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Fluorescence Quenching of Fluorenone by Alcohols

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The absorption and fluorescence spectra of fluorenone have been observed in various solvents. The fluorescence intensity increases with increasing solvent polarity, except in alcoholic solvents. The relative fluorescence intensity of fluorenone in acetonitrile is about 14-times greater than that in methanol. There are isosbestic points in the absorption spectra of fluorenone in mixed solvents comprising ethanol–cyclohexane and ethanol–acetonitrile, indicating the formation of a 1 : 1 hydrogen-bonded complex between fluorenone and ethanol. The equilibrium constants for the complex formation are estimated to be 2.0±0.5 and 0.6±0.2 $\text{mol}^{-1}\,\text{dm}^3$ in ethanol–cyclohexane and ethanol–acetonitrile solvents, respectively. The results indicate that the complex formation changes the relative energy of the singlet and triplet states, which have n–π* and π–π* characters, respectively. The complex formation causes a strong fluorescence quenching of fluorenone in the alcohols. A plot of the fluorescence quenching also shows that there is a route for excited-state quenching. It is concluded that the S_1 state has mainly an n–π* character in both nonpolar and alcoholic solvents, while a π–π* character in the S_1 state increases in polar and non-hydrogen bonding solvents. CNDO/S calculations support the experimental results.

The photophysical characteristics of aromatic carbonyl compounds which contain nonbonding(*n*) electrons are strongly dependent on the solvent properties.[1,2] The characteristic changes have been substantially explained by the close proximity of the n–π* and π–π* levels in both the singlet and triplet states. The increase in the solvent polarity shifts the n–π* level up to a higher energy and the π–π* level down to a lower energy. Therefore, they are nonfluorescent in nonpolar solvents and fluorescent in polar solvents as a result of their level inversion.

Fluorenone has a carbonyl group, and its photophysical and photochemical characteristics are dependent on the solvent properties.[3—14] The fluorescence yield, fluorescence lifetime, and intersystem crossing yield vary with the solvent character. Most of studies for these solvent effects relate to the role of the relative energy levels among the triplet and singlet excited states, as well as their n–π* and π–π* characters.[3,5—9,11—15] Kobayashi and Nagakura successfully explained the energy levels of fluorenone using a diagram.[11] They concluded that S_1 is an n–π* state in polar solvents, while it is a π–π* state in nonpolar solvents.

In this paper we report on the absorption and fluorescence spectra, relative fluorescence intensity, and Stokes shift of fluorenone in various solvents. The relative fluorescence intensity of fluorenone, in general, increases along with an increase in the solvent polarity. The fluorescence quantum yields of fluorenone are estimated to be ca. 0.005, 0.01, 0.02, and 0.003 in cyclohexane, benzene, acetone, and 2-propanol, respectively.[6,12—14] Among the polar solvents, the relative fluorescence intensity is abnormally weak in alcoholic solvents. Although Kuboyama,[3] Yoshihara, and Kearns,[5] Monroe and Groff,[10] and Gastilovich et al.[14] have suggested a somewhat different photophysical behavior of fluorenone in alcohols, there is no explanation for the abnormal photophysical behavior of fluorenone in alcoholic solvents. As a consequence of careful measurements of the absorption spectra in mixed solvents of ethanol and cyclohexane and of ethanol and acetonitrile, it has become apparent that fluorenone molecules form a 1 : 1 hydrogen-bonding complex with the alcohol molecules, and that this complex formation is responsible for the abnormal photophysical behavior of fluorenone. Furthermore, the influence of complex formation on the relative position of the energy levels for the n–π* and π–π* states and the photophysical properties of fluorenone was examined by CNDO/S calculations[16,17] and by spectroscopic studies.[3—14,18—23]

Experimental

Fluorenone and anthracene (Wako JIS 1 grade) were purified by repeated recrystallization from a water–ethyl alcohol mixture. 2-Methylbutane(1), hexane(2), cyclohexane(3), decalin(4), benzene(5), carbon tetrachloride(6), dioxane(7), butyl ether(8), bromobenzene(9), chloroform(10), 3-methylbutyl acetate(11), diethyl ether(12), chlorobenzene(13), ethyl acetate(14), methyl acetate(15), *o*-dichlorobenzene(16), dichloromethane(17), pyridine(18), acetone(19), acetonitrile(20), decyl alcohol(21), nonyl alcohol(22), octyl alcohol(23), heptyl alcohol(24), hexyl alcohol(25), pentyl alcohol(26), butyl alcohol(27), isobutyl alcohol(28), isopropyl alcohol(29), propyl alcohol(30), ethyl alcohol(31), methyl alcohol(32), and glycerol (Wako or Merck, Luminasol, spectrosol, JIS S, or reagent grade) were used without further purification. Water was deionized and distilled. Prepared fluorenone solutions ($1.0\times\text{mol}\,\text{dm}^{-3}$) were stored under a dark condition at room temperature. The absorption and emission spectra were observed using a Hitachi U-3210 recording spectrophotometer and a Shimadzu RF-5000 fluorescence spectrometer. The data were transferred to an NEC PC-9801 personal computer for processing. The relative fluorescence intensity of fluorenone in the various solvents was corrected by referring the fluorescence intensity of anthracene in ethanol. The CNDO/S calculations were carried out for the free fluorenone and hydrogen-bonded fluorenone with H_2O. The lowest 150 singly excited electronic configurations were included in the CI calculations. The geometry of fluorenone for the calculations was determined from the crystal data.[24] The calculations were performed using an NEC-9801 personal computer.

Results and Discussion

Absorption and Fluorescence Spectra of Fluorenone in Typical Solvents. The absorption spectra of fluorenone obtained in typical solvents are shown in Fig. 1. There are three apparent absorption bands in the observed region (0–0 peaks are located at 422, 321, and 293 nm in cyclohexane, respectively. See Fig. 1 and Refs. 3, 5, and 25). The absorption intensity of fluorenone increases at around 440, 455, and 470 nm, in cyclohexane, acetonitrile, and ethanol, respectively. It is noted that the spectrum in ethanol is located at the longer wavelength side than that in acetonitrile, though the polar character of ethanol is less than that of acetonitrile.[2,25] Kuboyama has suggested the possibility of hydrogen-bond formation between the carbonyl oxygen atom of fluorenone and ethanol.[3]

The fluorescence spectra of fluorenone can be characterized by the solvent properties, although all of them have a broad feature.[5,6,12] Figure 2 shows typical fluorescence bands of fluorenone. The spectra are classified into three groups. The first is observed in nonpolar solvents, such as cyclohexane etc., and the fluorescence spectrum (Bn) shows a peak at around 465 nm. The second is observed in polar solvents, such as ethyl acetate, dichloromethane, and acetonitrile, and the spectrum (Bp) shows a peak at around 510 nm. The third is observed in polar and hydrogen-bonding solvents (alcohols), and the fluorescence spectrum of fluorenone (Bh) shows a peak at around 550 nm and a shoulder at around 465 nm. Yoshihara and Kearns showed similar fluorescence features of fluorenone in an ethanol–methanol mixed solvent.[5] In the above, B means that the fluorescence is broad and n, p, and h mean that the fluorescence is observed in nonpolar solvents, in polar solvents, and in hydrogen-bonding solvents, respectively. There is no excitation wavelength dependence in the fluorescence spectrum, except in ethanol. The excitation-wavelength dependence in the fluorescence spectra of fluorenone in ethanol indicates that there are more than two ground-state species of fluorenone in ethanol.

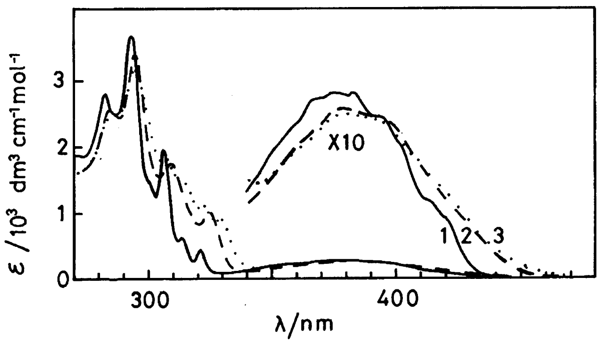


Fig. 1. The absorption spectra of fluorenone in 1: cyclohexane, 2: acetonitrile, and 3: ethanol.

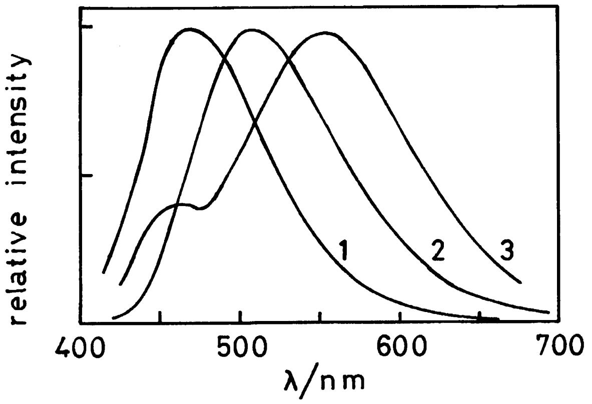


Fig. 2. The fluorescence spectra of fluorenone in 1: cyclohexane, 2: acetonitrile, and 3: ethanol. Excitation wavelength is 360 nm. There is no excitation wavelength dependence except in ethanol.

Stokes Shifts and Relative Fluorescence Intensity. The solvent effects on the electronic spectra give reliable information about the electronic state of molecules in the excited or the ground state.[2,26—29] Gastilovich et al. have classified the solvent effects into three categories depending on the photophysical properties of fluorenone: (I) cyclohexane and methylcyclohexane, (II) benzene, toluene, and tetrahydrofuran, and (III) acetone and acetonitrile. In order to characterize the photophysical properties of fluorenone, the relationship between f' and the Stokes shifts of fluorenone in various solvents is shown in Fig. 3, where f' is defined as

$$f'(D,n) = \left[\frac{(D-1)}{(2D+1)} - \frac{(n^2-1)}{2(2n^2+1)}\right]. \qquad (1)$$

Here, D is the dielectric constant and n is the refractive index of the individual solvents. The factor 1/2 in the second term of Eq. 1 is used for cases in which the dipole moment in the equilibrium excited state is much larger than the dipole moment in the ground state, exciplex, and CT complex.[26,28,29]

A glimpse of the data plotted in Fig. 3 seems to show that there are two straight lines between the Stokes shift and f'; straight line (1) is independent of f' and straight line (2) is directly proportional to f'. Compounds with small f' values belong to line (1). Acetone and acetonitrile with high f' values belong to this category. The points from 21 to 32 are the data in alcoholic solvents, and fall on line (2).

The relationship between f' and the relative fluorescence intensity of fluorenone is shown in Fig. 4. Figure 4 shows that the fluorescence intensity generally increases with increasing polarity of the solvents, except for those in alcoholic solvents. A possible relation is given by a dotted line. On the other hand, the values in the alcoholic solvents are extremely low compared with the values of the polar solvents having a

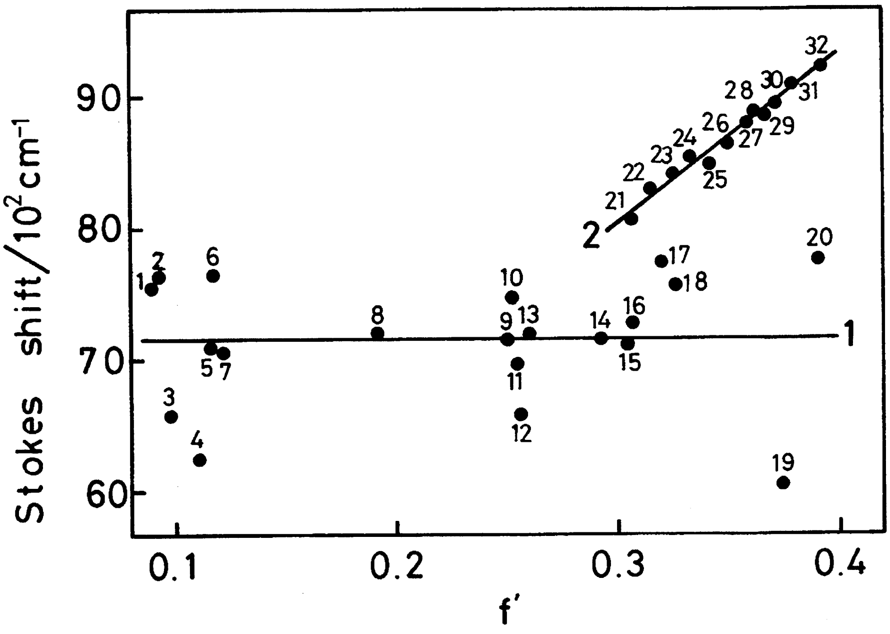


Fig. 3. Relationship between f' and the Stokes shift. The numbers correspond to those given in the experimental section.

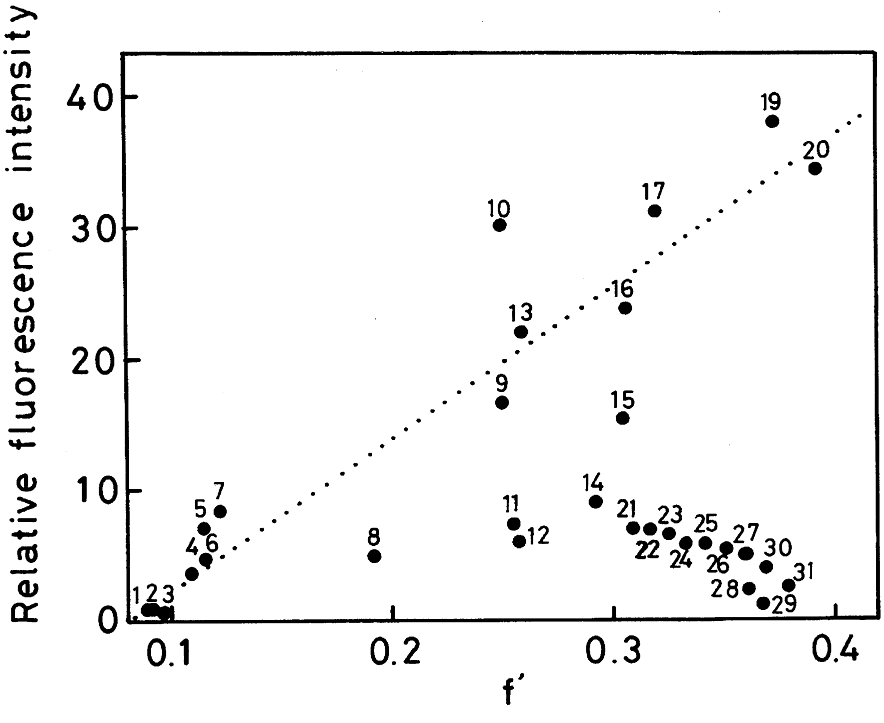


Fig. 4. Relationship between f' and the relative fluorescence intensity. The numbers correspond to those given in the experimental section.

similar polarity index. The results given in Figs. 3 and 4 indicate that photophysical processes of fluorenone in the alcohols are different from those in nonpolar solvents and polar non-hydrogen bonding solvents.

Absorption Spectra in Mixed Solvents. The absorption spectra of fluorenone in cyclohexane–ethanol and acetonitrile–ethanol mixed solvents are shown in Figs. 5 and 6. It can be seen that there are isosbestic points at 345 and 396 nm in cyclohexane–ethanol and at around 355 and 410 nm in acetonitrile–ethanol systems. This shows that there is 1 : 1 hydrogen-bond formation between fluorenone molecules (M) and the complex of M with ethanol molecule (R–OH) in the ground state:[2)]

$$\mathrm{M}+\mathrm{HO{-}R} \underset{}{\overset{K_\mathrm{g}}{\rightleftharpoons}} \mathrm{M}\cdots\mathrm{HO{-}R} \tag{2a}$$

and

$$K_\mathrm{g}=\frac{[\mathrm{MC}]}{[\mathrm{M}][\mathrm{C}]}, \tag{2b}$$

where [M], [C], and [MC] are the stoichiometric concentra-

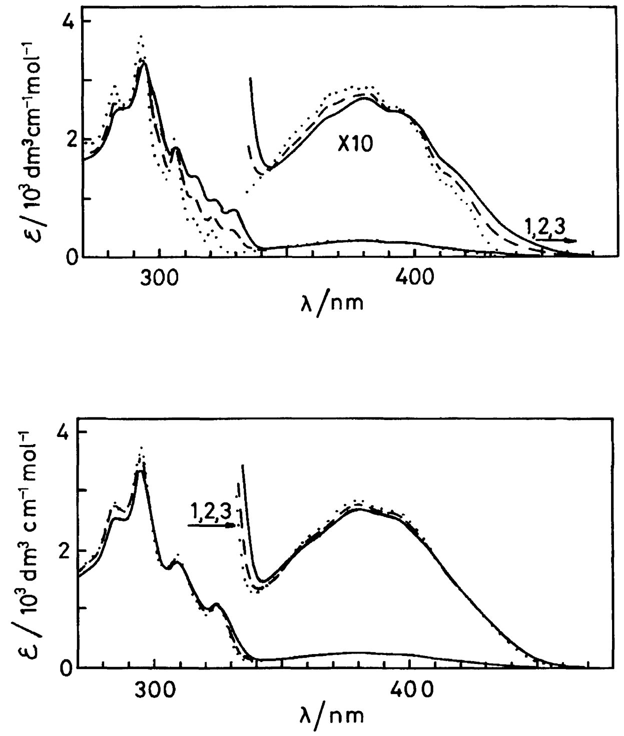


Fig. 5. The absorption spectra of fluorenone in (a) cyclohexane–ethanol and (b) acetonitrile–ethanol binary mixed solvents. Concentration of ethanol in mol dm^{-3} unit is a: (1) 0; (2) 1.73; and (3) 8.57 and b: (1) 0; (2) 1.73; and (3) 8.57.

tions of the ground-state fluorenone, ethanol, and the hydrogen-bonded complex, respectively, and K_g is the equilibrium constant defined by Eq. 2b.

To estimate the equilibrium constant (K_g) the following Ketelaar plot is applicable to the systems:[30,31]

$$\frac{1}{\varepsilon-\varepsilon_{M}}=\frac{1}{K_{g}(\varepsilon_{MC}-\varepsilon_{M})}\cdot\frac{1}{C}+\frac{1}{\varepsilon_{MC}-\varepsilon_{M}}, \tag{3}$$

where ε, ε_{MC}, and ε_{M}, are the apparent absorption coefficient, the absorption coefficient of the complex, and the absorption coefficient of free fluorenone, respectively. Since plots of $1/(\varepsilon-\varepsilon_{M})$ against $1/C$ (see Fig. 6) show a straight line, K_g in cyclohexane–ethanol and acetonitrile–ethanol systems is estimated to be 2.0±0.5 and 0.6±0.2 mol^{-1} dm^3, respectively.

Fluorescence Spectra in Mixed Solvents. Just 40 years ago, Mataga and his co-workers[32] were directed toward quantitative studies of the effect of hydrogen bonding upon the fluorescence of π-electron systems. The influence of hydrogen bonding on the photophysical properties of molecules with close-lying n–π* and π–π* excited states have been studied by many authors.[21—23] In order to clarify the difference in the fluorescence spectra of fluorenone in mixed binary solvents, the fluorescence spectra of fluorenone in acetonitrile–ethanol mixed solvent are shown in Fig. 7. From a pure acetonitrile solvent to a mixed solvent, the spectral peak shifts to the red and the fluorescence intensity decreases along with the addition of ethanol.

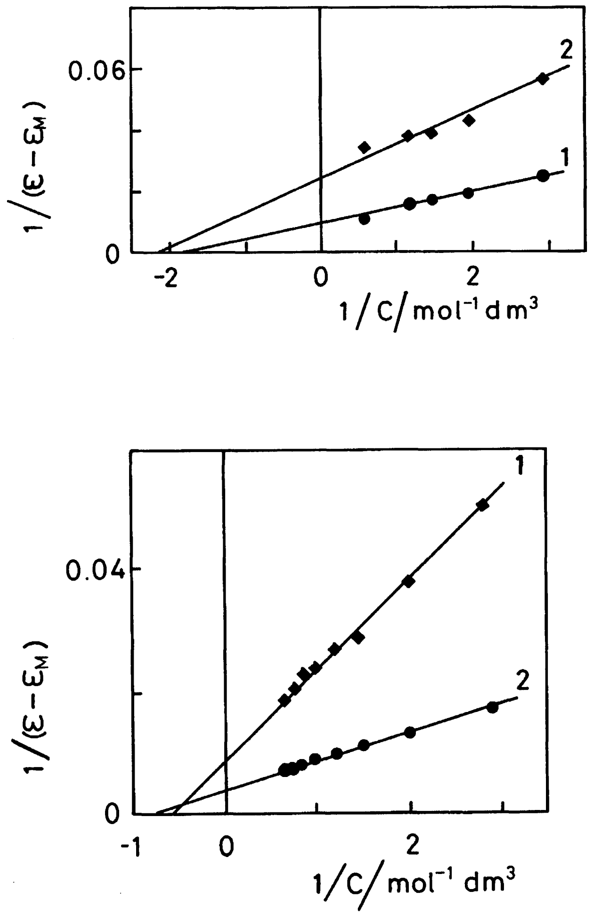


Fig. 6. Plot of $(\varepsilon-\varepsilon_{M})^{-1}$ against C^{-1} for the values at (1) 430 and (2) 400 nm for (a) cyclohexane–ethanol system and at (1) 442 and (2) 438 nm for (b) acetonitrile–ethanol system.

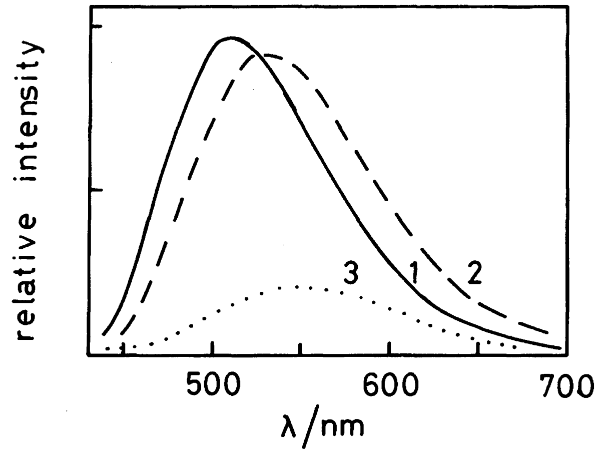


Fig. 7. The fluorescence spectra of fluorenone in acetonitrile–ethanol binary mixed solvent. Concentration of ethanol in mol dm^{-3} unit is (1) 0: (2) 1.73; and (3) 8.57. Excitation wavelength: 354 nm.

Figures 2 and 7 indicate that the fluorescence spectra in alcoholic solvents shift to the red, and are broader compared to those in polar and non-hydrogen bonding solvents. These behaviors indicate that there is a hydrogen-bonding interaction between fluorenone and the alcoholic solvents, not only in the ground state, but also in the excited states,

$$M^* + \text{HO–R} \overset{K_e}{\rightleftarrows} (M\cdots\text{HO–R})^* \tag{2c}$$

and

$$K_e = \frac{[\text{MC}^*]}{[\text{M}^*][\text{C}]}. \tag{2d}$$

Here, $[\text{M}^*]$ and $[\text{MC}^*]$ are the stoichiometric concentrations of the excited-state fluorenone and the hydrogen-bonded complex, respectively, and K_e is the equilibrium constant, defined by Eq. 2d.

Taking into account this process, the probable photophysical processes of fluorenone in hydrogen-bonding solvents is illustrated in Scheme 1. Based on the photophysical processes, the following simplification can be applied:[2,32)]
(a) when $k_1 \gg (1/\tau)$ and $k_2 \gg (1/\tau')$;

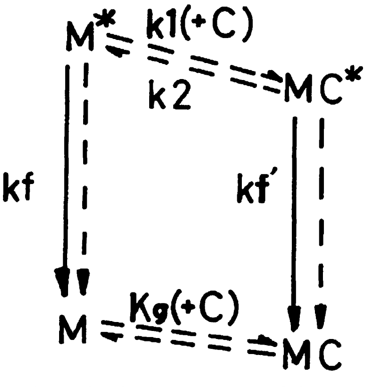
$$\frac{\left(\frac{F}{F_0}-1\right)}{[\text{C}]} \approx \alpha\left(\frac{\tau}{\tau'}\right) - \left(\frac{\tau}{\tau'}\right)K_e\left(\frac{F}{F_0}\right) \tag{4a}$$

(b) when $k_1 \ll (1/\tau)$ and $k_2 \ll (1/\tau')$;

$$\frac{\left(\frac{F}{F_0}-1\right)}{[\text{C}]} \approx \alpha\left(\frac{\varepsilon_{\text{MC}}}{\varepsilon_{\text{M}}}\right) - \left(\frac{\varepsilon_{\text{MC}}}{\varepsilon_{\text{M}}}\right)K_g\left(\frac{F}{F_0}\right). \tag{4b}$$

Here, k_1 and k_2 are the rate constants of hydrogen-bond formation and decomposition reactions in the excited state; F_0 and F are the fluorescence intensity without and with ethanol; τ and τ' are the fluorescence lifetimes of the free (in acetonitrile) and hydrogen-bonded complex (in ethanol), respectively; $K_e = k_1/k_2$; and $\alpha = (k_{f'} \times \tau')/(k_f \times \tau)$, where $k_{f'}$ and k_f are the fluorescent rate constants for free and hydrogen-bonded fluorenone (see Scheme 1), respectively.

Figure 8 shows plots $((F/F_0)-1)/[\text{C}]$ vs. F/F_0 for this system. The straight line indicates that the photophysical processes obey Eq. 4a or Eq. 4b. A least-square calculation shows that the line is represented as follows:



Scheme 1. Photophysical processes of fluorenone in hydrogen-bonding solvents. Where, M and M* are ground and excited states of free fluorenone, MC and MC* are ground and excited state of hydrogen-bonded fluorenone, K_g is an equilibrium constants between M and C, k_1 and k_2 are the rate constants of the hydrogen bond formation and decomposition reactions in the excited state, k_f and $k_{f'}$ are the fluorescent rate constants of M* and MC*, respectively.

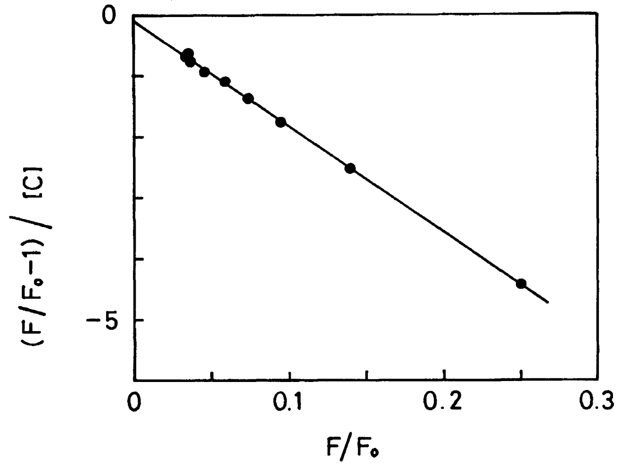


Fig. 8. $((F/F_0)-1/[\text{C}])$ vs. F/F_0 relation of fluorenone fluorescence in acetonitrile–ethanol binary mixed solvents. Excitation wavelength is 354 nm.

$$((F/F_0) - 1/[\text{C}]) = -0.03 \pm 0.06 - 17.5 \pm 0.3 \times (F/F_0). \tag{5}$$

The reported values in acetonitrile for $\tau(1/\tau)$ and k_f of fluorenone are 21.5×10^{-9} s (4.7×10^{7} s^{-1}) and 0.16×10^{7} s^{-1} by Andrews et al.[12)] and 18.6×10^{-9} s (5.4×10^{7} s^{-1}) and 0.17×10^{7} s^{-1} by Bliczók and Bérces;[13)] the reported τ value in ethanol for τ ($\approx\tau'$) ($1/\tau$) is 1.8×10^{-9} s (5.5×10^{-8} s^{-1}) by Monroe and Groff.[10)] Thus, (τ/τ') is estimated to be ca. 11. However, the k_1 and k_2 values are unknown at the present, and we cannot decide which case is dominant in present system. Since the excitation wavelength is almost the isosbestic point of this system and K_g is 0.6 ± 0.2 mol^{-1} dm^3, $(\varepsilon_{\text{MC}}/\varepsilon_{\text{M}})\times K_g$ is estimated to be 1 mol^{-1} dm^3. This is not the case of Eq. 5. Therefore, the value of 17.5 is to be the case (a), and K_e is estimated to be 1.6 mol^{-1} dm^3. This indicates that the excited-state equilibrium between M* and MC* is rapidly attained because fluorenone molecules are surrounded by many ethanol molecules,[27)] and this route is the main quenching process of fluorenone. A similar value of $K_e = 1.3$ mol^{-1} dm^3 has been reported in the case of the acridine N-oxide and ethanol system.[33)]

The results described above support the idea that the Bp and Bh bands of fluorenone fluorescence originate from fluorenone molecules surrounded by polar and non-hydrogen-bonding solvents such, as acetonitrile, and polar hydrogen-bonding molecules, such as alcohols, respectively. Therefore, the complex formation between fluorenone and alcoholic solvents in both the ground and excited states are responsible for the fluorescence quenching of fluorenone in the hydrogen-bonding solvents. In conclusion, both static and dynamic mechanisms are responsible for the quenching of fluorescence of fluorenone in alcoholic solvents.

Figure 9 shows the fluorescence spectra of fluorenone in cyclohexane–ethanol mixed solvents. The spectrum observed in pure cyclohexane is weak, and shows a broad peak at around 465 nm. The fluorescence intensity increases along with a small addition of ethanol, while a further addition of ethanol decreases the intensity. This behavior is completely

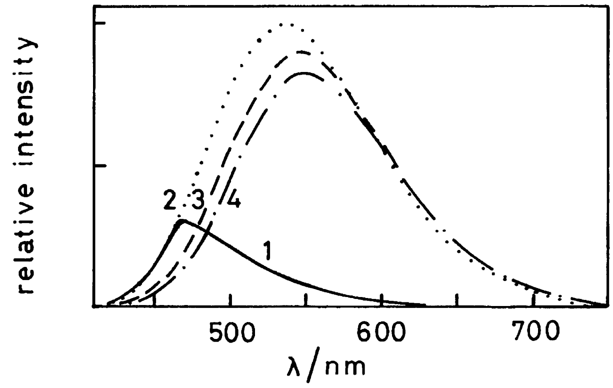


Fig. 9. The fluorescence spectra of fluorenone in cyclohexane–ethanol binary mixed solvent. Concentration of ethanol in mol dm^{-3} unit: (1) 0: (2) 1.73; (3) 5.14; and (4) 8.57. Excitation wavelength: 345 nm.

different from that observed in acetonitrile–ethanol mixed solvents. We have classified the fluorenone fluorescence spectra into three classes (Bn, Bp, and Bh), which correspond to the fluorescence peak at around 465, 510, and 550 nm, respectively. Based on the resolved spectra of fluorenone, we can estimate the relative contributions of the Bn, Bp, and Bh components to the total fluorescence of fluorenone in the cyclohexane–ethanol mixed solvents using the Simplex method.[34,35] The results are given in Table 1. In a pure ethanol solution, there is no contribution from the Bn and Bp components. The contribution of the Bn component, however, decreases rapidly along with the addition of ethanol. The contributions of Bp and Bh are comparable in a solution which includes 1.73 mol dm^{-3} ethanol. A further addition of ethanol results in a decrease in the Bp component, and an increase in the Bh component. These behaviors are completely different from the behavior of the fluorescence intensity in mixed polar solvents, such as the acetonitrile–ethanol system. The results suggest that both singlet and triplet electronic levels of fluorenone in various circumstance are important to elucidate the complete photophysical behavior of fluorenone. In addition to these experiments, though the results are not given here, we examined the influence of viscosity-water on the fluorescence spectra of fluorenone in mixed binary solvents of glycerol and ethanol (10 to 90 vol. % of glycerol) and water–ethanol (0.00025 to 0.04 mol of water) systems. The difference in the viscosity and the addition of water showed no substantial influence on the spectral feature.

Table 1. Relative Contribution (%) of Bn, Bp, and Bh to the Total Fluorescence Spectrum of Fluorenone in Cyclohexane–Ethanol Mixed Solvents

Ethanol mol dm^{-3}	Bn	Bp	Bh
0.0	100	0	0
1.73	3	48	49
3.43	2	32	60
5.14	1	26	73
6.85	1	21	75
8.57	0	15	85
10.3	0	11	89
12.0	0	9	91
13.7	0	5	95
15.4	0	2	98
17.1	0	0	100

It is concluded that the S_1 state has mainly the n–π* character in both nonpolar solvents, such as cyclohexane, and in alcoholic solvents, while the π–π* character in S_1 increases in polar non-hydrogen bonding solvents, such as acetonitrile. The fluorescence quantum yield is very low when S_1 has the n–π* character. The yield increases to a certain extent when the π–π* character increases in the S_1 state. The change of the electronic levels in fluorenone is responsible for the complicated photophysical behaviors of the fluorescence intensity and Stokes shift of fluorenone in various solvents.

CNDO/S-CI Calculations. The fluorescence spectra of fluorenone shifted to the red with increasing the solvent polarity, as shown in Figs. 2 and 3. Figure 5 shows that the fluorescence intensity also increases along with increasing the solvent polarity, except for alcoholic solvents. The results suggest that the relative position of the n–π* and π–π* states in both the singlet and triplet states plays an important role in the photophysical processes of fluorenone. There are three competitive processes from the S_1 state: fluorescence, intersystem crossing, and internal conversion. Among these processes, effective intersystem crossing depends on the n–π* and π–π* character in both the S_1 and T_i states. El-Sayed showed that the spin-orbit coupling between ^{1}(n–π*)→^{3}(π–π*) in molecules having nonbonding electrons is a dominant factor for governing the competition processes.[18]

The effects of hydrogen bonding on the electronic transition were performed by ab initio SCF-CI calculations. Del Bene[36] showed a blue shift of the n→π* band upon hydrogen-bond formation of R–OH···OCH$_3$. Nagaoka and Nagashima[37] investigated the influence of intramolecular hydrogen bonding on the various electronic states of *o*-hydroxybenzaldehyde. CNDO/S calculations are a useful tool for considering complicated photophysical processes.[17] In order to study the electronic structure of the fluorenone and to clarify the relative position of the n–π* and π–π* levels, CNDO/S calculations were carried out for free fluorenone as an example of fluorenone in nonpolar solvents and hydrogen-bonding fluorenone with H_2O. Table 2 gives the results of CNDO/S calculations for the two cases. The calculated energies of the two fluorenones are in good agreement with the observed values. The results indicate that S_1 is an n–π* state, S_2 is a π–π* state, T_1 is a π–π* state, and T_2 is an n–π* state for fluorenone in both nonpolar solvents and the hydrogen-bonded form. It is noted that the n–π* state shifts to blue upon the formation of the complex, while the π–π* states shift to the red. These relative positions of the π–π* and n–π* states in both the singlet and triplet states should be responsible for the low fluorescence quantum yield of free and hydrogen-bonded fluorenone. The results of CNDO/S

Table 2. The Lower Excited States Energy and Oscillator Strength of Free Fluorenone and Hydrogen-Bonded Fluorenone with H_2O Calculated by the CNDO/S Method (in eV Unit) Oscillator strength for the singlet states is written in under part.

State	Obsd in cyclohexane	Free fluorenone		Hydrogen-bonded fluorenone with H_2O[a]	
	Singlet	Singlet	Triplet	Singlet	Triplet
Ψ_1	2.94	2.94 (n–π^*) 0.0000	2.41 (π–π^*)	3.04 (n–π^*) 0.0000	2.45 (π–π^*)
Ψ_2	3.86	3.92 (π–π^*) 0.0629	2.94 (n–π^*)	3.83 (π–π^*) 0.0567	3.04 (n–π^*)
Ψ_3	4.23	4.45 (π–π^*) 0.0340	3.05 (π–π^*)	4.44 (π–π^*) 0.0158	3.08 (π–π^*)

a) >C=O···H–O–H bond length is fixed to be 1.5 Å.

calculations support the conclusions obtained from the experimental results and the El-Sayed rule.[18] In spite of the agreement among the relative energy levels of the π–π^* and n–π^* states in both the singlet and triplet states, it is worth pointing out the possibility that hydrogen-bond formation may activate an efficient $S_0 \leftarrow S_1$ internal conversion channel.[12,23]

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