 © 1991 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 64, 431—438 (1991)

Exciplex Formation between Perylene and *N,N*-Dimethylaniline in a Ternary Inclusion Compound with γ-Cyclodextrin in H_2O-Ethanol (7:3) Mixture

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(Received August 1, 1990)

Inclusion compounds in the system of γ-cyclodextrin (γ-CD)-*N,N*-dimethylaniline (DMA)-perylene (Pe) have been studied in an H_2O-ethanol (7:3) mixture by means of absorption and fluorescence spectral measurements. A ternary 1:1:1 inclusion compound of γ-CD-ethanol-Pe is formed by the addition of γ-CD to an H_2O-ethanol solution of Pe. In the presence of γ-CD, a further addition of DMA results in the formation of a γ-CD-DMA-Pe inclusion compound followed by association with a 1:1 γ-CD-DMA inclusion compound to form a ternary 2:2:1 inclusion compound of γ-CD-DMA-Pe. The exciplex fluorescence of Pe-DMA within the γ-CD cavity has been observed from the ternary inclusion compound. Equilibrium constants for the formation of these inclusion compounds have been evaluated.

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of at least six glucose residues which are joined by α-(1→4) linkages. Commercially available α-, β-, and γ-CD have six, seven, and eight glucose units, respectively, and are shaped like a truncated cone having a narrower and a wider end, which has the cavity capable of accommodating many kinds of organic and inorganic substances in aqueous solutions.[1] Among these CDs, γ-CD possessing the largest cavity has been suggested to form 1:2 and 2:2 host-guest inclusion compounds,[2-8] and ternary inclusion compounds.[9-15]

From an induced circular dichroism study, an inclusion of two chlorpromazine molecules entering the single γ-CD cavity has been pointed out.[16] Pyrene and sodium 1-naphthylacetate excimer emissions have been observed in γ-CD aqueous solutions.[7,8,11,17] The 1-naphthylacetate excimer emission has been ascribed to an excimer arising from a ground-state dimer of the guest within the single γ-CD cavity. For the pyrene excimer, however, it has been revealed that the ground-state dimer of pyrene is formed within two γ-CD cavities associating with each other.[8] Owing to the ground-state dimer formation of substrates, themselves, within the γ-CD cavity, it is difficult to investigate the interaction of substrates with other kinds of organic substances within the γ-CD cavity. Until now, there have been few studies on the interaction between different kinds of organic substances bound to the γ-CD cavity in solutions. Thus, as a guest molecule, we selected perylene (Pe), which seems to be too large to form a ground-state dimer within the cavity of a single γ-CD molecule. Because Pe is insoluble in water, an H_2O-ethanol (7:3) mixture was used as the solvent. Although, in general, the formation of inclusion compounds of CDs is unfavored in organic solvents, an alcohol molecule in water associates with 1:1 inclusion complexes of β-CD with pyrene, acenaphthene, fluorene, and 1-naphthonitrile to produce ternary 1:1:1 inclusion compounds.[12,13,15,18-21] In addition, for aromatics such as pyrene, an alcohol molecule included in the β-CD cavity promotes the formation of ternary inclusion compounds formed among β-CD, alcohol, and aromatics. With γ-CD, 1-butanol enables a ground-state pyrene dimer that is positioned inside the γ-CD cavity to dissociate, resulting in the formation of a γ-CD-1-butanol-pyrene inclusion compound.[11] The formation of ternary inclusion compounds of γ-CD-pyrene-alcohol (including ethanol) has also been confirmed.[12-15] Consequently, ethanol as a solvent is anticipated to inhibit the formation of the ground-state Pe dimer within the γ-CD cavity. In this respect, the use of a mixture containing ethanol simplifies the investigation of the interaction between different kinds of guests entering the γ-CD cavity.

Experimental

Perylene (Pe) was purchased from Aldrich and purified by column chromatography. γ-CD (Nakarai) and ethanol (Wako) were used as received. Benzene (Wako) was distilled. Aniline (Wako), *N,N*-Dimethylaniline (Tokyo Kasei), and *N,N*-diethylaniline (Tokyo Kasei) were distilled under reduced pressure.

The absorption spectra were recorded on a Shimadzu 260 spectrophotometer with which spectral data accumulation was repeated 20 times. The fluorescence spectra were obtained with a Shimadzu RF-501 spectrofluorometer equipped with a cooled Hamamatsu R-943 photomultiplier, and were corrected for the wavelength dependence of the sensitivity of the fluorometer. Aerated sample solutions were employed throughout this study, and measured at 25±0.1 °C. A water-ethanol (7:3) mixture was used as the solvent. The concentration of Pe was 3.0×10^{-7} mol dm^{-3}, unless otherwise stated.

Results and Discussion

Inclusion Compound of γ-CD with Pe. Figure 1 shows the absorption spectra of Pe solutions contain-

ing various concentrations of γ-CD. The absorption peaks are red shifted and sharpened accompanied by isosbestic points at 392, 397, 413, 423, and 437 nm, indicating the formation of an inclusion compound consisting of at least γ-CD and Pe. The red shift of the 0-0 band peak from 435 to 445 nm amounts to an energy gap of 520 cm^{-1}, which is comparable to those of 440 and 640 cm^{-1} for the absorption peaks between 1 : 1 : 1 inclusion compounds of β-CD-alcohol-pyrene and -fluorene and free pyrene and fluorene in water, respectively.[18,20] The red shifts are only 90 and 200 cm^{-1} for the peaks of 1 : 1 inclusion compounds of pyrene and fluorene, respectively. In contrast to 1 : 1 inclusion compounds of these aromatics, sharp vibronic bands are characteristic of ternary inclusion compounds containing alcohol, except for a β-CD-alcohol-acenaphthene inclusion compound. This is the case of the inclusion compound of Pe. Furthermore, considerable quantities of ethanol exist in the solvent used in this work. Consequently, the most plausible species responsible for the absorption spectral change shown in Fig. 1 is a ternary inclusion compound comprising γ-CD, ethanol, and Pe. Figure 2 exhibits the absorption spectra of Pe solutions with a fixed concentration of γ-CD (1.0×10^{-3} mol dm^{-3}) and varying amounts of cyclohexane. The addition of cyclohexane results in an enhancement of the 445-nm band at the expense of the 435-nm band. This spectral change resembles that shown in Fig. 1 where the γ-CD concentration is increased. In Fig. 2, cyclohexane acts as if it is γ-CD in Fig. 1. For pyrene solutions with β-CD, cyclohexane or hexane was found to induce an absorption spectral change similar to those observed for the addition of alcohols, indicating the formation of a 1 : 1 : 1 inclusion complex of β-CD with cyclohexane (hexane) and pyrene. Since cyclohexane is much more hydrophobic than ethanol, cyclohexane is expected to readily associate with γ-CD, thereby forming a γ-CD-cyclohexane-Pe inclusion compound analogous to the γ-CD-ethanol-Pe inclusion compound. This explains the effect of added cyclohexane on the absorption spectrum of Pe shown in Fig. 2. The finding of the effect of cyclohexane provides additional evidence for the ternary inclusion compound of γ-CD-ethanol-Pe. As revealed for the β-CD-alcohol-pyrene,[18] -acenaphthene,[19] -fluorene,[20] and -1-naphthonitrile systems,[21] it is most likely that the γ-CD-ethanol-Pe inclusion compound (PEC) comprises a single γ-CD, a single ethanol, and a single Pe molecule:

$$\mathrm{Pe} + \mathrm{EtOH} + \gamma\text{-CD} \overset{K_1}{\rightleftarrows} \mathrm{PEC}, \qquad (1)$$

where EtOH is ethanol, and K_1 is an equilibrium constant for the formation of PEC.

Figure 3 depicts the fluorescence spectra of Pe in the absence and presence of γ-CD. When γ-CD is added to a Pe solution, the fluorescence maxima are red shifted, and isoemissive points are observed at 445, 473, 494, and 506 nm. The spectral change in the fluorescence by the addition of γ-CD is also due to the 1 : 1 : 1 inclusion compound of γ-CD-ethanol-Pe.

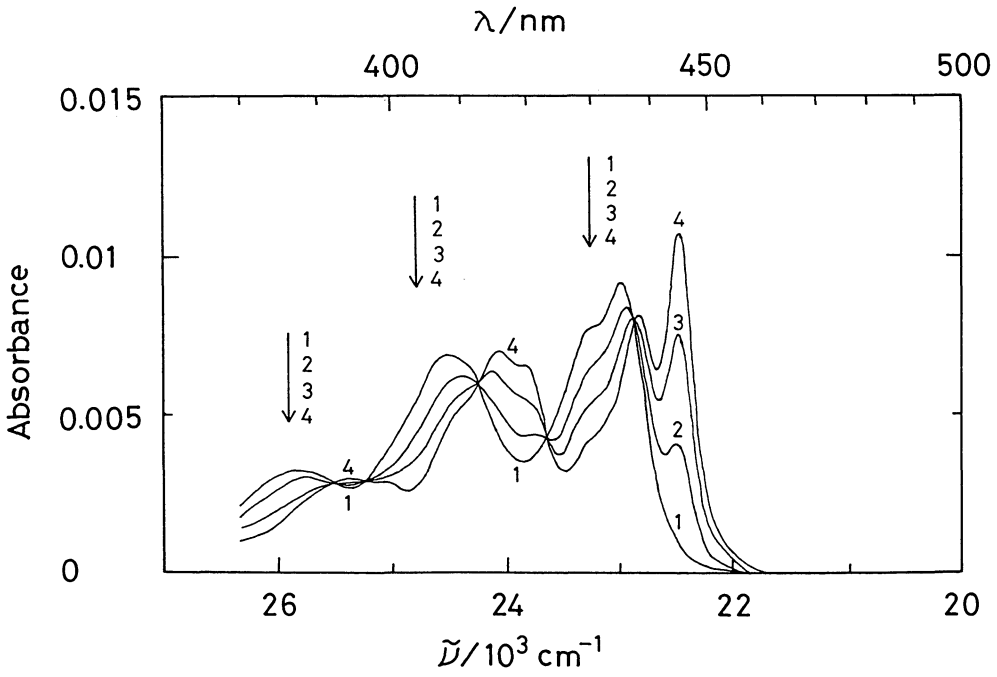

Fig. 1. Absorption spectra of Pe (3.0×10^{-7} mol dm^{-3}) in H_2O-ethanol (7 : 3) containing varying concentrations of γ-CD. Concentration of γ-CD: (1) 0, (2) 1.0×10^{-3}, (3) 2.0×10^{-3}, and (4) 4.0×10^{-3} mol dm^{-3}.

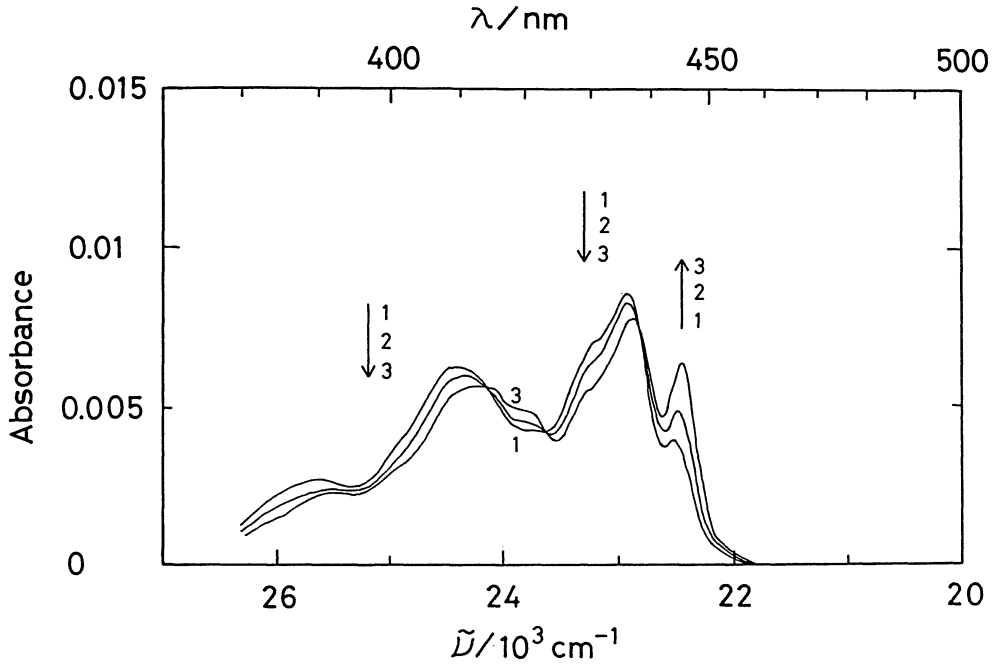

Fig. 2. Absorption spectra of Pe (3.0×10^{-7} mol dm^{-3}) in H_2O-ethanol (7 : 3) containing a fixed concentration of γ-CD (1.0×10^{-3} mol dm^{-3}) and varying concentrations of cyclohexane. Concentration of cyclohexane: (1) 0, (2) 1.85×10^{-3}, and (3) 4.63×10^{-3} mol dm^{-3}.

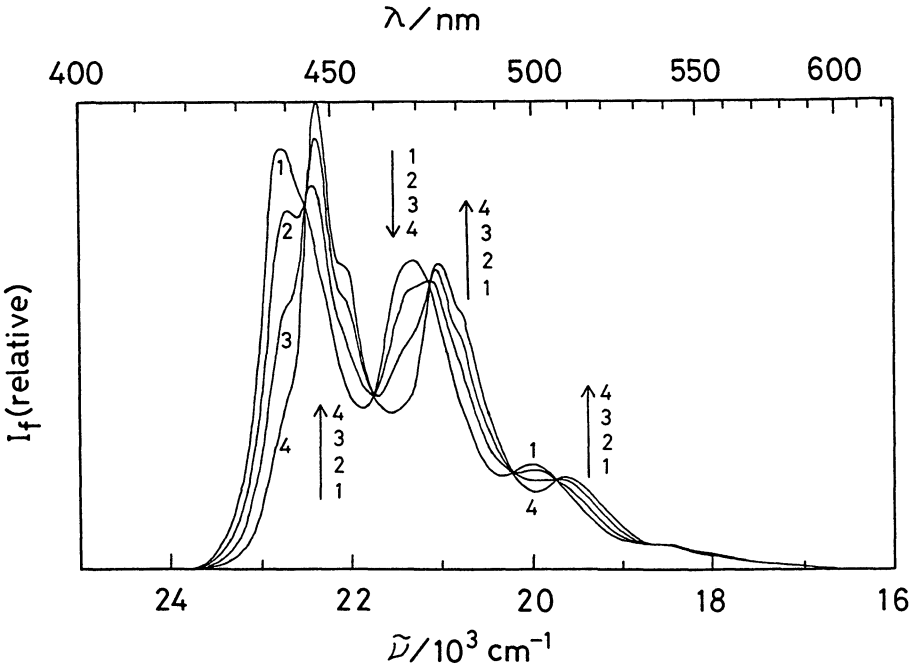

Fig. 3. Fluorescence spectra of Pe (3.0×10^{-7} mol dm^{-3}) in H_2O-ethanol (7 : 3) containing varying concentrations of γ-CD. Concentration of γ-CD: (1) 0, (2) 1.0×10^{-3}, (3) 2.0×10^{-3}, and (4) 4.0×10^{-3} mol dm^{-3}. λ_{ex}=413 nm.

For the equilibrium represented by Eq. 1, the following equation holds:

$$1/\Delta I_f = 1/a + 1/aK_1[\mathrm{EtOH}]_0[\gamma\text{-CD}]_0, \quad (2)$$

where ΔI_f is the difference in the integrated fluorescence intensity between a Pe solution with γ-CD and that without γ-CD, a is a constant, subscript 0 stands for the initial concentration, and $[EtOH]_0$ is 5.11 mol dm^{-3}. According to Eq. 2, K_1 was evaluated to be 37 ± 10 mol^{-2} dm^6. Upon the addition of cyclohexane

to a γ-CD solution of Pe, the Pe fluorescence spectrum shows a change similar to that shown in Fig. 3 where γ-CD is added to a Pe solution without cyclohexane. This spectral change for the fluorescence upon adding cyclohexane corresponds to that for the absorption change shown in Fig. 2.

Inclusion Compound of γ-CD with *N,N*-Dimethylaniline (DMA). DMA was confirmed to form an inclusion compound with γ-CD from the absorption and fluorescence spectral changes. Although there is a possibility that a ternary inclusion compound of γ-CD-ethanol-DMA is formed, we could not obtain evidence for its existence from spectroscopic measurements. Therefore, it is most likely that the spectral change is due to a 1 : 1 inclusion compound of γ-CD-DMA (DC) which is formed according to the equation

$$\text{DMA} + \gamma\text{-CD} \overset{K_2}{\rightleftarrows} \text{DC}, \tag{3}$$

where K_2 is an equilibrium constant for the formation of DC. A fluorometric method was used to determine K_2:

$$1/\Delta I_f = 1/b + 1/bK_2[\gamma\text{-CD}]_0, \tag{4}$$

where b is a constant. From an analysis based on Eq. 4, 27±14 $mol^{-1}\,dm^3$ was obtained as K_2.

Inclusion Compound of γ-CD with *N,N*-Dimethylaniline (DMA) and Pe. In the DMA concentration range below ca. 1×10^{-3} mol dm^{-3}, addition of DMA to a γ-CD (4.0×10^{-3} mol dm^{-3}) solution of Pe results in red shifts of the absorption maxima accompanied by isosbestic points at 421, 429, and 447 nm (Fig. 4). The absorption change can be attributed to the formation of an inclusion compound consisting of γ-CD, DMA, and Pe. It is most likely that the spectral change at low DMA concentrations is caused by the formation of a 1 : 1 : 1 inclusion compound of γ-CD-DMA-Pe. Above ca. 1×10^{-3} mol dm^{-3} of DMA, however, isosbestic points disappear with further red shifts of the absorption maxima. The absorption bands are broadened as the DMA concentration is raised. Because, as is described later, any benzene that cannot form an electron donor-acceptor complex with Pe causes an absorption spectral change similar to that produced by DMA, this change in the absorption is not due to a charge-transfer interaction between Pe and DMA but, rather, due to a kind of microscopic solvent effect exerted by neighboring DMA. Figure 5 illustrates the fluorescence spectrum of a Pe solution containing γ-CD (4.0×10^{-3} mol dm^{-3}) and DMA (3.16×10^{-3} mol dm^{-3}). Upon the addition of DMA, the Pe monomer band (447-nm band) is quenched. At the same time, a broad emission that is located at longer wavelengths appears with a maximum at 599 nm. For the Pe solution with γ-CD and DMA, the excitation spectrum observed at 580 nm was almost identical to the absorption spectrum. This broad emission is assigned to an exciplex fluorescence of Pe and DMA which enter the γ-CD cavity. If a Pe ground-state dimer within the γ-CD cavity exists in

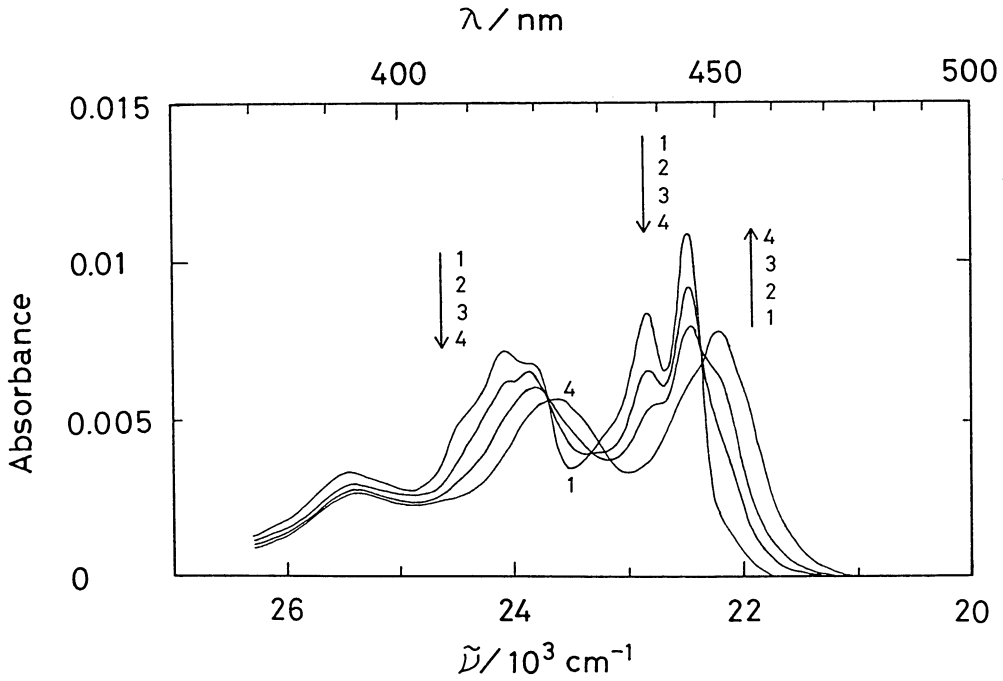

Fig. 4. Absorption spectra of Pe (3.0×10^{-7} mol dm^{-3}) in H_2O-ethanol (7 : 3) containing a fixed concentration of γ-CD (4.0×10^{-3} mol dm^{-3}) and varying concentrations of DMA. Concentration of DMA: (1) 0, (2) 3.16×10^{-4}, (3) 7.89×10^{-4}, and (4) 3.16×10^{-3} mol dm^{-3}.

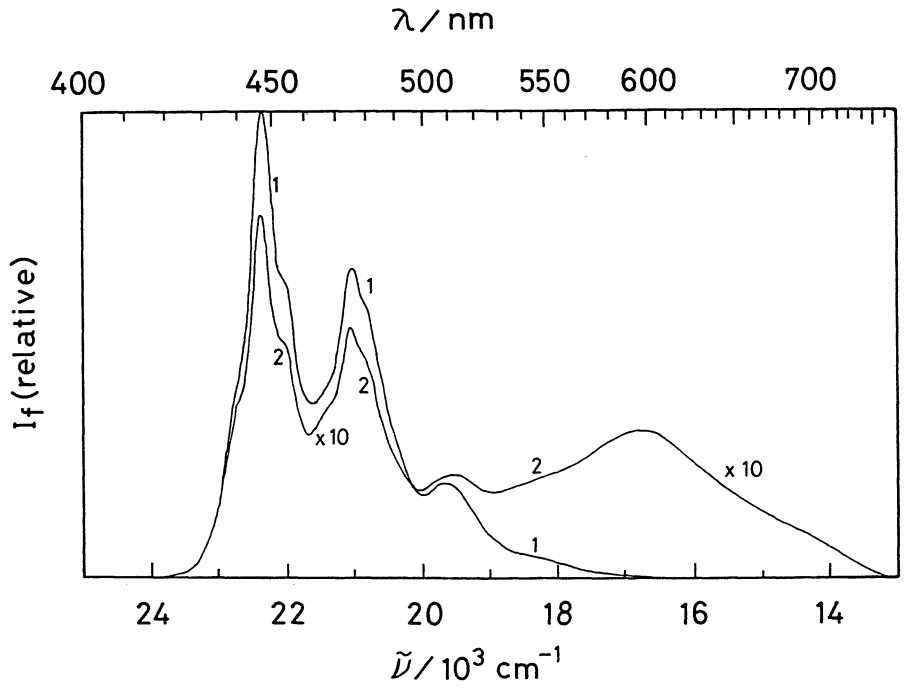

Fig. 5. Fluorescence spectra of Pe (3.0×10^{-7} mol dm^{-3}) in H_2O-ethanol (7 : 3) containing γ-CD (4.0×10^{-3} mol dm^{-3}) in the absence (Spectrum 1) and presence (Spectrum 2) of DMA (3.16×10^{-3} mol dm^{-3}). The fluorescence intensity of a Pe solution with DMA is multiplied by 10. λ_{ex}=402 nm.

H_2O-ethanol (7 : 3), it might be responsible for the broad emission. However, this possibility is excluded due to the following result. Nitrobenzene, which has been found to form an inclusion compound similar to that for DMA, only quenches the Pe monomer band, and does not induce the longer-wavelength emission, as does DMA.

For a Pe solution with both γ-CD (4.0×10^{-3} mol dm^{-3}) and DMA (3.16×10^{-3} mol dm^{-3}), an experiment on the concentration dependence of Pe was performed. The normalized absorption spectrum for 3.0×10^{-7} mol dm^{-3} Pe was identical to that for 1.0×10^{-7} mol dm^{-3} Pe, indicating that only one Pe molecule is included in the inclusion compound responsible for the exciplex fluorescence. A continuous variation plot of the absorbance at 437 nm, which is an isosbestic point for γ-CD-Pe solutions without DMA, against the molar fraction of γ-CD ($[\gamma\text{-CD}]_0/([\gamma\text{-CD}]_0+[\text{DMA}]_0)$) was made in order to identify the relevant inclusion compound under the condition of $[\gamma\text{-CD}]_0+[\text{DMA}]_0=2.0\times10^{-3}$ mol dm^{-3}. The result that the absorbance passes through a minimum at a molar fraction of 0.5 (not shown) revealed that the inclusion compound has a 1 : 1 stoichiometry concerning γ-CD and DMA. Combined with no concentration effect of Pe on the absorption spectrum, both the absorption change shown in Fig. 4 and the exciplex fluorescence in Fig. 5 are evidently due to a complex that includes a single Pe molecule, with a 1 : 1 stoichiometry of γ-CD and DMA. Therefore, as candidates responsible for the exciplex fluorescence, there are a 1 : 1 : 1 inclusion compound of γ-CD-DMA-Pe (PDC) and an inclusion compound (PDC · DC) formed by the association between PDC and DC:

$$\text{PEC}+\text{DMA}\overset{K_3}{\rightleftarrows}\text{PDC}+\text{EtOH}, \quad (5)$$

and

$$\text{PDC}+\text{DC}\overset{K_4}{\rightleftarrows}\text{PDC}\cdot\text{DC}, \quad (6)$$

where K_3 and K_4 are equilibrium constants for the formation of PDC and PDC · DC, respectively. Because the exciplex fluorescence intensity is proportional to the concentration of the emitting species under our experimental conditions, the exciplex fluorescence intensities which are a function of DMA concentration were compared with the concentration curves of the candidates in order to clarify the inclusion compound emitting the exciplex fluorescence. The concentrations of PDC and PDC · DC were calculated from the following equations:

$$[\text{PDC}]=K_1K_3[\text{DMA}][\gamma\text{-CD}]_0[\text{Pe}]_0/(1+K_1[\gamma\text{-CD}]_0([\text{EtOH}]_0+K_3[\text{DMA}])), \quad (7)$$

with $[\text{DMA}]=[\text{DMA}]_0/(1+K_2[\gamma\text{-CD}]_0)$

and

$$[\text{PDC}\cdot\text{DC}]=K_1K_2K_3K_4[\text{DMA}]^2[\gamma\text{-CD}]_0^2[\text{Pe}]_0/(1+K_1[\gamma\text{-CD}]_0([\text{EtOH}]_0+K_3[\text{DMA}]+K_2K_3K_4[\text{DMA}]^2[\gamma\text{-CD}]_0)). \quad (8)$$

The results are given in Fig. 6 together with the

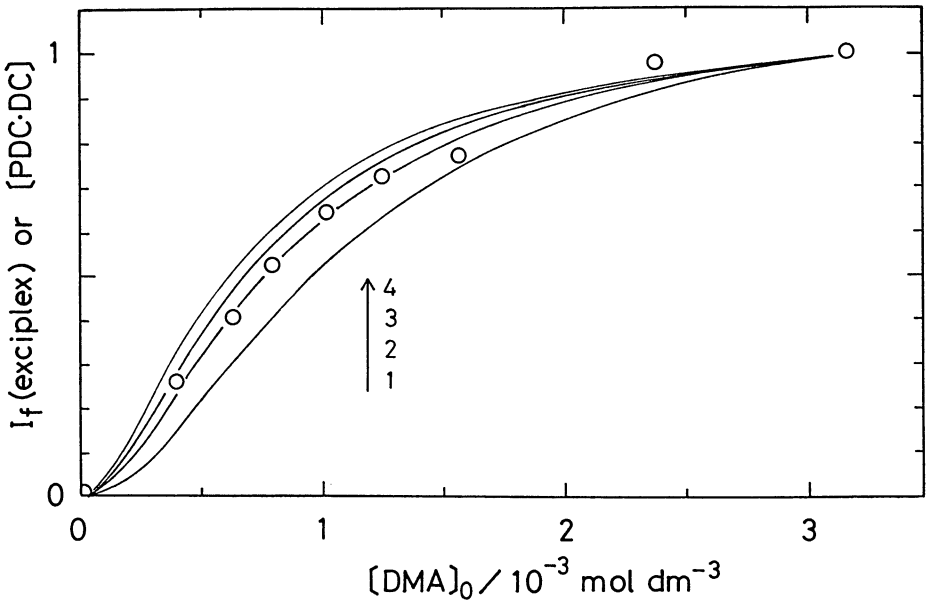

Fig. 6. Comparison of intensities of the Pe-DMA exciplex fluorescence in H_2O-Ethanol (7:3) containing both γ-CD (4.0×10^{-3} mol dm^{-3}) and DMA with calculated curves which are obtained with assumed K_3 and K_4 (20000 mol^{-1} dm^3). The exciplex fluorescence intensities and the curves are normalized to unity at the highest DMA concentration, respectively. Assumed K_3 value: (1) 10000, (2) 20000, (3) 30000, and (4) 40000. $[Pe]_0=3.0\times10^{-7}$ mol dm^{-3}. λ_{ex}=402 nm.

observed intensities of the exciplex fluorescence as a function of DMA concentration. Under the condition that $[\gamma\text{-CD}]_0=4.0\times10^{-3}$ mol dm^{-3}, a calculated curve for PDC·DC with assumed values of K_3=20000 and K_4=20000 mol^{-1} dm^3 was in good agreement with the observed data points, whereas a best-fit curve for PDC afforded K_3=10000. Because these comparisons could not identify the relevant inclusion compound, we next compared the data with calculated curves as a function of γ-CD concentration, keeping the initial DMA concentration at 3.16×10^{-3} mol dm^{-3}. The fitting procedure for PDC·DC gave K_3=20000 and K_4=15000 mol^{-1} dm^3 (not shown), which well agreed with the values evaluated from the previous simulation as a function of DMA concentration. From a similar procedure for PDC, on the other hand, K_3 was estimated to be 2000, which was in disagreement with the K_3 value obtained above for the mechanism of PDC formation. Therefore, we conclude that the exciplex fluorescence is due to PDC·DC. Upon diluting the initial concentration of DMA from 3.16×10^{-3} to 7.89×10^{-4} mol dm^{-3}, the same simulation method for PDC·DC in which comparisons were made as a function of γ-CD concentration afforded K_3=20000 and K_4=20000 mol^{-1} dm^3, which were in excellent agreement with the values already obtained, while the procedure for PDC could not give any K_3 value. These results provide additional evidence that PDC·DC is responsible for the exciplex fluorescence.

The inclusion compound PDC·DC closely resembles in form an association complex of a β-CD-aniline-sodium 1-pyrenesulfonate (or -pyrene) 1:1:1 inclusion compound with a β-CD-aniline 1:1 inclusion compound in the system of β-CD-aniline-sodium 1-pyrenesulfonate (or -pyrene), although a different CD (β-CD) is used.[22] In addition, the charge-transfer fluorescence of sodium 1-pyrenesulfonate- or pyrene-aniline has been observed from the β-CD association complexes. At low DMA concentrations (below ca. 1×10^{-3} mol dm^{-3}), PDC may exist predominantly in a Pe solution with γ-CD, since, as stated previously, there are isosbestic points in the low DMA concentration range. Inclusion compounds similar in form to PDC have also been suggested for the systems of β-CD-aniline-sodium 1-pyrenesulfonate and -pyrene.[22] In contrast to 2:2:1 inclusion compounds, such as PDC·DC, exciplex or charge-transfer emissions are not detected for the 1:1:1 inclusion compounds, such as PDC, probably because the polarity around an excited species within the CD cavity is very high, owing to the smaller degree of shielding from the aqueous phase, compared with the 2:2:1 inclusion compounds including two CD molecules.

Effects of Benzene, Aniline, and *N,N*-Diethylaniline on the Absorption and Fluorescence Spectra of Pe Solutions with γ-CD. When benzene was added to a Pe solution containing γ-CD, the Pe absorption spectrum changed in a fashion similar to that for DMA. This finding shows the formation of an inclusion compound, being of the PDC·DC type, which con-

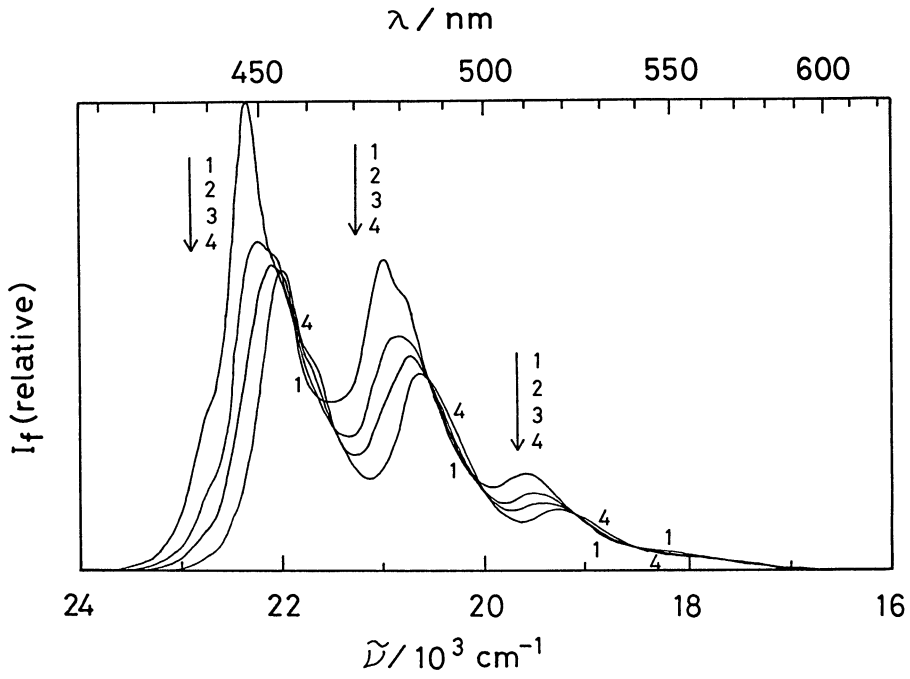

Fig. 7. Fluorescence spectra of Pe (3.0×10^{-7} mol dm^{-3}) in H_2O-ethanol (7 : 3) containing a fixed concentration of γ-CD (4.0×10^{-3} mol dm^{-3}) and varying concentrations of benzene. Concentration of benzene: (1) 0, (2) 5.63×10^{-3}, (3) 1.13×10^{-2}, and (4) 2.25×10^{-2} mol dm^{-3}. λ_{ex}=413 nm.

tains benzene instead of DMA. As the benzene concentration is increased, the fluorescence spectrum exhibits red shifts of peaks accompanied by a slight broadening of bands (Fig. 7). No appearance of long-wavelength emission is observed. In this case, benzene within the γ-CD cavity accommodating Pe exerts microscopic solvent effects, in which, depending on the strength of the interaction with Pe, a microscopic medium (neighboring benzene) influences the band position and band width, etc. Aniline as well as benzene showed similar effects on the absorption and fluorescence spectra, although the Pe monomer fluorescence was relatively efficiently quenched. For aniline, the exciplex fluorescence of Pe was not observed in 1-propanol and ethyl acetate. Consequently, no observation of the Pe-aniline exciplex fluorescence is reasonable for an inclusion compound including Pe and aniline. However, the behavior of *N,N*-diethylaniline towards the Pe fluorescence is intermediate between that of aniline and DMA. That is, both spectral shifts of the Pe monomer fluorescence and the weak exciplex fluorescence of Pe-*N,N*-diethylaniline are observed. In this case, owing to a bulkier diethylamino group in *N,N*-diethylaniline than a dimethylamino group in DMA, a smooth reorientation within the lifetime of excited Pe may be sterically hindered for Pe and *N,N*-diethylaniline molecules inside the γ-CD cavities, resulting in both the exertion of a kind of microscopic solvent effect (the spectral shifts of the monomer fluorescence bands, etc.) and the appearance of the weak exciplex fluorescence.

Polarity of the Interior of the γ-CD Cavities. In order to investigate the polarity within the γ-CD cavities, the exciplex fluorescence maximum (599 nm) was compared with the maxima of the Pe-DMA exciplex fluorescence in organic solvents. This examination has revealed that the dielectric constant around the Pe-DMA exciplex within the γ-CD cavities is close to that of 1-pentanol (ε=13.9), in which the exciplex fluorescence is centered at 600 nm. This value is rather greater than the dielectric constants obtained previously from charge-transfer emissions of a 2-methoxynaphthalene-phthalonitrile complex within the β-CD cavities and 1-pyrenesulfonate- and pyrene-aniline complexes within the β-CD cavities,[22,23] but less than that from a 1-naphthonitrile-anisole exciplex emission in the β-CD-anisole-1-naphthonitrile system.[21] Such differences are, of course, unlikely to be attributed to the differences in property between β- and γ-CD. There have been several studies concerning the polarity of the interior of the CD cavity:[21,22-29] The dielectric constants experienced by fluorescent probes have been reported to be in the very wide range from 2.2 to 55. These results imply that the intrinsic dielectric constant of the CD cavity interior is close to that of 1,4-dioxane (ε=2.2). As pointed out by Cox et al.,[25] the location of a probe molecule inside the cavity is quite critical for the evaluation of the dielectric constants of CDs. A probe molecule does not neces-

sarily totally enter the cavity, since the interior of the CD cavity is not so wide and deep for probes usually used. The polarity sensed by a probe molecule varies from point to point within the cavity. Consequently, the polarity determined from such a probe technique conversely indicates the location of a probe incorporated into the cavity.[21] If the estimated dielectric constant is large, the probe molecule inside the cavity seems to reside near the aqueous phase or to be in contact with water.

The author thanks Professor Fumio Hirayama for his valuable discussion.

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