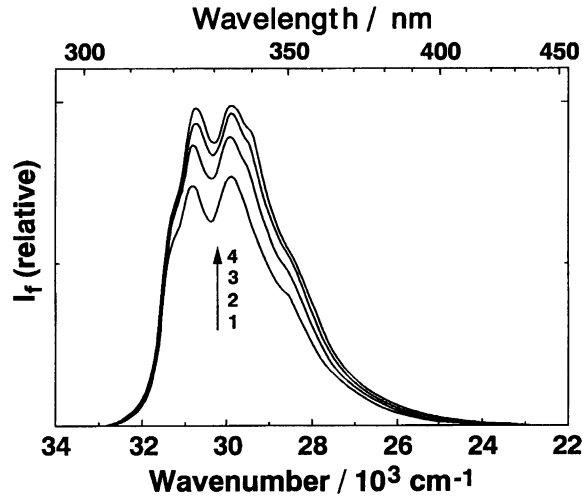

Fig. 3. Fluorescence spectra of 1-methylnaphthalene (3.3×10^{-6} mol dm^{-3}) aqueous solutions containing various concentrations of β-CD. Concentration of β-CD: (1) 0, (2) 1.0×10^{-3}, (3) 3.0×10^{-3}, and (4) 1.0×10^{-2} mol dm^{-3}. λ_{ex} = 273 nm.

rescence of 1-methylnaphthalene is monotonously enhanced, with a very slight peak shift to longer wavelengths, in contrast to the fluorescence spectral changes (Fig. 2) obtained for concentrated solutions of 1-methylnaphthalene (1.0×10^{-4} mol dm^{-3}). This finding indicates that a 1 : 1 β-CD–1-methylnaphthalene inclusion complex alone exists as an inclusion complex in dilute solutions of 1-methylnaphthalene:

$$\beta\text{-CD} + 1\text{MN} \overset{K_1}{\rightleftarrows} \beta\text{-CD}\cdot 1\text{MN}. \quad (1)$$

Here, 1MN stands for 1-methylnaphthalene, and K_1 is the equilibrium constant for the formation of the 1 : 1 inclusion complex (β-CD·1MN). When only one equilibrium involving free 1-methylnaphthalene and the 1 : 1 inclusion complex is established, a Benesi–Hildebrand type relation is hold between the monomer fluorescence intensity and the β-CD concentration:[3]

$$1/(I_f - I_f^0) = 1/a + 1/(aK_1[\beta\text{-CD}]_0), \quad (2)$$

where I_f, I_f^0, and a are the monomer fluorescence intensity in the presence of β-CD, that in the absence of β-CD, and a constant, respectively. From a plot of $1/(I_f - I_f^0)$ against $1/[\beta\text{-CD}]_0$, the value of K_1 is evaluated to be 340±40 mol^{-1} dm^3 (Fig. 4). This K_1 value is about half of K_1 (685 mol^{-1} dm^3) for naphthalene,[3] and is 3.5-fold less than K_1 (1190±40 mol^{-1} dm^3) for 2-methylnaphthalene[8] (Table 1). A similar position effect of a methyl substituent on K_1 has been reported, although an inclusion complex other than a 1 : 1 inclusion complex is not taken into account in estimating K_1 values.[17] These results suggest that in contrast to a methyl group substituted on the 2-position of a naphthalene ring, a methyl group on the 1-position imparts a steric hindrance in forming a 1 : 1 inclusion complex. Consequently, an axial inclusion is the most probable inclusion mode for the formation of the 1 : 1 inclusion complex of β-CD with 1-methylnaphthalene.

In the case of 2-methylnaphthalene, a 2 : 2 β-CD–2-methylnaphthalene inclusion complex, which is formed by the self-association of 1 : 1 inclusion complexes, is concluded to be responsible for the excimer fluorescence.[8] As with

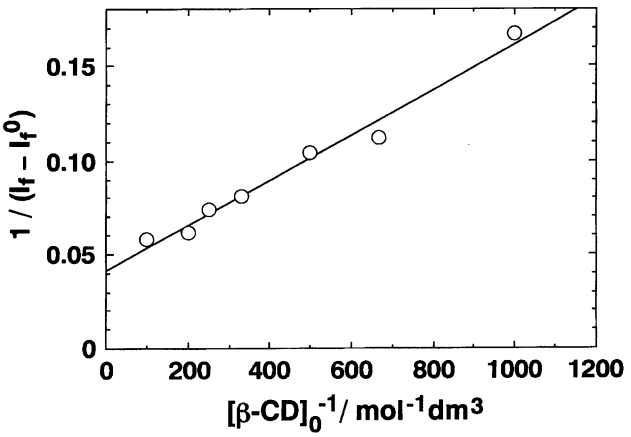

Fig. 4. Plot of $1/(I_f - I_f^0)$ against $1/[\beta\text{-CD}]_0$ for 1-methylnaphthalene (3.3×10^{-6} mol dm^{-3}). λ_{obsd}=334 nm.

1-methylnaphthalene, there are two possibilities concerning an excimer formation scheme; one excimer-emitting species is a 2 : 2 β-CD–1MN inclusion complex ((β-CD·1MN)$_2$), and the other a 1 : 2 β-CD–1MN inclusion complex (β-CD·(1MN)$_2$). These inclusion complexes are respectively formed through the following equilibria:

$$2(\beta\text{-CD}\cdot 1\text{MN}) \overset{K_2}{\rightleftarrows} (\beta\text{-CD}\cdot 1\text{MN})_2, \quad (3)$$

and

$$\beta\text{-CD}\cdot 1\text{MN} + 1\text{MN} \overset{K_2'}{\rightleftarrows} \beta\text{-CD}\cdot(1\text{MN})_2, \quad (4)$$

where K_2 and K_2' are the equilibrium constants for the formation of the 2 : 2 β-CD–1MN inclusion complex and the 1 : 2 β-CD–1MN inclusion complex, respectively.

Under our experimental conditions, the excimer fluorescence intensity is proportional to the concentration of the relevant excimer-emitting species. Hence, we have compared concentration curves calculated for the 2 : 2 inclusion complex with the observed excimer fluorescence intensities to identify an excimer-emitting species. The concentration of the 2 : 2 inclusion complex can be calculated according to the following equations:

$$[(\beta\text{-CD}\cdot 1\text{MN})_2] = ([1\text{MN}]_0 - [1\text{MN}] - [\beta\text{-CD}\cdot 1\text{MN}])/2, \quad (5)$$

$$2K_1^2K_2[\beta\text{-CD}]_0^2[1\text{MN}]^2 + (1+K_1[\beta\text{-CD}]_0)[1\text{MN}] - [1\text{MN}]_0 = 0, \quad (6)$$

$$[\beta\text{-CD}\cdot 1\text{MN}] = K_1[\beta\text{-CD}]_0[1\text{MN}]. \quad (7)$$

Here, $[1\text{MN}]_0$ and [1MN] are the initial concentration of 1-methylnaphthalene and the concentration of free 1-methylnaphthalene, respectively. As a function of β-CD concentration, Fig. 5 depicts the best fit concentration curve for the 2 : 2 inclusion complex, in which K_2 is assumed to be

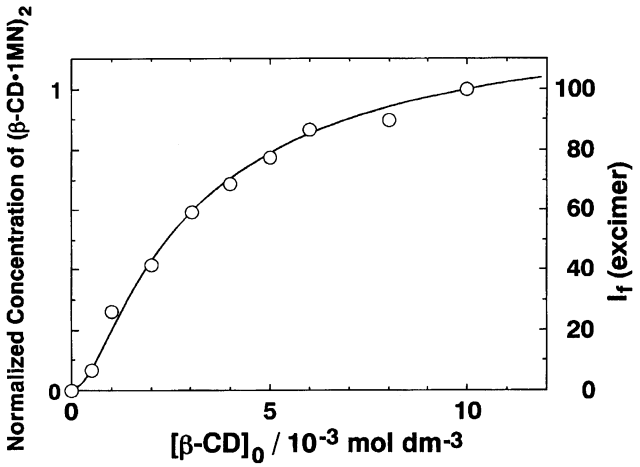

Fig. 5. Comparison between the best fit curve for the concentration of the 2 : 2 inclusion complex and the observed excimer fluorescence intensities (○). The best fit curve was calculated with the evaluated K_1 value of 340 mol^{-1} dm^3 and an assumed K_2 value of 5830 mol^{-1} dm^3. The simulated curve and the observed excimer fluorescence intensities were normalized to unity and 100 at a β-CD concentration of 1.0×10^{-2} mol dm^{-3}, respectively.

Table 1. Equilibrium Constants for the Formation of Inclusion Complexes in Aqueous Solutions at 25 °C

Host	Guest	K_1/mol^{-1} dm^3	K_2/mol^{-1} dm^3	K[a]/mol^{-3} dm^9
β-CD	Naphthalene[b]	685	4000	1.9×10^9
β-CD	1-Methylnaphthalene[c]	340±40	5820	6.7×10^8
β-CD	1-Ethylnaphthalene[c]	630±70	—	—
β-CD	1-(Chloromethyl)naphthalene[c]	190±40	—	—
β-CD	1-Cyanonaphthalene[d]	120±10	70000	1.0×10^9
β-CD	2-Methylnaphthalene[e]	1190±40	1400	1.98×10^9
β-CD	2-Ethylnaphthalene[c]	2000±200	3370	1.35×10^{10}
β-CD	Sodium 2-naphthalenesulfonate[f]	340	150	1.7×10^7
β-CD	Sodium 2-anthracenesulfonate[f]	4800	76	1.8×10^9
γ-CD	2-Methylnaphthalene[e]	9±3	3.38×10^6	2.7×10^8
γ-CD	Pyrene[g]	300	1.3×10^6	1.2×10^{11}
γ-CD	Sodium 1-pyrenebutyrate[h]	1280	5.2×10^4	8.5×10^{10}
γ-CD	Sodium 1-pyrenesulfonate[h]	ca. 130	ca. 1×10^6	ca. 2×10^{10}

a) K is the equilibrium constant for the formation of a 2:2 inclusion complex from two host and two guest molecules; $K=K_1{}^2K_2$. b) Ref. 3. c) This work. d) Ref. 6. e) Ref. 8. f) Ref. 5. g) Ref. 11. h) Ref. 9.

5830 mol^{-1} dm^3, together with the observed excimer fluorescence intensities. The simulation curve for the concentration of the 2:2 inclusion complex fits the observed excimer fluorescence intensities excellently, evidently indicating that the 2:2 β-CD–1MN inclusion complex is responsible for the excimer fluorescence of 1-methylnaphthalene. The estimated K_2 value of 5830 mol^{-1} dm^3 is close to that (4000 mol^{-1} dm^3) for naphthalene, but is greater than that for 2-methylnaphthalene (1400 mol^{-1} dm^3) and one order of magnitude less than that for 1-cyanonaphthalene (70000 mol^{-1} dm^3) (Table 1).[3,6,8]

On the other hand, the concentration of the 1:2 β-CD–1MN inclusion complex is expressed by

$$[\beta\text{-CD}\cdot(1\text{MN})_2] = ([1\text{MN}]_0 - [1\text{MN}] - [\beta\text{-CD}\cdot1\text{MN}])/2. \quad (8)$$

$$2K_1K_2'[\beta\text{-CD}]_0^2[1\text{MN}]^2+(1+K_1[\beta\text{-CD}]_0)[1\text{MN}]-[1\text{MN}]_0=0. \quad (9)$$

To further confirm the excimer-emitting species being the 2:2 inclusion complex, we next simulated the concentration curves of the 1:2 inclusion complex as a function of β-CD concentration. The calculated concentration curves of the 1:2 inclusion complex are shown along with the observed excimer fluorescence intensities (Fig. 6). As seen from Fig. 6, the simulation curves never fit the observed intensity data even when the value of K_2' is widely varied from 1×10^2 to 1×10^7 mol^{-1} dm^3. This result provides additional evidence that the 1-methylnaphthalene excimer fluorescence is not due to the 1:2 β-CD–1MN inclusion complex but is due to the 2:2 β-CD–1MN inclusion complex.

The formation of a 2:2 β-CD–1-methylnaphthalene inclusion complex is in sharp contrast to the results for sodium 1-naphthalenesulfonate and sodium 1-anthracenesulfonate, for which 2:2 inclusion complexes with β-CD are not formed.[5] In the inclusion complexation with β-CD, it is expected that a methyl group can be incorporated into the cavity while a hydrophilic sulfonato group is not bound to the cavity but protrudes into the bulk water. Consequently, the lack of reports of a 2:2 inclusion complex for the aromatics with a sulfonato group is likely due to the steric obstruction of a protruding sulfonato group on the aromatics contained in the 1:1 inclusion complex as well as the bulkiness of a sulfonato group.

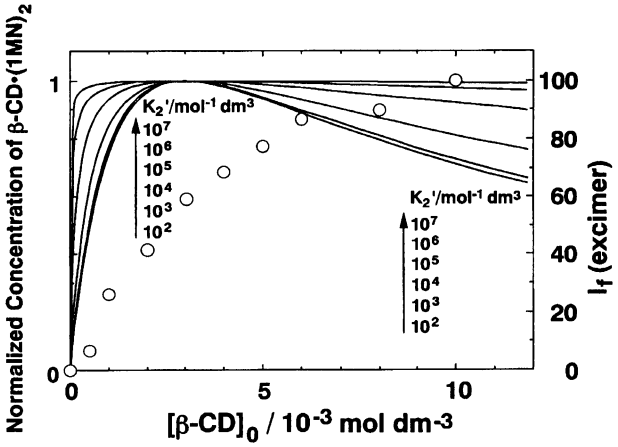

Fig. 6. Comparison between the concentration curves calculated for the 1:2 β-CD–1MN inclusion complex and the observed excimer fluorescence intensities (○). The concentration curves were calculated with the evaluated K_1 value of 340 mol^{-1} dm^3 and assumed K_2' values from 1.0×10^2 to 1.0×10^7 mol^{-1} dm^3.

There is another method for identifying an excimer-emitting species.[8,11] Above the pK_a value of the secondary hydroxy group of β-CD, a 2:2 inclusion complex dissociates to two 1:1 inclusion complexes because of the electrostatic repulsion between negative charges on the secondary hydroxy groups of associating β-CDs. Consequently, a drastic decrease in the excimer fluorescence intensity is expected above the pK_a value when an excimer-emitting species is truly a 2:2 inclusion complex. On the other hand, if a 1:2 β-CD–1MN inclusion complex is an excimer-emitting species, there is little or no pH dependence of the excimer fluorescence intensity. We, thus, attempted to examine the pH dependence of the excimer fluorescence intensity of 1-methylnaphthalene in β-CD (1.0×10^{-2} mol dm^{-3}) solution. However, in alkaline β-CD solutions of 1-methylnaphtha-

lene, a new, broad absorption band overlapped the absorption around 260 nm, so that a reliable titration curve could not be obtained with respect to the excimer fluorescence intensity. Nonetheless, the excimer fluorescence intensity of 1-methylnaphthalene was considerably reduced above about pH 10.5. This finding supports our conclusion that the excimer fluorescence is due to the 2 : 2 inclusion complex.

It should be noted that in spite of the existence of the 2 : 2 inclusion complex, the isosbestic points are observed in the absorption spectra (Fig. 1) of 1-methylnaphthalene. This result for 1-methylnaphthalene is in contrast to the results for 2-methylnaphthalene and naphthalene.[3,8] The observation of the isosbestic points implies that in the electronic ground state of 1-methylnaphthalene, there are few intermolecular interactions between two 1-methylnaphthalene molecules within the β-CD cavities.

Inclusion of 1-Ethylnaphthalene by β-CD. Figure 7 illustrates absorption spectra of 1-ethylnaphthalene (6.3×10^{-5} mol dm^{-3}) in aqueous solutions containing various concentrations of β-CD. When the β-CD concentration is increased, absorption maxima are shifted to longer wavelengths, with an enhancement of the absorbance. Unlike 1-methylnaphthalene, isosbestic points are not observed in the absorption spectra, suggesting the existence of at least two kinds of inclusion complexes. Fluorescence spectra of 1-ethylnaphthalene (6.3×10^{-5} mol dm^{-3}) in aqueous solutions in the absence and presence of β-CD are shown in Fig. 8. Upon adding β-CD, the monomer fluorescence of 1-ethylnaphthalene is enhanced in intensity, with slight red shifts of fluorescence peaks. However, the excimer fluorescence of 1-ethylnaphthalene is not observed as shown in Fig. 8. This emission behavior for the concentrated solutions of 1-ethylnaphthalene is similar to that for dilute solutions of 1-ethylnaphthalene. The results obtained from the absorption and fluorescence spectral changes suggest that, although a 2 : 2 β-CD–1-ethylnaphthalene inclusion complex is formed,

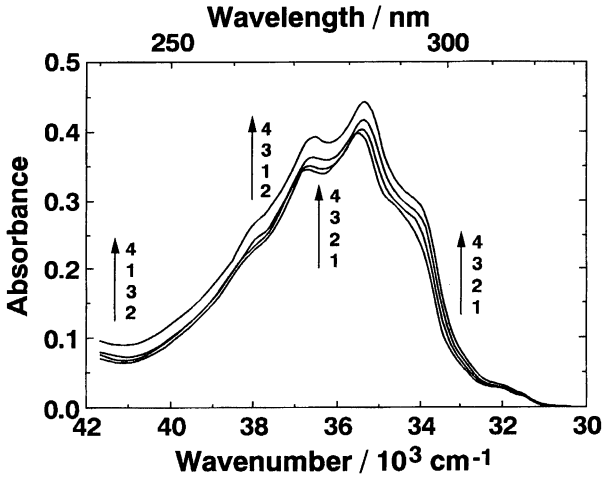

Fig. 7. Absorption spectra of 1-ethylnaphthalene (6.3×10^{-5} mol dm^{-3}) in aqueous solutions containing various concentrations of β-CD. Concentration of β-CD: (1) 0, (2) 1.0×10^{-3}, (3) 3.0×10^{-3}, and (4) 1.0×10^{-2} mol dm^{-3}.

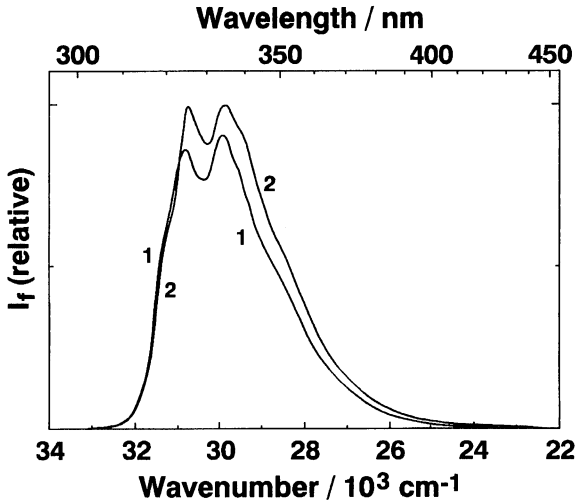

Fig. 8. Fluorescence spectra of 1- ethylnaphthalene (6.3×10^{-5} mol dm^{-3}) in aqueous solutions in the absence (spectrum 1) and presence (spectrum 2) of β-CD (1.0×10^{-2} mol dm^{-3}). λ_{ex}=270 nm.

the 1-ethylnaphthalene excimer is not produced within the narrow β-CD cavities. Because of the restricted motions of 1-ethylnaphthalene molecules carrying a bulky substituent, they cannot adopt a sandwich-type orientation within the β-CD cavities. In contrast to 1-methylnaphthalene, in the electronic ground state of 1-ethylnaphthalene, there are some intermolecular interactions between two 1-ethylnaphthalene molecules within the β-CD cavities as seen from Fig. 7, although an ethyl substituent is much bulkier than a methyl substituent. The intermolecular interactions between two 1-ethylnaphthalene molecules in the ground state may be due to a partial overlap of two naphthalene rings.

The lack of appearance of isosbestic points shown in Fig. 7, however, may suggest that a 1 : 2 β-CD–1-ethylnaphthalene inclusion complex rather than the 2 : 2 inclusion complex is formed in the concentrated 1-ethylnaphthalene solutions. If the 1 : 2 inclusion complex is formed, the freedom of 1-ethylnaphthalene molecules in a single β-CD cavity is much greater than that in two associating β-CD cavities of the 2 : 2 inclusion complex. Consequently, it is expected that the excimer fluorescence is observed from the 1 : 2 inclusion complex. In the case of 2-methylnaphthalene, even γ-CD whose cavity is greater than that of β-CD prefer the formation of the 2 : 2 inclusion complex rather than the 1 : 2 inclusion complex.[8] As stated previously, therefore, it is likely that the 2 : 2 β-CD–1-ethylnaphthalene inclusion complex is formed in concentrated 1-ethylnaphthalene solutions containing β-CD.

In dilute solutions of 1-ethylnaphthalene, only a 1 : 1 inclusion complex is most likely to exist as an inclusion complex. From a double-reciprocal plot based on Eq. 2, a K_1 value for 1-ethylnaphthalene has been estimated to be 630±70 mol^{-1} dm^3 (not shown), which is about twice as large as K_1 (340±40 mol^{-1} dm^3) for 1-methylnaphthalene. If a naphthalene moiety of 1-ethylnaphthalene is a binding site for the inclusion complexation by β-CD, a similar or smaller

K_I value is expected for 1-ethylnaphthalene compared to 1-methylnaphthalene because an ethyl group bulkier than a methyl group severely obstructs the accommodation of 1-ethylnaphthalene by β-CD. This is not true for the K_I of 1-ethylnaphthalene. Consequently, the naphthalene ring in 1-ethylnaphthalene is unlikely to be a binding site for a 1 : 1 inclusion complex between β-CD and 1-ethylnaphthalene; 1-ethylnaphthalene seems to be incorporated into the β-CD cavity from the ethyl substituent.

Inclusion of 1-(Chloromethyl)naphthalene by β-CD. Figure 9 shows absorption spectra of 1-(chloromethyl)naphthalene (1.0×10^{-4} mol dm^{-3}) in aqueous solutions containing various concentrations of β-CD. When the β-CD concentration is increased, the absorption peaks are red-shifted, with an isosbestic point of 267.5 nm, indicating the formation of an inclusion complex between β-CD and 1-(chloromethyl)naphthalene. Upon the addition of β-CD to a 1-(chloromethyl)naphthalene (1.0×10^{-4} mol dm^{-3}) solution, the monomer fluorescence intensity of 1-(chloromethyl)naphthalene was enhanced without an appearance of the excimer fluorescence (not shown). These findings may suggest that a 1 : 1 inclusion complex alone is formed. As in the case of 1-methylnaphthalene, however, the appearance of the isosbestic point does not directly lead to the formation of only one kind of inclusion complex. Consequently, the other possible explanation is that the 1-(chloromethyl)naphthalene excimer cannot be produced within a 2 : 2 inclusion complex owing to the steric hindrance of a chloromethyl group if a 2 : 2 inclusion complex is formed.

In a dilute solution (1.1×10^{-5} mol dm^{-3}) of 1-(chloromethyl)naphthalene, a 1 : 1 β-CD–1-(chloromethyl)naphthalene inclusion complex alone is most likely formed. Thus, from the fluorescence intensity changes for dilute solutions of 1-(chloromethyl)naphthalene by the addition of β-CD, K_I was estimated to be 190±40 mol^{-1} dm^3, which is about half of that (340±40 mol^{-1} dm^3) for 1-methylnaphthalene. Taking into account the fact that a chloromethyl group exerts a profound steric hindrance effect on the binding of a guest to the β-CD cavity compared to a methyl group, this finding implies that 1-(chloromethyl)naphthalene molecule is bound into the β-CD cavity from a naphthalene ring first.

Inclusion of 2-Ethylnaphthalene by β-CD. 2-Methylnaphthalene has already been found to emit the excimer fluorescence in aqueous β-CD solutions.[8] For comparison with 1-alkylnaphthalenes, we thus investigated the spectroscopic behavior of 2-ethylnaphthalene in aqueous β-CD solutions. Figure 10 illustrates absorption spectra of 2-ethylnaphthalene (4.2×10^{-5} mol dm^{-3}) in aqueous solutions containing various amounts of β-CD. In the low β-CD concentration range below approximately 1.0×10^{-3} mol dm^{-3}, absorption peaks are red-shifted upon the addition of β-CD, accompanied by an isosbestic point of 274 nm, indicating the formation of a 1 : 1 β-CD–2-ethylnaphthalene inclusion complex. When β-CD is further added, absorption peaks are further red-shifted with an enhancement of absorbance in the entire wavelength range examined. This finding indicates the existence of an inclusion complex other than the 1 : 1 inclusion complex. Figure 11 shows fluorescence spectra of 2-ethylnaphthalene (4.6×10^{-5} mol dm^{-3}) in aqueous solutions containing various concentrations of β-CD. As the β-CD concentration is increased, the vibronic bands of the 2-ethylnaphthalene monomer fluorescence is sharpened with a remarkable increase in the monomer fluorescence intensity. At the same time, a broad, structureless emission assignable to the 2-ethylnaphthalene excimer fluorescence appears at around 410 nm. Like 1-methylnaphthalene, upon the dilution of the 2-ethylnaphthalene concentration to about 1/10 (4.2×10^{-6} mol dm^{-3}), the excimer fluorescence of 2-ethylnaphthalene could not be detected. Thus, using the dilute solutions of 2-ethylnaphthalene, the K_I for 2-ethylnaphthalene was determined to be 2000±200 mol^{-1} dm^3 from the fluorescence intensity change with the β-CD concentration. This K_I value

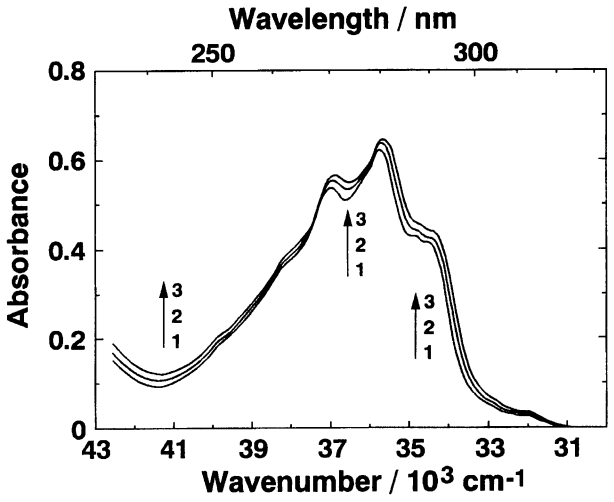

Fig. 9. Absorption spectra of 1-(chloromethyl)naphthalene (1.0×10^{-4} mol dm^{-3}) in aqueous solutions containing various concentrations of β-CD. Concentration of β-CD: (1) 0, (2) 3.0×10^{-3}, and (3) 1.0×10^{-2} mol dm^{-3}.

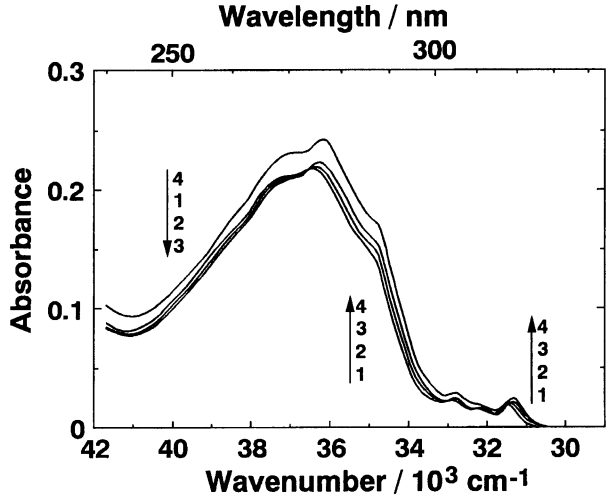

Fig. 10. Absorption spectra of 2- ethylnaphthalene (4.2×10^{-5} mol dm^{-3}) in aqueous solutions containing various concentrations of β-CD. Concentration of β-CD: (1) 0, (2) 3.0×10^{-4}, (3) 1.0×10^{-3}, and (4) 5.0×10^{-3} mol dm^{-3}.

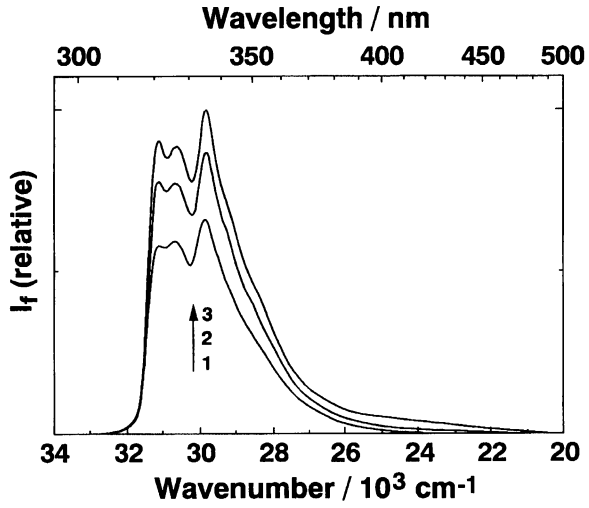

Fig. 11. Fluorescence spectra of 2- ethylnaphthalene (4.6×10^{-5} mol dm^{-3}) in aqueous solutions containing various concentrations of β-CD. Concentration of β-CD: (1) 0, (2) 3.0×10^{-4}, and (3) 5.0×10^{-3} mol dm^{-3}. $\lambda_{ex}=290$ nm.

is about 1.7 times greater than that for 2-methylnaphthalene, indicating the strong hydrophobicity compared to 2-methylnaphthalene.

The simulation methods used for the analysis of an excimer-emitting species in the β-CD–1-methylnaphthalene system were applied for the identification of an excimer-emitting species existing in the β-CD–2-ethylnaphthalene system. When K_2 was assumed to be 3370 mol^{-1} dm^3, the concentration curve simulated for a 2 : 2 β-CD–2-ethylnaphthalene inclusion complex best fitted the observed excimer fluorescence intensities (not shown), indicating that a 2 : 2 inclusion complex is responsible for the 2-ethylnaphthalene excimer fluorescence. This K_2 value is comparable to that for naphthalene (4000 mol^{-1} dm^3) but greater than that for 2-methylnaphthalene (1400 mol^{-1} dm^3). On the other hand, simulation curves for a 1 : 2 β-CD–2-ethylnaphthalene inclusion complex could not reproduce the observed excimer fluorescence intensities. This finding provides additional evidence for the existence of the 2 : 2 inclusion complex which emits the excimer fluorescence.

Self-Association of 1 : 1 Inclusion Complexes in Aqueous Solutions. Table 1 summarizes K_1, K_2, and equilibrium constants (K) for the formation of a 2 : 2 inclusion complex from two β-CD molecules and two guest molecules, together with literature data for these equilibrium constants of other guests. In Table 1 also shown are those reported for γ-CD. According to the relationships among the equilibria for the inclusion complex formation, K is expressed by $K_1{}^2K_2$. In the complexation with β-CD, K for 2-methylnaphthalene is 1.98×10^9 mol^{-3} dm^9, which is nearly the same as that for naphthalene, suggesting that the substitution of a methyl group on the 2-position of a naphthalene ring has little or no effect on K. On the other hand, K for 2-ethylnaphthalene is one order of magnitude greater than that for naphthalene, indicating the significant promotion of the formation of a 2 : 2 inclusion complex. This result is due probably to the extension of the molecular length of a guest; a hydrophobic moiety, of a guest, protruding from the β-CD cavity in a 1 : 1 inclusion complex effectively facilitates the binding with the β-CD cavity of another 1 : 1 inclusion complex. Upon substitution of a cyano or methyl group on the 1-position of a naphthalene ring, K is about 2- or 3-fold less than that for parent naphthalene, indicating that the substituent on the 1-position diminishes K owing to the steric hindrance of the substituent.

In the case of γ-CD, K_2 values are three orders of magnitude greater than those for β-CD, except for the β-CD–1-cyanonaphthalene and γ-CD–sodium 1-pyrenebutyrate systems. This result implies that, irrespective of dimensions of a guest, 1 : 1 γ-CD inclusion complexes considerably prefer the self-association compared to 1 : 1 β-CD inclusion complexes. In addition, except for 2-methylnaphthalene and sodium 1-pyrenesulfonate, the K values for γ-CD are on the order of 10^{11} mol^{-3} dm^9, which is two orders of magnitude greater than those (e. g., 1.9×10^9 mol^{-1} dm^3 for naphthalene) for β-CD except for the β-CD–2-ethylnaphthalene and β-CD–sodium 2-naphthalenesulfonate systems. Although there is a trend that the formation of a 2 : 2 inclusion complex of γ-CD is promoted to a great extent compared to β-CD, K is dependent on the kind of guest molecule as well as CD. From a binding point of view of two CD molecules, two guest molecules within the two CD cavities act as "non-covalent molecular adhesive" in constructing a supramolecular structure of CD.

In aqueous solutions without a guest, the existence of an α-CD or γ-CD dimer has been suggested from studies on activity coefficients of CDs.[18] A self-aggregation of CD has also been pointed out from a series of light-scattering experiments.[19] Aggregate sizes of α-, β-, and γ-CDs have been estimated to be 200—210 nm at 25 g dm^{-3} of CDs. In our studies, however, dimerization of 1 : 1 inclusion complexes shows different features depending on the respective characters of CD; two orders of magnitude greater K values and three orders of magnitude greater K_2 values are obtained for γ-CD compared to β-CD, although there are some exceptions. In addition, there is no example for the excimer formation in solutions with α-CD, although an inclusion mode of α-CD toward guests may be different from those of other CDs. Therefore, self-association of 1 : 1 inclusion complexes seems to be different from the reported dimer formation and aggregation of CDs themselves.

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