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Separation into Polar and Hydrogen-Bonding Factors of the Effects of Alcohols on the Emission Spectrum of 4-Phenyl-1-*N,N*-dimethylaminobutane in THF

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Abstract

The effects of the additions of protic and aprotic polar solvents on the emission spectrum of 4-phenyl-1-*N,N*-dimethylaminobutane (PDAB) in THF have been studied under conditions of steady-state illumination. The fluorescence spectrum of PDAB in THF was reported to consist of three component bands (band A at 285 nm (fluorescence of the phenyl group), band B at 343 nm (fluorescence of the amino group) and band C at 385 nm (emission from an intramolecular exciplex)). The intensities of bands B and C decreased with increasing solvent polarity. They also decreased owing to the hydrogen-bonding interaction between the amino group in PDAB and protic solvents, but in this case the intensity of band A was found to increase. Acetonitrile has only a polar effect and trichloroacetic acid only a hydrogen-bonding (or protonation) effect, while alcohols have both effects. The equilibrium constants for the formation of intermolecular hydrogen-bonded complexes of the amino group with alcohols were estimated from the intensity change of band A. The hydrogen-bonding and polar effects of alcohols on the intensities of bands B and C could be separately evaluated. The decrease in the intensities of bands B and C with increasing solvent polarity in THF-AN and THF-alcohol mixtures is considered to be caused by the conversion of the exciplex to an ion-pair enhanced by the increase in solvent polarity.

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

1. Introduction

In the presence of tertiary aliphatic amines several aromatic compounds show fluorescence quenching and exciplex emission [1-11]. With naphthylalkylamines [12, 13] and anthrylalkylamines [14] intramolecular exciplex formation was observed. Formation of intramolecular exciplexes between phenyl and amino groups was also observed in some ω -phenyl- α -(*N,N*-dimethylamino)alkanes [15-19]. Schryver *et al.* [17, 18] observed that in THF the emission of 4-phenyl-1-*N,N*-dimethylaminobutane (PDAB) at room temperature consists of a broad structureless band at about 372 nm and a shoulder at 286 nm. The emission at 286 nm was assigned to the phenyl chromophore and the broad band to the intramolecular exciplex and the locally excited state of the amino chromophore. The emission spectrum of 3-phenyl-1-*N,N*-dimethylaminopropane (PDAP) at room temperature consists of a band with a maximum at 377 nm. Emission from the phenyl chromophore was scarcely observed for this compound at room temperature. Multi-component emission spectra of intermolecular and intramolecular toluene-diamine systems were observed in THF [20].

In a previous letter [21], we briefly reported the effects of the addition of 1-butanol (BuOH), trichloroacetic acid (TCAA) and acetonitrile (AN) on the emission spectrum of PDAB in THF. The results showed that AN has only a polar effect and TCAA only a hydrogen-bonding (or protonation) effect, while BuOH has both effects. The relative magnitude of each effect was evaluated as a function of vol% of BuOH. It was pointed out that this method of separately evaluating the hydrogen-bonding and polar effects can be applied to other protic solvents.

The present paper reports the details of the effects of protic and aprotic polar solvents on the emission spectrum of PDAB in THF.

2. Experimental

PDAP and PDAB were prepared from 3-phenylpropylamine and 4-phenylbutylamine, respectively, according to the method of Halpern [19]. $^1\text{H-NMR}$ of the products confirmed their structures and they were purified by vacuum distillation. THF, AN, methanol (MeOH), ethanol (EtOH), 1-propanol (PrOH), BuOH and cyclohexane (CH) were of spectroscopic grade and were used as supplied. TCAA was of extra purity grade and was used as received.

The emission spectra were measured by a Shimadzu spectrofluorophotometer, model RF 1500 (typically 10 nm bandpass). Correction for the wavelength dependence of the sensitivity of the detection system was found to be unnecessary in practice between 280 and 550 nm using standard fluorescence solutions [20]. Excitation was effected at 270 nm in each case, a wavelength at which the radiation is nearly absorbed by the phenyl group. The concentration of PDAB and PDAP were kept below 10^{-3} mol dm^{-3} to avoid intermolecular interaction (the shapes of the emission spectra were observed not to depend on their concentration below 10^{-3} mol dm^{-3}). The solutions were degassed by four freeze-pump-thaw cycles. The relative permittivity (ϵ) of the several 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 the known values of relative permittivity for pure solvents.

3. Results

Fig. 1 shows the emission spectra of PDAB in some THF-BuOH mixtures. The emission spectrum of PDAB in THF was previously found to change with temperature and to decompose into three component bands (band A at 285 nm, band B at 343 nm and band

C at 385 nm) [20]. Bands A, B and C were assigned to the fluorescence of the phenyl group, fluorescence of the amino group and emission from an intramolecular exciplex, respectively (the wavelengths of the peaks of bands B and C are similar to those of dimethylethylamine fluorescence and the emission from the intermolecular exciplex between toluene and amine, respectively). [17, 20].

As shown in Fig. 1, the intensity of band A increases and those of bands B and C decrease with increasing amounts of BuOH. The shape of the combined band of bands B and C is little affected by the addition of BuOH. This indicates that the intensity ratio of bands B and C is almost constant in various THF-BuOH mixtures (the intensity ratio of about 1/3.5 for bands B and C was obtained) and the spectrum of PDAB behaves like a two-band spectrum (this also holds for the other mixtures except for THF-CH mixtures examined in this study).

For THF-MeOH, EtOH and PrOH mixtures, similar spectral changes were observed. Since no isosbestic point was seen in these spectral changes in THF-alcohol mixtures, there seem to be more than two causes for the spectral change.

Figs. 2 (a) and (b) show the changes in the intensities of band A and of the combined band of bands B and C 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 amounts of alcohols.

The addition of alcohol will cause hydrogen-bonding interaction with the amino group and a decrease in the concentration of species with the free amino group. The hydrogen-bonding interaction suppresses the formation of the intramolecular exciplex and that of the excited amino group which is formed through the exciplex. These effects cause an increase in the intensity of band A and decreases in those of bands B and C. On the other hand, the increase in solvent polarity will convert the exciplex to a non-fluorescent radical ion-pair [22, 23]. This conversion also decreases the intensities of bands B and C, but does not influence band A. As shown below, band A was found to be little affected by

the increase in the solvent polarity. The intensity change becomes greater in the order: BuOH <PrOH <EtOH <MeOH.

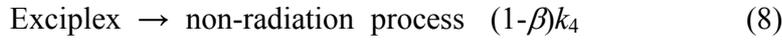
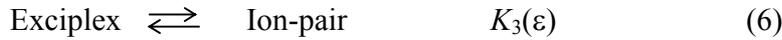
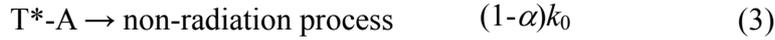
The intensities of bands B and C also decrease with increasing amounts of AN, but that of band A does not change (Figs. 2(a) and (b)). The addition of AN to THF will cause an increase in the polarity of the medium, but not in the hydrogen-bonding interaction. As mentioned above, the increase in the solvent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

Fig. 3 shows the effect of the addition of TCAA on the emission spectrum of PDAB 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 and a clear isosbestic point exists in the spectral change. This indicates that there is just one cause of the spectral change induced by TCAA. The addition of TCAA to THF will cause hydrogen-bonding interaction between the amino group of PDAB and TCAA (or the protonation on the amino group). Since the amounts of TCAA are very small, however, the polarity of the medium is little affected by the addition of TCAA. Fig. 4 shows the changes in the intensities of band A and of the combined band of bands B and C with [TCAA]/[PDAB].

Fig. 5 shows the relative permittivity (ϵ) of mixed solvents of THF with AN, MeOH, EtOH, PrOH and BuOH as functions of vol% of co-solvents.

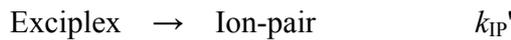
4. Discussion

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, the following reactions are considered.



Here, (T-A) denotes PDAB in the ground state, (T*-A) the PDAB having an excited phenyl chromophore, Exciplex the intramolecular exciplex, (T-A*) PDAB having an excited amino group and Ion-pair the non-fluorescent radical ion-pair formed by intramolecular electron transfer from the amino group to the phenyl group. $K_3(\varepsilon)$ shows the equilibrium constant that depends on solvent polarity (as described later). The proportions of radiation 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 of dependence of lifetime and relative emission intensity of the exciplex on the solvent polarity in an anthracene-*N,N*-diethylaniline system:



In this case the formation of the ion-pair occurs through and parallel to the formation of exciplex. They pointed out that k_{IP} and $k_{\text{IP}'}$ depend on the solvent polarity, whereas k_e

should be virtually independent of the 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, similarly to many other systems.

In the present system, as shown in Fig. 2, the fluorescence intensity of the phenyl group is little affected by the addition of AN to the THF solution. Therefore, the direct formation of the ion-pair from the excited phenyl group can be neglected. In polar solvents dissociation of exciplex to solvent-shared ion-pair occurs, and in high polar solvents as in AN this dissociation is essentially irreversible. In the above reaction mechanism, it was assumed that equilibrium between the exciplex and the ion-pair is attained in the moderately polar solvents and that the equilibrium constant depends on the solvent polarity.

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



Here, T-AH denotes PDAB having the hydrogen-bonded (or protonated) amino group in the ground state and T*-AH the corresponding PDAB having an excited phenyl chromophore.

Since the formation of hydrogen-bonded (or protonated) amino group with TCAA must occur quantitatively (Fig. 4), the following equations can be obtained:

$$X = \frac{I_A - I_A^\circ}{I_A^{\text{ex}} - I_A^\circ} = \frac{[\text{TCAA}]}{[\text{PDAB}]} \quad (16)$$

$$Y = \frac{I_{\text{B,C}}^\circ - I_{\text{B,C}}}{I_{\text{B,C}}^\circ} = \frac{[\text{TCAA}]}{[\text{PDAB}]} \quad (17)$$

where I_A° and I_A are the intensities of band A in the absence and presence of TCAA, respectively, I_A^{ex} is that in the presence of excess TCAA (the intensity of band A at

[TCAA] = 6.0×10^{-4} M was used as I_A^{ex} , see Fig. 4), and $I_{B,C}^{\circ}$ and $I_{B,C}$ are the total intensity of bands B and C in the absence and presence of TCAA, respectively.

As shown in Fig. 6, linear relationships with slopes equal to 1.0 between X and Y and [TCAA]/[PDAB] are obtained. This indicates that eqn. (16) and (17) hold. In this manner, X and Y can be used as a measure of the hydrogen-bonding interaction in THF-TCAA mixtures.

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



Here, T-AHOR denotes PDAB having a hydrogen-bonded amino group with alcohol and T*-AHOR the corresponding PDAB having an excited phenyl chromophore. The proportion factors of the radiation processes (α , β and γ) are assumed to be unaffected by the addition of alcohols.

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

$$I_A = I_0[T-A] \left(\frac{\alpha k_0}{k_0 + k_1} \frac{1}{1 + K_9[\text{ROH}]} + \frac{\alpha K_9[\text{ROH}]}{1 + K_9[\text{ROH}]} \right) \quad (22)$$

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

$$X(\text{ROH}) = \frac{I_A - I_A^0}{I_A^{\text{ex}} - I_A^0} = \frac{K_9[\text{ROH}]}{1 + K_9[\text{ROH}]} \quad (23)$$

where I_A^0 and I_A are the intensities of band A in the absence and presence of ROH, respectively, I_A^{ex} is that in the presence of excess alcohol (actually, the limiting intensities of band A in the presence of excess alcohols could not be obtained exactly, and therefore,

instead of these values the intensity of band A in the presence of excess TCAA shown above was used as I_A^{ex}).

As shown in Fig. 7, linear relationships with intercepts equal to 1.0 between $1/X$ and $1/[\text{ROH}]$ are obtained. The values of the equilibrium constant are obtained from the slopes of the straight lines ($K_9 = 0.43, 0.31, 0.21$ and 0.12 M^{-1} were obtained for MeOH, EtOH, PrOH and BuOH, respectively). These values are similar to the values reported for these alcohols and triethylamine in AN [24, 25].

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 $K_3(\epsilon)$ depends on the solvent polarity, as mentioned above, in order to discuss the effect of the solvent polarity on the intensities of bands B and C quantitatively, it is necessary to know the extent of the conversion from the exciplex to the ion-pair in pure THF. It was found that the intensities of bands B and C increased with increasing amounts of CH in THF-CH mixtures (with decreasing solvent polarity). The total intensity of bands B and C in pure CH (in which $K_3(\epsilon)$ was assumed to be zero) can be considered as a standard. However, since the shifts of bands B and C with changing solvent polarity are large in THF-CH mixtures and bands A, B and C largely overlap in CH, the intensities of bands B and C could not be obtained in pure CH.

As reported previously [20], the emission spectrum of PDAP only consists of band C. Using the ratio of the emission intensity of PDAP in CH and THF, the ratio of the total intensity of bands B and C of PDAB in CH and THF was estimated by considering that the intensity ratio of bands B and C is almost constant, as mentioned above (the value of $I_{B,C}(\text{CH})/I_{B,C}(\text{THF}) = 1.39$ was obtained).

The following equation of the total intensity of bands B and C in THF-AN mixtures was derived from reactions (1)-(11) by a steady-state treatment based on the assumption

that fast equilibria among Exciplex, T-A* and Ion-pair were attained:

$$I_{B,C} = I_0[T - A]_0 \frac{k_1}{k_0 + k_1} \frac{\beta k_4 + \gamma k_5 K_2}{k_4 + k_5 K_2 + k_6 K_3(\varepsilon)} \quad (24)$$

From this equation, $Y(\varepsilon)$ (modified Y) can be expressed as follows:

$$Y'(\varepsilon) = \frac{I_{B,C}(\text{CH}) - I_{B,C}}{I_{B,C}(\text{CH})} = \frac{k_6 K_3(\varepsilon)}{k_4 + k_5 K_2 + k_6 K_3(\varepsilon)} \quad (25)$$

where $I_{B,C}(\text{CH})$ and $I_{B,C}$ are the intensities of bands B and C in CH and THF-AN mixtures, respectively. This equation shows that since $K_3(\varepsilon)$ increases with increasing solvent polarity (ε), $Y(\varepsilon)$ increases with increasing relative permittivity of the solvent.

As is shown in Fig. 8, $Y(\varepsilon)$ increases steeply with increasing relative permittivity and approaches unity. These tendencies are consistent with the expectation from the above equation.

Similarly, since the total intensity of bands B and C in THF-alcohol mixtures is expressed by the following equation,

$$I_{B,C}(\text{ROH}) = I_0 \frac{k_1}{k_0 + k_1} \frac{[T - A]_0}{1 + K_9[\text{ROH}]} \frac{\beta k_4 + \gamma k_5 K_2}{k_4 + k_5 K_2 + k_6 K_3(\varepsilon)} \quad (26)$$

$Y(\text{ROH})$ can be expressed as follows:

$$\begin{aligned} Y'(\text{ROH}) &= \frac{I_{B,C}(\text{CH}) - I_{B,C}(\text{ROH})}{I_{B,C}(\text{CH})} \\ &= \frac{K_9[\text{ROH}]}{1 + K_9[\text{ROH}]} + \frac{1}{1 + K_9[\text{ROH}]} \frac{k_6 K_3(\varepsilon)}{k_4 + k_5 K_2 + k_6 K_3(\varepsilon)} \end{aligned} \quad (27)$$

Since $X(\text{ROH}) = K_9[\text{ROH}]/(1 + K_9[\text{ROH}])$ and $Y(\varepsilon) = k_6 K_3(\varepsilon)/(k_4 + k_5 K_2 + k_6 K_3(\varepsilon))$, the following equation is obtained:

$$Y'(\varepsilon) = (1 + K_9[\text{ROH}])(Y'(\text{ROH}) - X(\text{ROH})) \quad (28)$$

This equation shows the contribution of the polar effect in various THF-alcohol mixtures to the intensity change of bands B and C can be estimated by the values of $Y'(\text{ROH})$, $X(\text{ROH})$ and K_9 .

In Fig. 8 the values of $Y(\varepsilon)$ for THF-MeOH, EtOH, PrOH and BuOH mixtures are

shown as functions of the relative permittivity. The values of $Y(\epsilon)$ in THF-alcohol mixtures increase with increasing relative permittivity like those in THF-AN mixtures. The increases in $Y(\epsilon)$ in THF-alcohol mixtures are consistent with each other among alcohols examined (the solid line in Fig. 8 is the best-fit curve of all points obtained for alcohols shown above), and are also roughly consistent with those in THF-AN mixtures. The cause of small differences in $Y(\epsilon)$ between THF-AN and THF-alcohol mixtures is not clear. $Y(\epsilon)$ for THF-alcohol mixtures was not directly determined, but estimated using the values of $Y(\text{ROH})$, $X(\text{ROH})$ and K_9 , as mentioned above. Therefore, this discrepancy may come from the accumulation of errors in the evaluation of $Y(\epsilon)$ in THF-alcohol mixtures, but some unknown factors may possibly affect these values. We tried to identify these factors, but could not. Moreover, the origins of these factors remain open questions.

Although quantitative agreement remains an open question, Eqn. (23) and (28) provide a means of evaluating separately the hydrogen-bonding and polar effects in THF-alcohol mixtures. Both the hydrogen-bonding and polar effects increase with increasing content of alcohol in THF-alcohol mixtures. Fig. 9 shows the ratio of hydrogen-bonding effect to polar effect as functions of vol% of alcohol in some THF-alcohol mixtures. As shown in Fig. 9, this ratio increases nearly linearly for BuOH, while it shows a saturation tendency for MeOH, EtOH and PrOH. The ratio decreases in the order; MeOH > EtOH > PrOH > BuOH.

5. Conclusions

The emission spectrum of PDAB in THF consists of three component bands, but it behaves like a two-band spectrum with changes in the polarity and hydrogen-bonding ability in THF-AN, TCAA and alcohol mixtures. The short-wavelength band (band A) is the fluorescence of the phenyl group and the long-wavelength band is the combined band of bands B (fluorescence of the amino group) and C (emission from the intramolecular

exciplex). The former is sensitive to the hydrogen-bonding (or protonation) interaction between the amino group and an alcohol or a TCAA molecule, while the latter two to both the polar and hydrogen-bonding effects. AN shows only a polar effect and TCAA only a hydrogen-bonding (protonation) effect, while alcohols have both effects.

From the intensity change of band A on the addition of alcohols, the equilibrium constants for the formation of a hydrogen-bonded complex between the amino group of PDAB and an alcohol molecule were estimated. The polar and hydrogen-bonding effects of alcohols on the intensities of bands B and C could be separated.

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Figure captions

- Fig. 1. Emission spectra of PDAB in THF-BuOH mixtures at room temperature: vol % of BuOH are (1) 0, (2) 5.0, (3) 10.0, (4) 20.0, (5) 30.0 and (6) 40.0. $[\text{PDAB}] = 3.7 \times 10^{-4} \text{ mol dm}^{-3}$.
- Fig. 2. Plots of relative intensities of (a) band A and (b) bands B and C against vol% of the co-solvent in THF-AN and THF-alcohol mixtures: () AN, () MeOH, () EtOH, () PrOH and () BuOH.
- Fig. 3. Emission spectra of PDAB in THF-TCAA mixtures at room temperature: [TCAA] are (1) 0, (2) 0.50, (3) 1.0, (4) 1.5, (5) 2.0, (6) 2.5, (7) 3.0 and (8) $6.0 \times 10^{-4} \text{ M}$. $[\text{PDAB}] = 3.7 \times 10^{-4} \text{ mol dm}^{-3}$.
- Fig. 4. Plots of relative intensities of band A () and bands B and C () against $[\text{TCAA}]/[\text{PDAB}]$ in THF-TCAA mixtures.
- Fig. 5. Relative permittivity of mixed solvents of THF with () AN, () MeOH, () EtOH, () PrOH and () BuOH.
- Fig. 6. Experimental plots of Eqn. (16) and (17) for changes in the emission intensities of band A and bands B and C in THF-TCAA mixtures. (): X, (): Y.
- Fig. 7. Plots of $1/X$ against $1/[\text{ROH}]$ for changes in the emission intensity of band A in THF-alcohol mixtures: () MeOH, () EtOH, () PrOH and () BuOH.
- Fig. 8. Plots of $Y(\epsilon)$ against the relative permittivity for changes in the emission intensities in THF-AN and THF-alcohol mixtures: () AN, () MeOH, () EtOH, () PrOH and () BuOH.
- Fig. 9. Plots of the ratio of hydrogen-bonding effect to polar effect against vol% of Alcohol: () MeOH, () EtOH, () PrOH and () BuOH.

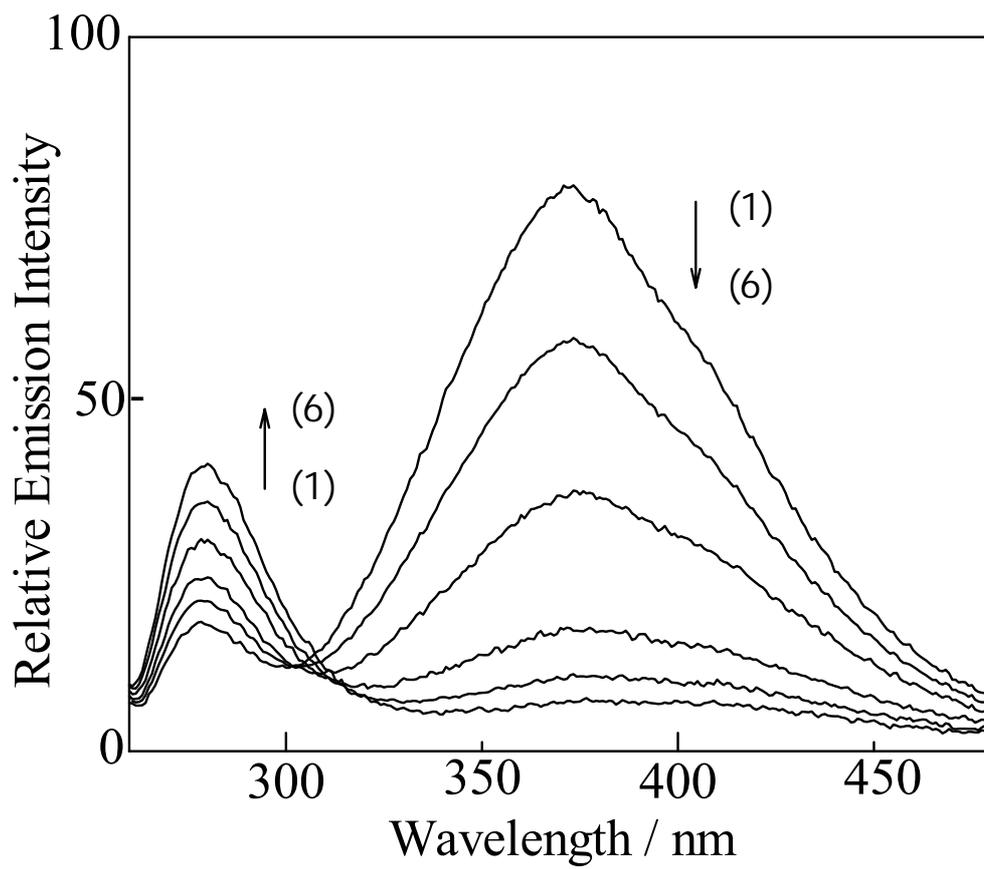


Fig. 1

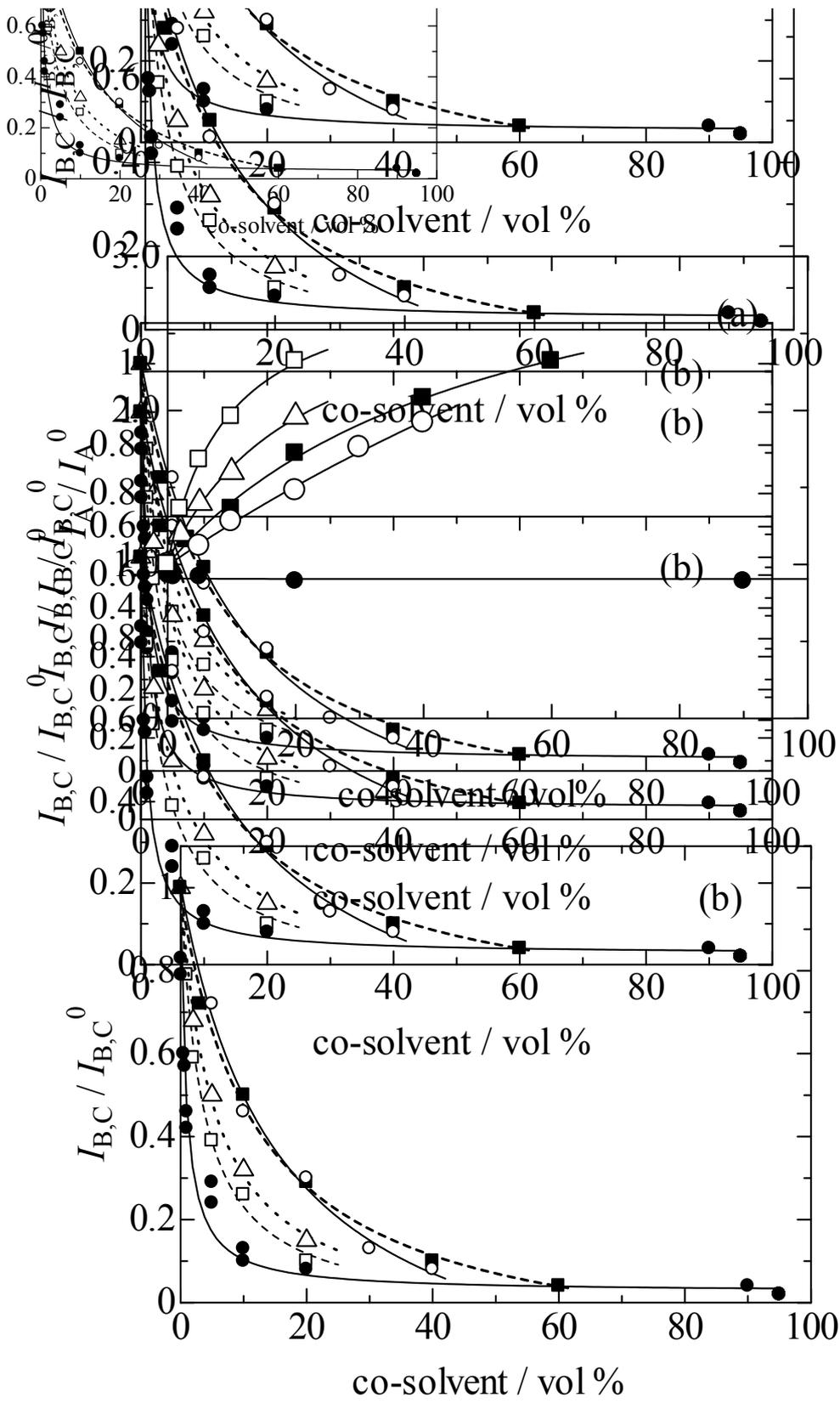


Fig.2

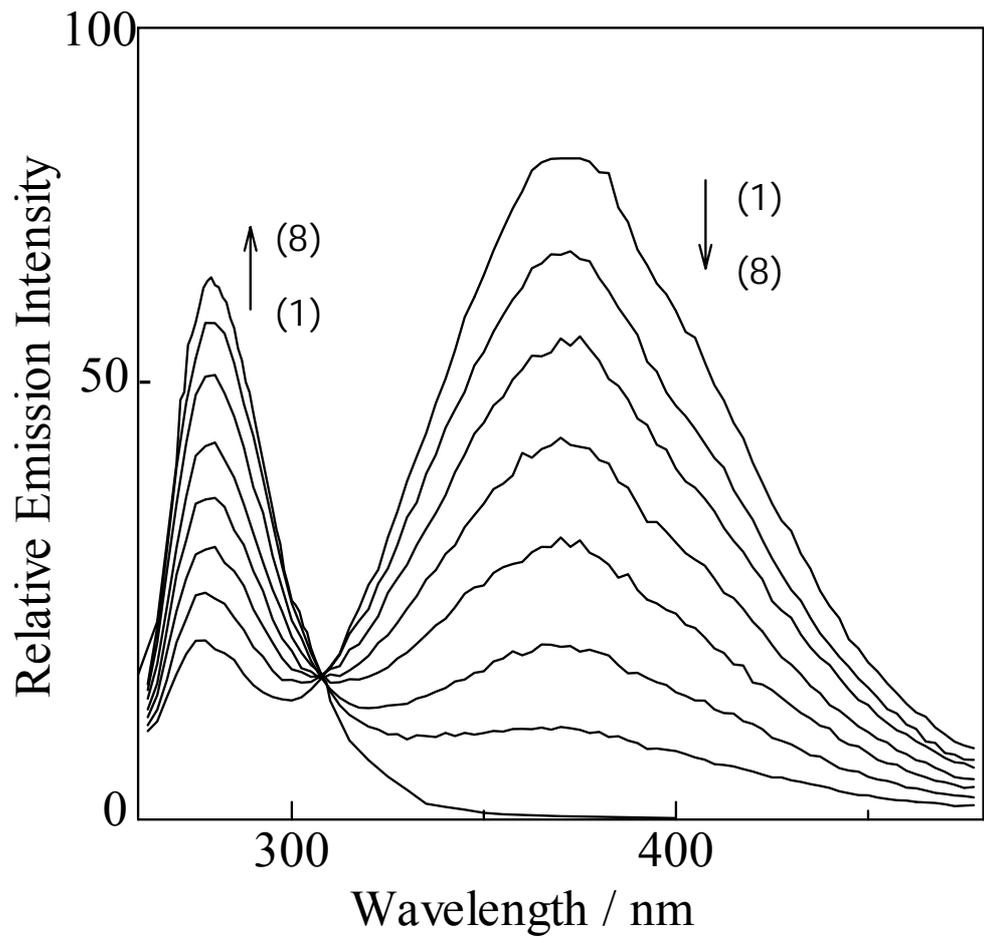


Fig. 3

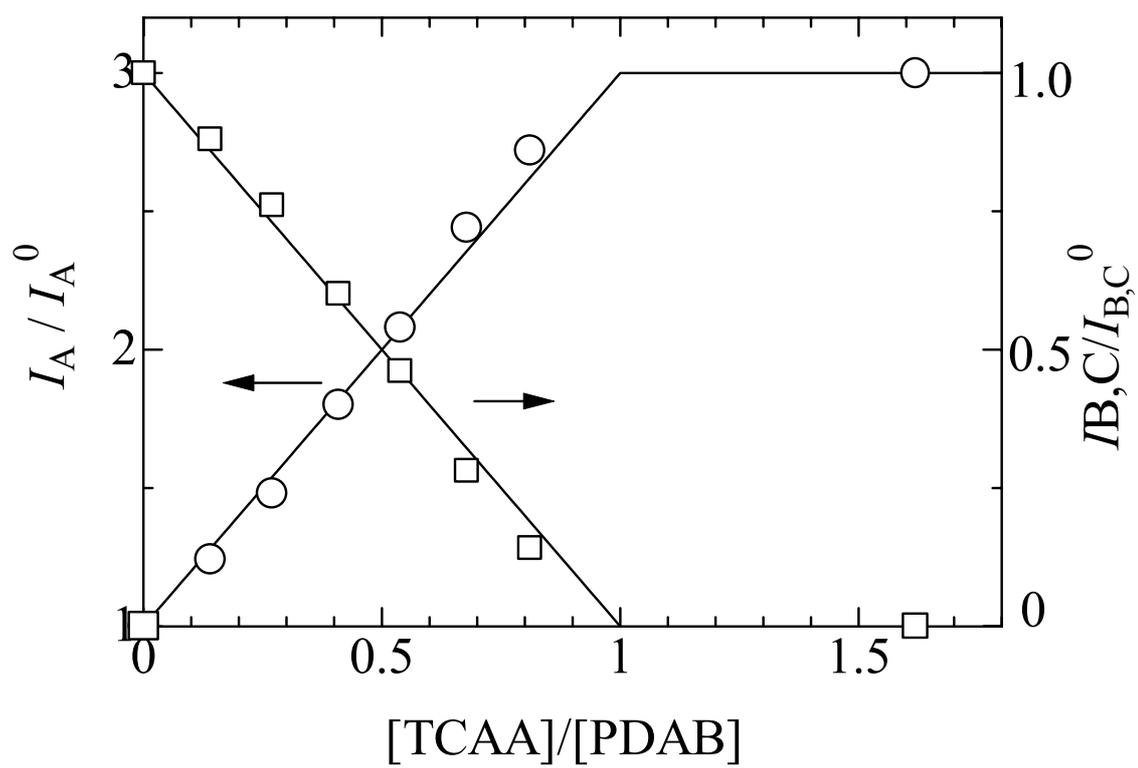


Fig. 4

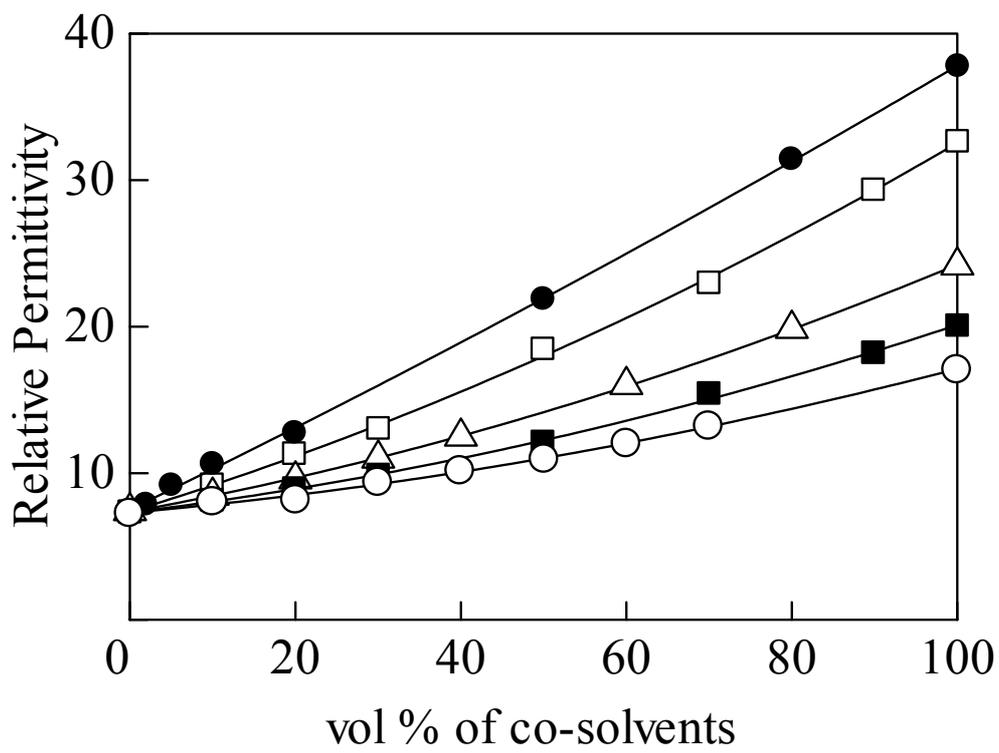


Fig. 5

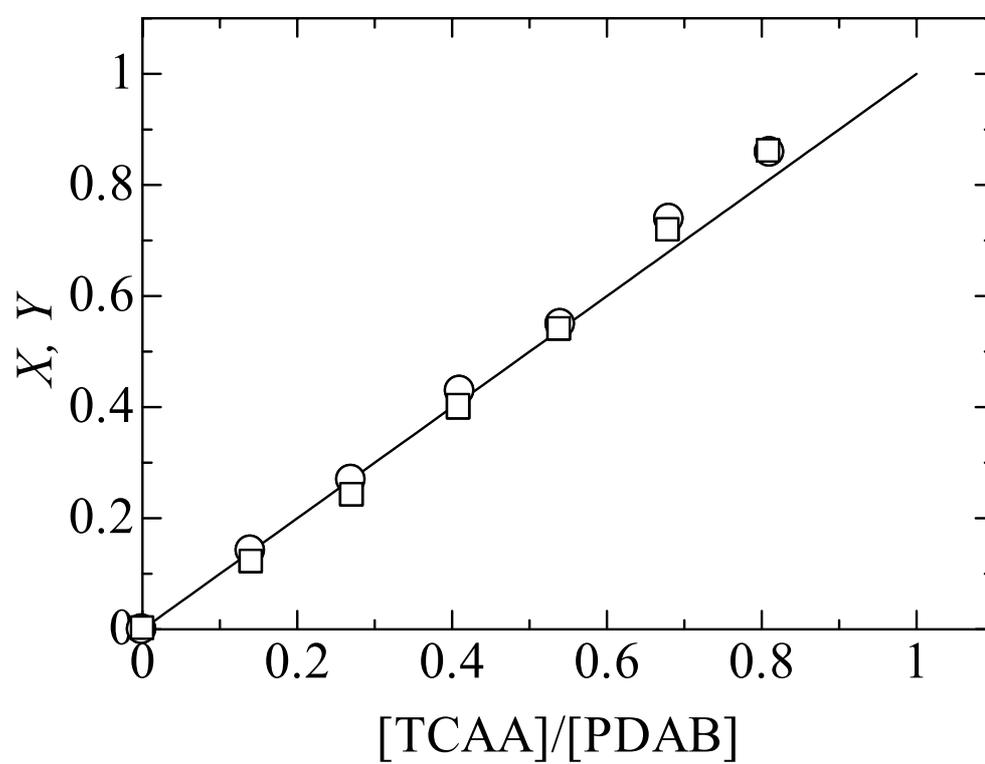


Fig. 6

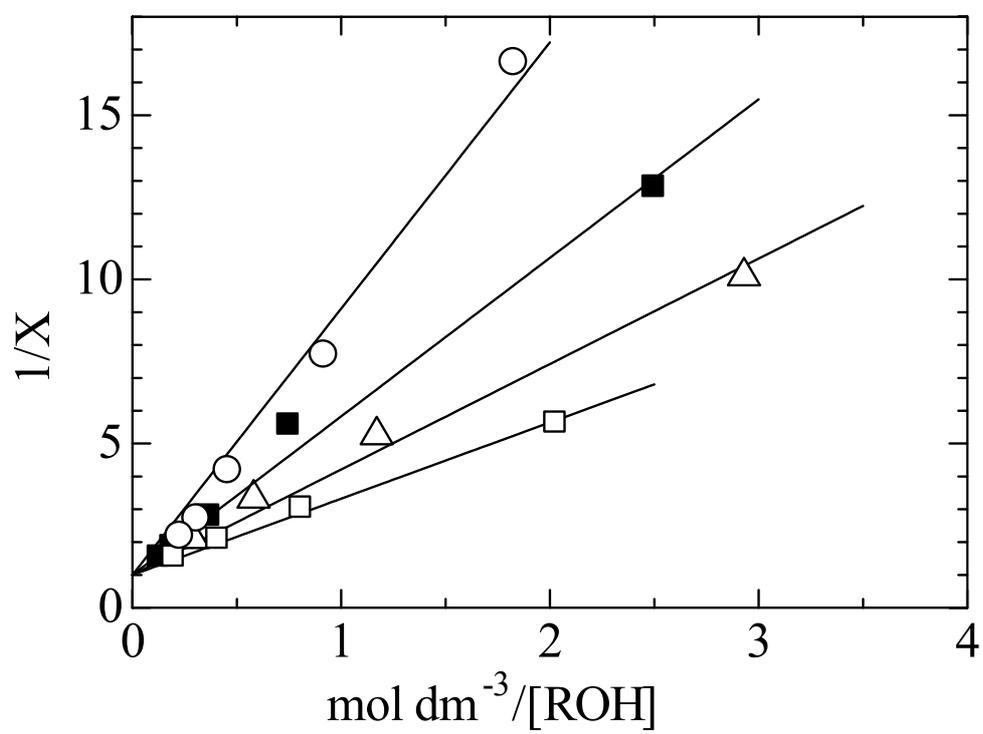


Fig. 7

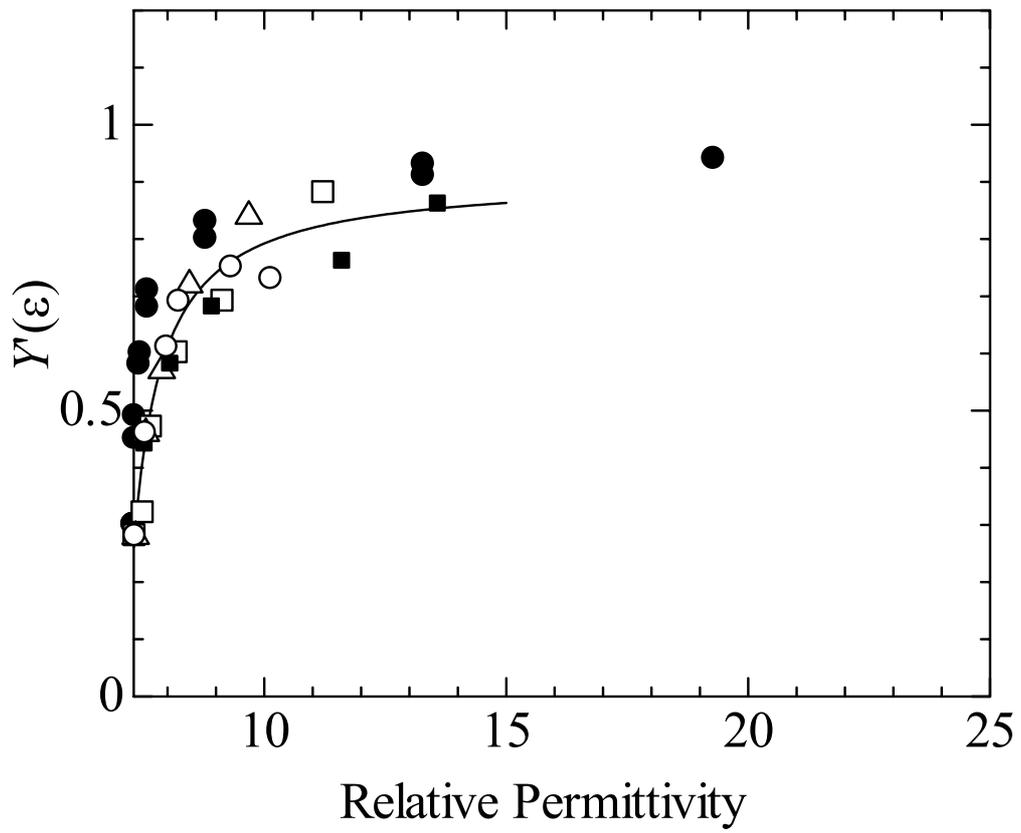


Fig. 8

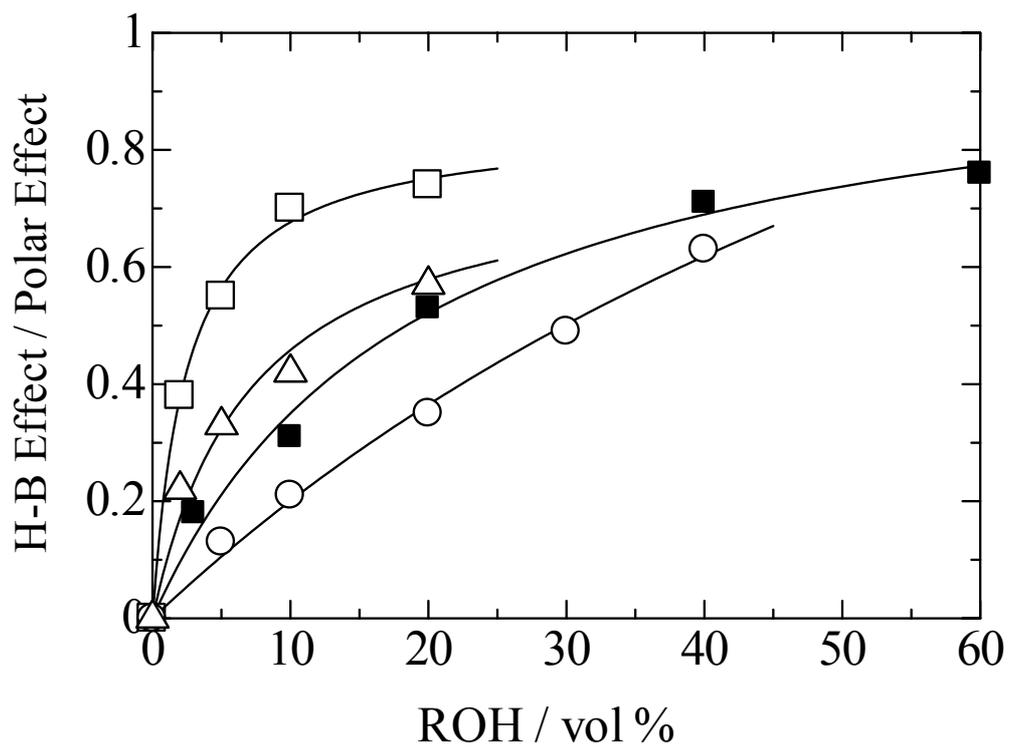


Fig. 9