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Effects of alcohols on emission spectra of toluene–triethylamine mixtures in THF: separation into polar and hydrogen-bonding interactions

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Abstract

The emission spectra of toluene (T)–triethylamine (TEA) systems were measured under conditions of steady-state illumination in some protic and aprotic solvent–THF mixtures. The fluorescence spectrum of the T–TEA system in THF could be separated into three component bands (band A at 279 nm (fluorescence of T), band B at 336 nm (fluorescence of TEA) and band C at 373 nm (emission from an intermolecular exciplex)). The intensities of bands B and C decreased with increasing solvent polarity. The decrease in the intensities of bands B and C is considered to be caused by the enhanced conversion of the exciplex to an ion-pair with increase in solvent polarity. The intensities of bands B and C also decreased owing to the hydrogen-bonding interaction between TEA and protic solvents, but in this case the intensity of band A increased. Acetonitrile only has a polar effect and trichloroacetic acid only has a hydrogen-bonding (or protonation) effect, while alcohols have both effects. The equilibrium constants for the formation of intermolecular hydrogen-bonded complexes of TEA with alcohols were estimated from the changes in the intensity of band A. The hydrogen-bonding and polar effects of alcohols on the intensities of bands B and C could be evaluated separately. The ratio of the hydrogen-bonding effect to the polar effect of alcohols was observed to increase with increasing vol.% of alcohol.

Keywords: Solvent effect; Polar effect; Hydrogen-bonding; Fluorescence; Exciplex

1. Introduction

It is well known that the fluorescence of aromatic compounds shows quenching and exciplex emission in the presence of tertiary amines in inter- and intramolecular systems [1–11]. The exciplexes are generally polar, but they prefer non- or low-polar media [12,13]. The photoinduced charge-transfer reactions are largely solvent dependent [14–16]. The separation of hydrogen-bonding interactions from the polar effect of the solvent has been discussed previously [14,17]. It was reported that the presence of hydrogen-bonding substances resulted in a decrease in the exciplex formation and an increase in the exciplex dissociation to the ion-pair in pyrene derivatives–triethylamine (TEA) mixtures [17]. Shirota et al. [18,19] observed that the addition of alcohols reduced the bimolecular rate constant for the quenching of naphthalene fluorescence and the quantum yield of product formation in the naphthalene–TEA system in acetonitrile (AN). They pointed out that the formation of intermolecular hydrogen bonds between the alcohol and TEA suppressed the electron-transfer process from TEA to the excited naphthalene.

The emission spectrum of 4-phenyl-1-*N*,*N*-dimethylaminobutane (PDAB) was found to show substantial changes upon the addition of alcohols to the PDAB solution in THF [20,21]. In this case, the emissions from the exciplex and the excited amino group decreased, but the fluorescence of the phenyl group increased. Such spectral changes suggested that alcohols have both polar and hydrogen-bonding effects. It was suggested that the relative importance of polar and hydrogen-bonding effects on the spectral changes could be estimated separately [21].

In this study, the effects of the addition of trichloroacetic acid (TCAA), AN and some alcohols on the fluorescence spectrum of a toluene (T)–TEA system in THF were studied, and the effects of hydrogen-bonding interactions and solvent polarity on the intermolecular charge-transfer process from TEA to the excited T molecule were examined.

2. Experimental

All of the reagents were purchased from commercial sources. TEA (Extra Purity Grade) was used after drying

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with potassium hydroxide and a trap-to-trap distillation. Methanol (MeOH), ethanol (EtOH), 1-propanol (PrOH) and 1-butanol (BuOH) (Extra Purity Grade) were dried over molecular sieves (4A) and distilled. T, THF, AN, cyclohexane (Spectroscopic Grade) and TCAA (Extra Purity Grade) were used as supplied.

The steady-state fluorescence spectra were measured by using a Shimadzu spectrofluorophotometer, model RF 1500 (band pass, typically 10 nm) at room temperature. The solutions were degassed by four freeze–pump–thaw cycles immediately prior to measurement. Excitation was effected at 270 nm in each case, a wavelength at which the radiation is nearly exclusively absorbed by toluene. The relative permittivities (ε) of mixed solvents were determined with a Dielectric Analyzer, Type FAM-3A, manufactured by Yamato Scientific Instrument Company. The oscillator, controlled by a quartz crystal, was operated at a frequency of 2 MHz. The values of the relative permittivities for THF–AN and THF–alcohol mixtures were shown in Ref. [21].

3. Results

The emission spectrum of the T–TEA system in THF was found to consist of three component bands (band A at 279 nm, band B at 336 nm and band C at 373 nm). As previously reported, bands A, B and C were assigned to the fluorescence of toluene, the fluorescence of the amine, and emission from an exciplex, respectively [11]. Fig. 1 shows the emission spectra of T–TEA systems in some THF–PrOH mixtures.

As shown in Fig. 1, the intensity of band A increases and the intensities of bands B and C decrease with increasing amounts of PrOH. Since the shape of the combined band that contains both bands B and C is only slightly affected by the addition of PrOH, the intensity ratio of bands B and C can be considered nearly constant in various THF–PrOH mixtures (the intensity ratio of about 1.8/1.0 for bands B and C), and the spectrum of the T–TEA system behaves like a two-band spectrum (this also holds for the other mixtures examined in this study). For THF–MeOH, –EtOH and –BuOH mixtures, similar spectral changes were observed. Since no isosbestic point was seen in the spectral changes in the THF–alcohol mixtures, there seem to be more than two causes for the spectral change.

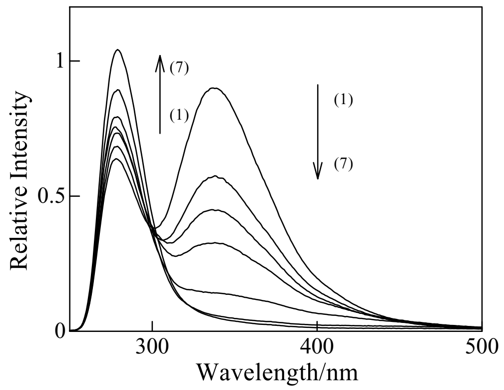

Fig. 1. Emission spectra of the T–TEA system in THF–PrOH mixtures at room temperature: vol.% of PrOH are (1) 0, (2) 3.0, (3) 5.0, (4) 10.0, (5) 20.0, (6) 40.0 and (7) 90.0. [T] = 1.0×10^{-3} mol dm^{-3} and [TEA] = 1.0×10^{-2} mol dm^{-3}.

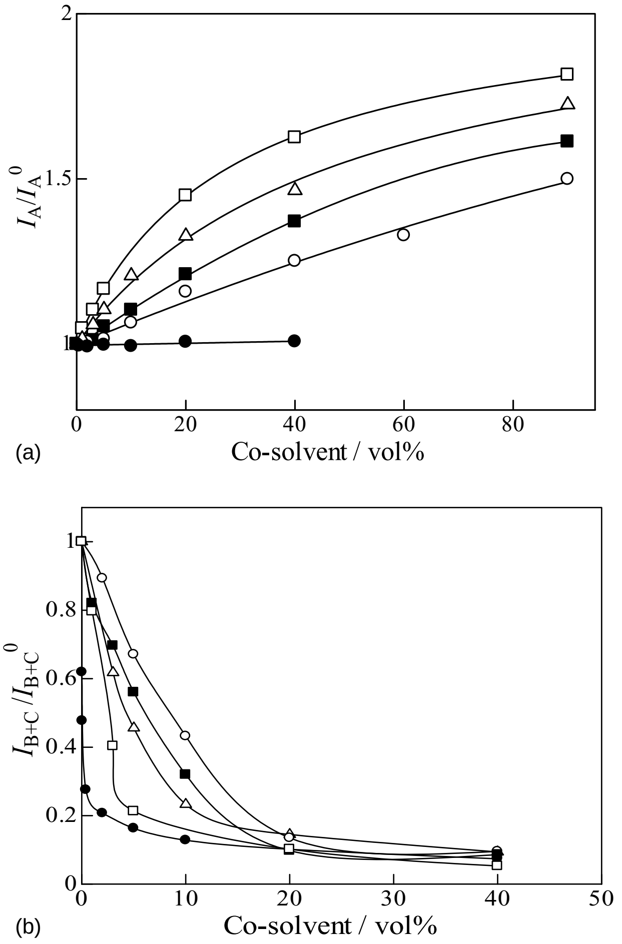

Fig. 2. Plots of relative intensities of (a) band A and (b) bands B and C against vol.% of the cosolvent in THF–AN and THF–alcohol mixtures: (●) AN, (□) MeOH, (△) EtOH, (■) PrOH and (○) BuOH.

Fig. 2(a) and (b) shows the changes in the intensities of band A and of the combined band with vol.% of alcohols, where the intensities were obtained by integrating band A and bands B and C. The intensity of band A increases and that of the combined band decreases with increasing alcohol content.

The addition of alcohol will cause a hydrogen-bonding interaction with TEA and a decrease in the concentration of the free amine. The hydrogen-bonding interaction suppresses the formation of the intramolecular exciplex and so that of the excited amine which is known to be formed through the exciplex. These effects cause an increase in the intensity of band A and decreases in the intensities of bands B and C. On the other hand, an increase in solvent polarity will convert

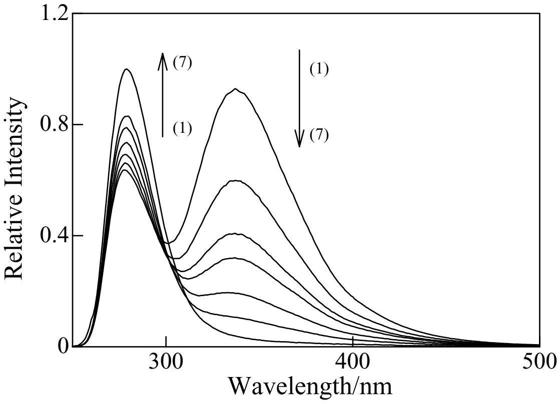

Fig. 3. Emission spectra of T–TEA system in THF–TCAA mixtures at room temperature: [TCAA] are (1) 0, (2) 1.0, (3) 2.0, (4) 3.0, (5) 5.0, (6) 7.0 and (7) $10.0 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$. $[\mathrm{T}] = 1.0 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ and $[\mathrm{TEA}] = 1.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$.

the exciplex to a non-fluorescent radical ion-pair. This conversion also decreases the intensities of bands B and C, but does not influence band A. The intensity change increases in the order: BuOH < PrOH < EtOH < MeOH.

The intensities of bands B and C also decrease with increasing amounts of AN, but that of band A does not change (Fig. 2(a) and (b)). The addition of AN to THF will cause an increase in the polarity of the medium, but not in the hydrogen-bonding interaction. As mentioned above, the increase in solvent polarity results in a decrease in the intensities of bands B and C.

Fig. 3 shows the effect of TCAA addition on the emission spectrum in THF. The spectral change seems to resemble that shown in Fig. 1. As shown in Fig. 3, however, the increase in the intensity of band A is larger than that in Fig. 1. The addition of TCAA to THF will cause a hydrogen-bonding interaction with the amine (or the protonation of the amine). Since the amounts of TCAA are very small, however, the polarity of the medium is little affected by the addition of TCAA.

4. Discussion

As mentioned in the previous section, the intensities of bands B and C decrease, but the intensity of band A does not change with increasing amounts of AN in THF–AN mixtures. These decreases must be caused by the conversion of the exciplex to the non-fluorescent ion-pair with increasing solvent polarity. To explain the experimental results in THF–AN mixtures, the following reactions are considered:

$$\mathrm{T} + h\nu \rightarrow \mathrm{T}^* \quad (I_0) \tag{1}$$

$$\mathrm{T}^* \rightarrow \mathrm{T} + h\nu_{\mathrm{A}} \quad (\alpha k_0) \tag{2}$$

$$\mathrm{T}^* \rightarrow \text{nonradiative process} \quad ((1-\alpha)k_0) \tag{3}$$

$$\mathrm{T}^* + \mathrm{TEA} \rightarrow \text{exciplex} \quad (k_1) \tag{4}$$

$$\text{exciplex} \rightleftarrows \mathrm{T} + \mathrm{TEA}^* \quad (K_2) \tag{5}$$

$$\text{exciplex} \rightleftarrows \text{ion-pair} \quad (K(\varepsilon)) \tag{6}$$

$$\text{exciplex} \rightarrow \mathrm{T} + \mathrm{TEA} + h\nu_{\mathrm{C}} \quad (\beta k_3) \tag{7}$$

$$\text{exciplex} \rightarrow \text{nonradiative process} \quad ((1-\beta)k_3) \tag{8}$$

$$\mathrm{TEA}^* \rightarrow \mathrm{TEA} + h\nu_{\mathrm{B}} \quad (\gamma k_4) \tag{9}$$

$$\mathrm{TEA}^* \rightarrow \text{nonradiative process} \quad ((1-\gamma)k_4) \tag{10}$$

$$\text{ion-pair} \rightarrow \mathrm{T} + \mathrm{A} \quad (k_5) \tag{11}$$

Here, exciplex denotes the intermolecular exciplex, TEA^* an excited amine and ion-pair the non-fluorescent radical ion-pair formed by the intermolecular electron transfer from TEA to T^*. $K(\varepsilon)$ shows the equilibrium constant that depends on solvent polarity. The proportions of radiative processes from excited species are shown by the factors α, β and γ.

Knibbe et al. [22] proposed the following reactions to explain their observations on the dependencies of the lifetime and relative emission intensities of exciplexes in an anthracene-*N*,*N*-diethylaniline system on solvent polarity:

$$\mathrm{A}^* + D \rightarrow \text{exciplex} \quad (k_{\mathrm{e}})$$

$$\mathrm{A}^* + D \rightarrow \text{ion-pair} \quad (k_{\mathrm{IP}})$$

$$\text{exciplex} \rightarrow \text{ion-pair} \quad (k'_{\mathrm{IP}})$$

In this case, 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, the exciplex emission was not detected in AN, as found in many other systems.

In the present system, as shown in Fig. 2(b), the fluorescence intensity of T is not affected much by the addition of AN in THF solution. Therefore, the direct formation of an ion-pair from the excited toluene can be neglected. In polar solvents, dissociation of exciplex to solvent-shared ion-pair occurs, and in highly polar solvents such as AN this dissociation is essentially irreversible. However, in moderately polar solvents the dissociation can be reversible, because the free energy difference between the exciplex and the ion-pair is nearly zero in these solvents, as shown later. In the above reaction mechanism, it is assumed that the equilibrium between the exciplex and the ion-pair is attained and that the equilibrium constant depends on solvent polarity.

The experimental results in THF–TCAA mixtures can be explained by reactions (1)–(11) and the following reactions:

$$\mathrm{TEA} + \mathrm{TCAA} \rightarrow \mathrm{TEAH}\,(+\mathrm{TCAA}') \quad (k_6) \tag{12}$$

Here, TEAH denotes the hydrogen bonded (or protonated) amine.

Since the formation of the hydrogen bonded (or protonated) amine with TCAA must occur quantitatively, the

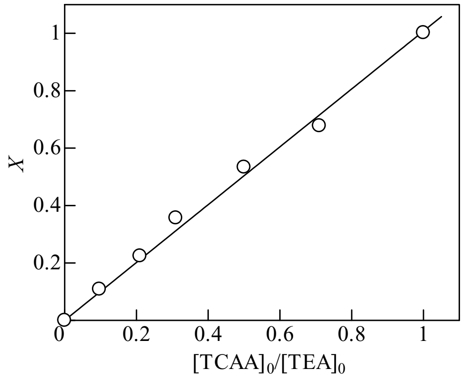

Fig. 4. Experimental plots of Eq. (13) for changes in the emission intensities of band A in THF–TCAA mixtures.

concentration of the free amine becomes $[\mathrm{TEA}] = [\mathrm{TEA}]_0 - [\mathrm{TCAA}]_0$ and the following equation can be obtained:

$$X = \frac{(1/I_{\mathrm{A}}^{0}) - (1/I_{\mathrm{A}})}{(1/I_{\mathrm{A}}^{0}) - (1/I_{\mathrm{A}}^{00})} = \frac{[\mathrm{TCAA}]_0}{[\mathrm{TEA}]_0} \tag{13}$$

where I_{A}^{0} and I_{A} are the intensities of band A in the absence and presence of TCAA, I_{A}^{00} the intensity of band A in the absence of both TEA and TCAA, and $[\mathrm{TEA}]_0$ and $[\mathrm{TCAA}]_0$ the initial concentrations of TEA and TCAA, respectively.

As shown in Fig. 4, a linear relationship between X and $[\mathrm{TCAA}]_0/[\mathrm{TEA}]_0$ with a slope equal to 1.0 is obtained. This indicates that Eq. (13) holds. In this manner, X can be used as a measure of the hydrogen-bonding (or protonation) interaction in THF–TCAA mixtures.

As mentioned previously, in THF–alcohol mixtures, bands B and C are influenced by both polar and hydrogen-bonding interactions, but band A is influenced only by the hydrogen-bonding interaction. In order to explain the results obtained in THF–alcohol mixtures, reactions (1)–(11) and the following reaction are considered:

$$\mathrm{TEA} + \mathrm{ROH} \rightleftarrows \mathrm{TEA}\cdots\mathrm{HOR} \quad (K_7) \tag{14}$$

Here, TEA···HOR denotes the amine hydrogen bonded to the alcohol.

The following equation for the intensity of band A is derived by a steady-state treatment:

$$\begin{aligned} I_{\mathrm{A}}(\mathrm{ROH}) &= \alpha I_0 \frac{k_0}{k_0 + k_1[\mathrm{TEA}]} \\ &= \alpha I_0 \frac{k_0}{k_0 + (k_1[\mathrm{TEA}]_0/(1 + K_7[\mathrm{ROH}]))} \end{aligned} \tag{15}$$

where I_0 is the absorption intensity of the exciting light by T (Eq. (1)).

From this equation, $X(\mathrm{ROH})$ can be expressed as follows:

$$\begin{aligned} X(\mathrm{ROH}) &= \frac{(1/I_{\mathrm{A}}^{0}) - (1/I_{\mathrm{A}}(\mathrm{ROH}))}{(1/I_{\mathrm{A}}^{0}) - (1/I_{\mathrm{A}}^{00})} \\ &= \frac{K_7[\mathrm{ROH}]}{1 + K_7[\mathrm{ROH}]} \end{aligned} \tag{16}$$

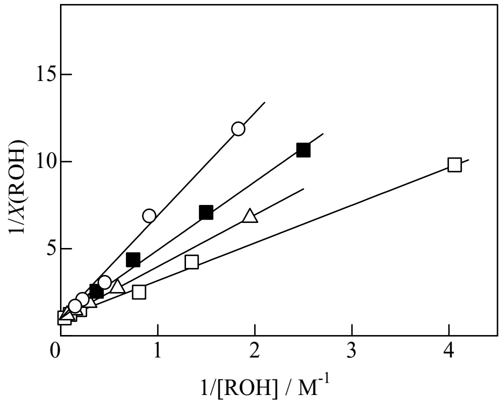

Fig. 5. Plots of $1/X(\mathrm{ROH})$ against $1/[\mathrm{ROH}]$ for changes in the emission intensity of band A in THF–alcohol mixtures: (□) MeOH, (△) EtOH, (■) PrOH and (○) BuOH.

where I_{A}^{0} and $I_{\mathrm{A}}(\mathrm{ROH})$ are the intensities of band A in the absence and presence of ROH, and I_{A}^{00} the intensity of band A in a toluene solution of the same concentration (in the absence of TEA and alcohol).

As shown in Fig. 5, linear relationships between $1/X(\mathrm{ROH})$ and $1/[\mathrm{ROH}]$ with intercepts equal to 1.0 are obtained. The values of the equilibrium constants were obtained from the slopes of the straight lines ($K_7 = 0.48$, 0.31, 0.25 and $0.18\,\mathrm{M}^{-1}$ were obtained for MeOH, EtOH, PrOH and BuOH, respectively). These values are similar to the values reported for these alcohols and TEA in AN [18,19].

As mentioned above, the intensities of bands B and C decrease with increasing amounts of AN in THF–AN mixtures, and these decreases must be caused by the conversion of the exciplex to the non-fluorescent ion-pair with increasing solvent polarity. To explain the experimental results in THF–AN mixtures, reactions (1)–(11) are considered. Since $K(\varepsilon)$ depends on the solvent polarity, it is necessary to know the extent of the conversion from the exciplex to the ion-pair in pure THF in order to quantitatively discuss the effect of solvent polarity on the intensities of bands B and C. It was found that the intensities of bands B and C increased with increasing amounts of cyclohexane (CH) in THF–CH mixtures (i.e. with decreasing solvent polarity). The total intensity of bands B and C in pure CH (in which $K(\varepsilon)$ is assumed to be zero) can be considered as a standard. However, since the shifts in bands B and C that correspond to changes in solvent polarity were large in THF–CH mixtures, and bands A and B largely overlapped in CH, the intensities of bands B and C could not be obtained in pure CH.

As reported previously [11], the emission spectrum of 3-phenyl-1-*N*,*N*-dimethylamino propane (PDAP) consists of band C only. In a similar manner to that mentioned for PDAB in a previous paper because of the similarity of the nature between the exciplexes of T–TEA system and PDAB [21], using the ratio of the emission intensities of PDAP in CH and THF, the ratio of the total intensities of bands B and C in the T–TEA system in CH and in THF was estimated (the value of $I_{\mathrm{B,C}}(\mathrm{CH})/I_{\mathrm{B,C}}(\mathrm{THF}) = 1.39$ was obtained).

The following equations for the total intensities of bands B and C in THF–AN mixtures and in CH were derived from reactions (1)–(11) by a steady-state treatment based on the assumption that fast equilibria between exciplex, TEA* and ion-pair were attained:

$$I_{\mathrm{B,C}}(\mathrm{AN}) = I_0 \frac{k_1[\mathrm{TEA}]_0}{k_0 + k_1[\mathrm{TEA}]_0} \frac{\beta k_3 + \gamma k_4 K_2/[\mathrm{T}]}{k_3 + k_4 K_2/[\mathrm{T}] + k_5 K(\varepsilon)} \tag{17}$$

$$I_{\mathrm{B,C}}(\mathrm{CH}) = I_0 \frac{k_1[\mathrm{TEA}]_0}{k_0 + k_1[\mathrm{TEA}]_0} \frac{\beta k_3 + \gamma k_4 K_2/[\mathrm{T}]}{k_3 + k_4 K_2/[\mathrm{T}]} \tag{18}$$

From these equations, the polar effect on the intensities of bands B and C ($Y(\varepsilon)$) can be expressed as follows (k_1-values in CH and THF–AN mixtures are assumed to be equal):

$$\begin{aligned} Y(\varepsilon) &= \frac{I_{\mathrm{B,C}}(\mathrm{CH}) - I_{\mathrm{B,C}}(\mathrm{AN})}{I_{\mathrm{B,C}}(\mathrm{CH})} \\ &= \frac{k_5 K(\varepsilon)}{k_3 + k_4 K_2/[\mathrm{T}] + k_5 K(\varepsilon)} \end{aligned} \tag{19}$$

This equation shows that since $K(\varepsilon)$ increases with increasing solvent polarity (the relative permittivity ε), $Y(\varepsilon)$ increases as the relative permittivity of the solvent increases.

As shown in Fig. 6, $Y(\varepsilon)$ initially increases steeply with increasing relative permittivity, and then approaches a constant value. These tendencies are consistent with the expectation from the above equation.

Similarly, since the total intensities of bands B and C in THF–alcohol mixtures (where both the hydrogen-bonding and polar effects work) are expressed by the following equation (see Appendix A):

$$\begin{aligned} I_{\mathrm{B,C}}(\mathrm{ROH}) &= I_0 \frac{k_1[\mathrm{TEA}]_0}{k_0(1 + K_7[\mathrm{ROH}]) + k_1[\mathrm{TEA}]_0} \\ &\quad \times \frac{\beta k_3 + \gamma k_4 K_2/[\mathrm{T}]}{k_3 + k_4 K_2/[\mathrm{T}] + k_5 K(\varepsilon)} \end{aligned} \tag{20}$$

the effects of alcohols on the intensities of bands B and C ($Y(\mathrm{ROH})$) can be expressed as follows (see Appendix B):

$$Y(\mathrm{ROH}) = \frac{m+1}{m + 1 + mK_7[\mathrm{ROH}]} Y(\varepsilon) + X'(\mathrm{ROH}) \tag{21}$$

where $m = k_0/k_1[\mathrm{TEA}]_0$ and $X'(\mathrm{ROH}) = mK_7[\mathrm{ROH}]/(m + 1 + mK_7[\mathrm{ROH}])$. Therefore, the following equation for $Y(\varepsilon)$ in THF–alcohol mixtures is obtained:

$$Y(\varepsilon) = \frac{m + 1 + mK_7[\mathrm{ROH}]}{m+1} (Y(\mathrm{ROH}) - X'(\mathrm{ROH})) \tag{22}$$

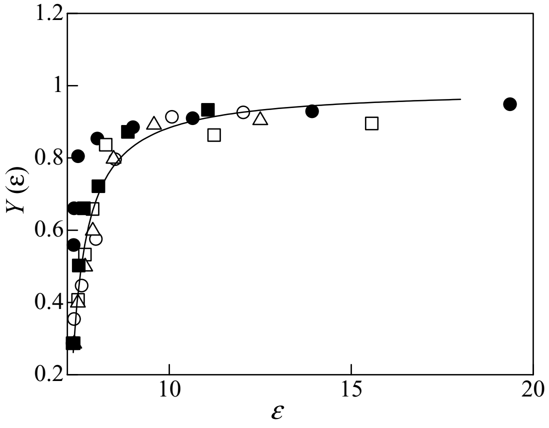

Fig. 6. Plots of $Y(\varepsilon)$ against relative permittivity (ε) for changes in the emission intensities in THF–AN and THF–alcohol mixtures: (●) AN, (□) MeOH, (△) EtOH, (■) PrOH and (○) BuOH. The solid line is the best-fit curve of all points obtained for alcohols.

This equation shows that the contribution of the change in solvent polarity in various THF–alcohol mixtures on the intensity change in bands B and C can be estimated by the values of $Y(\mathrm{ROH})$, $X'(\mathrm{ROH})$, m and K_7. The value of m can be estimated by the Stern–Volmer plots for the quenching of toluene fluorescence by TEA ($m = 0.6$ for $[\mathrm{TEA}]_0 = 1.0 \times 10^{-2}\ \mathrm{mol\,dm^{-3}}$).

In Fig. 6 the values of $Y(\varepsilon)$ for THF–MeOH, –EtOH, –PrOH and –BuOH mixtures are shown as functions of the relative permittivity. The values of $Y(\varepsilon)$ in THF–alcohol mixtures increase with increasing relative permittivity. The increases in $Y(\varepsilon)$ in THF–alcohol mixtures are consistent with each other among the alcohols examined, but are largely different from those in THF–AN mixtures. As previously shown [21], the values of $Y(\varepsilon)$ in THF–AN mixtures are different from those in THF–alcohol mixtures, as with the case of 4-phenyl-1-*N*,*N*-dimethylaminobutane (PDAB). The cause of this difference in $Y(\varepsilon)$ could not be shown in the previous paper [22].

In the present study, the fluorescence of TEA was observed to be quenched by AN, but not by alcohols in THF. The quenching of band B by AN was not taken into account in the evaluation of $Y(\varepsilon)$. This must be the cause of the deviation of the values of $Y(\varepsilon)$ in THF–AN mixtures from those in THF–alcohol mixtures. Since the proportion of band B in the combined band of the T–TEA system is larger than that in PDAB, the deviation in the former is considerably larger.

Weller [23] calculated the solvent dependent free energy of exciplex and radical ion-pair formation 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 solvated ion-pair for the present case:

$$\begin{aligned}\Delta\Delta G^\circ\,(\mathrm{kJ\,mol^{-1}}) &= \Delta G^\circ(\text{exciplex}) - \Delta G^\circ(\text{ion-pair})\\ &= -\frac{\mu^2}{\rho^3}\left(\frac{\varepsilon-1}{2\varepsilon+1}-\frac{\varepsilon_{\mathrm{hex}}-1}{2\varepsilon_{\mathrm{hex}}+1}\right)\\ &\quad +69.5\left(\frac{1}{r_+}+\frac{1}{r_-}\right)\left(\frac{1}{\varepsilon_{\mathrm{AN}}}-\frac{1}{\varepsilon}\right)+\frac{139}{\varepsilon d}+36.7\end{aligned} \tag{23}$$

where μ is the dipole moment of the exciplex, ρ the cavity radius according to Onsager's definition, r_+ and r_- the radii of the cation and anion formed by the intermolecular electron transfer from TEA to T and d the distance between the centers of the cation and the anion in the solvated ion-pair (r_+, r_- and d are given in nm). $\varepsilon_{\mathrm{hex}}$ and $\varepsilon_{\mathrm{AN}}$ denote the relative permittivities of hexane and AN ($\varepsilon_{\mathrm{hex}} = 1.89$ and $\varepsilon_{\mathrm{AN}} = 37.5$). When $r_+ = r_- = 0.30$ and $d = 0.65$ nm (r_+ and r_- were evaluated from the Corey–Pauling–Koltum models for T and TEA, and d was assumed to be somewhat larger than the sum of r_+ and r_-), the above equation can be rewritten as follows:

$$\Delta\Delta G^\circ\,(\mathrm{kJ\,mol^{-1}})=-\frac{\mu^2}{\rho^3}\left(\frac{\varepsilon-1}{2\varepsilon+1}-0.19\right)-\frac{249}{\varepsilon}+49.2 \tag{24}$$

The value of μ^2/ρ^3 can be estimated by the solvent shift of the exciplex band using the following relation:

$$\overline{\nu_{\max}} = -\frac{2\mu^2}{hc\rho^3}\left[\frac{\varepsilon-1}{2\varepsilon+1}-\frac{n^2-1}{2(2n^2+1)}\right]+\text{const.} \tag{25}$$

and the value of 110 kJ mol^{-1} was obtained (Fig. 7).

The following equation was then obtained:

$$\Delta\Delta G^\circ\,(\mathrm{kJ\,mol^{-1}}) = 110\left(\frac{\varepsilon-1}{2\varepsilon+1}\right)+\frac{249}{\varepsilon}-70.1 \tag{26}$$

In Fig. 8, $\Delta\Delta G^\circ$ is shown as a function of ε. Since $K(\varepsilon)$ at various values of ε can be calculated from $\Delta\Delta G^\circ$($\ln K(\varepsilon)= -\Delta\Delta G^\circ/RT$), $Y(\varepsilon)$ is shown as a function of $K(\varepsilon)$ in Fig. 9.

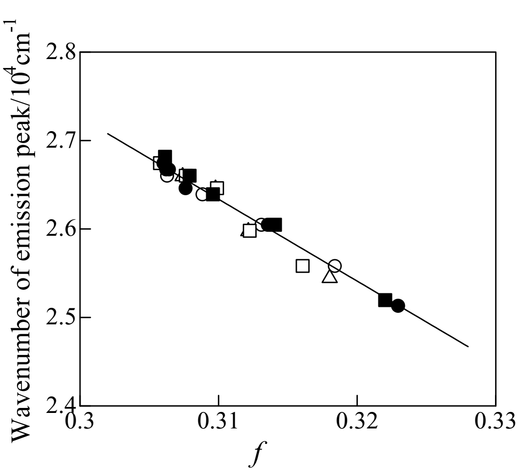

Fig. 7. Wavenumber of the emission peak vs. f (=[($\varepsilon-1$)/($2\varepsilon+1$) − (n^2-1)/2($2n^2+1$)]) relation for band C in: (●)THF–AN, (□) THF–MeOH, (△) THF–EtOH, (■) THF–PrOH and (○) THF–BuOH mixtures.

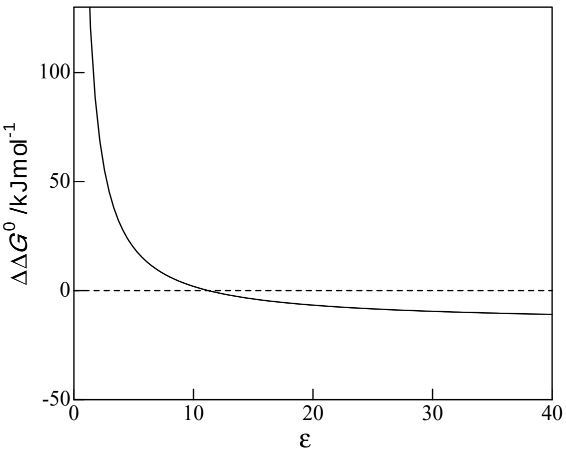

Fig. 8. Plots of $\Delta\Delta G^\circ$ calculated by Eq. (27) against relative permittivity (ε).

Eq. (19) can then be rewritten as follows

$$Y(\varepsilon) = \frac{aK(\varepsilon)}{1+aK(\varepsilon)} \tag{27}$$

where $a = k_5/(k_3 + k_4K_2/[\mathrm{T}])$.

The solid line in Fig. 9 shows the values of $Y(\varepsilon)$ calculated by Eq. (22) for THF–alcohol mixtures, using a-values obtained by the curve fitting method ($a = 20$). As is shown in Fig. 9, the agreement between the calculated and the experimentally obtained values is fairly good in the region where the polarity is low. The a-value obtained shows that the rate constant for the disappearance of the solvated ion-pair is considerably larger than those for deactivations of the exciplex and the excited TEA.

X'(ROH) and $Y(\varepsilon)$ provide a means of evaluating the hydrogen-bonding and polar effects in THF–alcohol mixtures separately (see Appendix C). Both the hydrogen-bonding and the polar effects increase with increasing alcohol content in THF–alcohol mixtures. Fig. 10 shows the ratio of hydrogen-bonding effect to polar effect as a function of vol.% of alcohol in some THF–alcohol mixtures. As

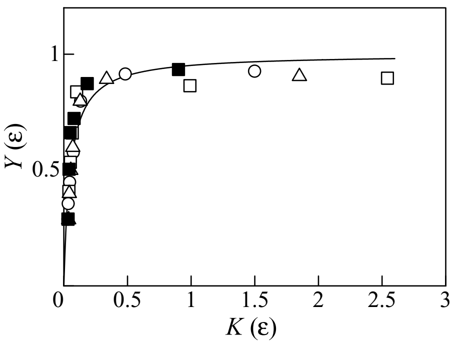

Fig. 9. Plots of $Y(\varepsilon)$ against $K(\varepsilon)$ in THF–alcohol mixtures: (□) MeOH, (△) EtOH, (■) PrOH and (○) BuOH.

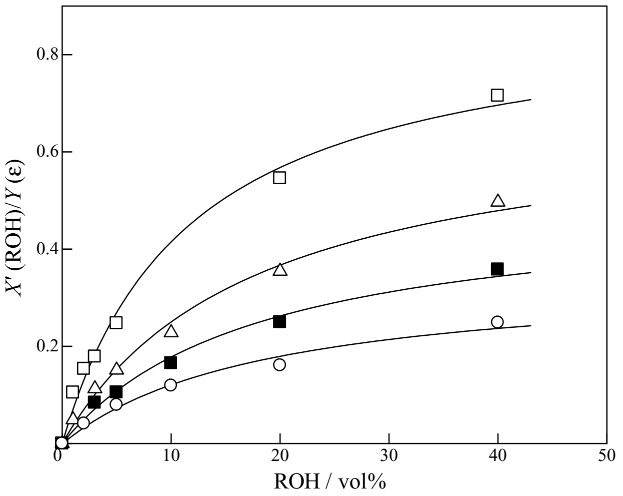

Fig. 10. Plots of the ratio of hydrogen-bonding effect to polar effect against vol.% of alcohol.

shown in Fig. 10, this ratio shows a saturation tendency for MeOH, EtOH, PrOH and BuOH. The ratio decreases in the order: MeOH > EtOH > PrOH > BuOH.

5. Conclusions

It was found that the emission spectrum of the T–TEA system in THF consists of three component bands, but it behaves like a two-band spectrum when changes in polarity and hydrogen-bonding ability are caused by different THF–AN, –TCAA and –alcohol mixtures. The short-wavelength band (band A) was attributed to the fluorescence of T and the long-wavelength band to a combination of bands B (fluorescence of TEA) and C (emission from intermolecular exciplex). The former was sensitive to the hydrogen-bonding (or protonation) interaction between the amine and an alcohol or a TCAA molecule, while the latter was sensitive to both polar and hydrogen-bonding effects.

From the changes in the intensity of band A upon addition of alcohols, the equilibrium constants for the formation of hydrogen-bonded complexes between TEA and alcohol molecules were estimated. The polar and hydrogen-bonding effects of alcohols on the intensities of bands B and C could be separated. The decrease in the intensities of bands B and C with increasing solvent polarity could be explained by the dependence of the equilibrium constant between the exciplex and radical ion-pair on the relative permittivity.

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Appendix A

The intensity of bands B and C in THF–alcohol mixtures is expressed as follows:

$$I_{\mathrm{B,C}}(\mathrm{ROH}) = I_0 \frac{k_1[\mathrm{TEA}]}{k_0 + k_1[\mathrm{TEA}]} \frac{\beta k_3 + \gamma k_4 K_2/[\mathrm{T}]}{k_3 + k_4 K_2/[\mathrm{T}] + k_5 K(\varepsilon)} \tag{A.1}$$

where [TEA] is the concentration of free TEA. From Eq. (14), the following equation is obtained:

$$[\mathrm{TEA}] = \frac{[\mathrm{TEA}]_0}{1 + K_7[\mathrm{ROH}]} \tag{A.2}$$

By inserting Eq. (A.2) into Eq. (A.1), the following equation is obtained:

$$\begin{aligned} I_{\mathrm{B,C}}(\mathrm{ROH}) &= I_0 \frac{k_1[\mathrm{TEA}]_0}{k_0(1 + K_7[\mathrm{ROH}]) + k_1[\mathrm{TEA}]_0} \\ &\quad \frac{\beta k_3 + \gamma k_4 K_2/[\mathrm{T}]}{k_3 + k_4 K_2/[\mathrm{T}] + k_5 K(\varepsilon)} \end{aligned} \tag{A.3}$$

Appendix B

$Y(\mathrm{ROH})$ is defined as follows:

$$Y(\mathrm{ROH}) = \frac{I_{\mathrm{B,C}}(\mathrm{CH}) - I_{\mathrm{B,C}}(\mathrm{ROH})}{I_{\mathrm{B,C}}(\mathrm{CH})} = 1 - \frac{I_{\mathrm{B,C}}(\mathrm{ROH})}{I_{\mathrm{B,C}}(\mathrm{CH})} \tag{B.1}$$

From Eqs. (A.3) and (18) the following equation is obtained:

$$\begin{aligned} \frac{I_{\mathrm{B,C}}(\mathrm{ROH})}{I_{\mathrm{B,C}}(\mathrm{CH})} &= \frac{k_0 + k_1[\mathrm{TEA}]_0}{k_0(1 + K_7[\mathrm{ROH}]) + k_1[\mathrm{TEA}]_0} \\ &\quad \times \frac{k_3 + k_4 K_2/[\mathrm{T}]}{k_3 + k_4 K_2/[\mathrm{T}] + k_5 K(\varepsilon)} \\ &= \frac{m + 1}{m(1 + K_7[\mathrm{ROH}]) + 1} \\ &\quad \times \frac{k_3 + k_4 K_2/[\mathrm{T}]}{k_3 + k_4 K_2/[\mathrm{T}] + k_5 K(\varepsilon)} \end{aligned} \tag{B.2}$$

where $m = k_0/k_1[\mathrm{TEA}]_0$. Inserting Eq. (B.2) into Eq. (B.1) gives the following equation:

$$\begin{aligned} Y(\mathrm{ROH}) &= \frac{m + 1}{m + 1 + mK_7[\mathrm{ROH}]} \frac{k_5 K(\varepsilon)}{k_3 + k_4 K_2/[\mathrm{T}] + k_5 K(\varepsilon)} \\ &\quad + \frac{mK_7[\mathrm{ROH}]}{m + 1 + mK_7[\mathrm{ROH}]} \end{aligned} \tag{B.3}$$

Since $Y(\varepsilon) = k_5 K(\varepsilon)/(k_3 + k_4 K_2/[\mathrm{T}] + k_5 K(\varepsilon))$ and by defining $X'(\mathrm{ROH})$ as $mK_7[\mathrm{ROH}]/(m + 1 + mK_7[\mathrm{ROH}])$, Eq. (B.3) becomes

$$\begin{aligned} Y(\mathrm{ROH}) &= \frac{m+1}{m+1+mK_7[\mathrm{ROH}]} Y(\varepsilon) + \frac{mK_7[\mathrm{ROH}]}{m+1+mK_7[\mathrm{ROH}]} \\ &= \frac{m + 1}{m+1 + mK_7[\mathrm{ROH}]} Y(\varepsilon) + X'(\mathrm{ROH}) \end{aligned} \tag{B.4}$$

Appendix C

Since $m = k_0/k_1[\mathrm{TEA}]_0$, Eq. (A.3) becomes

$$\begin{aligned} I_{\mathrm{B,C}}(\mathrm{ROH}) &= I_0 \frac{1}{m(1+K_7[\mathrm{ROH}])+1} \\ &\quad \times \frac{\beta k_3 + \gamma k_4 K_2/[\mathrm{T}]}{k_3 + k_4 K_2/[\mathrm{T}] + k_5 K(\varepsilon)} \\ &= I_0 \frac{1}{m(1+K_7[\mathrm{ROH}])+1} J \end{aligned} \tag{C.1}$$

where $J = (\beta k_3 + \gamma k_4 K_2/[\mathrm{T}])/(k_3 + k_4 K_2/[\mathrm{T}] + k_5 K(\varepsilon))$. If it is assumed that only the hydrogen-bonding effect of alcohols affects the intensities of bands B and C, J does not depend on the composition of THF–alcohol mixtures. In this case, the total intensity of bands B and C in pure THF is expressed as follows:

$$I^0_{\mathrm{B,C}}(\mathrm{ROH}) = I_0 \frac{1}{m+1} J \tag{C.2}$$

From Eqs. (C.1) and (C.2), the effect of hydrogen-bonding on the intensities of bands B and C is expressed as follows:

$$\begin{aligned} &\frac{I^0_{\mathrm{B,C}}(\mathrm{ROH}) - I_{\mathrm{B,C}}(\mathrm{ROH})}{I^0_{\mathrm{B,C}}(\mathrm{ROH})} \\ &\quad = \frac{I_0 J((1/(m+1)) - (1/(m(1+K_7[\mathrm{ROH}])+1))}{I_0 J(1/(m+1))} \\ &\quad = \frac{mK_7[\mathrm{ROH}]}{(m+1) + mK_7[\mathrm{ROH}]} = X'(\mathrm{ROH}) \end{aligned} \tag{C.3}$$

Thus, $X'(\mathrm{ROH})$ shows the hydrogen-bonding effect of alcohols on the intensities of bands B and C.

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