The Excimer Fluorescence of 2-Methylnaphthalene in β- and γ-Cyclodextrin Aqueous Solutions

Sanyo Hamai

Department of Chemistry, College of Education, Akita University, Tegata Gakuen-machi 1-1, Akita 010

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2-Methylnaphthalene (MN) exhibits MN excimer fluorescence in both β-cyclodextrin (β-CD) and γ-cyclodextrin (γ-CD) neutral aqueous solutions. β-CD forms a 1 : 1 inclusion complex with MN, which self-associates to form a 2 : 2 inclusion complex emitting the MN excimer fluorescence. In 0.4 mol dm^{-3} NaOH solutions, no excimer fluorescence has been observed, indicating that the 2 : 2 inclusion complex dissociates to two 1 : 1 inclusion complexes because of an electrostatic repulsion between the negatively charged hydroxy groups of the two β-CD molecules contained in the 2 : 2 inclusion complex. For the γ-CD–MN system as well as the β-CD–MN system, the excimer fluorescence can be explained in terms of the formation of a 2 : 2 inclusion complex through a self-association of 1 : 1 inclusion complexes.

Naturally occurring β- and γ-cyclodextrins (β-CD and γ-CD) are seven- and eight-membered cyclic oligosaccharides of D-glucose, which are able to accommodate a wide variety of guest molecules into their hydrophobic cavities. Due to the binding of a guest molecule to the CD cavity, the fluorescence properties of a guest are often affected; changes in fluorescence intensity, fluorescence band shape, and fluorescence lifetime, etc. are observed for CD inclusion complexes of indole derivatives,[1] naphthalene,[2] 2-methoxynaphthalene,[2] pyrene,[3—7] fluorene,[8] acenaphthene,[9] 1-cyanonaphthalene,[10] perylene,[11] azulene,[12] and 2-chloronaphthalene,[13] etc. In the systems of β-CD–naphthalene,[2] β-CD–1-cyanonaphthalene,[10] β-CD–2-chloronaphthalene,[13] β-CD–sodium 2-anthracenesulfonate,[14] γ-CD–pyrene,[3,4,7] and γ-CD–sodium 1-pyrenebutyrate,[15] excimer fluorescence of guests is observed in aqueous solutions. In these systems, the association of 1 : 1 host (β-CD or γ-CD)–guest inclusion complexes results in the formation of a 2 : 2 inclusion complex that exhibits excimer fluorescence.

The pK_a value of the secondary hydroxy groups of γ-CD is 12.1.[16,17] It is difficult for two γ-CD anions to associate together because of an electrostatic repulsion between the negatively charged, deprotonated hydroxy groups of the two γ-CD anions. When the pyrene excimer fluorescence is due to a 2 : 2 γ-CD–pyrene inclusion complex, the anionization of a neutral γ-CD molecule to a γ-CD anion is expected to induce the dissociation of a 2 : 2 inclusion complex to two 1 : 1 inclusion complexes, resulting in a disappearance of the excimer fluorescence. From the pH dependence of the pyrene excimer fluorescence intensity, a pK_a value of 12.0, which is in good agreement with the pK_a value (12.1) of the secondary hydroxy groups of γ-CD, has been obtained.[7] Therefore, the 2 : 2 γ-CD–pyrene inclusion complex has been concluded to be responsible for the pyrene excimer fluorescence. As exemplified for pyrene, γ-CD as well as β-CD can form a 2 : 2 inclusion complex.

Ueno et al. have suggested that two 1-naphthaleneacetate ions are incorporated into the cavity of a single γ-CD molecule.[18] In addition, they have investigated the intramolecular self-inclusion of guests that are grafted in a γ-CD molecule through a molecular chain.[19—21] From studies on the fluorescence properties of γ-CD derivatives bearing two 2-naphthylsulfonyl moieties, the intramolecular incorporation of two 2-naphthylsulfonyl moieties has been revealed.

The excimer fluorescence of a guest has so far been observed in aqueous solutions containing β-CD (e.g., naphthalene[2] and 1-cyanonaphthalene,[10] etc.) or γ-CD (e.g., pyrene[3,4,7]). To our knowledge, however, there has been no report that the excimer fluorescence of a guest is detected in both β-CD and γ-CD aqueous solutions. 2-Methylnaphthalene (MN) was found to exhibit excimer fluorescence in both β-CD and γ-CD aqueous solutions. We thus examined the interactions between MN and β- or γ-CD by means of absorption, fluorescence, and induced circular dichroism (icd) spectroscopies. In this paper, we report on the formation and MN excimer fluorescence of 2 : 2 host–MN inclusion complexes in β- and γ-CD aqueous solutions.

Experimental

2-Methylnaphthalene (MN) purchased from Tokyo Kasei Kogyo Co., Ltd. was purified using silica-gel column chromatography. β-CD (Nacalai Tesque, Inc.) was twice recrystallized from water. γ-CD (Nacalai Tesque, Inc.) was used as received. Aqueous solutions of MN were prepared by plunging purified MN crystals into water for several days in the dark.

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, respectively. Fluorescence spectra were corrected for the wavelength-dependent sensitivity of the detection system. Induced circular dichroism (icd) spectra were obtained with a JASCO

J-600 spectropolarimeter. Spectroscopic measurements were made at 25 °C, except for icd spectra that were taken on at room temperature.

Results and Discussion

Inclusional Complexation of 2-Methylnaphthalene with β-CD in Neutral Aqueous Solutions. Figure 1 shows absorption spectra of 2-methylnaphthalene (MN) (1.3×10^{-4} mol dm^{-3}) in aqueous solutions containing varying concentrations of β-CD. As the β-CD concentration is increased, absorption maxima are red-shifted, and the absorbances of the maxima are increased, accompanied by isosbestic points at 267, 316, and 318 nm. In the wavelength range below 250 nm, however, no isosbestic point has been observed. This finding indicates that there is an inclusion complex other than a 1 : 1 inclusion complex formed between β-CD and MN.

Figure 2 shows fluorescence spectra of MN (1.3×10^{-4} mol dm^{-3}) in aqueous solutions containing varying concentrations of β-CD. With an increase in the β-CD concentration, intensities of the monomer fluorescence bands are enhanced accompanied by a sharpening of the bands. The peak positions of the monomer fluorescence bands are unchanged by the addition of β-CD. However, the addition of β-CD results in the emergence of a broad, structureless emission at longer wavelengths (ca. 410 nm). This broad emission is assignable to the excimer fluorescence of MN. For naphthalene, the naphthalene excimer fluorescence, which is due to a 2 : 2 β-CD–naphthalene inclusion complex formed by the self-association of 1 : 1 β-CD–naphthalene inclusion complexes, is observed upon adding β-CD.[2] As in the case of naphthalene, β-CD seems to form a 1 : 1 inclusion complex with MN, followed by the formation of a 2 : 2 inclusion complex that emits MN excimer fluorescence.

When a dilute MN (1.3×10^{-5} mol dm^{-3}) solution containing β-CD was excited, no excimer fluorescence was observed (Fig. 3), suggesting that the 1 : 1 β-CD–MN inclusion complexes self-associate at a higher concentration (1.3×10^{-4} mol dm^{-3}) of MN. As shown in Fig. 3, the monomer fluorescence intensity is enhanced in the presence of β-CD. Thus, from the fluorescence intensity change by the β-CD addition we can determine an equilibrium constant (K_1(β-CD)) for the formation of a 1 : 1 β-CD–MN inclusion complex (β-CD·MN):

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

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

where I_f and I_f^0 are the fluorescence intensity in the presence and absence of β-CD, respectively, a is a constant, and [β-CD]$_0$ is the initial concentration of β-CD.[2] From a plot (Fig. 4) based on Eq. 2, a value of 1190±40 mol^{-1} dm^3

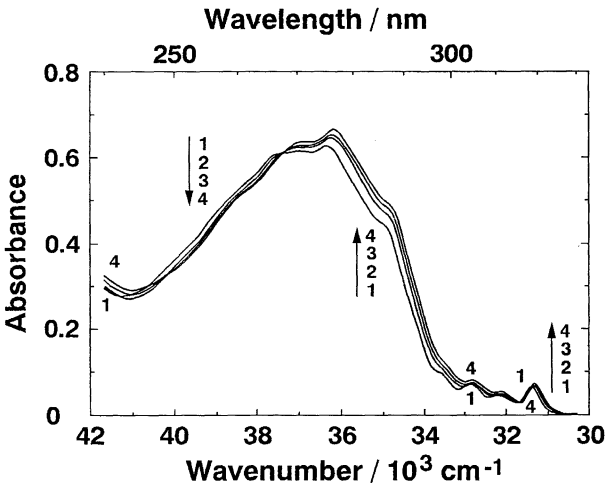

Fig. 1. Absorption spectra of MN (1.3×10^{-4} mol dm^{-3}) in aqueous solutions containing varying concentrations of β-CD. Concentration of β-CD: (1) 0, (2) 1.0×10^{-3}, (3) 3.0×10^{-3}, and (4) 1.0×10^{-2} mol dm^{-3}.

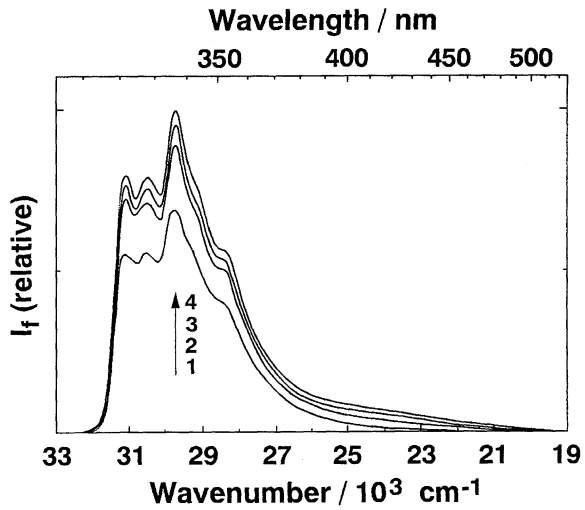

Fig. 2. Fluorescence spectra of MN (1.3×10^{-4} mol dm^{-3}) in aqueous solutions containing varying concentrations of β-CD. Concentration of β-CD: (1) 0, (2) 1.0×10^{-3}, (3) 3.0×10^{-3}, and (4) 1.0×10^{-2} mol dm^{-3}. λ_{ex} = 267 nm.

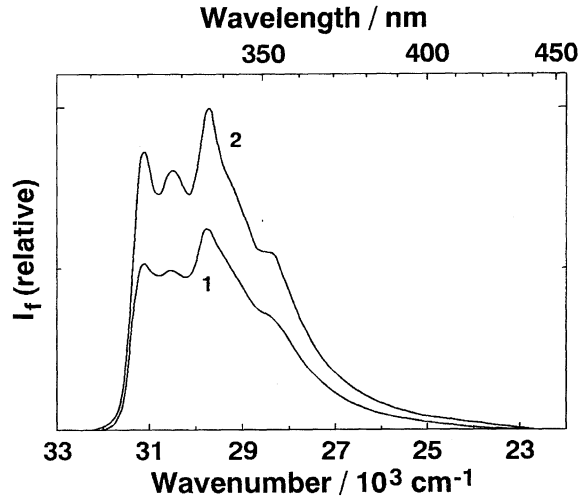

Fig. 3. Fluorescence spectra of dilute MN (1.3×10^{-5} mol dm^{-3}) solutions in the absence (spectrum 1) and presence (spectrum 2) of β-CD (1.0×10^{-2} mol dm^{-3}). λ_{ex}=267 nm.

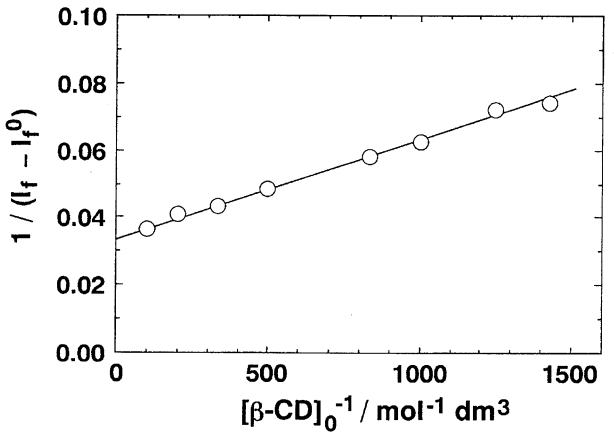

Fig. 4. Plot of $1/(I_f - I_f^0)$ against $1/[\beta\text{-CD}]_0$ for dilute MN (1.3×10^{-5} mol dm^{-3}) solutions. λ_{ex}=267 nm, λ_{obs}=336 nm.

is obtained as $K_1(\beta\text{-CD})$. This $K_1(\beta\text{-CD})$ value for MN is about 1.7 times greater than that for naphthalene, suggesting a stronger hydrophobicity of MN compared to naphthalene.

Taking into account the β-CD–naphthalene system, in which a 2 : 2 inclusion complex is responsible for the excimer fluorescence, the excimer fluorescence in the β-CD–MN system is most likely to be due to the formation of the 2 : 2 β-CD–MN inclusion complex ($(\beta\text{-CD}\cdot\text{MN})_2$):

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

where $K_2(\beta\text{-CD})$ is the equilibrium constant for the formation of the 2 : 2 inclusion complex. When the above-described scheme is true, the excimer fluorescence intensity should be proportional to the concentration of the 2 : 2 β-CD–MN inclusion complex under our experimental conditions. Thus, comparisons were made between the β-CD concentration dependence of the observed excimer fluorescence intensity and simulation curves for the $(\beta\text{-CD}\cdot\text{MN})_2$ concentration, which was calculated using the evaluated $K_1(\beta\text{-CD})$ and an assumed $K_2(\beta\text{-CD})$ value, according to the following equations:

$$[(\beta\text{-CD}\cdot\text{MN})_2] = ([\text{MN}]_0 - [\text{MN}] - [\beta\text{-CD}\cdot\text{MN}])/2. \quad (4)$$

$$2K_1(\beta\text{-CD})^2K_2(\beta\text{-CD})[\beta\text{-CD}]_0^2[\text{MN}]^2 + (1 + K_1(\beta\text{-CD})[\beta\text{-CD}]_0)[\text{MN}] - [\text{MN}]_0 = 0. \quad (5)$$

$$[\beta\text{-CD}\cdot\text{MN}] = K_1(\beta\text{-CD})[\beta\text{-CD}]_0[\text{MN}]. \quad (6)$$

Here, $[\text{MN}]_0$ and [MN] are the initial concentration of MN and the concentration of free MN, respectively. Figure 5 shows the best fit curve of $[(\beta\text{-CD}\cdot\text{MN})_2]$ calculated with $K_2(\beta-\text{CD})$=1400 mol^{-1} dm^3. The quality of the fit to the observed intensity data is satisfactory. For the β-CD–naphthalene system, $K_2(\beta\text{-CD})$ has been estimated to be 4000 mol^{-1} dm^3, which is comparable to that for MN.[2)]

There may be the possibility, however, that the excimer fluorescence is due to a 1 : 2 β-CD–MN inclusion complex (β-CD·$(\text{MN})_2$). Thus, to investigate this possibility, we compared observed data of the excimer fluorescence intensity with concentration curves calculated for the 1 : 2 β-CD–MN inclusion complex, as a function of β-CD concentration (not shown). However, even when an equilibrium constant for the formation of β-CD·$(\text{MN})_2$ from β-CD·MN and MN was varied from 10^2 to 10^7 mol^{-1} dm^3, the calculated curves could not reproduce the β-CD concentration dependence of the observed excimer fluorescence intensity, evidently indicating that the 1 : 2 β-CD–MN inclusion complex is not responsible for the excimer fluorescence. This finding provides additional evidence concerning the formation of the 2 : 2 inclusion complex exhibiting the excimer fluorescence.

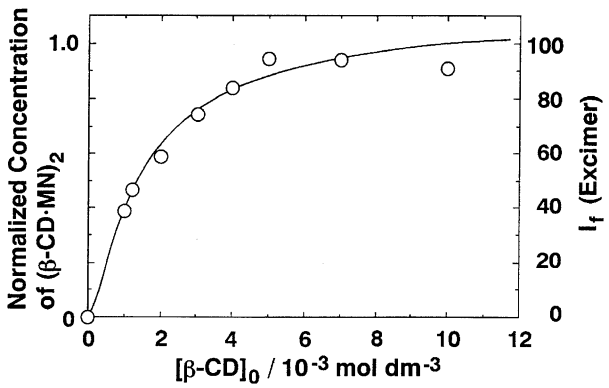

Fig. 5. Best fit curve simulated for the concentration of the 2 : 2 β-CD–MN inclusion complex, with an assumed $K_2(\beta\text{-CD})$=1400 mol^{-1} dm^3, together with observed excimer fluorescence intensity data (○). The best fit curve is normalized to unity at a β-CD concentration of 1.0×10^{-2} mol dm^{-3}. λ_{ex}=267 nm.

Inclusional Complexation of MN in Alkaline Aqueous Solutions Containing β-CD. Figure 6 shows absorption spectra of MN (1.2×10^{-4} mol dm^{-3}) in 0.4 mol dm^{-3} NaOH aqueous solutions (pH=13.3) containing varying concentra-

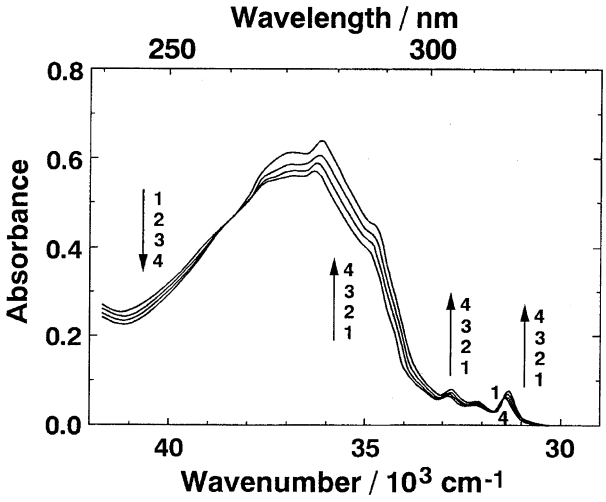

Fig. 6. Absorption spectra of MN (1.2×10^{-4} mol dm^{-3}) in 0.4 mol dm^{-3} NaOH aqueous solutions containing varying concentrations of β-CD. Concentration of β-CD: (1) 0, (2) 1.0×10^{-3}, (3) 3.0×10^{-3}, and (4) 1.0×10^{-2} mol dm^{-3}.

tions of β-CD. When the β-CD concentration is increased, absorption peaks are shifted to longer wavelengths, and are increased in intensity, accompanied by isosbestic points at 264, 316, and 318 nm. The absorption spectral change for the alkaline solutions (Fig. 6) is similar to that for neutral solutions (Fig. 1), except for the spectral change in the short-wavelength region (below ca. 250 nm). In this wavelength region, the absorbance for the alkaline solution is regularly reduced with an increase in the β-CD concentration, in contrast to that for the neutral solutions. This finding suggests that a 1 : 1 β-CD–MN inclusion complex alone exists as an inclusion complex in alkaline solutions.

Figure 7 illustrates fluorescence spectra of MN (1.2×10^{-4} mol dm^{-3}) in 0.4 mol dm^{-3} NaOH solutions in the absence and presence of β-CD. As shown in Fig. 7, the excimer fluorescence is not observed upon the addition of 1.0×10^{-2} mol dm^{-3} β-CD, in contrast to neutral solutions (Fig. 2). A pKa value of 12.2 has been reported for β-CD.[17] At pHs above 12.2, the 2 : 2 inclusion complex dissociates into two 1 : 1 inclusion complexes because the electrostatic repulsion works between negatively charged hydroxy groups of two associating β-CD molecules that are contained in the 2 : 2 inclusion complex. Consequently, no observation of the excimer fluorescence in the alkaline solutions is consistent with our conclusion that the excimer fluorescence arises from a 2 : 2 β-CD–MN inclusion complex that is formed by the self-association between 1 : 1 β-CD–MN inclusion complexes.

If an excimer-emitting species is a 1 : 2 β-CD–MN inclusion complex, in a 0.4 mol dm^{-3} NaOH solution, the 1 : 2 β-CD–MN inclusion complex would be produced by the association of a second MN molecule with a 1 : 1 β-CD–MN inclusion complex, since the electrostatic repulsion does not work between a neutral MN molecule and a β-CD anion. However, this is not the case for the β-CD–MN system in an alkaline solution because of no appearance of the excimer fluorescence. Therefore, the 1 : 2 β-CD–MN inclusion complex is formed in neither neutral β-CD solutions nor alkaline β-CD solutions.

The pH dependence of the excimer fluorescence intensity is exhibited in Fig. 8. In the pH range from 7 to 11.5, the excimer fluorescence intensity remains constant. However, it drastically drops from pH 12, and excimer fluorescence is not detected above pH 13. From the titration curve concerning the excimer fluorescence intensity, a value of 12.2 has been evaluated as a pK_a value, which is identical to the pK_a value of the secondary hydroxy groups of β-CD.[17] As a consequence, the 1 : 1 β-CD–MN inclusion complexes associate to the 2 : 2 inclusion complex in neutral aqueous solutions.

On the basis of the fluorescence intensity change of MN by the β-CD addition, K_1(anionic β-CD) for a 0.4 mol dm^{-3} NaOH solution was determined to be 520 ± 10 mol^{-1} dm^3. This value is about half of K_1(β-CD) for neutral solutions, indicating that it is unfavorable for anionic β-CD to accommodate MN compared to neutral β-CD. This unfavorable inclusion of MN within the cavity may imply that β-CD experiences a conformational change upon anionization.

Inclusional Complexation of MN with γ-CD in Neutral Aqueous Solutions. At an MN concentration of approximately 1.3×10^{-4} mol dm^{-3}, the addition of γ-CD to a neutral MN solution resulted in precipitation. Thus, dilute MN (1.3×10^{-5} mol dm^{-3}) solutions, in which precipitation did not take place upon adding γ-CD, were used in experiments with γ-CD. Figure 9 depicts fluorescence spectra of MN (1.3×10^{-5} mol dm^{-3}) in γ-CD aqueous solutions containing varying concentrations of γ-CD. As the γ-CD concentration is increased, the monomer fluorescence grows in intensity without any sharpening of the vibronic bands. As in the case of β-CD, the MN excimer fluorescence appears upon the addition of γ-CD. In spite of the low MN concentration, the excimer fluorescence is more prominent for γ-CD solutions than for β-CD solutions. Like the β-CD–MN

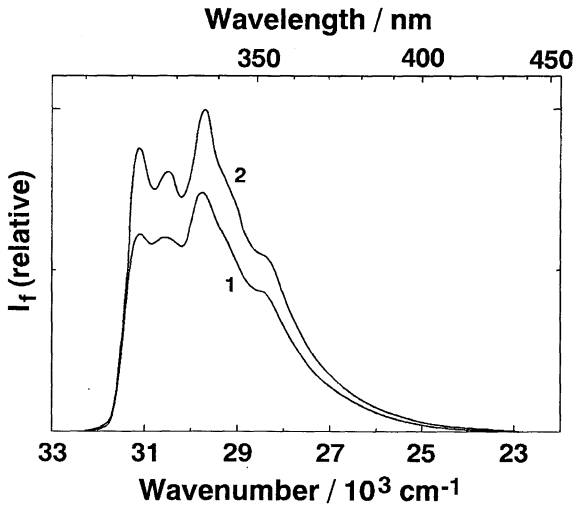

Fig. 7. Fluorescence spectra of MN (1.2×10^{-4} mol dm^{-3}) in 0.4 mol dm^{-3} NaOH aqueous solutions in the absence (spectrum 1) and presence (spectrum 2) of β-CD (1.0×10^{-2} mol dm^{-3}). λ_{ex}=264 nm.

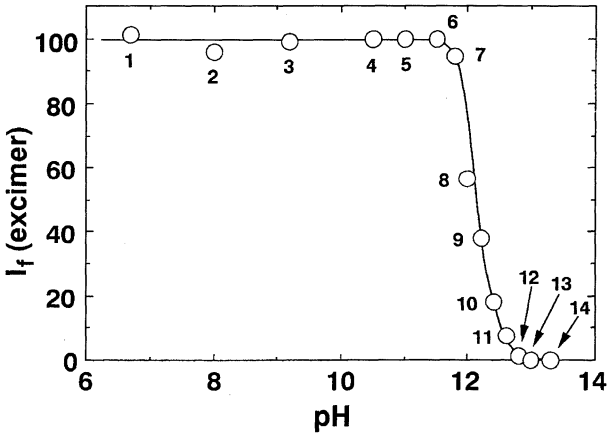

Fig. 8. pH dependence of the excimer fluorescence intensity in aqueous solutions with β-CD (1.0×10^{-2} mol dm^{-3}). Buffer: (1) without buffer, (2) and (3) 0.01 mol dm^{-3} boric acid–0.01 mol dm^{-3} KCl–NaOH buffer, (4) 0.05 mol dm^{-3} $NaHCO_3$–NaOH buffer, (5)—(7) 0.05 mol dm^{-3} Na_2HPO_4–NaOH buffer, (8)—(13) 2 mol dm^{-3} KCl–NaOH buffer, and (14) 0.4 mol dm^{-3} NaOH solution. λ_{ex}=264 nm.

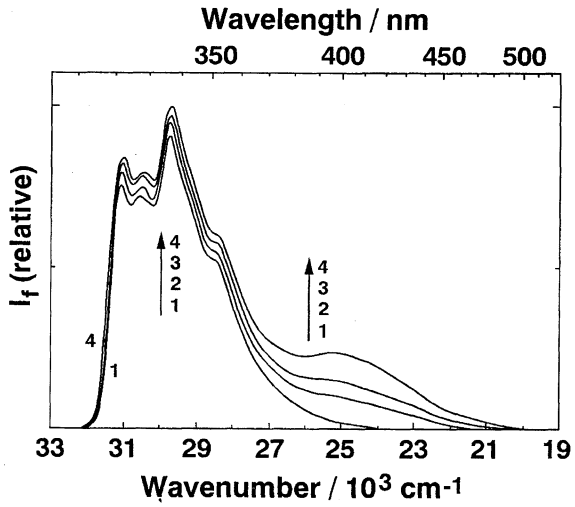

Fig. 9. Fluorescence spectra of dilute MN (1.3×10^{-5} mol dm^{-3}) solutions containing varying concentrations of γ-CD. Concentration of γ-CD: (1) 0, (2) 3.0×10^{-3}, (3) 5.0×10^{-3}, and (4) 1.0×10^{-2} mol dm^{-3}. λ_{ex}=290 nm.

system, the excimer fluorescence in γ-CD solutions is likely to be due to the 2:2 inclusion complex. Since the cavity diameter of γ-CD is greater than that of β-CD, however, two MN molecules may enter the cavity of a single γ-CD molecule.

When the MN concentration was decreased to 1.3×10^{-6} mol dm^{-3}, the addition of γ-CD resulted in an enhancement of the monomer fluorescence of MN, accompanied by slight red-shifts of the fluorescence maxima (not shown). However, the excimer fluorescence was not observed, indicating that at a very low MN concentration, such as 1.3×10^{-6} mol dm^{-3}, γ-CD cannot induce the association of MN. Consequently, only an equilibrium involving free MN and a 1:1 γ-CD–MN inclusion complex is established at an MN concentration as low as 1.3×10^{-6} mol dm^{-3}:

$$\gamma\text{-CD} + \text{MN} \overset{K_1(\gamma\text{-CD})}{\rightleftarrows} \gamma\text{-CD}\cdot\text{MN}. \quad (7)$$

Here, $K_1(\gamma$-CD) is the equilibrium constant for the formation of a 1:1 γ-CD–MN inclusion complex (γ-CD·MN). According to Eq. 2, the $K_1(\gamma$-CD) value was evaluated to be 9±3 mol^{-1} dm^3 from the fluorescence intensity change, in very dilute MN (1.3×10^{-6} mol dm^{-3}) solutions, by the addition of γ-CD.[22] This $K_1(\gamma$-CD) value is significantly less than $K_1(\beta$-CD) (1190±40 mol^{-1} dm^3) for β-CD, indicating the considerably poor fit of MN into the γ-CD cavity compared to the β-CD cavity. The less snug fit between MN and the γ-CD cavity is due to the cavity diameter of γ-CD greater than that of β-CD.

As stated previously, there are two schemes that can explain the observation of the excimer fluorescence in MN solutions containing CD. One possibility is the self-association of 1:1 γ-CD–MN inclusion complexes; the other is the incorporation of MN by a 1:1 γ-CD–MN inclusion complex:

$$2(\gamma\text{-CD}\cdot\text{MN}) \overset{K_2(\gamma\text{-CD})}{\rightleftarrows} (\gamma\text{-CD}\cdot\text{MN})_2, \quad (8)$$

and

$$\gamma\text{-CD}\cdot\text{MN} + \text{MN} \overset{K_2'(\gamma\text{-CD})}{\rightleftarrows} \gamma\text{-CD}\cdot(\text{MN})_2, \quad (9)$$

where $K_2(\gamma$-CD) and $K_2'(\gamma$-CD) are the equilibrium constants for the formation of a 2:2 γ-CD–MN inclusion complex ((γ-CD·MN)$_2$) and a 1:2 γ-CD–MN inclusion complex (γ-CD·(MN)$_2$), respectively.

To identify a species that emits the MN excimer fluorescence, the concentrations of (γ-CD·MN)$_2$ and γ-CD·(MN)$_2$ were simulated using a known $K_1(\gamma$-CD) value and an assumed $K_2(\gamma$-CD) or $K_2'(\gamma$-CD) value, as a function of γ-CD concentration. The best fit curves for the concentrations of (γ-CD·MN)$_2$ and γ-CD·(MN)$_2$, with $K_2(\gamma$-CD)=3.38×10^6 mol^{-1} dm^3 and $K_2'(\gamma$-CD)=2.67×10^5 mol^{-1} dm^3, respectively, are shown in Fig. 10, together with the observed excimer fluorescence intensities. The best fit curve for (γ-CD·MN)$_2$, which exhibits a sigmoidal character, is in good agreement with the observed data, particularly in the low γ-CD concentration range compared to the best fit curve for γ-CD·(MN)$_2$, evidently indicating that the excimer fluorescence is due to the formation of the 2:2 inclusion complex, (γ-CD·MN)$_2$, as in the case of β-CD. Since $K_1(\gamma$-CD) is very small, $K_2(\gamma$-CD) is expected to be considerably large in order to be able to observe the excimer fluorescence. A remarkably large $K_2(\gamma$-CD) value has indeed been obtained from the above simulation. For the γ-CD–pyrene system, a similar, very large $K_2(\gamma$-CD) value (1.3×10^6 mol^{-1} dm^3) has been estimated.[7] The finding that the $K_2(\gamma$-CD) values for MN and pyrene are three orders of magnitude greater than the $K_2(\beta$-CD) values for MN and naphthalene suggests that γ-CD inclusion complexes self-associate much more favorably than do β-CD inclusion complexes.

The formation of the 2:2 γ-CD–MN inclusion complex is in contrast to the results of the γ-CD–sodium 1-naph-

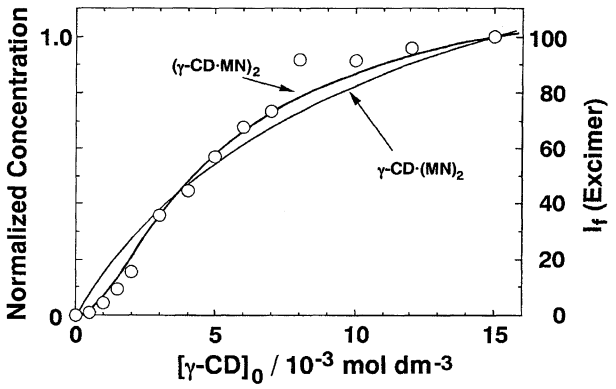

Fig. 10. Best fit curve simulated for the concentration of the 2:2 γ-CD–MN inclusion complex, with an assumed $K_2(\gamma$-CD)=3.38×10^6 mol^{-1} dm^{-3}, and that of the 1:2 γ-CD–MN inclusion complex, with an assumed $K_2'(\gamma$-CD)=2.67×10^5 mol^{-1} dm^3, together with observed excimer fluorescence intensity data (○). The best fit concentration curves are normalized to unity at a γ-CD concentration of 1.5×10^{-2} mol dm^{-3}. λ_{ex}=290 nm.

thaleneacetate system and γ-CD derivatives bearing two 2-naphthylsulfonyl moieties, where 1 : 2 host–guest inclusion complexes are formed.[18—21] The intramolecular self-incorporation of two 2-naphthylsulfonyl groups appended to γ-CD is most likely promoted by the first binding of the 2-naphthylsulfonyl group, thereby leading to the formation of an intramolecular 1 : 2 self-inclusion complex. The difference in inclusion behavior of γ-CD between sodium 1-naphthaleneacetate and 2-methylnaphthalene may be due to a difference in substitution position on a naphthalene ring between these two naphthalene derivatives.

Inclusional Complexation of MN in Alkaline Aqueous Solutions Containing γ-CD. Since no precipitation occurred in a 0.4 mol dm^{-3} NaOH solution of 1.2×10^{-4} mol dm^{-3} MN upon the addition of γ-CD, spectroscopic measurements were made at an MN concentration of approximately 1.2×10^{-4} mol dm^{-3}. The addition of 1.0×10^{-2} mol dm^{-3} γ-CD to 0.4 mol dm^{-3} NaOH solutions of MN resulted in slight red-shifts of absorption peaks (not shown), indicating the formation of a γ-CD–MN inclusion complex. In 0.4 mol dm^{-3} NaOH solutions with γ-CD, the excimer fluorescence could not be observed. Consequently, it is most likely that a 1 : 1 γ-CD–MN inclusion complex alone is formed in 0.4 mol dm^{-3} NaOH solutions. As the γ-CD concentration was increased, the monomer fluorescence of MN was slightly enhanced without any peak shifts. From the intensity change of the monomer fluorescence, K_1(anionic γ-CD) for a 0.4 mol dm^{-3} NaOH solution has been estimated to be 60±20 mol^{-1} dm^3, which is about 7 times greater than K_1(γ-CD) for neutral solutions. Consequently, MN very snugly fits into the cavity of anionic γ-CD compared to neutral γ-CD. This finding is contrary to the result for β-CD solutions; K_1(anionic β-CD) is conversely about half of K_1(β-CD) for neutral solutions. These results, that the binding abilities of anionic β- and γ-CD are different from those of neutral β- and γ-CD, respectively, imply that anionic β- and γ-CD cause some conformational changes.

To further confirm the self-association of γ-CD·MN to (γ-CD·MN)$_2$, the pH dependence of the excimer fluorescence intensity was examined as in the case of the β-CD–MN system (Fig. 11). From the pH dependence, a pK_a value of 12.2 was obtained. This pK_a value is in excellent agreement with the pK_a value for the secondary hydroxy groups of γ-CD,[17] providing further evidence that (γ-CD·MN)$_2$ is responsible for the excimer fluorescence. In (γ-CD·MN)$_2$, the coulombic repulsion between the deprotonated hydroxy groups of two γ-CD molecules causes the dissociation of (γ-CD·MN)$_2$ to two γ-CD·MNs, leading to a disappearance of the excimer fluorescence.

Induced Circular Dichroism Spectra of MN in β-CD and γ-CD Solutions. For naphthalene, the 300—320-nm, 240—290-nm, and 200—240-nm bands are assigned to the ^1L_b, ^1L_a, and ^1B_b transitions, respectively. The directions of the ^1L_b and ^1B_b transitions are parallel to the longitudinal axis of a naphthalene molecule. On the other hand, the ^1L_a transition moment is directed along the transverse axis of naphthalene. The 300—320-nm, 245—300-nm, and 240—245-nm bands for MN correspond to the ^1L_b, ^1L_a, and ^1B_b transitions for naphthalene, respectively. Consequently, it is likely that the directions of the ^1L_b and ^1B_b transitions in MN are nearly parallel to the longitudinal axis, although a methyl substituent slightly perturbs the directions of these transitions. Similarly, the direction of the ^1L_a transition for MN is anticipated to be nearly perpendicular to the longitudinal axis.

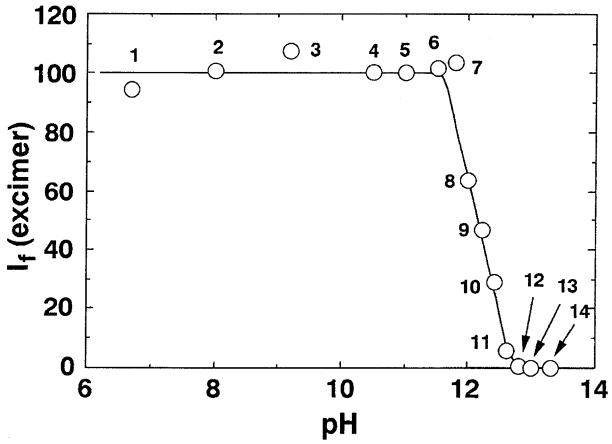

Fig. 11. pH dependence of the excimer fluorescence intensity in aqueous solutions with γ-CD (1.0×10^{-2} mol dm^{-3}). Buffer: (1) without buffer, (2) and (3) 0.01 mol dm^{-3} boric acid–0.01 mol dm^{-3} KCl–NaOH buffer, (4) 0.05 mol dm^{-3} $NaHCO_3$–NaOH buffer, (5)—(7) 0.05 mol dm^{-3} Na_2HPO_4–NaOH buffer, (8)—(13) 2 mol dm^{-3} KCl–NaOH buffer, and (14) 0.4 mol dm^{-3} NaOH solution. λ_{ex}=290 nm.

Figure 12a illustrates the induced circular dichroism (icd) spectrum of MN in a neutral aqueous solution containing 1.0×10^{-2} mol dm^{-3} β-CD. In the wavelength range from 300 to 320 nm, the icd band exhibits a very small positive

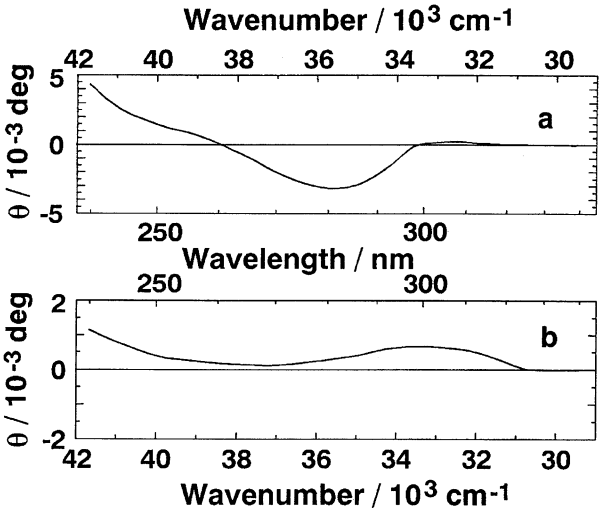

Fig. 12. a) Induced circular dichroism spectrum of MN (1.3×10^{-4} mol dm^{-3}) in aqueous solution containing β-CD (1.0×10^{-2} mol dm^{-3}). b) Induced circular dichroism spectrum of MN (1.2×10^{-4} mol dm^{-3}) in 0.4 mol dm^{-3} NaOH aqueous solution containing γ-CD (2.0×10^{-2} mol dm^{-3}).

signal. On the other hand, the 240—260-nm and the 260—300-nm bands of the icd spectrum distinctly show positive and negative signs, respectively.

When the angle between the direction of a transition moment existing within the CD cavity and the symmetry axis of CD is between $-54.44°$ and $54.44°$, the sign of an icd spectrum is positive.[23] Taking into account this criterion, MN is bound to the β-CD cavity, its longitudinal axis being almost parallel to the symmetry axis of β-CD. The icd spectrum of MN in a 0.4 mol dm^{-3} NaOH solution with β-CD was similar to that in a neutral solution with β-CD (not shown). Consequently, the relative location of MN within the β-CD cavity in an alkaline solution is nearly the same as that in a neutral solution. In a neutral solution with β-CD, a 2 : 2 inclusion complex as well as a 1 : 1 inclusion complex is present, whereas, in an alkaline solution, a 1 : 1 inclusion complex exists without self-association. Nonetheless, the fact that similar icd spectra are obtained for both neutral and alkaline solutions indicates that the disposition of MN with respect to the β-CD cavity is nearly identical to each other in the 1 : 1 and the 2 : 2 inclusion complexes. This conclusion is consistent with the finding that the absorption spectra of MN in neutral solutions exhibit isosbestic points in the wavelength range above 250 nm, as shown in Fig. 1. As evidenced by the existence of the isosbestic points, within the 2 : 2 β-CD–MN inclusion complex, there are few interactions between the two MN molecules in the ground state. In the case of naphthalene, no isosbestic points have been observed in the absorption spectra for β-CD solutions.[2] Unlike naphthalene, a methyl substituent at the 2 position provides a steric hindrance to some extent, thereby resulting in significantly weak intermolecular interactions between the two ground-state MN molecules residing in $(\beta\text{-CD}\cdot\text{MN})_2$, compared to naphthalene.

Unfortunately, an icd spectrum for a neutral γ-CD solution of MN could not be obtained because of an extremely low MN concentration (1.3×10^{-6} mol dm^{-3}). In a 0.4 mol dm^{-3} NaOH solution with γ-CD (2.0×10^{-2} mol dm^{-3}), the sign of the MN icd spectrum corresponding to the ^1L_a transition is reversed to be slightly positive, compared to that in solutions with β-CD, whereas the signs for the other transitions remain unaltered (Fig. 12b). This finding suggests that the molecular axis of MN is slightly tilted relative to the γ-CD symmetry axis, keeping the signs of the icd bands for the ^1L_b and ^1B_b transitions unchanged. This may also imply that the angle between the directions of the ^1L_a and ^1L_b (or ^1B_b) transitions for MN is less than 90°.

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