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THREE COMPONENT COMPLEXES OF CYCLOHEPTAAMYLOSE. FLUORESCENCE QUENCHING OF PYRENES AND NAPHTHALENES IN AQUEOUS MEDIA

Koji KANO, Itsuro TAKENOSHITA, and Teiichiro OGAWA
Department of Molecular Science and Technology, Kyushu University,
Hakozaki, Higashi-ku, Fukuoka 812

Fluorescence quenching of pyrenes and naphthalenes by diethylamine and di-n-butylamine has been measured in aqueous media with and without cycloheptaamylose. Formation of three component complexes of cycloheptaamylose with a fluorophore and a quencher has been indicated from the catalytic effects of cycloheptaamylose on quenching.

It has been well known that cycloamyloses catalyze various kinds of reactions by including substrates within their cyclic cavities.1) Formation of cycloamylose complexes has been proved by kinetic analyses and/or by means of NMR, ESR, and absorption spectroscopy. Fluorescence spectroscopy is also a powerful means to study the complexation of cycloamyloses. Upon complexation, fluorescence intensities of 1-anilino-8-naphthalenesulfonate increase together with a blue shift of the emission maximum.2) Recently, Edwards and Thomas have studied the interaction between cycloheptaamylose (β-cyclodextrin, β-CD) and pyrene by measuring fluorescence spectra and fluorescence lifetimes of pyrene.3)

The present study deals with the catalytic action of β-CD on fluorescence quenching of pyrenes and naphthalenes by aliphatic amines as well as an evidence for the formation of three component complexes of arene, amine, and β-CD.

The fluorescence lifetimes of pyrene in air-saturated water ([pyrene] = 5 x 10^{-7} M) in the absence and presence of β-CD (1 x 10^{-2} M) were 154 and 226 ns, respectively; fluorescence decay curves were measured by using a nitrogen laser (10 ns pulse width) as an exciting light source. Since no excimer emission from pyrene was observed under the present conditions, it may be reasonable to assume that the complexation between pyrene and β-CD prevents the pyrene fluorescent state from quenching by O_2.3,4) In general, fluorescence intensity (I) and fluorescence lifetime (τ) are related to quenching rate constant (k_q) and concentration of quencher ([Q]) by the Stern-Volmer equation (eq. 1);

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + k_q\tau_0[Q] = 1 + K_{SV}[Q] \qquad (1)$$

where I_0 and τ_0 are fluorescence intensity and fluorescence lifetime, respectively, in the absence of quencher and K_{SV} is the Stern-Volmer constant. Figure 1 shows two types of the Stern-Volmer plots for the pyrene-diethylamine (DEA) system, I_0/I versus [Q] and τ_0/τ versus [Q]. A quenching rate constant (k_{q1}) derived from a plot of I_0/I versus [Q] should be the same as that (k_{q2}) from a plot of τ_0/τ versus [Q] if diffusional collisions induce deactivation of the excited fluorophore. In the pyrene-DEA system, the value of k_{q1} was the same as that of k_{q2} in the absence of β-CD ($k_q = 0.36 \times 10^8\ M^{-1}s^{-1}$). The steady-state fluorescence intensity measurements indicate that the quenching of pyrene is greatly accelerated by β-CD ($k_{q1} = 3.8 \times 10^8\ M^{-1}s^{-1}$). In this case, however, the fluorescence lifetimes of pyrene scarecely decreased upon addition of DEA as is shown in Fig. 1, the k_{q2}-value being $0.36 \times 10^8\ M^{-1}s^{-1}$. The fact that the k_{q2}-value is much smaller than the k_{q1}-value in the presence of β-CD clearly indicates that the complex of pyrene and DEA is formed in the ground state and the pyrene fluorescent state is statically quenched by DEA. In other words, both pyrene and DEA molecules are included within the same cavity of a β-CD molecule where the pyrene molecule is located within an interaction radius of the pyrene-DEA system. Figure 1 also shows that the I_0/I values increase linearly with increasing [Q] at lower quencher concentrations and level off at higher DEA concentrations. This finding suggests the saturation of the binding sites of β-CD-pyrene complex with DEA. Judging from the saturation-type profile, it seems to be reasonable to conclude that the complexation of pyrene, DEA, and β-CD

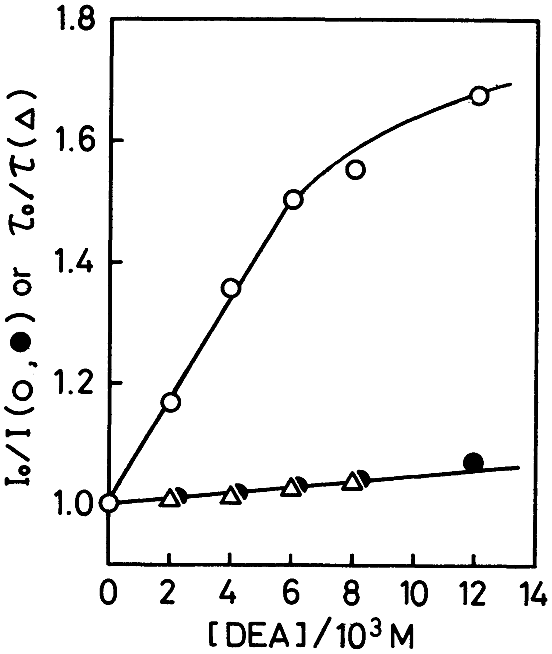

Fig. 1. Stern-Volmer plots of the pyrene-DEA system at 25°C: [pyrene] = 5×10^{-7} M; [β-CD] = 1×10^{-2} M; ●, I_0/I versus [DEA] in the absence of β-CD; ○, I_0/I versus [DEA] in the presence of β-CD; △, τ_0/τ versus [DEA] in the presence of β-CD.

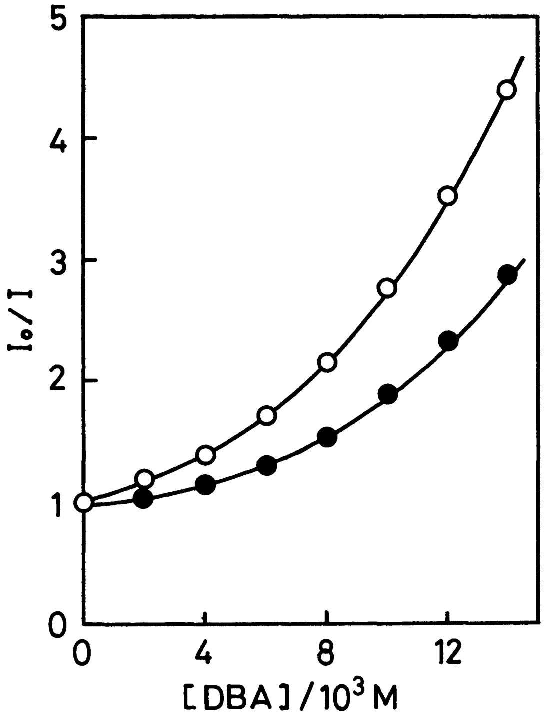

Fig. 2. Relationships between relative fluorescence intensities of naphthalene and DBA concentrations in SDS micellar system in the presence (○) and absence (●) of β-CD at 25°C: [naphthalene] = 1×10^{-5} M; [β-CD] = 1×10^{-2} M; [SDS] = 2×10^{-2} M.

Table 1. Effects of β-CD on Fluorescence Quenching of Arenes by Diethylamine in Aerobic Water at 25°C[a)]

Fluorophore	[β-CD] = 0 M			[β-CD] = 1×10^{-2} M		
	τ_0 b)	K_{SV} c)	k_q d)	τ_0 b)	K_{SV} c)	k_q d)
	ns	M^{-1}	$10^{-8}M^{-1}s^{-1}$	ns	M^{-1}	$10^{-8}M^{-1}s^{-1}$
Pyrene	154	5.5	0.36	226	85.0	3.8
Na 3-pyrenesulfonate	90	23.1	2.6	86	34.9	4.1
Naphthalene	-	17.5	-	-	110	-
Na 1-naphthalenesulfonate	-	13.4	-	-	46.7	-

a) [pyrene] = 5×10^{-7} M, [sodium 3-pyrenesulfonate] = 1×10^{-6} M, [naphthalene] = [sodium 1-naphthalenesulfonate] = 1×10^{-5} M.

b) Fluorescence lifetime of fluorophore in air-saturated water without quencher.

c) Stern-Volmer constant determined from a plot of I_0/I versus [Q].

d) Quenching rate constant.

takes place prior to the quenching reaction. Thus the data of steady-state fluorescence intensity are consistent with those of fluorescence lifetimes.

When DEA, a water soluble aliphatic secondary amine, was used as a quencher, the fluorescence quenching of arenes such as pyrene, 3-pyrenesulfonate, naphthalene, and 1-naphthalenesulfonate was catalyzed by β-CD. The Stern-Volmer constants ($K_{SV} = k_q\tau_0$) obtained from the plots of I_0/I versus [DEA] and the quenching rate constants (k_q) of the pyrene derivatives are listed in Table 1. In the cases of water soluble fluorophores such as 3-pyrenesulfonate and 1-naphthalenesulfonate, the effects of β-CD on the quenching were smaller than those for pyrene and naphthalene. This may be ascribed to the lower affinities of these hydrophilic fluorophores to β-CD.

Surfactant micelles can solubilize various kinds of hydrophobic compounds into water. Then the effects of β-CD on the fluorescence quenching of pyrene and naphthalene were studied by using di-n-butylamine (DBA), a water insoluble aliphatic amine, which was solubilized by sodium dodecylsulfate (SDS) micelles. Figure 2 shows the relationships between the relative fluorescence intensities and the concentrations of DBA in the absence and presence of β-CD. As have been reported,[5)] the plots of I_0/I versus [DBA] cannot be expressed by a simple Stern-Volmer equation. This is ascribed to the statistic distribution of quencher among micelles. As can be seen in Fig. 2, the acceleration of quenching by β-CD was observed even if the reaction was carried out in the SDS micellar phase. This catalytic effects of β-CD in SDS micellar system may also indicate the formation of three component complex as in the case of DEA. On the other hand, β-CD scarcely affected the quenching of pyrene fluorescence by DBA in the presence of SDS micelles. This shows that the higher affinity of surfactant molecule to β-CD causes the transfer of pyrene molecule from the β-CD cavity to the micellar phase.[3)]

The structure of three component complexes of arene, aliphatic amine, and β-CD

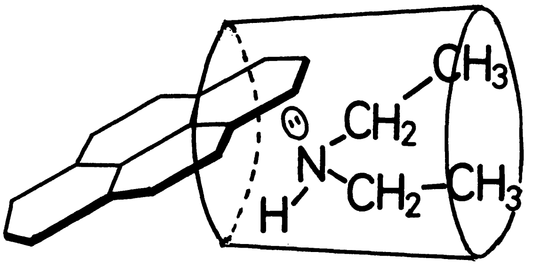

Fig. 3. One of the possible structures of the pyrene-DEA heteroexcimer in the β-CD cavity.

has not been clarified yet. It is known that the internal diameter of the β-CD ring is 7.0-7.5 Å. Judging from the molecular size estimated by using the Corey-Pauling-Koltun (CPK) molecular model, pyrene cannot completely be included within the cavity of β-CD. Therefore, a part of a pyrene molecule seems to be placed within the β-CD cavity as schematically shown in Fig. 3. The pyrene molecule has to tilt in the β-CD cavity in order to interact with the lone-pair electrons of DEA.

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