

THREE-COMPONENT COMPLEXES OF CYCLODEXTRINS. EXCIPILEX FORMATION IN CYCLODEXTRIN CAVITY

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ABSTRACT. The fluorescence quenching of naphthalene, 1-methylnaphthalene, and acenaphthene by trimethylamine (TMA) was studied in aqueous  $\beta$ -cyclodextrin ( $\beta$ -CD) solutions to know the structural requirements for guest molecules to form three-component complexes. The apparent rates for the fluorescence quenching of the naphthalene derivatives by TMA markedly increased in the presence of  $\beta$ -CD. The fluorescence quenching of 1-methylnaphthalene and acenaphthene by TMA was accelerated by  $\beta$ -CD more efficiently than that of naphthalene. These results suggest the structures of the three-component complexes as the arene-capped  $\beta$ -CD including TMA in its cavity.

## 1. INTRODUCTION

In order to develop catalytic effects of cyclodextrins for bimolecular reactions, it needs to include two guest molecules simultaneously in a cyclodextrin (CD) cavity. Several examples of cyclodextrin-catalyzed bimolecular reactions have been reported. Rideout and Breslow have found that Diels-Alder reactions of cyclopentadiene with butenone, cyclopentadiene with acrylonitrile, and anthracene-9-carbinol with N-ethylmaleimide in water are markedly accelerated by  $\beta$ -cyclodextrin ( $\beta$ -CD) (1). Komiyama and Hirai have reported site-selective Reimer-Tiemann reactions of phenols in cyclodextrin solutions (2). In most of these reactions, however, each substrate molecule is relatively small so that a  $\beta$ -CD cavity may include simultaneously an additional reactant molecules. We found previously that the fluorescence quenching of pyrene and naphthalene by trimethylamine (TMA) or dimethylamine (DMA) in water is catalyzed by  $\beta$ -CD (3). Since the pyrene molecule is too large to be incorporated completely in the  $\beta$ -CD cavity, it has been assumed that pyrene binds to a rim of the CD cavity to form a pyrene-capped CD complex and a remain-

ing space in the cavity of the complex is occupied by TMA or DMA (3).

The fluorescence quenching can be regarded as a probe reaction for investigating the effects of CD on bimolecular reactions. Especially, the structural requirements for guest molecules to form three-component complex can be studied by this method. Formation of three-component complexes is essentially important to realize CD-catalyzed bimolecular reactions. In the present work, we studied the fluorescence quenching of naphthalene, 1-methylnaphthalene, and acenaphthene by TMA in aqueous  $\beta$ -CD solutions to clarify the steric factors affecting the formation of the three-component complexes.

## 2. MATERIALS AND METHODS

### 2.1. Materials

$\beta$ -CD (Nakarai) was purchased and used without purification because unknown fluorescent species was produced during recrystallization from aqueous 2-propanol. Sodium salt of sulfopropylated  $\beta$ -CD was prepared by a method reported by Lammers et al. (4). A mixture of 12 g of  $\beta$ -CD and 7.2 g of NaOH in 15 ml of water in a flask was stirred and added dropwise to 3.08 g of molten propanesultone during 3 h under a nitrogen atmosphere at 30°C. The reaction mixture was neutralized by HCl to pH 9 and added to methanol. The colorless precipitates were collected and washed by acetone. After drying under vacuum at 80°C, the product was analyzed by  $^1\text{H-NMR}$  and elemental analysis. The average number of the sulfopropyl groups introduced to  $\beta$ -CD was 2. The position of sulfopropyl groups in  $\beta$ -CD have not been determined in this study. We use an abbreviation,  $\beta$ -CD-2, for this compound. Naphthalene and 1-methylnaphthalene were purified by sublimation and vacuum distillation, respectively. Reagent grade acenaphthene (Nakarai) was used without further purification after the purity was checked by its melting point. Concentration of TMA (Nakarai) in water was determined by pH titration. Water was deionized by passing through an ion exchange resin column and distilled.

### 2.2. Methods

The fluorescence quenching experiments were carried out according to the following procedures. The stock solution of naphthalene derivative in methanol ( $1 \times 10^{-3}$  M) was injected to the  $1 \times 10^{-3}$  M aqueous  $\beta$ -CD solution to adjust  $[\text{naphthalene derivative}] = 1 \times 10^{-5}$  M. An appropriate amount of TMA was added and the sample solution was shaken gently before fluorescence spectral measurement. Since the fluorescence intensities of naphthalene derivatives gradually decreased upon aging and no reproducible result was obtained, the fluorescence spectrum of each solution was measured immediately after the preparation of sample by using a Hitachi 650-60 spectrofluorimeter. The

fluorescence lifetimes of the naphthalene derivatives were determined by an Ortec-PRA single-photon-counting apparatus.

All measurements were carried out under aerobic conditions at 25°C.

### 3. RESULTS

#### 3.1. Binding Constants of Naphthalenes with $\beta$ -CD and $\beta$ -CD-2

The binding constants ( $K$ ) of naphthalene, 1-methylnaphthalene, and acenaphthene with  $\beta$ -CD and  $\beta$ -CD-2 were determined by Benesi-Hildebrand plots for fluorescence intensities (5):

$$\Delta F^{-1} = (\alpha [N]_0 K [CD]_0)^{-1} + (\alpha [N]_0)^{-1} \quad (1)$$

where  $\Delta F$  is the change of fluorescence intensity upon addition of CD,  $[N]_0$  and  $[CD]_0$  are the initial concentrations of naphthalenes and CD, respectively, and  $\alpha$  is the proportionality constant. The  $K$  values of naphthalene, 1-methylnaphthalene, and acenaphthene with  $\beta$ -CD were  $730 \pm 10$ ,  $570 \pm 30$ , and  $260 \pm 50 \text{ M}^{-1}$ , respectively. The  $K$  values for  $\beta$ -CD-2 were  $1100 \pm 100 \text{ M}^{-1}$  for naphthalene and ca.  $300 \text{ M}^{-1}$  for 1-methylnaphthalene. The  $K$  value for the naphthalene- $\beta$ -CD system ( $730 \text{ M}^{-1}$ ) is in good agreement with the reported value ( $685 \text{ M}^{-1}$ ) (5c).

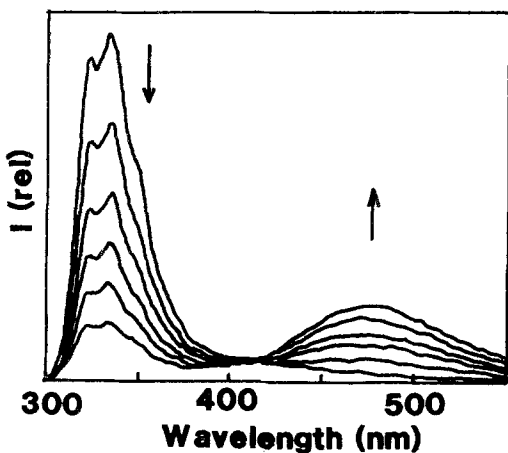


Fig. 1. Fluorescence spectral changes of naphthalene ( $1 \times 10^{-5} \text{ M}$ ) in aqueous  $\beta$ -CD ( $1 \times 10^{-2} \text{ M}$ ) solution upon addition of TMA. Naphthalene was excited at 282 nm.  $[TMA] = (0, 0.49, 0.97, 1.5, 2.0, \text{ and } 2.9) \times 10^{-2} \text{ M}$ .

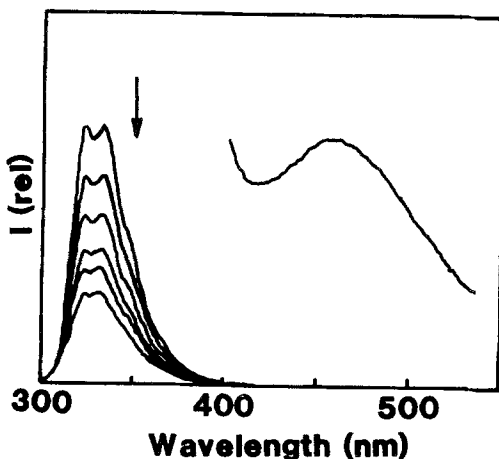


Fig. 2. Fluorescence spectral changes of naphthalene ( $1 \times 10^{-5} \text{ M}$ ) in aqueous  $\beta$ -CD ( $1 \times 10^{-3} \text{ M}$ ) solution upon addition of TMA. Naphthalene was excited at 277 nm.  $[TMA] = (0, 0.31, 0.62, 1.0, 1.6, \text{ and } 2.1) \times 10^{-2} \text{ M}$ .

### 3.2. Exciplex Emissions in CD Solutions

TMA quenched the naphthalene fluorescence in water with the quenching rate constant ( $k_q$ ) of  $1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ . Of course, no exciplex emission was observed in the aqueous solution. In the presence of  $1 \times 10^{-2} \text{ M}$   $\beta$ -CD, however, the exciplex emission having a maximum intensity at 477 nm was clearly observed as shown in Fig. 1. Virtually the same results were obtained for the 1-methylnaphthalene-TMA system. Since the  $\beta$ -CD-1-methylnaphthalene complex precipitated in the  $1 \times 10^{-2} \text{ M}$   $\beta$ -CD solution,  $\beta$ -CD-2 was used in place of  $\beta$ -CD. The  $k_q$  value was  $6.2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$  and no exciplex emission was observed in the aqueous solution without  $\beta$ -CD-2. In the presence of  $\beta$ -CD-2 ( $1 \times 10^{-2} \text{ M}$ ), a broad exciplex emission having a  $\lambda_{\text{max}}$  at 473 nm was measured. A relatively weak fluorescence band of exciplex of acenaphthene and TMA was observed at around 450 nm in the  $1.0 \times 10^{-2} \text{ M}$   $\beta$ -CD solution.

The effect of the CD concentration on the exciplex emission was remarkable. The fluorescence spectral change of naphthalene in the aqueous  $1 \times 10^{-3} \text{ M}$   $\beta$ -CD upon addition of TMA is shown in Fig. 2 as an example. Reduction of the  $\beta$ -CD concentration caused the marked decrease in the fluorescence intensity of the exciplex. The same result was obtained for the 1-methylnaphthalene- $\beta$ -CD-2 system.

In all cases, very weak exciplex emissions were observed even in the  $1 \times 10^{-3} \text{ M}$   $\beta$ -CD solutions.

### 3.3. Fluorescence Quenching

In homogeneous fluid solution, a Stern-Volmer equation (eq 2) can be applied to fluorescence quenching:

$$I_0/I = \tau_0/\tau = 1 + K_{\text{SV}}[Q] = 1 + k_q\tau_0[Q] \quad (2)$$

where  $I_0$  and  $I$  are the fluorescence intensities in the absence and in presence of quencher (Q), respectively,  $\tau_0$  and  $\tau$  are the fluorescence lifetimes in the absence and in presence of Q, respectively,  $K_{\text{SV}}$  is the Stern-Volmer constant, and  $k_q$  is the rate constant for fluorescence quenching.

In a homogeneous aqueous solution, the Stern-Volmer equation could be applied to the fluorescence quenching of the naphthalene derivatives ( $1 \times 10^{-5} \text{ M}$ ) by TMA; i.e., the  $K_{\text{SV}}$  values from the fluorescence intensities were in good agreement with those from the fluorescence lifetimes. The determined  $k_q$  value for each system is shown in Table I along with the fluorescence lifetime in the absence of quencher. In the presence of  $1 \times 10^{-3} \text{ M}$   $\beta$ -CD, however, the simple Stern-Volmer relationship expressed by eq 2 is not valid for the fluorescence quenching of naphthalene ( $1 \times 10^{-5} \text{ M}$ ) by TMA as shown in Fig. 3. Namely, the  $I_0/I$  value at a given [TMA] was much larger than the  $\tau_0/\tau$  value, which indicates clearly that the static quenching competes with the dynamic quenching. The apparent  $k_q$  value ( $k_{\text{app}}$ ) was determined from the plot of  $I_0/I$  vs. [TMA] as  $1.7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  which is much larger than the  $k_q$  value for the fluorescence quenching in the absence

of  $\beta$ -CD ( $k_q = 1.0 \times 10^{-8} \text{ M}^{-1} \text{ s}^{-1}$ ). The rate constant for the dynamic fluorescence quenching ( $k_{\text{dyn}}$ ) can be evaluated from the plot of  $\tau_0/\tau$  vs. [TMA]. The  $k_{\text{dyn}}$  thus determined was  $9.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  which was significantly larger than the  $k_q$  value for the reaction in the bulk water ( $k_q = 1.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>4</sup> Virtually the same results were obtained for the fluorescence quenching of 1-methylnaphthalene and acenaphthene and the results are summarized in Table I.

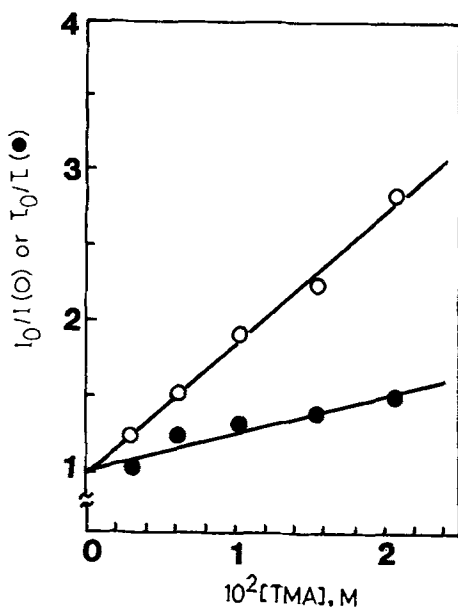


Fig. 3. Plots of  $I_0/I$  and  $\tau_0/\tau$  vs. [TMA] for the naphthalene- $\beta$ -CD system. [Naphthalene] =  $1 \times 10^{-5} \text{ M}$  and [ $\beta$ -CD] =  $1 \times 10^{-3} \text{ M}$ .

TABLE I. Effects of  $\beta$ -CD and  $\beta$ -CD-2 ( $1 \times 10^{-3} \text{ M}$ ) on the Fluorescence Quenching of Naphthalene, 1-Methylnaphthalene, and Acenaphthene ( $1 \times 10^{-5} \text{ M}$ ) by TMA in Water at  $25^\circ \text{C}$

Fluorescer	CD	$\tau_0$ (ns)	$10^{-9}k_{\text{app}}$ ( $\text{M}^{-1}\text{s}^{-1}$ )	$10^{-9}k_{\text{dyn}}$ ( $\text{M}^{-1}\text{s}^{-1}$ )	$k_{\text{app}}^{\text{CD}}/k_{\text{app}}^{\text{H}_2\text{O}}$
Naphthalene		30.1	0.10	0.10	1
	$\beta$ -CD	47.8	1.7	0.56	17
	$\beta$ -CD-2	46.5	1.3	0.34	13
1-Methylnaphthalene		27.6	0.062	0.062	1
	$\beta$ -CD	35.3	9.1	0.45	147
	$\beta$ -CD-2	36.3	5.0	0.23	81
Acenaphthene		24.0	0.029	0.029	1
	$\beta$ -CD	26.0	28	0.62	966

### 3.4. Effects of CD Concentrations on Fluorescence Quenching

In a previous paper (3b), we reported the effect of  $\beta$ -CD ( $1 \times 10^{-2}$  M) on the fluorescence quenching of naphthalene by TMA. The reported  $k_{app}$  value for the  $1 \times 10^{-2}$  M  $\beta$ -CD solution is  $4.06 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  which is larger than  $k_{app}$  obtained in the present study where  $[\beta\text{-CD}]_0$  is  $1 \times 10^{-3}$  M. Then we reexamined the fluorescence quenching of naphthalene by TMA in the  $1 \times 10^{-2}$  M  $\beta$ -CD solution. Although the reproducibility was somewhat poor, the plot of  $I_0/I$  vs. [TMA] curved slightly upward. If the plot was approximated by a straight line, the  $k_{app}$  value was in agreement with the previous value. The repeated experiments, however, revealed that the quenching efficiency increased with increasing the TMA concentration in the case of  $1 \times 10^{-2}$  M  $\beta$ -CD solution. Similar results were obtained for the naphthalene- and 1-methylnaphthalene- $\beta$ -CD-2 systems. In the case of 1-methylnaphthalene, the complex with  $\beta$ -CD precipitated in the  $1 \times 10^{-2}$  M  $\beta$ -CD solution. The sulfopropylated  $\beta$ -CD is useful for such case.

## 4. DISCUSSION

The first step of a CD-catalyzed reaction is inclusion of substrate molecule into the CD cavity. Ester hydrolyses are typical reactions which are accelerated by CD (6). If the geometrical orientation of the complex is favorable for the attack of the hydroxide or hydroxyl groups, the ester hydrolysis may be accelerated by CD. These typical reactions require the formation of a 1:1 complex of the substrate molecule with CD. In order to use cyclodextrins more widely as catalysts for bimolecular reactions, however, it needs to include both substrate and reactant molecules in the same CD cavity. Recent studies have shown the possibility that two guest molecules are included in the same CD cavity (7-14). Except for adamantane and tropolone derivatives (13,14), most of the 2:1 complexes are formed by using  $\gamma$ -CD having larger cavity. Little has been known about the complexes which are composed of two different kinds of guest molecules and a CD. It has been reported that the intermolecular Diels-Alder reactions are accelerated by  $\beta$ -CD (1). In these reactions, diene and dienophile seem to be included simultaneously in the same  $\beta$ -CD cavity. Kobayashi et al. have found that an absorption band of the charge-transfer complex of 1-naphthylacetate and picric acid is enhanced by  $\gamma$ -CD (7c). The CD cavities are structurally rigid so that steric requirements for the guest molecules should be strict to form the three-component complex. In a previous paper, we reported the  $\beta$ -CD-enhanced fluorescence quenching of pyrene by alkylamines (3). The catalytic effect of  $\beta$ -CD is ascribed to the formation of the three-component complexes of pyrene, alkylamine, and  $\beta$ -CD. Judging from a CPK molecular model, the pyrene molecule seems to be too large to be incorporated completely into the  $\beta$ -CD cavity. We have postulated that the three-component complex is formed when one guest molecule binds shallowly to  $\beta$ -CD leading to a complex whose cavity still has a space to include an additional guest molecule. In the present study, we tried to con-

firm this assumption. Naphthalene has a size of  $8.5 \text{ \AA} \times 6.8 \text{ \AA}$  and is expected to be included in the  $\beta$ -CD cavity whose inner diameter is ca.  $7 \text{ \AA}$ . Meanwhile, 1-methylnaphthalene has a size of  $8.5 \text{ \AA} \times 7.6 \text{ \AA}$  and may bind shallowly to  $\beta$ -CD. Acenaphthene will bind more shallowly than 1-methylnaphthalene. We studied how the difference in the structures between these naphthalene derivatives affects the fluorescence quenching of these fluorescers by TMA in  $\beta$ -CD solutions.

At first, the binding constants of the naphthalene derivatives with  $\beta$ -CD and  $\beta$ -CD-2 were determined from the Benesi-Hildebrand plots for fluorescence intensities. Except for the naphthalene- $\beta$ -CD system, the reproducibility was considerably poor. Especially, it was very difficult to determine the  $K$  values of the naphthalenes with  $\beta$ -CD-2. For freshly prepared samples, eq 1 could be applied for determining  $K$ , suggesting the 1:1 complex formation. Both fluorescence intensities and apparent  $K$  values decreased upon aging of the CD solutions when the sample solutions were in contact with air. The self quenching was greatly accelerated by bubbling air or nitrogen gas through the sample solutions. The fluorescence of naphthalene in the  $\beta$ -CD ( $1 \times 10^{-3}$  and  $1 \times 10^{-2}$  M) solutions completely disappeared upon aeration. These results clearly indicate that the complexes of the naphthalene derivatives and  $\beta$ -CD and/or  $\beta$ -CD-2 aggregate each other at the water-air interface to form nonfluorescent species. Then the fluorescence measurements in this study were performed immediately after the sample was prepared.

The  $K$  values for the  $\beta$ -CD systems decreased in the order of naphthalene, 1-methylnaphthalene, and acenaphthene (see Results section). Shallow binding may provide smaller  $K$  value.

Addition of TMA into the naphthalene- $\beta$ -CD complex system caused the static quenching of the naphthalene fluorescence and the appearance of the exciplex emission. The progress of the static quenching was proved by the facts that the  $K_{SV}$  value obtained from the plot of  $I_0/I$  vs. [TMA] is much larger than that from the plot of  $\tau_0/\tau$  vs. [TMA] (see Fig. 3). The static quenching can occur when a ground state complex of naphthalene and TMA is formed. It is likely that both naphthalene and TMA were included in a  $\beta$ -CD cavity to form the three-component complex. In the  $1 \times 10^{-2}$  M  $\beta$ -CD solution, a considerably intense emission from the exciplex of naphthalene and TMA was observed at around  $477 \text{ nm}$  (Fig. 1). The exciplex emission decayed single-exponentially without rise, suggesting that naphthalene associates with TMA in the ground state. It is well known that the structure of the exciplex is so polar that the emission maximum of the exciplex shifts to longer wavelength with increasing solvent polarity. Indeed, we found that the wavelength of the emission maximum ( $\lambda_{\text{max}}$ ) of the naphthalene-TMA exciplex shifted from  $406 \text{ nm}$  in hexane (dielectric constant ( $\epsilon$ ) = 1.89) to  $522 \text{ nm}$  in amyl alcohol ( $\epsilon$  = 13.9). From Lippert-Mataga's equation (15,16), the dipole moment of the exciplex was determined to be  $11.5 \text{ D}$  by using an effective radius of the exciplex of  $4.0 \text{ \AA}$ . Van and Hammond reported the dipole moment of the exciplex of naphthalene and triethylamine as  $11.1 \text{ D}$  (17) which is very close to that of the naphthalene-TMA exciplex. If the 1:1:1 complex of naphthalene, TMA, and  $\beta$ -CD shows the exciplex emission, it can be concluded

that  $\beta$ -CD provides considerably less polar environment in water. The  $\lambda_{\max}$  (477 nm) of the exciplex in the  $1 \times 10^{-2}$  M  $\beta$ -CD solution suggests that the microenvironment of the  $\beta$ -CD cavity is less polar than dichloromethane ( $\lambda_{\max} = 484$  nm,  $\epsilon = 9.08$ ). It is surprising that very polar exciplex can exist in the  $\beta$ -CD cavity without interaction with surrounding water. Quite recently, Cox et al. have found the intramolecular exciplex emission of 1- $\alpha$ -naphthyl-3-(dimethylamino)propane in the aqueous  $\beta$ -CD ( $1 \times 10^{-2}$  M) solution (18). From the  $\lambda_{\max}$  (500 nm) of the intramolecular exciplex, the  $\beta$ -CD cavity where the probe molecule is located seems to have a polarity similar to that of ethanol ( $\epsilon = 24.3$ ). The fluorescence intensity of the naphthalene-TMA exciplex, however, markedly decreased in the  $1 \times 10^{-3}$  M  $\beta$ -CD solution as shown in Fig. 2. From the K value of naphthalene with  $\beta$ -CD ( $730 \text{ M}^{-1}$  at  $25^\circ\text{C}$ ), it is calculated that 89 and 42 % of the naphthalene molecules ( $1 \times 10^{-5}$  M) bind to  $\beta$ -CD in the  $1 \times 10^{-2}$  and  $1 \times 10^{-3}$  M aqueous  $\beta$ -CD solutions, respectively. The difference in the binding cannot interpret the difference in the fluorescence intensities between  $1 \times 10^{-2}$  and  $1 \times 10^{-3}$  M  $\beta$ -CD solutions. Presumably, the three-component complex of naphthalene, TMA, and  $\beta$ -CD in the  $1 \times 10^{-2}$  M  $\beta$ -CD solution associates spontaneously to form aggregates whose insides should be less polar than the cavity of  $\beta$ -CD of the 1:1:1 complex. Another possibility is the formation of a 1:1:2 complex of naphthalene-TMA- $\beta$ -CD at higher  $\beta$ -CD concentration. A very weak exciplex emission having  $\lambda_{\max}$  at 458 nm was observed even in the  $1 \times 10^{-3}$  M  $\beta$ -CD solution (Fig. 2). Although it is estimated from  $\lambda_{\max}$  that the polarity of the microenvironment is similar to that of diisopropyl ether ( $\lambda_{\max} = 457$  nm,  $\epsilon = 3.88$ ), the fluorescence intensity of the exciplex in the  $1 \times 10^{-3}$  M  $\beta$ -CD solution was much smaller than that in diisopropyl ether. These results indicate that most of the ground state complex molecules of naphthalene and TMA are located at relatively polar environment. The emission of the exciplex of naphthalene and TMA is not observed in the solvents having  $\epsilon$  above 14. The intermolecular exciplex system, therefore, does not prefer to probe the microscopic polarity of the  $\beta$ -CD cavity. Virtually the same results were obtained for the 1-methylnaphthalene and acenaphthene systems.

The fluorescence quenching of the naphthalene derivatives by TMA in water was markedly accelerated by  $\beta$ -CD (Table I). The effect of  $\beta$ -CD greatly depends on the structure of fluorescer. The apparent  $k_q$  value for naphthalene in the presence of  $1 \times 10^{-3}$  M  $\beta$ -CD was 17 times greater than that in water. The catalytic effect of  $\beta$ -CD was more remarkable in the cases of 1-methylnaphthalene and acenaphthene, the  $k_{\text{app}}^{\text{CD}}/k_{\text{app}}^{\text{H}_2\text{O}}$  being 147 for 1-methylnaphthalene and 966 for acenaphthene. It is noteworthy that the fluorescence quenching of the naphthalene derivative which forms a loose complex with  $\beta$ -CD was catalyzed more efficiently by  $\beta$ -CD, the K values for naphthalene, 1-methylnaphthalene, and acenaphthene being 730, 570, and  $260 \text{ M}^{-1}$ , respectively. The CPK molecular model suggests that the naphthalene molecule can be included completely in the  $\beta$ -CD cavity to form a tight complex whereas 1-methylnaphthalene and acenaphthene bind shallowly to  $\beta$ -CD because of the steric hindrances. Presumably, these two fluorescers occlude onto the  $\beta$ -CD cavity to form the fluorescer-capped  $\beta$ -CD complexes. The



capped  $\beta$ -CD complex still has the space where a TMA molecule is included. The three-component complex thus formed can interpret reasonably the static quenching and the difference in the catalytic effects of  $\beta$ -CD between these three naphthalene derivatives. The tight complex such as the naphthalene- $\beta$ -CD complex can hardly include an additional guest molecule.

The K values suggest that over 50% of the naphthalene derivative molecules does not bind to  $\beta$ -CD under the conditions of [naphthalene derivative] =  $1 \times 10^{-5}$  M and [ $\beta$ -CD] =  $1 \times 10^{-3}$  M, the ratios of the free molecules being 58% for naphthalene, 64% for 1-methylnaphthalene, and 79% for acenaphthene. The K value of TMA with  $\beta$ -CD has been determined as  $51 \text{ M}^{-1}$  at  $25^\circ\text{C}$  (3b), suggesting that the concentration of the TMA- $\beta$ -CD complex is  $3.3 \times 10^{-4}$  M when TMA was added into the  $1 \times 10^{-3}$  M  $\beta$ -CD solution to adjust [TMA] =  $1 \times 10^{-2}$  M. If the fluorescer molecules distribute between the  $\beta$ -CD cavities and the aqueous bulk phase, it is expected that the plot of  $I_0/I$  vs. [TMA] for each system levels off. The plot of  $I_0/I$  vs. [TMA], however, was linear till over 80% of the added fluorescer molecules was quenched. This novel phenomenon may be interpreted as that the TMA- $\beta$ -CD complex tends to bind strongly with naphthalene derivatives. Further studies need to clarify this point.

In order to use  $\beta$ -CD as a catalyst for bimolecular reactions, the formation of a three-component complex of substrate, reactant, and  $\beta$ -CD is essentially important. The present study as well as a previous one (3b) revealed the structural requirements of the guest molecules for forming a three-component complex of  $\beta$ -CD. One of the guest molecules needs to occlude onto the  $\beta$ -CD cavity to form a guest molecule-capped  $\beta$ -CD whose cavity still has a space for including an additional guest molecule. We found previously that the size of diethylamine is too large to give the static quenching of pyrene and naphthalene in the  $\beta$ -CD cavity (3b). The size of TMA is one of the standards for the guest molecule which is included in the cavity of arene-capped  $\beta$ -CD.

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