Effects of 1-Butanol on Emission Spectrum of 4-Phenyl-1-*N*,*N*-dimethylaminobutane in THF: Separation into Polar and Hydrogen-Bonding Interactions

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The effects of the addition of 1-butanol (BuOH), trichloroacetic acid (TCAA) and acetonitrile (AN) on the emission spectrum of 4-phenyl-1-*N*,*N*-dimethylaminobutane in THF have been studied. The results show 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.

Several aromatic compounds show fluorescence quenching and exciplex emission in the presence of tertiary amines.[1] As noted below, the emission spectrum of 4-phenyl-1-*N*,*N*-dimethylaminobutane (PDAB) in THF decomposes into three component bands (one of them was assigned to the emission from an intramolecular exciplex).[2–4]

In this study we examined the effects of the addition of 1-butanol (BuOH) on the emission spectrum of PDAB in THF. The addition of BuOH to THF will cause an increase in the solvent polarity and in the hydrogen-bonding interaction with an amino group. The results were found to provide valuable information about the change in the relative importance of the polar and hydrogen-bonding interactions by the amount of BuOH.

The emission spectra were measured by a Shimadzu spectrofluorophotometer, model RF 1500 (typically 10 nm bandpass). Excitation was at 270 nm, a wavelength at which radiation is nearly exclusively absorbed by phenyl ring. The concentrations of PDAB were kept below 10^{-3} M ($1\,\mathrm{M} = 1\,\mathrm{mol\,dm^{-3}}$) to avoid intermolecular interaction. The solutions were degassed by four freeze-pump-thaw cycles.

Figure 1 shows the emission spectra of PDAB in some THF-butanol mixtures. The emission spectrum of PDAB in THF was previously found to change with temperature and decompose into three component bands (band A at 285 nm, band B at 343 nm and band C at 385 nm).[4] Bands A, B and C were assigned to the fluorescence of phenyl group, that of the amino group and the emission from an intramolecular exciplex, respectively.

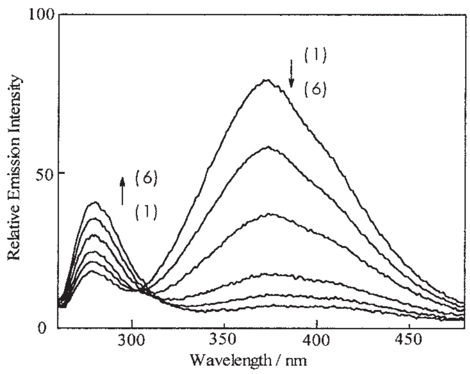


Figure 1. Emission spectra of PDAB in THF-BuOH mixtures at room temperature: vol% of BuOH are (1) 0, (2) 5.0, (3) 10, (4) 20, (5) 30, and (6) 40. [PDAB] = 3.7×10^{-4} M.

As shown in Figure 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 and the spectrum of PDAB behaves like a two-band spectrum (this also holds for other systems examined in this study). Since no isosbestic point is seen in the spectral change, there seem to be more than two causes for the spectral change.

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 nonfluorescent radical ion-pair.[5] 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.

Figure 2(a) shows the emission spectrum of PDAB in some THF-acetonitrile (AN) mixtures. The intensities of bands B and C decrease with increasing amounts of AN, but that of band A does not change. 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.

Figure 2(b) shows the effect of the addition of trichloroacetic acid (TCAA) on the emission spectrum of PDAB in THF. The spectral change seems to resemble that shown in Figure 1. As

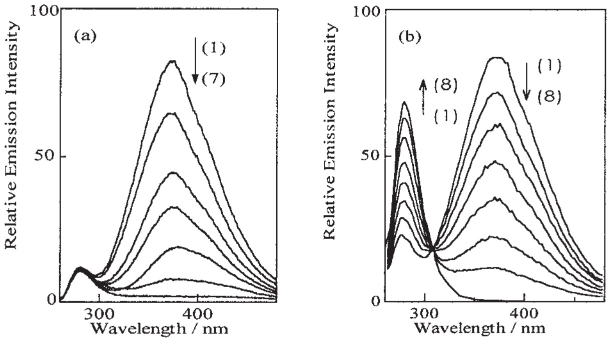
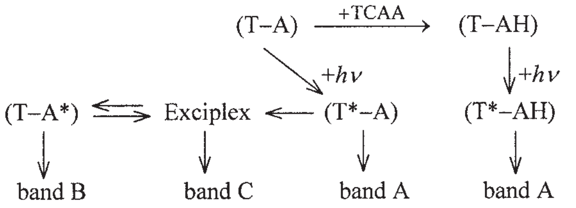


Figure 2. Emission spectra of PDAB in (a) THF-acetonitrile and (b) THF-TCAA mixtures at room temperature: (a) vol% of acetnitrile are (1) 0, (2) 0.10, (3) 0.50, (4) 1.0, (5) 5.0, (6) 20, and (7) 90. [PDAB] = 3.8×10^{-4} M; (b) [TCAA] are (1) 0, (2) 0.5, (3) 1.0, (4) 1.5, (5) 2.0, (6) 2.5, (7) 3.0, and (8) 6.0 ($\times 10^{-4}$ M). [PDAB] = 3.9×10^{-4} M.

shown in Figure 2(b), however, the increase in the intensity of band A is larger than that in Figure 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 the hydrogen-bonding interaction between the amino group of PDAB and TCAA (or the protonation on the amino group). Since the amounts of TCAA is very small, however, the polarity of the medium is little affected by the addition of TCAA.

To explain the experimental results in THF-TCAA mixtures, Scheme 1 is considered.



Scheme 1.

In Scheme 1, (T–A) and (T–AH) denote PDAB molecules having the free and hydrogen-bonded (or protonated) amino groups in their ground states, (T*–A) and (T*–AH) are the corresponding PDAB molecules having an excited toluene chromophore, and Exciplex is the intramolecular exciplex and (T–A*) the PDAB molecule having an excited amino group.

If it is simply assumed that the formation of hydrogen-bonded (or protonated) amino group with TCAA occurs quantitatively, the following equations can be obtained from Scheme 1:

$$X = \frac{I_A - I_A^\circ}{I_A^{ex} - I_A^\circ} = \frac{[\mathrm{TCAA}]}{[\mathrm{PDAB}]} \tag{1}$$

$$Y = \frac{I_{B,C}^\circ - I_{B,C}}{I_{B,C}^\circ} = \frac{[\mathrm{TCAA}]}{[\mathrm{PDAB}]} \tag{2}$$

where I_A° and I_A are the intensities of band A in the absence and presence of TCAA, I_A^{ex} is that in the presence of excess TCAA (the intensity of band A at $[\mathrm{TCAA}] = 6.0 \times 10^{-4}$ M was used as I_A^{ex}, see Figure 2(b)), and $I_{B,C}^\circ$ and $I_{B,C}$ are the combined intensity of bands B and C in the absence and presence of TCAA.

As shown in Figure 3, the linear relationships with slopes equal to 1.0 between X and Y and [TCAA]/[PDAB] are obtained. This indicates that equations (1) and (2) 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-BuOH mixtures bands B and C are influenced by the polar and hydrogen-bonding interactions, but band A only by the hydrogen-bonding interaction. Therefore, we can evaluate the hydrogen-bonding effect from intensity change of band A (X) and the total effect from the combined intensity of bands B and C (Y). In Figure 4 the values of X and Y are plotted against vol% of BuOH. As shown in Figure 4, the hydrogen-bonding effect increases almost linearly with increasing vol% of BuOH, while the polar effect shows, somewhat, a saturation tendency. Shirota et al. investigated the effect of the addition of alcohols on the photoinduced electron transfer reaction of a naphthalene-triethylamine (NP-TEA) system in AN[6,7] and observed the decrease in the bimolecular rate constant for the quenching of the NP fluorescence by TEA. They pointed out that the hydrogen-bonding interaction between the amine and alcohol suppresses the electron transfer process owing to the decrease in the concentration of free TEA. Their investigation is closely related to the present study. However, in the present study THF was used as a solvent instead of AN and both toluene fluorescence and emission from the exciplex could be observed.

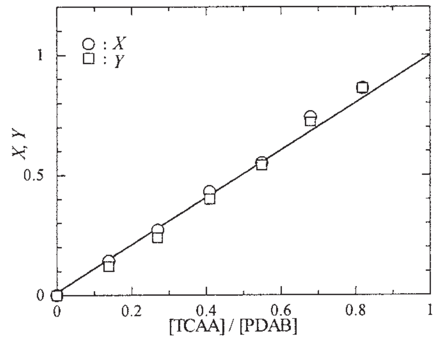


Figure 3. Experimental plots of Eqs. (1) and (2) for changes in emission intensities in THF-TCAA mixtures.

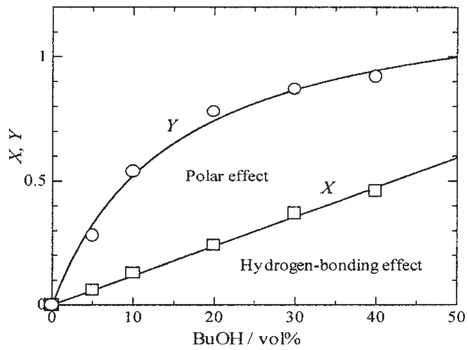


Figure 4. Plots of X and Y against vol% of BuOH for changes in emission intensities in THF-BuOH mixtures.

This method of evaluating the hydrogen-bonding and polar effects separately can also be applied to other protic solvents.

References and Notes

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