

*Chemistry*

*Physical & Theoretical Chemistry fields*

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Okayama University

Year 2006

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Shunzo Yamamoto  
Okayama University, [yamashun@cc.okayama-u.ac.jp](mailto:yamashun@cc.okayama-u.ac.jp)

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# Polar and Hydrogen-Bonding Effects of Alcohols on the Emission Spectrum of Styrene–Triethylamine System

Siqintuya,<sup>1</sup> Yoshimi Sueishi,<sup>1</sup> and Shunzo Yamamoto<sup>1,\*</sup>

Received March 17, 2005; accepted April 18, 2005

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The emission spectra of styrene (ST)–triethylamine (TEA) systems were measured under steady-state illumination conditions in some tetrahydrofuran (THF)–protic solvent mixtures. The fluorescence spectrum of the ST–TEA system in THF consists of two bands (band A at 304 nm (fluorescence of ST) and band B at 460 nm (emission from an exciplex)). The intensity of band A increased and that of band B decreased with increasing amounts of protic solvents in THF–protic solvent mixtures. The increase in the intensity of band A was explained by the decrease in the concentration of free amine owing to the hydrogen-bonding interaction (or protonation) between TEA and protic solvents. The decrease in the intensity of band B was considered to be caused by the decrease in the concentration of free amine upon the addition of protic solvents and the enhanced conversion of the exciplex to an ion pair with increasing solvent polarity. The polar effect was expressed as a function of the relative permittivity of the solution.

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

## 1. INTRODUCTION

It is well known that the fluorescence of aromatic compounds shows quenching and exciplex formation in the presence of tertiary aliphatic amines in non- and slightly-polar solvents.<sup>(1–7)</sup> 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.<sup>(8–10)</sup> Shirota *et al.*<sup>(11,12)</sup> observed that the addition of alcohols to the naphthalene (NP)–TEA system in acetonitrile (AN) reduced 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

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<sup>1</sup>Graduate School of Natural Science and Technology, Okayama University, 3-1-1, Tsushima-naka, Okayama 700-8530, Japan; e-mail: yamashun@cc.okayama-u.ac.jp.

electron-transfer process owing to the decrease in the concentration of free TEA. Since AN was used as a solvent in their study, the effect of alcohols on the emission from the exciplex could not be examined. We have recently reported that the effects of the addition of alcohols on the intra- and intermolecular exciplex systems (4-phenyl-1-*N,N*-dimethylaminobutane (PDAB),<sup>(13,14)</sup> toluene (T)-TEA<sup>(15)</sup> and NP-TEA systems<sup>(16)</sup>) could be separated into solvent polarity and hydrogen bonding effects. In our studies, THF was used as a solvent instead of AN, so both aromatic fluorescence and exciplex emissions could be observed, and more detailed information was obtained on the solvent effects. It would be interesting to understand how these two factors affect other intermolecular exciplex systems.

Fluorescent exciplexes were observed in inter- and intramolecular styrene-amine systems in non- and weakly-polar solvents.<sup>(17-21)</sup> The exciplex fluorescence was observed to show a red shift with increasing solvent polarity from hexane to THF, but the exciplex emission was not observed in AN.<sup>(18,19)</sup> The solvent dependence of the exciplex fluorescence was investigated in aprotic solvents, but the effects of protic solvents were not reported. The information is insufficient on spectral changes in aromatic compound-amine systems resulting from the polarity change from THF to AN and the addition of protic solvents.

As mentioned above, we have recently studied the effects of alcohols on the emission spectra in the T-TEA and NP-TEA systems. It was found that in the T-TEA system, energy transfer from excited toluene to TEA through the exciplex occurred and the emission spectrum could be separated into three bands (fluorescence of T and TEA, and exciplex emission). On the other hand, the emission spectrum of the NP-TEA system was found to consist of two bands (fluorescence of NP and exciplex emission), but the spectral changes resulting from the additions of alcohols to this system were complicated, because both bands were affected by polar and hydrogen-bonding effects of alcohols. Since the emission spectrum and the spectral changes resulting from the additions of alcohols to the ST-TEA system adopted in this study were found to be simple in the preliminary study, a more typical evaluation of solvent effects is expected to be possible.

In the present study, spectral changes of the ST-TEA system in THF upon the addition of trichloroacetic acid (HTCA) and some alcohols were studied and the effects of the hydrogen-bonding interaction and the change in solvent polarity on the emission spectrum of the ST-TEA system are discussed.

## 2. EXPERIMENTAL

All reagents were obtained from commercial sources. TEA (extra purity grade) was used after drying with sodium hydroxide and trap-to-trap distillation. Methanol (MeOH), ethanol (EtOH), butanol (BuOH), cyclohexane (CH), THF, and AN were of spectroscopic grade and were used as supplied. HTCA (extra

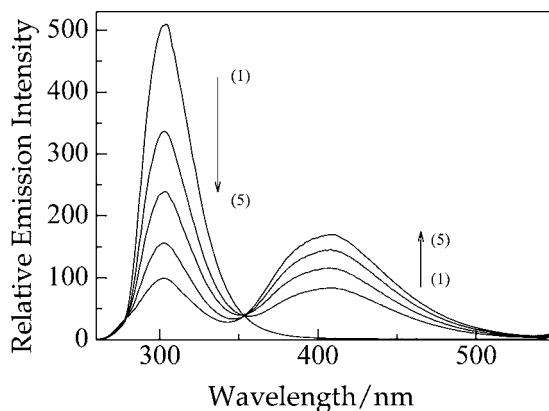
purity grade) was used as obtained. ST (extra purity grade) was purified by trap-to-trap distillation.

The emission spectra were measured using a Shimadzu spectrofluorophotometer, model RF-5300PC (band-pass, typically 10 nm), at room temperature. Excitation was effected at 280 nm to avoid the local excitation of the TEA. The concentrations of ST and TEA were chosen to be  $1.2 \times 10^{-4}$  and  $3.5 \times 10^{-2}$  mol-dm<sup>-3</sup>, respectively. The relative permittivity ( $\epsilon$ ) of the 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 THF ( $\mu = 7.58$ ) and AN ( $\mu = 35.9$ ).

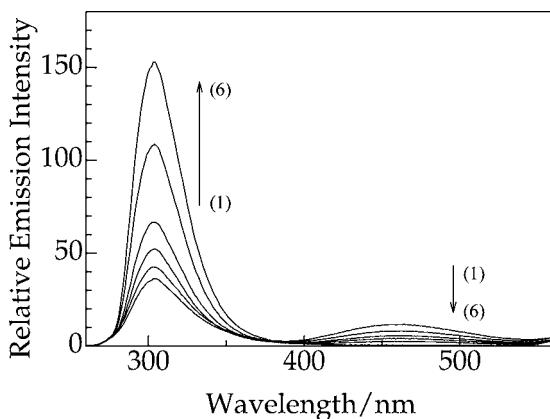
### 3. RESULTS AND DISCUSSION

The fluorescence of ST was quenched by TEA and a new emission band appeared on the long wavelength side of ST fluorescence in CH (Fig. 1) and THF. The emission spectrum of the ST-TEA system consists of two emission bands; the ST fluorescence band (band A with a peak at 304 nm in CH and THF) and the exciplex emission band (band B with a peak at 408 nm in CH and 460 nm in THF).

Upon addition of trichloroacetic acid to the THF solutions, the intensity of band B decreased, while that of band A increased (Fig. 2). Since the concentrations of HTCA are low, the change in the polarity of the solution is small (the relative permittivity of the solution was found to increase from 7.58 to 7.87 when the concentration of HTCA was increased from 0 to 0.035 mol-dm<sup>-3</sup>). The main effect was attributed to the hydrogen-bonding interaction between TEA and HTCA (or



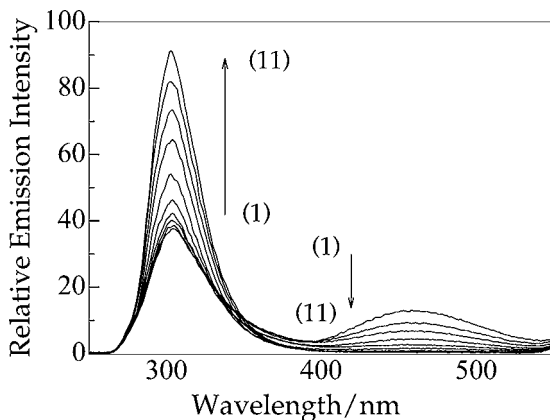
**Fig. 1.** Emission spectra of the ST-TEA system in CH at room temperature: [TEA]: (1) 0, (2) 0.44, (3) 0.88, (4) 1.8, and (5)  $3.5 \times 10^{-2}$  mol-dm<sup>-3</sup>. [ST] =  $1.2 \times 10^{-4}$  mol-dm<sup>-3</sup>.



**Fig. 2.** Emission spectra of the ST-TEA system in THF-HTCA mixtures at room temperature: [HTCA]: (1) 0, (2) 0.7, (3) 1.4, (4) 2.1, (5) 2.8, and (6)  $3.5 \times 10^{-2} \text{ mol-dm}^{-3}$ , [ST] =  $1.2 \times 10^{-4} \text{ mol-dm}^{-3}$ , [TEA] =  $3.5 \times 10^{-2} \text{ mol-dm}^{-3}$ .

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.

Spectra of the ST-TEA system in some THF-MeOH mixtures are shown in Fig. 3. Upon the addition of MeOH, the intensity of band B decreased, while that of



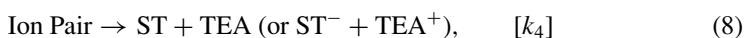
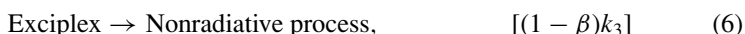
**Fig. 3.** Emission spectra of the ST-TEA system in THF-MeOH mixtures at room temperature: [MeOH]: (1) 0, (2) 0.07, (3) 0.15, (4) 0.30, (5) 0.64, (6) 1.23, (7) 2.46, (8) 3.69, (9) 4.92, and (10) 6.15  $\text{mol-dm}^{-3}$ , [ST] =  $1.2 \times 10^{-4} \text{ mol-dm}^{-3}$ , [TEA] =  $3.5 \times 10^{-2} \text{ mol-dm}^{-3}$ .

band A increased. Similar spectral changes were observed for other alcohols. The spectral changes increased in the order: butanol < 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. The intensities of bands A and B in HTCA– and alcohol–THF mixtures are listed in Table I.

Table II shows the relative permittivity ( $\epsilon$ ) of mixed solvents of THF with MeOH, EtOH, BuOH and HTCA as functions of [ROH] and [HTCA].

### 3.1. Basic Mechanism for Exciplex Formation

The following reactions are considered to explain the emission spectrum of the ST–TEA system:



Here,  $\text{ST}^*$  denotes ST in the excited singlet state. Exciplex and Ion Pair denote the intermolecular exciplex and the ion pair formed by the electron transfer from TEA to  $\text{ST}^*$ .  $K(\epsilon)$  shows the equilibrium constant that depends on solvent polarity.<sup>(22)</sup>

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

$$\frac{I_A}{I_A^0} = \frac{1}{1 + K_{\text{SV}}[\text{TEA}]_f} \quad (9)$$

$$I_B = \beta I_0 \frac{K_{\text{SV}}[\text{TEA}]_f}{1 + K_{\text{SV}}[\text{TEA}]_f} \frac{k_3}{k_3 + k_4 K(\epsilon)} \quad (10)$$

Here,  $I_A^0$  denotes the intensity of band A in the absence of TEA,  $K_{\text{SV}} = k_2/k_1$ , and  $[\text{TEA}]_f$  denotes the concentration of free TEA. Figure 4 shows the relationships between  $I_A/I_A^0$  and  $[\text{TEA}]_f$  ( $[\text{TEA}]_0$  equals to the initial concentration of TEA in THF). The solid line was obtained by the nonlinear least-square method. The  $K_{\text{SV}}$  value obtained is  $143 \text{ dm}^{-3}\text{-mol}$ .

**Table I.** Intensities of Bands A and B and Values of  $X$ ,  $Y$  and  $X/Y$  for the ST-TEA System in Some Protic Solvent-THF Mixtures

[Protic solvent]/ mol-dm <sup>-3</sup>	$I_A/I_A^0$	$I_B$	$X$	$Y$	$X/Y$
HTCA					
0	0.17	12.8	1.00	1.00	1.00
0.007	0.20	9.0	0.70	0.95	0.74
0.014	0.24	6.2	0.48	0.89	0.54
0.021	0.31	4.6	0.35	0.80	0.44
0.028	0.50	2.9	0.22	0.58	0.38
0.033	0.71	0	—	—	—
MeOH					
0	0.16	12.8	1.00	1.00	1.00
0.07	0.17	9.0	0.70	0.99	0.71
0.15	0.18	6.5	0.50	0.98	0.51
0.30	0.19	4.3	0.33	0.97	0.34
0.64	0.21	2.6	0.20	0.95	0.21
1.23	0.24	1.6	0.12	0.91	0.14
2.46	0.29	0.9	0.07	0.83	0.08
3.69	0.33	0.7	0.06	0.77	0.07
4.92	0.37	0.4	0.03	0.71	0.05
6.15	0.41	0.3	0.02	0.66	0.03
EtOH					
0	0.17	12.8	1.00	1.00	1.00
0.09	0.17	10.4	0.81	0.99	0.82
0.20	0.18	7.0	0.55	0.98	0.55
0.44	0.19	4.6	0.36	0.97	0.36
0.85	0.20	2.4	0.18	0.96	0.19
1.71	0.23	1.3	0.10	0.92	0.11
2.56	0.25	0.8	0.06	0.88	0.07
3.41	0.28	0.6	0.05	0.85	0.06
4.27	0.31	0.5	0.04	0.81	0.05
BuOH					
0	0.17	12.8	1.00	1.00	1.00
0.13	0.17	9.3	0.72	0.99	0.72
0.46	0.17	5.6	0.44	0.98	0.44
0.88	0.18	4.0	0.31	0.97	0.32
1.09	0.19	2.1	0.16	0.97	0.20
1.63	0.20	1.5	0.11	0.96	0.12
2.17	0.21	1.0	0.8	0.95	0.09
2.72	0.22	0.9	0.07	0.94	0.07

### 3.2. Effect of Protonation of Amine on Emission Spectra

As mentioned previously, the emission spectra of PDAB and the T-TEA system in THF were only affected by the protonation of the amine upon HTCA addition. Since the concentrations of HTCA were very small in these

**Table II.** Relative Permittivities of Mixed Solvents of THF with HTCA, MeOH, EtOH and BuOH

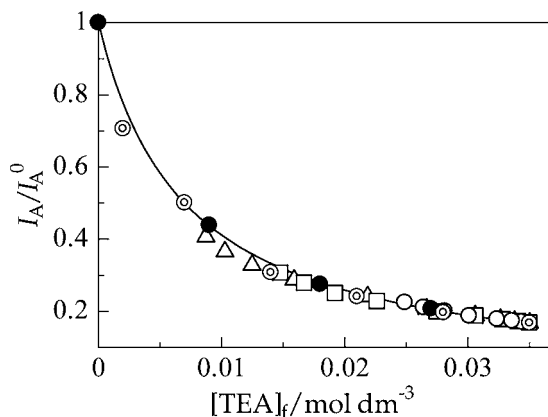
HTCA (mol-dm <sup>-3</sup> )	Relative permittivity	MeOH (mol-dm <sup>-3</sup> )	Relative permittivity	EtOH (mol-dm <sup>-3</sup> )	Relative permittivity	BuOH (mol-dm <sup>-3</sup> )	Relative permittivity
0	7.58	0	7.58	0	7.58	0	7.58
0.010	7.63	0.07	7.63	0.09	7.64	0.13	7.64
0.0010	7.72	0.15	7.68	0.20	7.70	0.46	7.72
0.057	7.87	0.30	7.79	0.44	7.85	0.88	7.85
0.127	7.94	0.64	8.02	0.85	8.11	1.09	8.14
		1.23	8.45	1.71	8.67	1.63	8.45
		2.46	9.37	2.56	9.32	2.17	8.79
		3.69	10.32	3.41	9.89	2.71	9.16
		4.92	11.32	4.27	10.56		
		6.15	12.35				

studies, the polarity of the solution was only slightly affected by the addition of HTCA.

The experimental results for the emission spectrum of the ST-TEA system in THF-HTCA mixtures can be explained by reactions (1)–(10) and the following reaction:



Here, TEAH<sup>+</sup> denotes the protonated amine. If formation of the protonated amine with HTCA is assumed to occur quantitatively, as proven previously,<sup>(13–15)</sup> the equation  $[\text{TEA}]_f = [\text{TEA}]_0 - [\text{HTCA}]_0$  can be obtained, where  $[\text{TEA}]_f$  is the



**Fig. 4.** Plots of relative intensity of band A against  $[\text{TEA}]_f$  in THF (●), THF-HTCA (⊙), THF-MeOH (Δ), THF-EtOH (□), and THF-BuOH (○) mixtures.



concentration of free amine, and  $[\text{TEA}]_0$  and  $[\text{HTCA}]_0$  are the initial concentrations of TEA and HTCA. In Fig. 4,  $I_A/I_A^0$  is plotted against  $[\text{TEA}]_f$  for the THF–HTCA mixtures. As seen in Fig. 4, the values of  $I_A/I_A^0$  obtained for the THF–HTCA mixtures lie on the curve showing the relationship between  $I_A/I_A^0$  and  $[\text{TEA}]_f$  for the ST–TEA system in THF. This indicates that the protonated TEA does not quench the ST fluorescence.

The values of  $I_B$  obtained for the THF–HTCA mixtures were found to be inconsistent with those for the ST–TEA system in THF. The intensity of band B must be influenced by the protonation of TEA and the increase in solvent polarity. Since the range of HTCA concentrations examined in the ST–TEA system was wide compared with those for the PDAB and the T–TEA systems studied previously, the effect of solvent polarity on the intensity of band B could not be neglected. The polar effect on the intensity of band B will be discussed later.

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

As shown in Fig. 3, the intensity of band A increases and that of band B decreases with increasing amounts of MeOH. For THF–EtOH and THF–BuOH mixtures, similar spectral changes were observed.

As reported previously, the emission spectrum of T–TEA mixtures was affected by the addition of alcohols. The emission spectrum of the T–TEA system in THF was found to consist of three component bands (band A at 274 nm, band B at 336 nm, and band C at 373 nm). Bands A, B, and C were assigned to the fluorescence of T, the fluorescence of TEA and emission from an exciplex, respectively. It was found that the intensity of band A increased whereas the intensities of bands B and C decreased with increasing amounts of alcohols. As mentioned previously, in THF–alcohol mixtures, bands B and C were influenced by both polar and hydrogen-bonding interactions, but band A was influenced only by the hydrogen-bonding interaction. The values of the equilibrium constants for the following reaction were estimated from the changes in the intensity of band A resulting from changes in the alcohol concentrations:



The  $K_H$  values obtained for MeOH, EtOH and BuOH were 0.48, 0.31 and  $0.18 \text{ dm}^3 \cdot \text{mol}^{-1}$ , respectively.<sup>(15)</sup> In Fig. 5, the  $[\text{TEA}]_f/[\text{TEA}]_0$  ratios are shown as functions of the concentration of alcohols for THF–MeOH, EtOH and BuOH mixtures.

The increase in the intensity of band A with increasing amounts of alcohols observed in the present study must also be caused by the hydrogen-bonding effect.

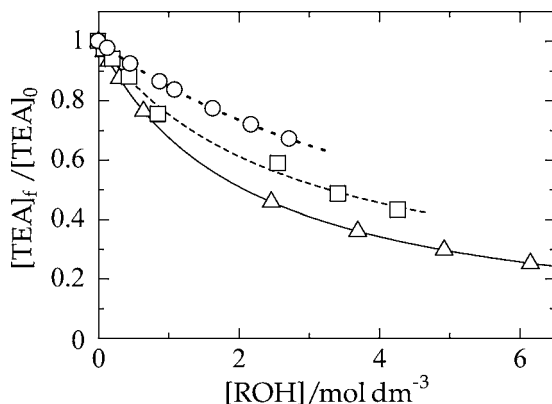


Fig. 5. Plots of  $[\text{TEA}]_f/[\text{TEA}]_0$  against  $[\text{ROH}]$  in THF–MeOH ( $\Delta$ ), THF–EtOH ( $\square$ ), and THF–BuOH ( $\circ$ ) mixtures.

In Fig. 4, the intensity of band A in THF–alcohol mixtures is shown as a function of  $[\text{TEA}]_f$ . The intensity of band A decreases with increasing  $[\text{TEA}]_f$ , as in the ST–TEA system in THF and in THF–HTCA mixtures. The decreases in the intensity of band A in THF–alcohol mixtures are consistent among the alcohols examined and also consistent with the results in THF and in THF–HTCA mixtures (as mentioned above, the solid line in Fig. 4 is the best-fit curve for points obtained in THF). This indicates that the increase in the intensity of band A with increasing alcohol concentration can only be explained by the decrease in the concentration of free TEA.

The following equations for the intensity of band B in THF ( $I_B^{\text{THF}}$ ) and that in THF–alcohol mixtures ( $I_B^{\text{ROH}}$ ) were derived from reactions (1)–(7) by a steady-state treatment:

$$I_B^{\text{THF}} = \beta I_0 \frac{K_{\text{SV}}[\text{TEA}]_0}{1 + K_{\text{SV}}[\text{TEA}]_0} \frac{k_3}{k_3 + k_4 K(\text{THF})} \quad (13)$$

$$I_B^{\text{ROH}} = \beta I_0 \frac{K_{\text{SV}}[\text{TEA}]_f}{1 + K_{\text{SV}}[\text{TEA}]_f} \frac{k_3}{k_3 + k_4 K(\varepsilon)} \quad (14)$$

where  $K(\text{THF})$  and  $K(\varepsilon)$  indicate the values of  $K(\varepsilon)$  in THF and the THF–ROH mixture whose relative permittivity is equal to  $\varepsilon$ , respectively. As described in two previous papers, conversion of the exciplex to an ion pair is enhanced by the increase in solvent polarity ( $K(\varepsilon)$  must increase with increasing  $\mu$ ). The total effects of alcohols on the intensity of band B can be expressed as follows:

$$X = \frac{I_B^{\text{ROH}}}{I_B^{\text{THF}}} = \frac{[\text{TEA}]_f}{[\text{TEA}]_0} \frac{1 + K_{\text{SV}}[\text{TEA}]_0}{1 + K_{\text{SV}}[\text{TEA}]_f} \frac{k_3 + k_4 K(\text{THF})}{k_3 + k_4 K(\varepsilon)} \quad (15)$$

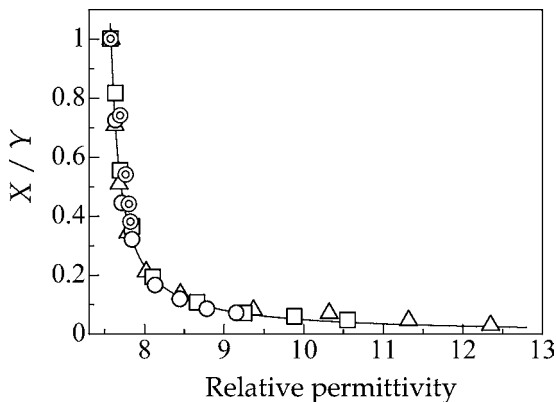


Fig. 6. Plots of  $X/Y$  against relative permittivity of the solutions in THF-HTCA ( $\odot$ ), THF-MeOH ( $\Delta$ ), THF-EtOH ( $\square$ ), and THF-BuOH ( $\circ$ ) mixtures.

When only the hydrogen-bonding effect of an alcohol affects the intensity of band B, the following equation is obtained by setting  $K(\text{THF}) = K(\epsilon)$ ;

$$Y = \frac{[\text{TEA}]_f}{[\text{TEA}]_0} \frac{1 + K_{\text{SV}}[\text{TEA}]_0}{1 + K_{\text{SV}}[\text{TEA}]_f} \quad (16)$$

Therefore, the relative effect of polarity in alcohol-THF mixtures to that in THF on the intensity of band B can be expressed from  $X$  and  $Y$  as follows:

$$\frac{X}{Y} = \frac{k_3 + k_4 K(\text{THF})}{k_3 + k_4 K(\epsilon)} \quad (17)$$

From the intensity of band B in THF and those in THF-HTCA or THF-ROH mixtures, the value of  $K_{\text{SV}}$  obtained above and the concentrations of free TEA, we can obtain the values of  $X$  and  $Y$  in various THF-HTCA or THF-ROH mixtures (Table I). In Fig. 6 the values of  $X/Y$  for THF-HTCA, THF-MeOH, -EtOH and -BuOH mixtures are shown as functions of the relative permittivity ( $\epsilon$ ). The values of  $X/Y$  in the THF-alcohol mixtures decrease with increasing relative permittivity. The decreases in  $X/Y$  in THF-alcohol mixtures are consistent among the mixtures (the solid line in Fig. 6 is the best fit curve of all points obtained for alcohols). The decreases in the value of  $X/Y$  are considered to be caused by the increase in  $K(\epsilon)$  with increasing solvent polarity. The values of  $K(\epsilon)$  must increase steeply with increasing relative permittivity of the solution in the range from 7.58 to about 8.

#### 4. CONCLUSIONS

The fluorescence spectrum of the ST-TEA system in THF consists of two emission bands [ST fluorescence (band A) and exciplex emission (band B)].

The intensity of band B decreased with increasing solvent polarity. However, the intensity of band A increased and that of band B decreased when a hydrogen-bonding interaction (or protonation) occurred between TEA and protic solvents.

The hydrogen-bonding interaction between the amine and protic solvents suppresses the exciplex formation 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 enhanced conversion of the exciplex to the ion pair under polar conditions. The polar effects of HTCA and alcohols were correlated to the relative permittivity of the solution.

## ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid for Scientific Research (No. 15550014) from the Ministry of Education, Culture, Sports, Science, and Technology.

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