

# Analysis of the Effects of Protic, Aprotic, and Multi-Component Solvents on the Fluorescence Emission of Naphthalene and its Exciplex with Triethylamine

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The emission spectra of naphthalene (NP)–triethylamine (TEA) systems were measured under steady-state illumination conditions in some protic and aprotic solvent–tetrahydrofuran (THF) mixtures. The fluorescence spectrum of the NP–TEA system in THF could be separated into two component bands (band A at 329 nm (fluorescence of NP) and band B at 468 nm (emission from an intermolecular exciplex)). The intensities of bands A and B decreased with increasing solvent polarity. The intensity of band B also decreased owing to the hydrogen-bonding interaction between TEA and protic solvents, but in this case the intensity of band A increased. The decrease in the intensity of band A with increasing solvent polarity is considered to be caused by the enhanced formation of an ion-pair parallel to the formation of an exciplex with increasing solvent polarity. The decrease in the intensity of band B is considered to be caused by the enhanced formation of ion-pair both parallel to and through the formation of the exciplex. The increase in the intensity of band A and the decrease in that of band B upon the addition of protic solvents is caused by the decrease in the concentration of free TEA. Acetonitrile only has a polar effect and trichloroacetic acid only has a hydrogen-bonding (protonation) effect, while alcohols have both the effects.

**KEY WORDS:** Solvent effect; hydrogen-bonding; polar effect; exciplex; fluorescence.

## INTRODUCTION

Effects of solvent–solute interactions on multi-component fluorescence and charge-transfer reactions of aromatic compound–amine mixtures have been subjects of intensive research. The fluorescence of naphthalene and other aromatic compounds is quenched by tertiary amines with the formation of fluorescent exciplexes [1–7], which is revealed by broad and structureless emission bands that appear on the red side of naphthalene fluorescence in low or non-polar solvents [8].

The intensity and position of the exciplex emission are highly solvent-dependent, and a large red shift and

decrease in the intensity were observed with increasing solvent polarity [8–10]. Shirota *et al.* [11, 12] observed that the addition of alcohols to an NP–TEA system in acetonitrile (AN) reduces both the bimolecular rate constants for the quenching by triethylamine (TEA) and the quantum yields of the photoinduced reactions, and suggested that the hydrogen-bonding interaction between the amine and alcohol suppressed the electron transfer process owing to the decrease in the concentration of free TEA. We reported previously that the effects of the addition of alcohols on the intra- and inter-molecular exciplex systems (4-phenyl-1-*N,N*-dimethylaminobutane (PDAB) [13, 14] and toluene–TEA system [15]) can be separated into solvent polarity and hydrogen bonding effects. These studies are closely related to the investigation by Shirota *et al.* However, in our studies tetrahydrofuran (THF) was used as a solvent instead of AN and both fluorescences of aromatics and emissions from the exciplexes could be observed and

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more detailed information about the emission intensities could be obtained. It would be interesting to understand how these two factors affect other intermolecular exciplex systems which show more complicated spectral changes.

In the present study, the spectral changes of the NP-TEA system in THF upon the addition of AN, trichloroacetic acid (TCAA) and some alcohols were studied, and the effects of the hydrogen-bonding interaction and the change in solvent polarity on the intermolecular photo-induced processes of the NP-TEA system are discussed.

## EXPERIMENTAL

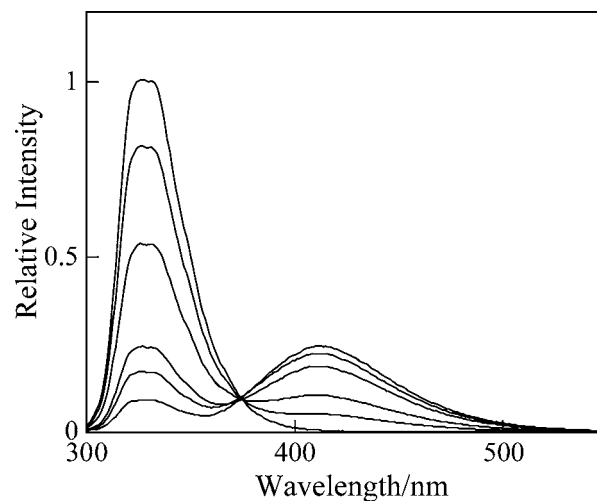
All the reagents were obtained from commercial sources. TEA (extra purity grade) was used after drying with sodium hydroxide and a trap-to-trap distillation. Methanol (MeOH), ethanol (EtOH), propanol (PrOH), Butanol (BuOH), cyclohexane (CH), tetrahydrofuran (THF) and acetonitrile (AN) were of spectroscopic grade and were used as supplied. TCAA (extra purity grade) was used as available. NP (extra pure grade) was purified by recrystallization from ethanol followed by sublimation.

The emission spectra were measured by a Shimadzu spectro-fluorophotometer, model RF1500 (band-pass, typically 10 nm), at room temperature. Excitation was effected at 290 nm to avoid the local excitation of TEA. The concentrations of NP and TEA were chosen to be  $1.0 \times 10^{-4}$  M and  $5.0 \times 10^{-2}$  M, respectively. The relative permittivity ( $\epsilon$ ) of mixed solvents was determined with a dielectric analyzer, Type FAM-3A, manufactured by Yamato Scientific Instrument Co. The oscillator, controlled by a quartz crystal, was operated at a frequency of 2 MHz. The cell constant was determined using CH ( $\epsilon = 2.02$ ), THF ( $\epsilon = 7.39$ ) and AN ( $\epsilon = 37.5$ ). These data have been reported previously [14].

## RESULTS

The fluorescence of NP was quenched by TEA, and a new emission band appeared on the long wavelength side of NP fluorescence in CH (Fig. 1) and THF. The emission spectrum of the NP-TEA system consists of two emission bands; the fluorescence of the NP (band A, with a peak at 329 nm) and the exciplex emission (band B, at 412 nm in CH and 468 nm in THF) (Table I). The wavelength of the peak and the bandwidth of band B were independent of the excitation wavelength.

Upon the addition of TCAA to THF solutions, the intensity of band B decreased, while that of band A in-



**Fig. 1.** Emission spectra of the NP-TEA system in cyclohexane at room temperature: [TEA] are (1)  $0$ , (2)  $1.0 \times 10^{-3}$ , (3)  $5.0 \times 10^{-3}$ , (4)  $1.5 \times 10^{-2}$ , (5)  $3.0 \times 10^{-2}$ , and (6)  $5.0 \times 10^{-2}$  mol dm $^{-3}$ , [NP] =  $1.0 \times 10^{-4}$  mol dm $^{-3}$ .

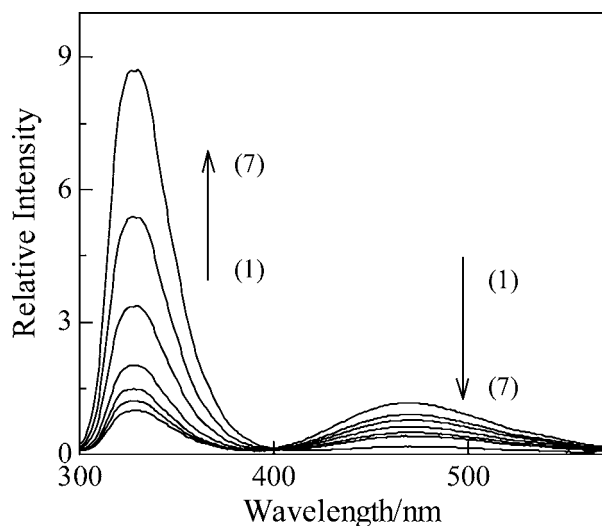
creased (Fig. 2). Since a clear isosbestic point is seen, there seems to be only one factor affecting the spectral changes. Since the concentrations of TCAA are very low, the polarity of the solution is kept almost constant (the relative permittivity of the solution was found to increase slightly from 7.39 to 7.52, when the concentration of TCAA increased from 0 to  $1 \times 10^{-2}$  M in THF). Therefore, the effect was attributed to the hydrogen-bonding interaction between TEA and TCAA (or the protonation of the amine). The decrease in the concentration of free amine suppresses the formation of the intermolecular exciplex, and results in the increase in the intensity of band A and the decrease in that of band B.

Figure 3 shows the emission spectra of the NP-TEA system in some THF-AN mixtures. The intensities of bands A and B decrease with increasing AN concentration, and the decrease in the intensity of band B is larger than that of band A. A red shift of band B upon the addition of AN was also observed.

The decrease in the intensity of band B on the addition of AN to THF must be attributed to the increase

**Table I.** Wavelengths (nm) (and Bandwidth) of Band B and the  $K_{SV}$  for Naphthalene Fluorescence Quenching by TEA in Different Solvents

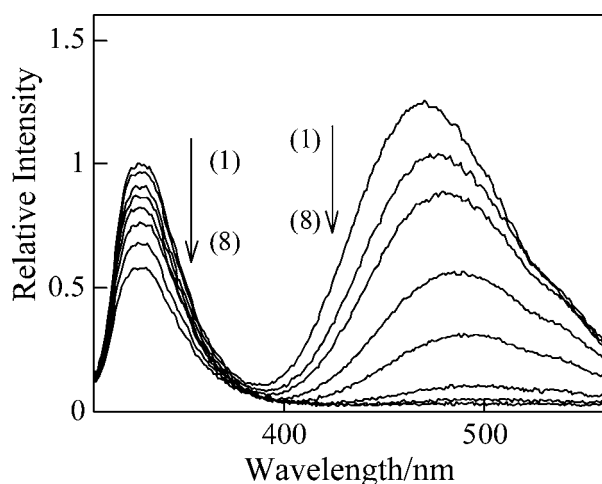
Solvent	Relative permittivity	$\lambda_B$ ( $\lambda_{1/2}$ )	$K_{sv}$ (dm $^3$ mol $^{-1}$ )
Cyclohexane	2.02	412 (76)	200
THF	7.39	468 (84)	330
Acetonitrile	37.5	—	725



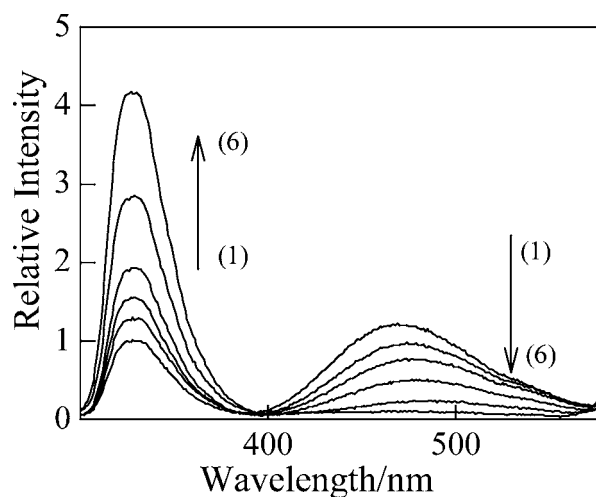
**Fig. 2.** Emission spectra of the NP-TEA system in THF-TCAA mixtures at room temperature:  $[TCAA]_0$  are (1) 0, (2)  $1.0 \times 10^{-2}$ , (3)  $2.0 \times 10^{-2}$ , (4)  $3.0 \times 10^{-2}$ , (5)  $4.0 \times 10^{-2}$ , (6)  $4.5 \times 10^{-2}$ , and (7)  $5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[NP] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$ , and  $[TEA] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ .

in the solvent polarity. The exciplex converts to a non-fluorescent ion-pair in polar medium. The red shift of band B shows that the exciplex is highly polar [16].

Spectra of the NP-TEA system in some THF-ethanol mixtures are shown in Fig. 4. Upon the addition of ethanol, the intensity of band B decreased, while that of band A increased. Similar spectral changes were ob-



**Fig. 3.** Emission spectra of the NP-TEA system in THF-AN mixtures at room temperature: vol% of AN are (1) 0, (2) 5.0, (3) 10, (4) 20, (5) 30, (6) 50, (7) 70, and (8) 90.  $[NP] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$ , and  $[TEA] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ .



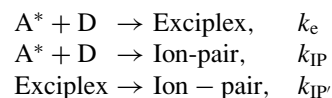
**Fig. 4.** Emission spectra of the NP-TEA system in THF-EtOH mixtures at room temperature: vol% of EtOH are (1) 0, (2) 10, (3) 20, (4) 30, (5) 60, and (7) 90.  $[NP] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$ , and  $[TEA] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ .

served for the other alcohols. Figure 5 shows the intensity changes of bands A and B resulted from the addition of alcohol. The spectral changes increased in the order: butanol < propanol < ethanol < methanol. Since the addition of alcohol results in increases in solvent polarity and hydrogen-bonding ability with TEA, the spectral changes resulting from alcohol additions must be a result of the effects of these two factors.

## DISCUSSION

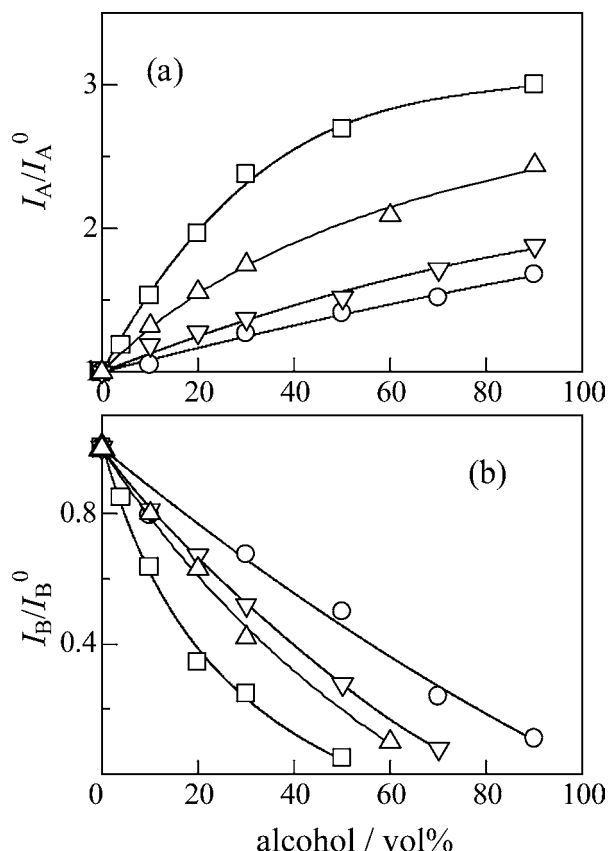
### Basic Mechanism for Exciplex and Ion-Pair Formation

Knibbe *et al.* [17] proposed the following reactions to explain their observations on the dependencies of the lifetime and relative emission intensity of the exciplex in the anthracene-*N,N*-diethylaniline system on solvent polarity:



where  $A^*$  and  $D$  denote an excited anthracene and *N,N*-diethylaniline, respectively.

In this scheme, the formation of the ion-pair occurs through and parallel to the formation of the exciplex. They pointed out that  $k_{IP}$  and  $k_{IP'}$  depend on solvent polarity, whereas  $k_e$  should be virtually independent of solvent polarity, and that these electron-transfer reactions are highly exergonic in AN and thus presumably irreversible. Indeed,



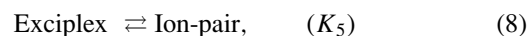
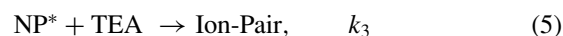
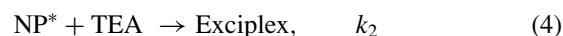
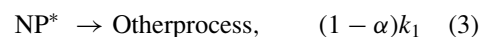
**Fig. 5.** Plots of relative intensities of bands A (a) and B (b) against vol.% of alcohols in THF-alcohol mixtures: (□) MeOH, (Δ) EtOH, (▽) PrOH, and (○) BuOH.  $[NP] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$ , and  $[TEA] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ .

the exciplex emission was not detected in AN, as with many other systems.

In the previous studies [13–15], it was observed that in the cases of 4-phenyl-1-*N,N*-dimethylaminopropane and toluene-TEA system, the emission intensity of exciplexes decreased with increasing solvent polarity as the present study, but the intensity of the fluorescence of phenyl group (or toluene) (band A) was independent of solvent polarity. The decrease in the intensity of exciplex emission was considered to be caused by the conversion of the exciplex to ion-pairs enhanced by the increase in solvent polarity. The finding that the intensity of band A was constant was thought to show that the rate of exciplex formation was independent of solvent polarity and the reaction for exciplex formation was not reversible.

As shown in Fig. 3, however, both the intensities of bands A and B decreased with increasing solvent polarity. As shown later, the value of  $K_{SV}$  for the quenching of band A by TEA increases with increasing solvent polarity. The

decrease in the intensity of band A seems to show that the rate of exciplex formation from the excited naphthalene and TEA increases with increasing solvent polarity or that the reaction for exciplex formation is reversible. As shown above, however, the rate of exciplex formation was found to be independent of solvent polarity for similar cases of exciplex formation. Further, any enhancement of the exciplex emission with increasing solvent polarity was not observed. Judging from these things, the rate of exciplex formation is not considered to increase with solvent polarity. Since the change in the intensity of band A was not parallel to that of band B and all Stern-Volmer plots for the quenching of band A by TEA in CH, THF, and AN were linear, the reaction for exciplex formation is thought not reversible. In the present study, to explain the decrease in the intensity of band A, the above reactions proposed by Kinbbe *et al.* were adopted. The direct formation of ion-pair from the excited naphthalene must occur and the rate constant of this reaction depend on the solvent polarity. In polar solvents, dissociation of the exciplex to a solvent-shared ion-pair occurs, and in highly polar solvents, such as AN, the dissociation is essentially irreversible (the exciplex emission was not observed in AN). However, in moderately-polar solvents, the dissociation can be considered to be reversible [14,15]. In the following reaction mechanism, it is assumed that the equilibrium between the exciplex and the ion-pair is attained:



Here  $NP^*$  denotes NP in the excited singlet state. Exciplex denotes the intermolecular exciplex, and ion-pair denotes the solvent-shared ion-pair. The proportions of radiation processes from the two excited species are shown by the factor  $\alpha$  and  $\beta$ , respectively.

The findings that the decrease in the intensity of band B was larger than that of band A show that both  $k_3$  and  $K_5$  depend on the solvent polarity.

The following equations for the intensities of bands A and B were derived by a steady-state treatment based on

the assumption that a fast equilibrium between Exciplex and ion-pair is attained:

$$I_A = \frac{\alpha k_1}{k_1 + (k_2 + k_3)[TEA]} I_0 \quad (10)$$

$$I_B = \frac{k_2[TEA]}{k_1 + (k_2 + k_3)[TEA]} \times \frac{\beta k_4}{k_4 + K_5 k_6} I_0 \quad (11)$$

Here [TEA] denotes the concentration of free TEA.

From Eq. (10), the following expression can be derived for the intensity changes in naphthalene fluorescence on TEA addition:

$$\begin{aligned} \frac{I_A^0}{I_A} &= 1 + \frac{k_2 + k_3}{k_1} [TEA] \\ &= 1 + K_{SV} [TEA] \end{aligned} \quad (12)$$

where  $I_A^0$  represents the intensity of naphthalene fluorescence in the absence of TEA, and  $K_{SV} = (k_2 + k_3)/k_1$ . The  $K_{SV}$  values in some solvents are shown in Table I.

As shown in Table I, the  $K_{SV}$  value increases significantly with increasing solvent polarity. The results indicate that the value of  $k_3$  increases with increasing solvent polarity.

### Effect of Protonation of Amine on Emission Spectra

The emission spectrum of the NP-TEA system in THF is only affected by the protonation of the amine upon TCAA addition. Since the concentrations of TCAA are very small, as mentioned above, the polarity of the solvent is only slightly affected by the addition of TCAA.

The experimental results for the THF-TCAA mixtures can be explained by reactions (1)–(9) and the following reaction:



Here  $TEAH^+$  denotes the protonated amine. Since formation of the protonated amine with trichloroacetic acid must occur quantitatively, the following equations can be obtained ( $[TEA] = [TEA]_0 - [TCAA]_0$  and  $k_3$  and  $K_5$  are independent of  $[TCAA]_0$ , where  $[TEA]$  is the concentration of the free amine and  $[TEA]_0$  and  $[TCAA]_0$  are the initial concentrations of TEA and TCAA):

$$\begin{aligned} X_{TCAA} &= \frac{I_A^{THF}}{I_A} = 1 - \frac{(k_2 + k_3^{THF})[TEA]_0}{k_1 + (k_2 + k_3^{THF})[TEA]_0} \\ &\times \frac{[TCAA]_0}{[TEA]_0} = 1 - \frac{K_{SV}^{THF}[TEA]_0}{1 + K_{SV}^{THF}[TEA]_0} \\ &\times \frac{[TCAA]_0}{[TEA]_0} \end{aligned} \quad (14)$$

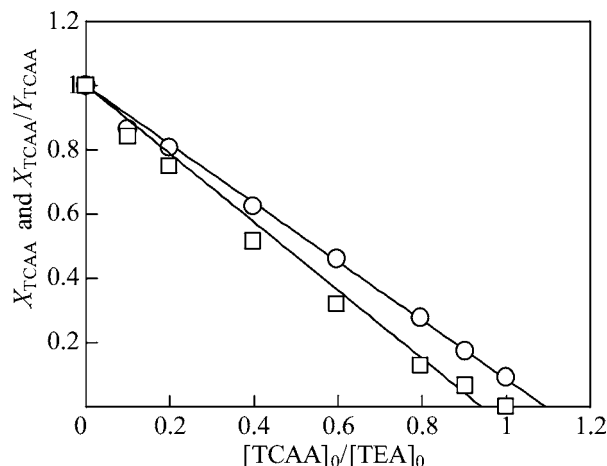


Fig. 6. Plots of  $X_{TCAA}$  (○) and  $X_{TCAA}/Y_{TCAA}$  (□) against  $[TCAA]_0/[TEA]_0$  for changes in the intensities of bands A and B in THF-TCAA mixtures.

$$Y_{TCAA} = \frac{I_B^{THF}}{I_B} = X_{TCAA} \times \frac{[TEA]_0}{[TEA]} \quad (15)$$

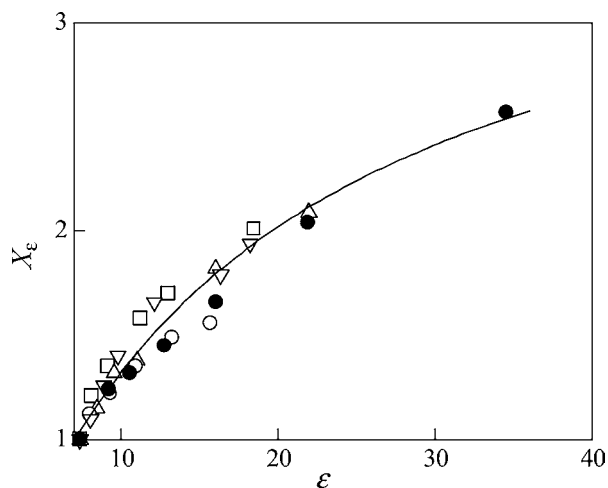
$$\frac{X_{TCAA}}{Y_{TCAA}} = \frac{[TEA]}{[TEA]_0} = 1 - \frac{[TCAA]_0}{[TEA]_0} \quad (16)$$

where  $I_A^{THF}$  and  $I_B^{THF}$  are the intensities of bands A and B, respectively, in pure THF.  $k_3^{THF}$  represents the rate constant of reaction (5) in pure THF.

As shown in Fig. 6, linear relationships between  $X_{TCAA}$  and  $[TCAA]_0/[TEA]_0$  and  $X_{TCAA}/Y_{TCAA}$  and  $[TCAA]_0/[TEA]_0$  were obtained. The slope of the straight line for the relationship between  $X_{TCAA}/Y_{TCAA}$  and  $[TCAA]_0/[TEA]_0$  is about  $-1.0$  and that for the relationship between  $X_{TCAA}$  and  $[TCAA]_0/[TEA]_0$  is  $-0.94$ . Since  $[TEA]_0$  is equal to  $5 \times 10^{-2} \text{ mol dm}^{-3}$ , the value of the latter slope ( $-0.94$ ) gives a value of  $K_{SV}^{THF}$  equal to 314. This value is in good agreement with the value of  $K_{SV}^{THF}$  shown in Table I. These findings indicate that the effect of TCAA addition on the intensities of bands A and B can be explained by the quantitative protonation of TEA.

### Direct Electron Transfer Between the Excited Naphthalene and TEA

For the toluene-TEA system in THF-AN mixed solvents, it was found that the intensity of band A was independent of the amount of AN, while that of band B decreased with increasing amount of AN [15]. However, as mentioned above, the intensity of band A decreased with increasing AN amount in the NP-TEA system. This must be caused by the direct formation of an ion-pair between the excited naphthalene and TEA as in the anthracene-*N,N*-diethylaniline system mentioned above.



**Fig. 7.** Plots of  $X_\epsilon$  against relative permittivity ( $\epsilon$ ) for changes in the intensities of Band A in THF-AN and THF-alcohol mixtures: (●) AN, (□) MeOH, (Δ) EtOH, (∇) PrOH, and (○) BuOH. The solid line is the best-fit curve of all points obtained.

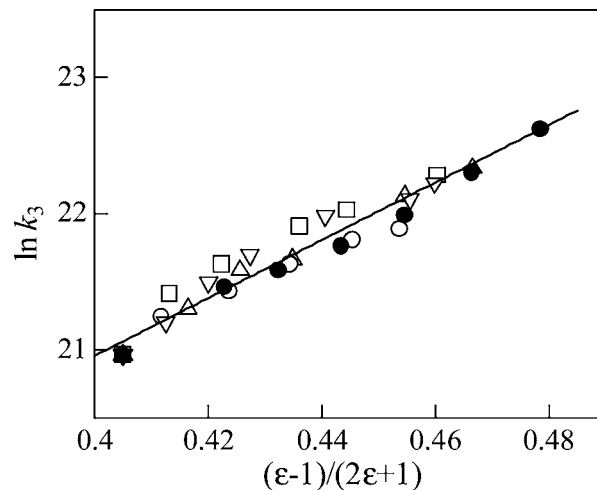
From Eq. (10),  $X_\epsilon$  can be expressed as follows:

$$\begin{aligned} X_\epsilon &= \frac{I_A^{\text{THF}}}{I_A} = \frac{k_1 + (k_2 + k_3^\epsilon)[\text{TEA}]_0}{k_1 + (k_2 + k_3^{\text{THF}})[\text{TEA}]_0} \\ &= \frac{k_1 + k_2[\text{TEA}]_0}{k_1 + (k_2 + k_3^{\text{THF}})[\text{TEA}]_0} + \frac{[\text{TEA}]_0}{k_1 + (k_2 + k_3^{\text{THF}})[\text{TEA}]_0} k_3^\epsilon \\ &= \frac{1 + K_{\text{SV}}^{\text{CH}}[\text{TEA}]_0}{1 + K_{\text{SV}}^{\text{THF}}[\text{TEA}]_0} + \frac{[\text{TEA}]_0}{1 + K_{\text{SV}}^{\text{THF}}[\text{TEA}]_0} \frac{k_3^\epsilon}{k_1} \quad (17) \end{aligned}$$

where  $K_{\text{SV}}^{\text{CH}}$  is the value of  $K_{\text{SV}}$  in CH ( $K_{\text{SV}}^{\text{CH}} = k_2/k_1$ ) and  $k_3^\epsilon$  denotes the value of  $k_3$  in a solvent with relative permittivity  $\epsilon$ . Since  $K_{\text{SV}}^{\text{CH}}$ ,  $K_{\text{SV}}^{\text{THF}}$ , and  $[\text{TEA}]_0$  are known, the values of  $k_3^\epsilon/k_1$  can be estimated from  $X_\epsilon$  in various THF-AN mixtures (see Fig. 7). Using the value reported for  $k_1$  ( $k_1 = 1/\tau_1$ ,  $\tau_1 = 104$  ns) [18],  $k_3^\epsilon$  can be obtained as a function of  $\epsilon$ . The values of  $k_3^\epsilon$  obtained in THF-AN mixtures are in the order of  $10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and they are a little smaller than the diffusion-controlled rate constant (those in THF-alcohol mixtures are also a little smaller than the diffusion-controlled rate constant).

Reichardt [19] discussed the dependence of the rate constant of the electron-transfer reaction on the solvent polarity using the difference in solvation Gibbs energy between the activated complex and the reactants. According to this theory, the dependence of  $k_3^\epsilon$  on the solvent polarity can be expressed as follows:

$$\begin{aligned} \ln k_3^\epsilon &= \ln k_3^0 + \frac{N_A}{4\pi\epsilon_0 RT} \\ &\times \left( \frac{\mu_{\neq}^2}{r_{\neq}^3} - \frac{\mu_{\text{NP}}^2}{r_{\text{NP}}^3} - \frac{\mu_{\text{TEA}}^2}{r_{\text{TEA}}^3} \right) \left( \frac{\epsilon - 1}{2\epsilon + 1} \right) \quad (18) \end{aligned}$$



**Fig. 8.** Correlation between  $\ln k_3$  and the Kirkwood function  $(\epsilon - 1)/(2\epsilon + 1)$  in THF-AN and THF-alcohol mixtures: (●) AN, (□) MeOH, (Δ) EtOH, (∇) PrOH, and (○) BuOH.

Here  $k_3^0$  is the reference rate constant when  $\epsilon = 1$ ,  $\epsilon_0$  is the permittivity of vacuum,  $N_A$  is the Avogadro's constant,  $\mu$  is the dipole moment,  $r$  is the radius of the spherical molecule described by Kirkwood [20], and the subscripts  $\neq$ , TEA and NP represent the activated complex, TEA, and excited naphthalene, respectively.

The linear relationship between  $\ln k_3$  and  $(\epsilon - 1)/(2\epsilon + 1)$  is shown in Fig. 8. Using Eq. (18), the dipole moment of the activated complex was estimated as  $5.8 \times 10^{-29} \text{ cm}$  (17 D) from the slope of the line by assuming that  $r_{\neq} = 0.7 \text{ nm}$ ,  $r_{\text{NP}} = 0.35 \text{ nm}$  and  $r_{\text{TEA}} = 0.30 \text{ nm}$ ,  $\mu_{\text{NP}} = 0$ , and  $\mu_{\text{TEA}} = 2.7 \times 10^{-30} \text{ cm}$  (0.8 D). The dipole moment of the exciplex of the NP-TEA system has been reported to be about  $(3.7 - 4.8) \times 10^{-29} \text{ cm}$  (11–12 D), [8, 21] and we also obtained the similar dipole moment of the exciplex ( $4.1 \times 10^{-29} \text{ cm}$  (12 D)). Although the crude assumption and approximation were used in the treatment, we can state that the activated complex for the direct electron transfer is more close to the ion-pair than the exciplex is.

### Conversion of Exciplex to Ion-Pair in Polar Solvent

The decrease in the intensity of band B that occurs on the addition of AN can be caused not only by the direct formation of the ion-pair, but also by the conversion of the exciplex to a non-fluorescent ion-pair. The following equation for the intensity changes of bands A and B was derived from Eqs. (11) and (17):

$$\frac{Y_\epsilon}{X_\epsilon} = \frac{k_4}{k_4 + K_5^{\text{THF}}k_6} + \frac{k_6}{k_4 + K_5^{\text{THF}}k_6} K_5^\epsilon \quad (19)$$

where  $Y_\varepsilon = I_B^{\text{THF}}/I_B$ , and  $K_5^{\text{THF}}$  and  $K_5^\varepsilon$  denote the values of  $K_5$  in THF and THF-AN mixtures.

Weller [22] calculated the solvent-dependent free energies of exciplex and radical ion-pair formations in solution on the basis of the experimentally-obtained thermodynamic and spectroscopic values, with the aid of theoretical considerations for solvent polarity effects. According to his method, the following equation was obtained for the difference in the free energy between the exciplex and the ion-pair for the present case:

$$\begin{aligned} \Delta\Delta G^\circ/\text{kJmol}^{-1} &= \Delta G^\circ(\text{exciplex}) - \Delta G^\circ(\text{ion-pair}) \\ &= -\frac{\mu^2}{\rho^3} \times \left( \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{\varepsilon_{\text{hex}} - 1}{2\varepsilon_{\text{hex}} + 1} \right) \\ &\quad + 69.5 \left( \frac{1}{r_+} + \frac{1}{r_-} \right) \times \left( \frac{1}{\varepsilon_{\text{AN}}} - \frac{1}{\varepsilon} \right) \\ &\quad + \frac{139}{\varepsilon d} + 36.7 \end{aligned} \quad (20)$$

where  $\mu$  is the dipole moment of the exciplex,  $\rho$  the cavity radius according to Onsager's definition,  $r_+$  and  $r_-$  are the radii of the cation and anion formed by the intermolecular electron transfer from TEA to naphthalene and  $d$  the distance between the centers of the cation and the anion in the ion-pair ( $r_+$ ,  $r_-$  and  $d$  are given in nm).  $\varepsilon_{\text{hex}}$  and  $\varepsilon_{\text{AN}}$  denote the relative permittivity of hexane and AN ( $\varepsilon_{\text{hex}} = 1.89$  and  $\varepsilon_{\text{AN}} = 37.5$ ).

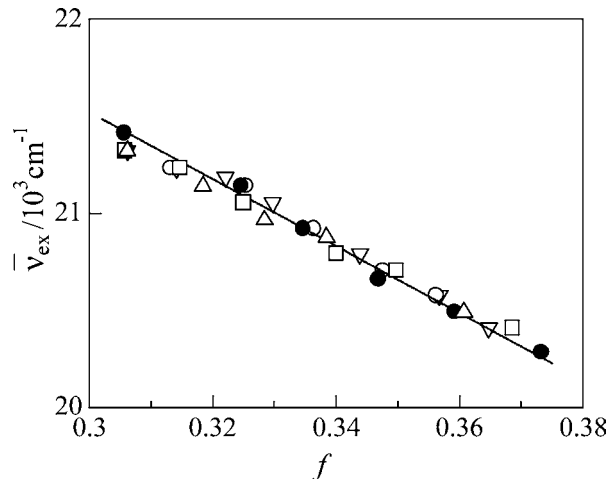
When  $r_+ = 0.30$ ,  $r_- = 0.35$  and  $d = 0.70$  nm ( $r_+$  and  $r_-$  were evaluated from the Corey-Pauling-Koltum models for TEA and NP, and  $d$  was assumed to be somewhat larger than the sum of  $r_+$  and  $r_-$ ), the above equation can be rewritten as follows:

$$\begin{aligned} -\Delta\Delta G^\circ/\text{kJmol}^{-1} &= \frac{\mu^2}{\rho^3} \times \left( \frac{\varepsilon - 1}{2\varepsilon + 1} - 0.19 \right) \\ &\quad + \frac{213}{\varepsilon} - 47.4 \end{aligned} \quad (21)$$

The value of  $\mu^2/\rho^3$  can be estimated from the solvent shift of the exciplex band (Fig. 9) using the following relation:

$$\begin{aligned} \bar{\nu}_{\text{ex}} &= -\frac{2\mu^2}{hc\rho^3} \times \left( \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{4n^2 + 2} \right) \\ &\quad + \text{constant} \end{aligned} \quad (22)$$

where  $\bar{\nu}_{\text{ex}}$  is the maximum wavenumber of exciplex emission,  $h$  the planck's constant,  $c$  the velocity of light, and  $n$  is the refractive index of the solvent. A value of  $103.2 \text{ kJmol}^{-1}$  was obtained (the dipole moment of the exciplex can be estimated to be  $4.1 \times 10^{-29} \text{ cm}$  (12 D) by assuming  $\rho = 0.45 \text{ nm}^8$ ).

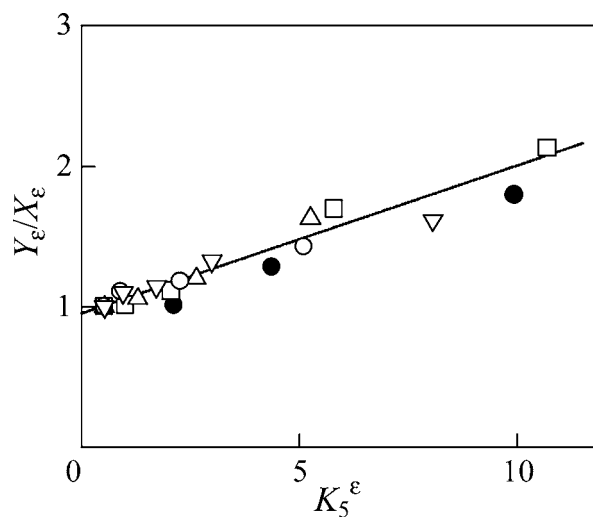


**Fig. 9.** Wavenumber of the emission peak ( $\bar{\nu}_{\text{ex}}$ ) vs.  $f (= [(\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1)])$  relation for band B in THF-AN and THF-alcohol mixtures: (●) AN, (□) MeOH, (Δ) EtOH, (▽) PrOH, and (○) BuOH.

Then, the following equation was obtained from Eq. (21):

$$\begin{aligned} -\Delta\Delta G^\circ/\text{kJmol}^{-1} &= 103.2 \left( \frac{\varepsilon - 1}{2\varepsilon + 1} \right) \\ &\quad + \frac{213}{\varepsilon} - 68 \end{aligned} \quad (23)$$

Figure 10 gives the linear relationship between  $Y_\varepsilon/X_\varepsilon$  and  $K_5^\varepsilon$  in the range  $K_5^\varepsilon < 10$ . This is consistent with the expectation from Eq. (19), because  $k_4$ ,  $k_6$  and  $K_5^{\text{THF}}$  do not

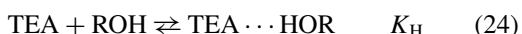


**Fig. 10.** Plots of  $Y_\varepsilon/X_\varepsilon$  calculated by Eq. (30) against  $K_5^\varepsilon$  in THF-AN and THF-alcohol mixtures: (●) AN, (□) MeOH, (Δ) EtOH, (▽) PrOH, and (○) BuOH.

depend on  $\varepsilon$ . The intercept and slope of the plot in Fig. 10 give  $k_6/k_4 = 0.12$ .

### Polar and Hydrogen-Bonding Effects on the Emission Spectra Resulting from the Addition of Alcohols

As shown above, the addition of alcohols will cause not only an increase in the relative permittivity of the solvent, but also in the hydrogen-bonding interaction between TEA and alcohol:



The concentration of free TEA is expressed as follows:

$$[\text{TEA}] = \frac{[\text{TEA}]_0}{1 + K_H[\text{ROH}]} \quad (25)$$

The addition of alcohols increases the polarity of the solvent and decreases the concentration of free TEA. The former effect decreases the intensity of band A and the latter effect increase that of band A, while these effects both decrease the intensity of band B.

From Eqs. (10), (17) and (25), the following equations for the intensity of band A in THF–alcohol mixtures can be derived:

$$\begin{aligned} X_{\text{ROH}} &= \frac{I_{\text{A}}^{\text{THF}}}{I_{\text{A}}^{\text{ROH}}} = \frac{k_1 + (k_2 + k_3^\varepsilon)[\text{TEA}]}{k_1 + (k_2 + k_3^{\text{THF}})[\text{TEA}]_0} \\ &= \frac{X_\varepsilon}{1 + K_H[\text{ROH}]} + \frac{k_1}{k_1 + (k_2 + k_3^{\text{THF}})[\text{TEA}]_0} \\ &\quad \times \frac{K_H[\text{ROH}]}{1 + K_H[\text{ROH}]} \end{aligned} \quad (26)$$

$$X_\varepsilon = (1 + K_H[\text{ROH}])X_{\text{ROH}} - \frac{K_H[\text{ROH}]}{1 + K_{\text{SV}}^{\text{THF}}[\text{TEA}]_0} \quad (27)$$

In the previous study [15], we estimated the value of  $K_H$  from the fluorescence intensity of the toluene–TEA system in various THF–alcohol mixed solvents, and  $K_H$  values of 0.48, 0.31, 0.25 and 0.18  $\text{dm}^3 \text{mol}^{-1}$  were obtained for MeOH, EtOH, PrOH and BuOH, respectively.

Since  $K_H$  and  $X_{\text{ROH}}$  are known, the polar effect ( $X_\varepsilon$ ) on band A from the addition of alcohols can be calculated as a function of  $[\text{ROH}]$  using Eq. (27) from the relationship between  $X_{\text{ROH}}$  and  $[\text{ROH}]$ . The  $X_\varepsilon$  values obtained for THF–alcohol mixtures are shown as a function of  $\varepsilon$  in Fig. 7. The  $X_\varepsilon$  values for THF–alcohol mixtures are consistent with those for THF–AN mixtures. The  $k_3^\varepsilon$  values in THF–alcohol mixtures can be calculated in a similar manner to the one above. As shown in Fig. 8, the plots of

$\ln k_3^\varepsilon$  against  $(\varepsilon - 1)/(2\varepsilon + 1)$  for THF–alcohol mixtures are also consistent with those for THF–AN mixtures.

As mentioned above, band B in THF–alcohol mixtures is influenced by three factors: (1) The decrease in the concentration of free TEA by the hydrogen-bonding effect, (2) the increase in the rate constant for the direct formation of the ion-pair by the polar effect and (3) the increase in the equilibrium constant between the exciplex and the ion-pair with the increase in the solvent polarity. These factors decrease the intensity of band B. The following equation for the intensity of band B in THF–alcohol mixtures can be derived from Eqs. (11) and (25):

$$\begin{aligned} Y_{\text{ROH}} &= \frac{I_{\text{B}}^{\text{THF}}}{I_{\text{B}}^{\text{ROH}}} = \frac{k_1(1 + K_H[\text{ROH}]) + (k_2 + k_3^\varepsilon)[\text{TEA}]_0}{k_1 + (k_2 + k_3^{\text{THF}})[\text{TEA}]_0} \\ &\quad \times \frac{\left(1 + \frac{k_6}{k_4} K_5^\varepsilon\right)}{\left(1 + \frac{k_6}{k_4} K_5^{\text{THF}}\right)} \end{aligned} \quad (28)$$

From Eqs. (25), (26) and (28), the following equation can be derived:

$$\frac{Y_{\text{ROH}}}{X_{\text{ROH}}} = \frac{[\text{TEA}]}{[\text{TEA}]_0} \times \frac{k_4 + K_5^\varepsilon k_6}{k_4 + K_5^{\text{THF}} k_6} \quad (29)$$

Using Eq. (19),  $Y_\varepsilon/X_\varepsilon$  in THF–alcohol mixed solvents can be expressed as follows:

$$\frac{Y_\varepsilon}{X_\varepsilon} = \frac{Y_{\text{ROH}}}{X_{\text{ROH}}} (1 + K_H[\text{ROH}]) \quad (30)$$

In Fig. 10, the  $Y_\varepsilon/X_\varepsilon$  values obtained from Eq. (30) are plotted against  $K_5^\varepsilon$ . As shown in Fig. 10, these values are in good agreement with each other, and also fairly consistent with those for THF–AN mixtures.

## CONCLUSIONS

The fluorescence spectrum of the NP–TEA system in THF consists of two emission bands (fluorescence of naphthalene (band A) and exciplex emission (band B)). The intensities of bands A and B decrease with increasing solvent polarity. However, the intensity of band A increases and that of band B decreases when a hydrogen-bonding interaction (or protonation) occurs between TEA and protic solvents. Acetonitrile shows only a polar effect and trichloroacetic acid only a hydrogen-bonding (protonation) effect, while alcohols have both effects.

In polar solvents, the fluorescence of naphthalene is quenched by TEA through electron transfer and exciplex formation. The electron transfer reaction is enhanced by the solvent polarity. The hydrogen-bonding interaction between amine and protic solvents suppresses these



reactions due to the decrease in the concentration of free amine. It was shown that the decrease in the intensity of band B can be ascribed to the suppression of exciplex formation and the conversion of the exciplex to the ion-pair under polar conditions.

The spectral changes resulting from the addition of AN and TCAA can be used as references for solvent polarity and hydrogen-bonding effects, respectively, whereas those resulting from alcohol addition could be considered to be the simultaneous effects of solvent polarity and hydrogen-bonding interactions.

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