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Cyanine Dye-Cyclodextrin Systems. Enhanced Dimerization of the Dye

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β-Cyclodextrin (CD), as well as γ-CD, enhances dimerization of some cyanine dyes, as revealed by the enhancement of dimer band in absorption spectra. The presence and absence of enhancement are governed by geometrical factors, i.e., the length of central methine chain and the size of the chromophore at each end.

The effect of inclusion of organic molecules in the cavity of cyclodextrin (CD) has been studied from many viewpoints.[1)] CD enhances the dimerization of some organic molecules, such as pyrene[2)] and anthracene derivatives.[3)] Many photochemical properties of organic molecules change on the inclusion in the CD cavity; emission intensity enhancement,[4,5)] intramolecular or intermolecular excimer or exciplex formation,[2,6)] fluorescence quenching due to the inclusion of the fluorophore and quencher in the same cavity,[7)] and a change in the rate of proton dissociation,[8)] to name a few.

Cyanine dyes are important as photographic sensitizing materials,[9)] mode-locking and lasing media for lasers,[10)] etc. Many physical and chemical properties of cyanine dyes are sensitive to the environment. The study of these environmental effects provides important information which is basic to the photochemical properties of these dyes. The monomer-dimer (or higher aggregate) equilibrium is very sensitive to the presence of additives like salts, organic

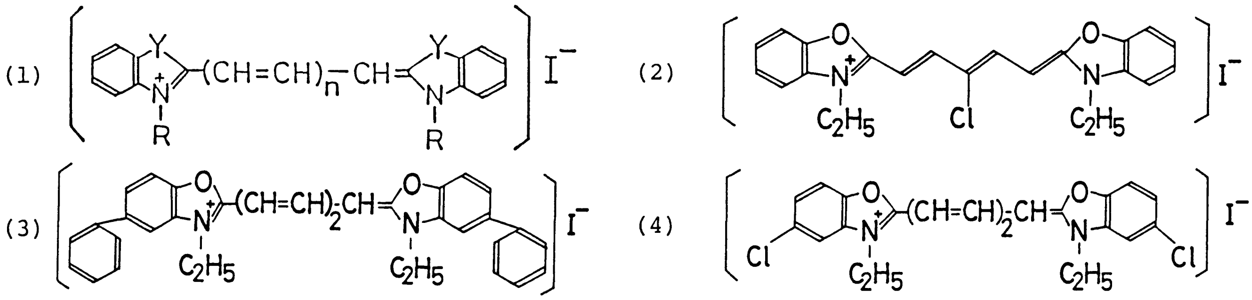

Fig. 1. Sturctural formulas of the cyanine dyes used. (1) Y=O, R=C_2H_5, n=1: 3,3'-diethyloxacarbocyanine iodide (DOC), Y=O, R=C_2H_5, n=2: 3,3'-diethyloxadicarbocyanine iodide (DODC), Y=O, R=C_3H_7, n=2: 3,3'-dipropylthiadicarbocyanine iodide (NK-2606), Y=O, R=C_2H_5, n=3: 3,3'-diethyloxatricarbocyanine iodide (DOTC), Y=S, R=C_2H_5, n=1: 3,3'-diethylthiacarbocyanine iodide (DTC), Y=S, R=C_2H_5, n=2: 3,3'-diethylthiadicarbocyanine iodide (DTDC), Y=S, R=C_2H_5, n=3: 3,3'-diethylthiatricarbocyanine iodide (DTTC), Y=C(CH_3)$_2$, R=CH_3, n=1: 1,3,3,1',3',3'-hexamethylindocarbocyanine iodide (HIC), Y=C(CH_3)$_2$, R=CH_3, n=2: 1,3,3,1',3',3'-hexamethylindodicarbocyanine iodide (HIDC), Y=C(CH_3)$_2$, R=CH_3, n=3: 1,3,3,1',3',3'-hexamethylindotricarbocyanine iodide (HITC), (2) NK-1165, (3) NK-2035, (4) NK-2038.

solvents[11)] or anionic detergent like sodium dodecyl sulfate.[11,12)]

In this letter, the effect of α-, β-, and γ-cyclodextrin on the aggregation state of some cyanine dyes was studied. The result of molecular mechanics calculation on this system with the MM2 program[13)] is briefly reported. The names and structural formulas of the cyanine dyes used are shown in Fig. 1, together with their abbreviated names and code numbers.

DOC, DODC, DOTC, DTC, DTDC, DTTC, HIC, HIDC, and HITC (Dojin, laser grade) and other dyes (Japanese Research Institute for Photosensitizing Dyes), α- and β-CD (Nakarai) and γ-CD (Tokyo Kasei) were used as received. Water was distilled twice. Absorption spectra were measured with a Hitachi 200-20 recording spectrophotometer at room temperature. The concentration of the dye was 2 x 10^{-5} M (1 M = 1 mol dm^{-3} in this letter) except the cases stated otherwise, and that of α-, β-, or γ-CD was 5 x 10^{-3} M.

Examples of absorption spectra of some dye-CD systems are shown in Fig. 2. The bands of DODC near 580 nm and 530 nm are, respectively, due to the monomer and dimer dye, since the increase in dye concentration in the absence of CD accompanied the appearance of the latter band at the expense of the former one. The monomer band of HIDC in the absence of CD is found near 635 nm with a shoulder near 590 nm. It is clear from Fig. 2 that dimerization of DODC is enhanced on the addition of β- or γ-CD, while no enhanced dimerization occurs for HIDC. The same criteria was applied for the other systems. The presence or absence of enhanced dimerization is clearly shown by the presence or absence of the dimer band. The results are summarized in Table 1.

As is clear in the table, α-CD does not enhance dimerization at all. This must be the result of its small cavity diameter (0.45 nm[1)]). To the contrary, γ-CD (cavity diameter 0.85 nm[1)]) enhances dimerization for most of the dyes studied. Its failure in enhancement of dimerization for HIC and HIDC will be due to the presence of bulky end groups. It enhances dimerization for HITC, however. The enhanced dimerization by β-CD (cavity diameter 0.70 nm[1)]) does not occur for dyes with a short methine chain (DOC, DTC, and HIC), dyes with a bulky end group (DTDC, HIDC, NK-2606), or the dye with a bulky atom attached on the central methine chain (NK-1165). Thus, the presence or absence of enhanced dimerization is governed by steric factors.

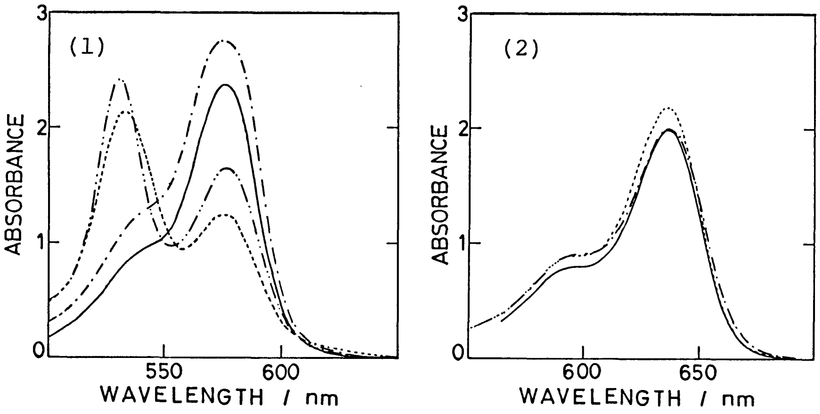

Fig. 2. Absorption spectra of some dye-CD systems. (1) DODC, (2) HIDC
———— : without CD, —-—: with α-CD,
—--—: with β-CD, -----: with γ-CD.
The concentration of dye: 2 x 10^{-5} M. That of CD: 5 x 10^{-3} M.

In order to know the stoichiometry of the inclusion complex, the absorbance at the dimer band of DODC in the DODC-β-CD system ([DODC] = 2.0×10^{-5} M) was measured as a function of [β-CD]. The result, shown in Fig. 3, was simulated for two cases D_2-CD and D_2-CD_2, where D denotes DODC. The concentration of monomer dye in the CD cavity([D-CD]) can be assumed to be very small compared to [D] and [D_2-CD], since the fluorescence quantum yield of the monomer dye was affected little by the addition of CD. For D_2-CD case, we have

$$K = [D_2\text{-}CD]/\ [D]^2[CD]\ , \qquad (1)$$

and

$$[D]_0 = [D] + 2[D_2\text{-}CD], \qquad (2)$$

where $[D]_0$ is the total dye concentration (initially dissolved). The absorbance at the dimer band is

$$A = (\varepsilon_D[D] + \varepsilon_{D_2\text{-}CD}[D_2\text{-}CD])L, \qquad (3)$$

where ε's are relevant molar extinction coefficients and L is the light path length. From Eqs. 1-3 we can make the simulation taking $\varepsilon_{D_2\text{-}CD}$ and K as adjustable parameters. The best-fit result is shown by the solid line in Fig. 3. The values of best-fit K and $\varepsilon_{D_2\text{-}CD}$ are 7×10^7 $mol^{-2}dm^6$ and $3.5 \times 10^5 mol^{-1}$ dm^3cm^{-1}, respectively. The best-fit simulation curve for the D_2-CD_2 case, obtained in a similar way, is shown by the broken line in the same figure. In this case the value of best-fit K is 4.4×10^{11} $mol^{-2}dm^6$, a totally unrealistic value. The results of these simulations strongly suggest the D_2-CD stoichiometry.

Tamaki and Kokubu[3)] showed that two molecules of anthracene sulfonate can be included in the cavity

Table 1. The enhanced dimerization of the dye by the addition of CD. The symbol o denotes the occurrence of enhancement, as judged by the absorption spectra, while x shows the absence of this effect.

Dye[a)]	α-CD[b)]	β-CD[b)]	γ-CD[b)]
DOC	x	x	o
DODC	x	o	o
NK-2606	x	x	o
DOTC	x	o	o
DTC	x	x	o
DTDC	x	x	o
DTTC	x	o	o
HIC	x	x	x
HIDC	x	x	x
HITC	x	o	o
NK-1165	x	x	o
NK-2035	x	o	o
NK-2038	x	o	o

a) Dye concentration: 2×10^{-5} M, except DOC and DTC (5×10^{-5} M) and DTDC (4×10^{-6} M).

b) Concentration of α-, β-, or γ-CD: 5×10^{-3} M.

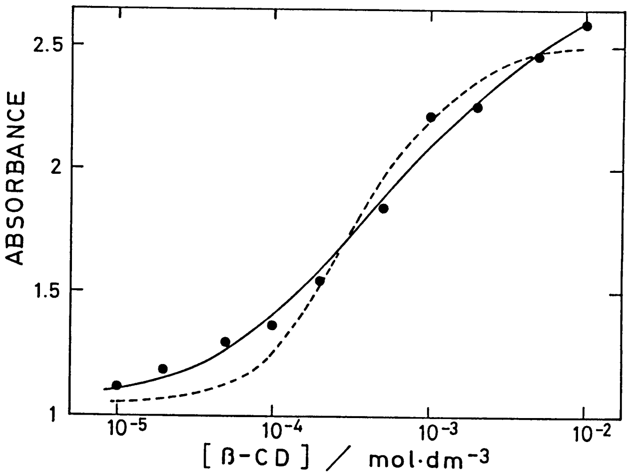

Fig. 3. The dependence of absorbance at the dimer band of DODC in the DODC-β-CD system ([DODC] = 2.0×10^{-5} M) as a function of β-CD concentration, and its simulation assuming two models for CD-enhanced dimer formation (See text.).

of γ-CD. Hirai et al.[14,15] studied dye-CD systems, using crystal violet, methylene blue, methyl orange, or Congo Red as the dye. According to them, two dye molecules are included in the γ-CD (except the case of Congo Red) and one dye molecule is included in the β-CD cavity. However, at first sight it might be hard to conceive that two dye molecules can be incorporated in the β-CD cavity, considering their molecular dimensions. A molecular mechanics calculation was performed by the MM2 program, with an NEC PC-9801 personal computer. The cavity of β- or γ-CD must expand to some extent when it allows inclusion of two dye molecules which are geometrically large compared to the cavity size. This is energetically feasible, however, when the destabilization due to CD ring expansion is compensated by energy gain due to hydrophobic stabilization plus dimerization of the dye. The destabilization energy can be, at least semiquantitatively, estimated as the sum of the incremental energy on stretching of each glycopiranoside unit. The preliminary result shows that the incremental energy caused by the inclusion of two DOTC molecules in a β-CD cavity is of comparable magnitude as that for two anthracence molecules in a γ-CD cavity. They amount only to 1 - 4 kcal per one glycopiranoside unit. Such a small destabilization energy must be well compensated by the hydrophobic stabilization energy on inclusion. As to the inclusion complex of two DODC molecules in a β-CD cavity, the experimental evidence points to its presence. The inclusion of two cyanine dye molecules in the β-CD cavity is a novel, rather unexpected, aspect in the CD chemistry.

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15) The value of $K = 7 \times 10^7$ $mol^{-2}dm^6$ in the simulation of β-CD-$(DODC)_2$ complex mentioned above is comparable with that of γ-CD-$(\text{crystal violet})_2$ in Ref. 14 (2×10^7 mol^{-2} dm^6 calculated from their dissociation constant).

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