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γ-CYCLODEXTRIN-ENHANCED EXCIMER FLUORESCENCE OF PYRENE AND EFFECT OF n-BUTYL ALCOHOL

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The fluorescence of pyrene has been measured in aqueous solutions in the presence of γ-cyclodextrin. The excimer emission of pyrene was enhanced upon addition of γ-cyclodextrin, indicating the formation of the 2:1 complex of pyrene with γ-cyclodextrin which degraded upon addition of n-butyl alcohol to yield the more stable three-component complex of pyrene, n-butyl alcohol, and γ-cyclodextrin.

Cyclodextrins (CD) in water include various kinds of compounds into their cyclic cavities.[1] The binding force for forming inclusion complex has been suggested to be hydrophobic interaction,[2] London dispersion force,[3] or hydrogen bonding.[3a,4] Since the cavities of the cyclodextrins are significantly rigid, the relative size of guest molecule and CD cavity is one of the essentially important factors to form stable inclusion complex. The internal diameters of α-, β-, and γ-CD are 4.5, 7.0, and 8.5 Å, respectively.[1] The CD chemistry has been focused only on α- and β-CD and little attention has been paid on inclusion complex of γ-CD, because the cavity size of γ-CD is too large to fit the benzene and naphthalene derivatives. However, it is assumed easily that, if a vacant space of a 1:1 complex of guest with γ-CD is filled with an additional guest molecule, the inclusion complex should be stabilized. Indeed, the recent studies revealed the formation of the complexes which consist of two guest molecules and one γ-CD molecule.[5-8]

The present study deals with the fluorescence behavior of pyrene in water in the presence of γ-CD. Judging from the CPK molecular model, pyrene molecule can be incorporated into the γ-CD cavity. Since pyrene is a structually rigid molecule, the considerable part of the space, which is exposed to water, remains in the cavity of the 1:1 complex of pyrene with γ-CD. Under such circumstances, an additional molecule may be incorporated into the γ-CD cavity. This is the case which we reported herein.

The dilute aqueous solution of pyrene (2×10^{-6} M) showed the monomer emission on its fluorescence spectrum. A broad emission band, however, appeared at longer wavelength upon addition of γ-CD (1×10^{-2} M). Since the excitation spectrum followed at the emission maximum of the broad band (475 nm) corresponds to the absorption spectrum of pyrene, the emission at the longer wavelength should be ascribed to the pyrene excimer. No enhancement of the pyrene excimer was observed when α- and/or β-CD was added into the aqueous pyrene solution. The γ-CD-concentration dependence on the pyrene monomer and excimer emission is shown in Fig. 1.

After an abrupt increase, the intensities of the monomer emission at 384 nm (I_M) decreased with increasing γ-CD concentrations and again increased at γ-CD concentrations higher than 5×10^{-3} M. On the other hand, the excimer emission was initially enhanced upon addition of γ-CD and diminished at higher γ-CD concentrations. The following three equilibria were considered to interpret the effect of γ-CD on the pyrene-excimer emission:

$$\mathrm{Py} + \mathrm{CD} \overset{K_1}{\rightleftharpoons} \mathrm{Py{\cdot}CD} \quad (1)$$

$$\mathrm{Py{\cdot}CD} + \mathrm{Py} \overset{K_2}{\rightleftharpoons} \mathrm{Py{\cdot}Py{\cdot}CD} \quad (2)$$

$$\mathrm{Py{\cdot}CD} + \mathrm{CD} \overset{K_3}{\rightleftharpoons} \mathrm{Py{\cdot}CD{\cdot}CD} \quad (3)$$

$$K_1 = \frac{[\mathrm{Py{\cdot}CD}]}{[\mathrm{Py}][\mathrm{CD}]} \quad (4)$$

$$K_2 = \frac{[\mathrm{Py{\cdot}Py{\cdot}CD}]}{[\mathrm{Py{\cdot}CD}][\mathrm{Py}]} \quad (5)$$

$$K_3 = \frac{[\mathrm{Py{\cdot}CD{\cdot}CD}]}{[\mathrm{Py{\cdot}CD}][\mathrm{CD}]} \quad (6)$$

$$2K_1K_2[\mathrm{CD}][\mathrm{Py}]^2 + (1 + K_1[\mathrm{CD}] + K_1K_3[\mathrm{CD}]^2)[\mathrm{Py}] - [\mathrm{Py}]_0 = 0 \quad (7)$$

The computer simulation was carried out for the plots of the fluorescence intensities of pyrene excimer (I_E) vs. [γ-CD] to estimate the K_1-, K_2-, and K_3 values by calculating [Py] (the concentration of pyrene which does not bind with γ-CD) from eq. 7 for given K_1-, K_2-, and K_3 values, [Py·CD] from eq. 4, and [Py·Py·CD] from eq. 5.[9] For calculation, we assumed that $[\mathrm{CD}] = [\mathrm{CD}]_0$ because the initial concentrations of γ-CD ($[\mathrm{CD}]_0$) were much higher than those of the total concentrations of the γ-CD complexes and the excimer fluorescence is emitted only from the 2:1 complex of pyrene with γ-CD. One of the calculated curves is given in Fig. 1. The simulated curve obtained by assuming $K_1 = 20\ \mathrm{M}^{-1}$, $K_2 = 5 \times 10^6\ \mathrm{M}^{-1}$, and $K_3 = 200\ \mathrm{M}^{-1}$ was well fitted

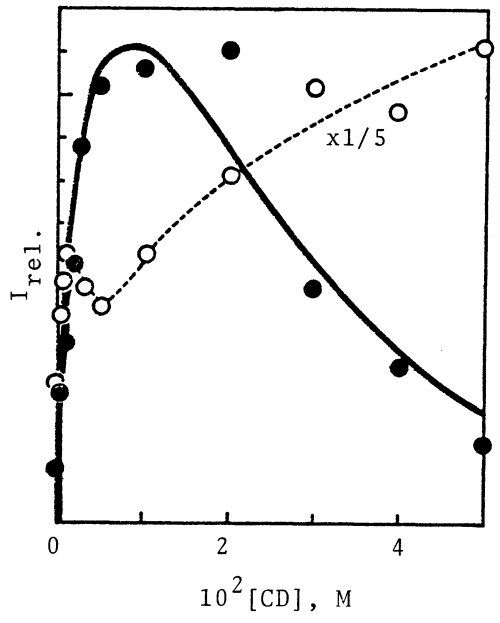

Fig. 1. Effect of γ-CD on the fluorescence intensities of the pyrene monomer (○, 384 nm) and excimer (●, 475 nm) at 25 °C. The fluorescence spectra were measured by exciting 2×10^{-6} M of pyrene in aerobic water in the absence and presence of γ-CD at 337 nm. The solid line shows the calculated fluorescence intensities of the pyrene excimer as a function of [γ-CD] when K_1, K_2, and K_3 are 20, 5×10^6, and $200\ \mathrm{M}^{-1}$, respectively. The fluorescence intensities of the excimer are normalized to coincide at their maximum values.

with the experimental one. We also considered the case where the formation of the 1:2 complex of pyrene with γ-CD (eq. 3) was excluded. In such case, the steep decrease in I_E at higher γ-CD concentrations could not be reproduced by computer simulation. Muramatsu et al. have indicated through spectroscopic analysis that a pyrene molecule binds with two β-CD molecules (Py + 2β-CD $\overset{K}{\rightleftharpoons}$ Py·β-CD·β-CD; log K = 3.3)[10]

The estimated binding constant for the formation of the 2:1 complex of pyrene with γ-CD was extremely large (K_2 = 5 x 10^6 M^{-1}) while that for the 1:1 complex was quite small (K_1 = 20 M^{-1}). Judging from the CPK molecular model, the 1:1 complex still has a space in its cavity which should be exposed to the aqueous phase. Such complex may be stabilized by including an additional hydrophobic guest molecule.[11] Further study should be undertaken to discuss the large K_2 and small K_1 values.

The 2:1 complex of pyrene with γ-CD degraded upon addition of n-butyl alcohol (n-BuOH). Figure 2 shows the effect of n-BuOH on the ratio of the relative fluorescence intensity of excimer (475 nm) to that of monomer (394 nm) when n-BuOH was added into the aqueous pyrene solutions (2 x 10^{-6} M) containing 1 x 10^{-2} M of γ-CD. Upon addition of n-BuOH, the intensities of the monomer emission increased at the expense of the excimer emission. It has been known that the intensities of the pyrene monomer fluorescence at 373 (Peak I) and 384 nm (Peak III) are very sensitive to polarity of medium: the ratio of the fluorescence intensity at 384 nm to that at 373 nm (I_{384}/I_{373}) increases with decreasing solvent polarity.[12] The values of the

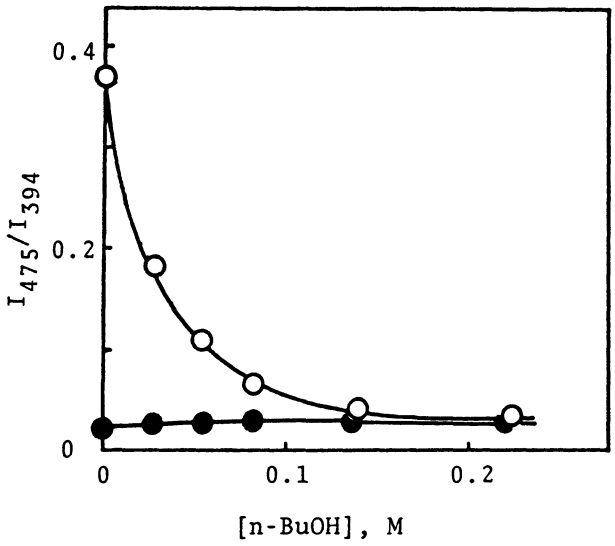

Fig. 2. Effects of n-BuOH on the ratios of the fluorescence intensities of pyrene monomer to those of excimer. n-BuOH was added into the aerobic aqueous solutions of pyrene (2 x 10^{-6} M) in the absence (●) and presence of 1 x 10^{-2} M γ-CD (○) at 25 °C.

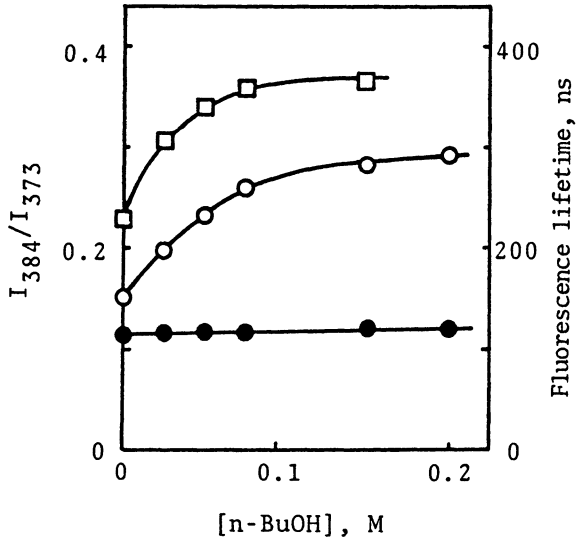

Fig. 3. Changes in the values of the polarity parameter (I_{384}/I_{373}, ○, ●) and the fluorescence lifetimes of pyrene monomer (□) upon addition of n-BuOH into the aerobic aqueous solutions of pyrene (2 x 10^{-6} M) in the absence (●) and presence of 1 x 10^{-2} M γ-CD (○, □) at 25 °C.

polarity parameter (I_{384}/I_{373}) as well as the lifetimes of pyrene monomer also increased upon addition of n-BuOH, as shown in Fig. 3. The increase in the I_{384}/I_{373} values indicates that the environment where the pyrene molecules are located becomes more hydrophobic upon addition of n-BuOH. In other words, n-BuOH does not exclude pyrene in the γ-CD cavity to the aqueous bulk phase. The most plausible explanation is that n-BuOH forms a three-component complex of pyrene, n-BuOH, and γ-CD which is more stable than the 2:1 complex of pyrene with γ-CD. The value of I_{384}/I_{373} obtained for the 1×10^{-2} M γ-CD solution in the absence of n-BuOH is not different significantly from that for water, suggesting that the most of the pyrene molecules in the monomer form are located in the aqueous phase under the conditions. Therefore, the following scheme may be reasonable for forming the pyrene-n-BuOH-γ-CD three-component complex:

$$\text{n-BuOH} + \text{CD} \overset{K_4}{\rightleftharpoons} \text{n-BuOH·CD} \qquad (8)$$

$$\text{n-BuOH·CD} + \text{Py} \overset{K_5}{\rightleftharpoons} \text{Py·n-BuOH·CD} \qquad (9)$$

The cavity size of γ-CD is so large that a stoicheiometry of 1:1 may be inadequate for the complex of n-BuOH with γ-CD. n-BuOH·CD in eqs. 8 and 9 does not mean the 1:1 complex. Recently, the same space-regulating effect of cyclohexanol has been reported for the α-naphthyloxyacetic acid-γ-CD complex.[7] Translocation of pyrene molecules from the aqueous phase to the CD cavity leads the protection of excited pyrene toward oxygen quenching to give longer fluorescence lifetime of pyrene monomer as shown in Fig. 3.

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