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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 with 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.

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 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 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 2MHz. 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.

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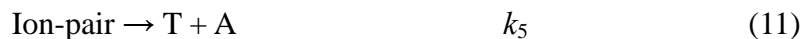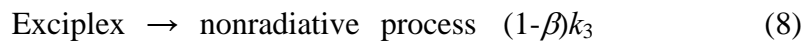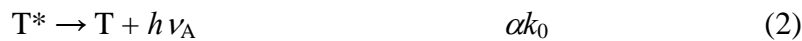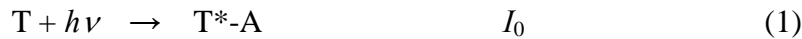
The intensities of bands B and C also decrease with increasing amounts of AN, but that of band A does not change (Figs. 2(a) and (b)). The addition of AN to THF will cause an increase in the polarity of the medium, but not in the hydrogen-bonding

interaction.   As mentioned above, the increase in 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.
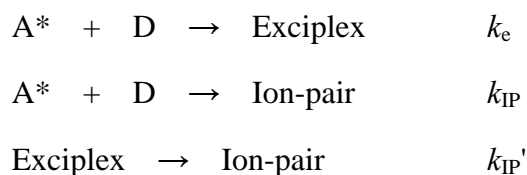
4. Discussion

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.

$$T + h\nu \quad \rightarrow \quad T^*\text{-A} \qquad\qquad I_0 \qquad\qquad (1)$$

$$T^* \rightarrow T + h\nu_A \qquad\qquad \alpha k_0 \qquad\qquad (2)$$

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

$$T^* + TEA \rightarrow \text{Exciplex} \qquad k_1 \qquad\qquad (4)$$

$$\text{Exciplex} \quad \rightleftarrows \quad TEA^* \qquad K_2 \qquad\qquad (5)$$

$$\text{Exciplex} \quad \rightleftarrows \quad \text{Ion-pair} \qquad K(\varepsilon) \qquad\qquad (6)$$

$$\text{Exciplex} \quad \rightarrow T + TEA + h\nu_C \qquad \beta k_3 \qquad (7)$$

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

$$TEA^* \rightarrow TEA + h\nu_B \qquad\qquad \gamma k_4 \qquad\qquad (9)$$

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

$$\text{Ion-pair} \rightarrow T + A \qquad\qquad k_5 \qquad\qquad (11)$$

Here, Exciplex denotes the intermolecular exciplex, TEA* denotes 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:

$$A^* \quad + \quad D \quad \rightarrow \quad \text{Exciplex} \qquad k_e$$

$$A^* \quad + \quad D \quad \rightarrow \quad \text{Ion-pair} \qquad k_{IP}$$

$$\text{Exciplex} \quad \rightarrow \quad \text{Ion-pair} \qquad k_{IP}'$$

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:

$$\text{TEA} + \text{TCAA} \quad \rightarrow \quad \text{TEAH} \; (+ \text{TCAA}') \qquad k_6 \qquad\qquad (12)$$

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 concentration of the free amine becomes [TEA] = [TEA]$_0$ – [TCAA]$_0$ and the following equation can be obtained:

$$X = \frac{\dfrac{1}{I_A^0} - \dfrac{1}{I_A}}{\dfrac{1}{I_A^0} - \dfrac{1}{I_A^{00}}} = \frac{[\text{TCAA}]_0}{[\text{TEA}]_0} \qquad\qquad (13)$$

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

As shown in Fig. 4, a linear relationship between X and [TCAA]$_0$/ [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:

$$\text{TEA} + \text{ROH} \quad \rightleftarrows \quad \text{TEA--HOR} \quad K_7 \qquad\qquad (14)$$

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

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

$$I_A(\text{ROH}) = \alpha I_0 \frac{k_0}{k_0 + k_1[\text{TEA}]} = \alpha I_0 \frac{k_0}{k_0 + \dfrac{k_1[\text{TEA}]_0}{1 + K_7[\text{ROH}]}} \qquad\qquad (15)$$

From this equation, X(ROH) can be expressed as follows:

$$X(\text{ROH}) = \frac{\dfrac{1}{I_A^0} - \dfrac{1}{I_A(\text{ROH})}}{\dfrac{1}{I_A^0} - \dfrac{1}{I_A^{00}}} = \frac{K_7[\text{ROH}]}{1 + K_7[\text{ROH}]} \qquad (16)$$

where I_A^0 and $I_A(\text{ROH})$ are the intensities of band A in the absence and presence of ROH, and I_A^{00} is 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 $1/X(\text{ROH})$ and $1/[\text{ROH}]$ with intercepts equal to 1.0 are obtained. The values of the equilibrium constants are obtained from the slopes of the straight lines (K_7 = 0.48, 0.31, 0.25 and 0.18 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 increased 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_ε 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 are large in THF-CH mixtures, and bands A and B largely

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