Effects of β-Cyclodextrin on Fluorescence Quenching of Sodium 1-Pyrenesulfonate by Aniline in Aqueous Media

Harumichi Kobashi,* Masatoshi Takahashi, Yasuyoshi Muramatsu, and Toshifumi Morita

Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376

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Synopsis. β-Cyclodextrin added to the fluorescence quenching system of the title compounds has two effect, depression on dynamic quenching and binding between the fluorescer and quencher causing rapid quenching.

Catalytic actions of cyclodextrins on various chemical reactions are well known.[1] Inclusion effects on excited state properties of organic molecules, such as fluorescence enhancement, have been investigated by several workers,[2] but studies of the effects on intermolecular interactions from photophysical view points are still scarce.[3]

This paper gives results of addition effects of β-cyclodextrin (CD) on fluorescence quenching of sodium 1-pyrenesulfonate (PS) by aniline (A) in aqueous solutions. It is concluded that CD acts as a mediator for ground state association between the fluorescer and the quencher as well as acting as a retarder for dynamic quenching. Immediately after this work had been completed, a similar effect of CD was reported by Kano *et al.*[4] for fluorescence quenching of pyrene and PS by diethylamine. The enhancement of the quenching induced by CD was very small because of a higher ionization potential of the aliphatic amine (8.51 eV) than that of the aromatic amine (7.68 eV) we used. A more efficient quenching induced by such association together with retardation for the dynamic quenching has been revealed from a general consideration of the intensities and lifetimes of fluorescence consisting of two components.

Experimental

After measurements of absorption and fluorescence spectra, fluorescence lifetimes were measured with a Hitachi time resolved photometer and an apparatus for ns flash photolysis.[5] All measurements were carried out at 22 °C unless otherwise stated. Concentrations of CD and A were $\leq 1.0\times10^{-2}$ and $\leq 6.0\times10^{-3}$ M (1 M=1 mol dm^{-3}), respectively. The PS was fixed at 2.0×10^{-5} M. Degassed solutions of these concentrations were stable.

Results and Discussion

The absorption and fluorescence spectra of PS alone agreed with those obtained by Klein *et al.*[6] Addition of CD caused a slight red shift in the L_a absorption band. This shift, similar to that in micellar systems[6,7] originates from the hydrophobic property of a central void of CD. It gives an evidence for inclusion by CD.

In order to study the inclusion further, the difference absorption spectra between PS with and without CD were measured (Fig. 1). With an increase in the amount of CD the positive (d_+) and negative (d_-) absorptions increase their amplitudes. No changes were observed in positions and shapes of the absorption bands. This indicates that PS included by CD has a characteristic absorption differing from that of the free PS. The separation of wavelength between d_- and d_+ of the maximum amplitudes are ≈460 cm^{-1} for the L_a band and ≈180 cm^{-1} for the L_b band, respectively. The dependence of d_+ and d_- on [CD] was analyzed by means of a modified Ketelaar equation, $a/d\pm=1/(b^nK\varepsilon_\lambda)+1/\varepsilon_\lambda$, where a and b are the initial concentrations of PS and CD, respectively, K is the association constant between PS and CD, ε_λ the difference of molar extinction coefficients between complexed PS and free PS at a wavelength λ, $d\pm$ denotes d_+ or d_-, and n is the number of CD concerning the complex formation. The equation with $n=1$ corresponds to the observed dependence, the K value for the 1:1 complex between PS and CD being obtained to be 46±9 M^{-1} at 15 °C.

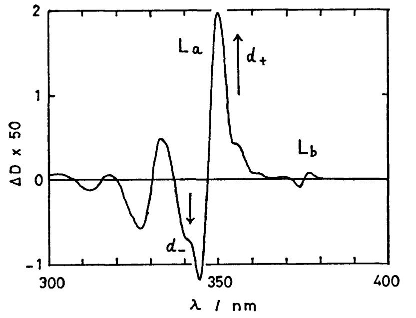

Fig. 1. Difference Spectrum of PS+CD against PS in aqueous solution at 15 °C. [PS]=2.0×10^{-5} M, [CD]=6.0×10^{-3} M.

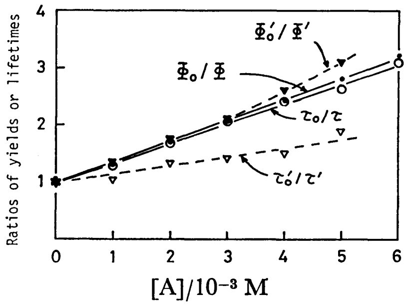

Fig. 2. Stern-Volmer plots for fluorescence yields and life-times of PS in the absence and presence of CD. [PS]=2.0×10^{-5} M, [CD]=1.0×10^{-2} M.

Fluorescence spectra with and without CD are very similar, their quantum yields being almost the same. The Stern-Volmer plots for the fluorescence quenching by A are shown in Fig. 2. In the case with no CD, both plots of Φ_0/Φ and τ_0/τ, where Φ_0/Φ and τ_0/τ have their usual meanings, are in good agreement with each other. The quenching rate con-

TABLE 1. LIFETIMES AND QUENCHING CONSTANTS AND RATE CONSTANTS FOR THE SYSTEM WITH AND WITHOUT CD

	τ_0/ns	K_{SV}/M^{-1}		$k_q/10^9\ M^{-1}\ s^{-1}$	
		a	b	a	b
Without CD	79±1	377±6	347±11	4.7±0.1	4.4±0.1
With CD	76±1	381±13	175±23	5.0±0.2	2.3±0.3

a) Obtained from the plots for Φ_0/Φ and Φ'_0/Φ'. b) Obtained from the plots for τ_0/τ and τ'_0/τ'.

stants (k_q) were obtained to be $4.7\times10^9\ M^{-1}\ s^{-1}$ from the Φ_0/Φ plot and $4.4\times10^9\ M^{-1}\ s^{-1}$ from the τ_0/τ plot. In the case with CD, however, each plot for Φ'_0/Φ' and τ'_0/τ' (the prime is used to distinguish the quantities from those in the former case) splits with increase in A. The difference in the Stern-Volmer constants (K_{SV}) estimated approximately from Φ'_0/Φ' and τ'_0/τ' is larger than that given by Kano *et al.*[4] For the purpose of comparison apparent quenching parameters and lifetimes in the presence and absence of CD are given in Table 1.

The τ'_0 and τ' have been calculated according to the statistical definition of the lifetime, $\tau_s=\int_0^\infty t\phi(t)\mathrm{d}t\Big/\int_0^\infty \phi(t)\mathrm{d}t$, where $\phi(t)$ is an observed decay function of the fluorescence. The decay function in the absence of the quencher is nearly exponential in both cases with and without CD. This might be due to a slight change between the fluorescence lifetimes of the free and the complexed PS. However, the non-exponential feature of the decay in the presence of CD becomes remarkable with increase of quencher. This indicates that at least these two kinds of fluorescers, the free PS and the (PS···CD) complex, are quenched by A with a different rate. Since the complex (the long life component) decays more slowly than the free PS, the excited PS in the complex has been protected to some extent from quenching. When the decay is non-exponential it is not correct to regard the discrepancy between Φ'_0/Φ' and τ'_0/τ' (Fig. 2) as being due to the static quenching. In the present case the following consideration may be possible. Since the inclusion rate constants (k_a) in the ground state are of an order less than $10^7\ M^{-1}\ s^{-1}$ in many cases,[1b)] the excited state equilibrium between PS and the complex would not be attained within the lifetime ($k_a\tau_0[\mathrm{CD}]\ll1$ for $\tau_0=79$ ns and $[\mathrm{CD}]=10^{-2}$ M). The excited species might decay independently of each other. If the observed decay functions can be expressed approximately by $\phi'(t)=A\ \exp(-\alpha't)+B\ \exp(-\beta't)$ and $\phi'_0(t)=C\ \exp(\alpha'_0t)$ in the presence and absence of the quencher, respectively, we have

$$\frac{\Phi'_0}{\Phi'}=\frac{\int_0^\infty \phi'_0(t)\mathrm{d}t/C}{\int_0^\infty \phi'(t)\mathrm{d}t/(A+B)}=\frac{\alpha'}{\alpha'_0}\cdot\frac{A+B}{A+(\alpha'/\beta')B}, \tag{1}$$

$$\frac{\tau'_0}{\tau'}=\frac{\int_0^\infty t\phi'_0(t)\mathrm{d}t\Big/\int_0^\infty \phi'_0(t)\mathrm{d}t}{\int_0^\infty t\phi'(t)\mathrm{d}t\Big/\int_0^\infty \phi'(t)\mathrm{d}t}=\frac{\alpha'}{\alpha'_0}\cdot\frac{A+(\alpha'/\beta')B}{A+(\alpha'/\beta')^2B}, \tag{2}$$

where α' and β' denote the rate parameters of the free and the complexed PS depending on [A], respectively, and α'_0 the one observed at [A]=0. A, B, and C are coefficients depending on [CD] and excitation wavelength. Since we can put $\alpha'=\alpha$, $\alpha'_0\approx\alpha_0$, $\alpha'>\beta'$, and $\alpha/\alpha_0=\Phi_0/\Phi=\tau_0/\tau$, the relations, $\tau'_0/\tau'<\tau_0/\tau$ (Eq. 3), $\tau'_0/\tau'<\Phi'_0/\Phi'$ (Eq. 4), and $\Phi'_0/\Phi'<\Phi_0/\Phi$ (Eq. 5), are obtained from Eqs. 1 and 2 at a certain concentration of the quencher. We see from Fig. 2 that Eqs. 3 and 4 fit the observed results, but not Eq. 5. The results obtained from fluorescence intensity give the relation, $\Phi'_0/\Phi'\gtrsim\Phi_0/\Phi$. There is a discrepancy between the yield (Φ') obtained by the intensity measurements and the one calculated from the decay functions, the former being smaller than the latter. This suggests that there exists an additional quenching so rapid that it is impossible to detect by decay experiments. It would be reasonable to take into account the ground state association between the fluorescer and the quencher induced by CD, because such quenching occurs only with the coexistence of CD. A 1:1:1 complex among PS, CD, and A is plausible as suggested by Kano *et al.*[4] Such a three component complex has also been suggested by Hamai in the system of 2-methoxynaphthalene and *p*-dicyanobenzene in the presence of CD.[8]

The effects of CD on the intermolecular quenching are summarized as follows. (1) Inclusion of the fluorescer and the quencher[9] depresses the dynamic quenching by diffusive collision. (2) Mutual association of the quenching pairs mediated by CD gives rise to rapid quenching. The second effect appears to be important as one of catalytic functions of CD in relation to the association between biological substances under a very low concentration.

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