Solvent Effects on the Flourescence Spectrum of the Ion-pair (Naphthol-Triethylamine System)

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It has been demonstrated[1] that the strong hydrogen bond between β-naphthol and triethylamine (TEA) in the equilibrium ground state and in the excited Franck-Condon state shifts to the ion-pair in the excited equilibrium state, from which fluorescent transition occurs, in benzene. This phenomenon has been interpreted[1] as due to a strong charge transfer from the nitrogen non-bonding orbital of TEA to the OH antibonding orbital of naphthol in the Franck-Condon excited state, which is followed by an almost complete proton transfer from oxygen to nitrogen in the excited equilibrium state.

We have extended the above work to systems including various solvents of different polarities, thus obtaining results which seem to support the above interpretation. The solvents used here were monochlorobenzene, dichloroethane and acetonitrile. The observed results are summarized in Table I. As one can see from the table, the red shift of the fluorescene band maximum due to the complex formation, ($\Delta\sigma_f$), is larger, the greater the dielectric constant (D) of the solvent, whereas that of the absorption band, ($\Delta\sigma_a$), which is much smaller than $\Delta\sigma_f$, decreases with an increase in the dielectric constant of the solvent.

TABLE I. WAVE NUMBER SHIFTS OF BAND MAXIMA DUE TO COMPLEX FORMATION

Solvent	D	$\Delta\sigma_f$ 10^4 cm^{-1}	$\Delta\sigma_a$ 10^4 cm^{-1}
Benzene	2.284	0.40	0.04
Monochlorobenzene	5.621	0.45	0.03
Dichloroethane	10.36	0.46	0.01
Acetonitrile	37.5	0.58	0.00

As is described elsewhere[2], by using the charge transfer model[3] of the hydrogen bond,

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[1] N. Mataga and Y. Kaifu, *J. Chem. Phys.*, 36, 2804 (1962).

[2] N. Mataga and Y. Kaifu, to be published.

[3] H. Tsubomura, This Bulletin, 27, 445 (1954); K. Nukasawa, J. Tanaka and S. Nagakura, *J. Phys. Soc. Japan*, 8, 792 (1953).

the wave function of the proton donor-acceptor pair may be expressed as a superposition of various resonance structures.

$$\Psi = a\Phi(\mathrm{D-A}) + b\Phi(\mathrm{D^- - A^+}) + c\Phi(\mathrm{D^*A-})$$

where D−A denotes the hydrogen-bonded pair when the proton donor D is in the ground state (no charge transfer), $\mathrm{D^- - A^+}$, the charge transfer structure, and $\mathrm{D^* - A}$, the hydrogen-bonded pair when D is in the fluorescent state (on charge transfer).

The energy difference between the charge transfer structure and the infinitely separated D−A pair may be written as:

$$\begin{aligned}\Delta E &= E(\mathrm{D^- - A^+}) - E(\mathrm{D-A}) \\ &= I_\mathrm{A} - A_\mathrm{D} + V(\mathrm{D^- - A^+}) + H_\mathrm{s}\end{aligned}$$

where I_A: the ionization potential of the non-bonding orbital of the proton acceptor, A_D: the electron affinity of the anti-bonding orbital of the O–H bond, $V(\mathrm{D^- - A^+})$: interaction energies between the pair, and H_s: the stabilization energy due to the solvation of the ion-pair.

Probably, $\Phi(\mathrm{D^- - A^+})$ may interact very strongly with $\Phi(\mathrm{D^* - A})$, but not so much with $\Phi(\mathrm{D-A})$, when D and A come close to each other because $E(\mathrm{D^- - A^+})$ may be rather small and almost comparable to $E(\mathrm{D^* - A})$ owing to the quite small I_A value of TEA. Hence, $a \gg b, c$ in the ground state and $b, c \gg a$ in the first excited electronic state of the D−A complex. These circumstances are indicated in Fig. 1, where the reaction coordinate represents the D−A distance, the degree of the charge transfer from A to D and the position of the O–H proton.

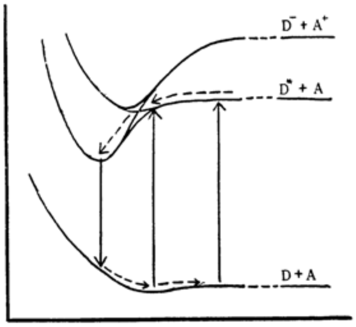

Fig. 1. Potential energy curves for D−A interaction.

Furthermore, H_s seems to play an important role in the present case. This quantity seems to be larger in the more polar solvent than in the less polar one, because of the greater dipole-dipole and dipole-polarization forces in the former solvent. The larger H_s value may be a main cause of the greater $\Delta\sigma_\mathrm{f}$ value in the polar solvent. However, hydrogen bonding between D and A may be very weak in the polar solvent, because either D or A may be solvated rather strongly, which seems to result in the very small $\Delta\sigma_\mathrm{a}$ value of this solvent.

Analogous phenomena have been observed when TEA was added to the solution of carbazole in acetonitrile and dichloroethane⁴⁾ respectively, and also when a rather large amount of primary or secondary aliphatic amines was added to the cyclohexane or benzene solution of β-naphthol⁵⁾. These phenomena may be interpreted on the basis of similar reasoning.

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4) N. Mataga and Y. Torihashi, unpublished.

5) N. Mataga and Y. Kawasaki, unpublished.