Solvent Effects on the Fluorescence of Some π-Electron Systems Naphthylamine and Naphthol

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Heretofore, in a series of investigations[1-5], we have examined some aspects of solvent effects on the fluorescence of π-electron systems, especially concerning the hydrogen bonding effect.

a) Firstly, a general formula for the difference of solvent shifts of fluorescence and absorption spectra in the approximation of long range dipolar interaction was derived using Ooshika's theory[6] of light absorption in solution. Measurements of fluorescence and absorption spectra of some naphthalene derivatives in various organic solvents were undertaken, and the experimental data were analyzed by the theoretical formula. The formula reproduces the experimental data satisfactorily, and from this fact it was concluded that the most predominant factor which determines the difference of solvent shifts of fluorescence and absorption spectra of these molecules is the interaction energy between solute and solvent molecules due to orientation polarization. The incremental values of dipole moments in the excited state were estimated, and those for α, β-naphthols and β-naphthyl methylether were interpreted as due to the increase of electron migration from the substituent in the excited state.

b) Secondly, the question whether a new and different equilibrium of the hydrogen bond formation is reached during the lifetime of the excited state, was examined using the solutions of α- and β-naphthol as fluorescers and proton donors in non-polar solvent mixed with various proton acceptors.

By quantitative treatment of the experimental results, it was confirmed that β-naphthol in the excited state has a greater tendency toward hydrogen bonding, a new equilibrium being attained during its lifetime.

c) Thirdly, the effect of hydrogen bond formation on the fluorescence yield of the mother substance was investigated, from which some facts of the mechanism of non-radiative degradation of excited state

1) N. Mataga, Y. Kaifu and M. Koizumi, This Bulletin, **28**, 690 (1955); **29**, 465 (1956).
2) N, Mataga, Y. Kaifu and M. Koizumi, *Nature*, **175**, 731 (1955); This Bulletin, **29**, 116 (1955).
3) N. Mataga and S. Tsuno, ibid., **30**, 368 (1957).
4) N. Mataga and S. Tsuno, *Naturwiss.*, **44**. 304 (1957).
5) N. Mataga and S. Tsuno, This Bulletin, **30**, 711 (1957).
6) Y. Ooshika, *J. Phys. Soc. Japan*, **9**, 594 (1954).

due to inter- or intra-molecular processes, were obtained. The role of non-bonding electrons in the inner quenching of some nitrogen heterocycles, and the effect of π-electronic state on the fluorescence quenching caused by the near-by existence of halogen atoms, were studied. The cause of the inner quenching in nitrogen heterocycles was attributed to the n-π interaction in the excited state. The difference between quinoline and acridine in their fluorescence quenching caused by the existence of a halogen atom was ascribed to the different emitting states in these molecules (^1L_b in quinoline, ^1L_a in acridine), and some considerations were made assuming a close similarity of the electronic states of nitrogen heterocycles to those of the parent hydrocarbons. This assumption has been confirmed by some quantum mechanical calculations[7,8].

Fluorescence quenching caused by the hydrogen bond formation between nitrogen heterocycles as proton acceptors and fluorescers, and proton donors such as phenol, naphthol, aniline and pyrrole which are capable of making hydrogen bond intimately related with π-electron systems, was investigated, and interpreted as due to the delocalization of π-electrons through the hydrogen bond, in the excited state.

In the present paper, we shall report other examples of the solvent effect on fluorescence spectra, the shift of the hydrogen bonding equilibrium in the excited state, and the fluorescence quenching due to hydrogen bond formation, in which naphthylamine and naphthol are used as fluorescers and proton donors, and pyridine and acetic acid esters as proton acceptors.

Experimental

Apparatus:—Absorption spectra were measured with a Beckman Spectrophotometer model DU. Fluorescence spectra were photographed with small-type glass prism spectrograph. The fluorometer was the same as described previously[2]. Filters used for naphthol are the same as before[2], and for naphthylamine, they are as follows: for exciting light, Matsuda color filter UV-DI which takes out 365 mμ line of mercury lamp, and for fluorescent light, the yellow filter, attached to Beckman photometer for fluorescence analysis, the transmittance of which is nearly 90% in all the visible spectral region longer than 410 mμ, were used.

Reagent:—β-Naphthol and β-naphthylmethyl ether were the same samples as used before[2]. Chemical-pure grade α- and β-naphthylamine were purified by repeated recrystallization from ligroin. Extra-pure grade N,N-dimethyl-β-naphthylamine was purified by repeated distillation in vacuo. Acetic acid esters[2] and trichloroacetic acid[3] were the same samples as described previously. Extra-pure grade pyridine was dried over sodium hydroxide and distilled carefully. Benzene was the same as described elsewhere[5].

Experimental Results and Discussion

When acetic acid esters are added to the solution of naphthylamine in benzene, the features of phenomena are similar to the case of naphthol. When hydrogen bonded with acetic acid esters, enhancement of fluorescence intensity compared with free molecules is observed, and the excited molecules have greater tendency to form hydrogen bonds, a new equilibrium being reached during the lifetime of the excited state.

When hydrogen bonded with pyridine, however, fluorescence is almost completely quenched, and it is also the case for naphthol. This quenching phenomenon is similar to the previously reported one[5] of non-radiative degradation caused by hydrogen bonding, but the fluorescer and the quencher have exchanged their roles as proton acceptor and donor, with each other.

A. Changes of Absorption Spectrum Caused by Hydrogen Bonding.—Absorption spectra are somewhat strengthened and shifted to red by hydrogen bonding. Some examples of these changes are shown

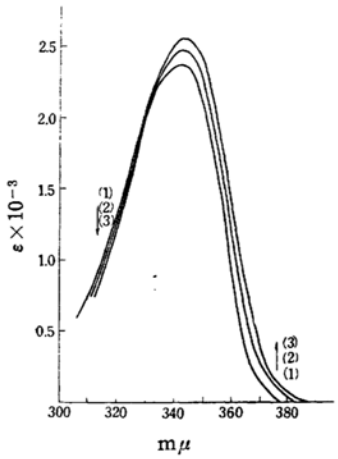

Fig. 1. Change of absorption spectrum of β-naphthylamine in benzene produced by added pyridine.
Concentration of pyridine: (1) 0, (2) 4.96×10^{-1} mole/l., (3) 1.24 mole/l.

7) N. Mataga, to be published in this Bulletin.
8) N. Mataga, to be published in this Bulletin.

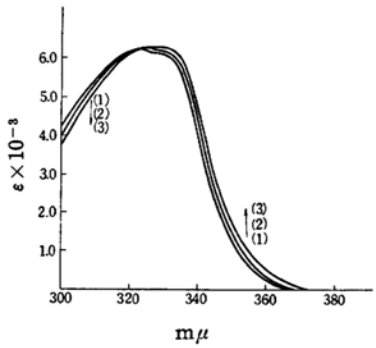

Fig. 2. Change of absorption spectrum of α-naphthylamine in benzene produced by added butyl acetate.
Concentration of butyl acetate: (1) 0, (2) 1.23 mole/l., (3) 2.76 mole/l.

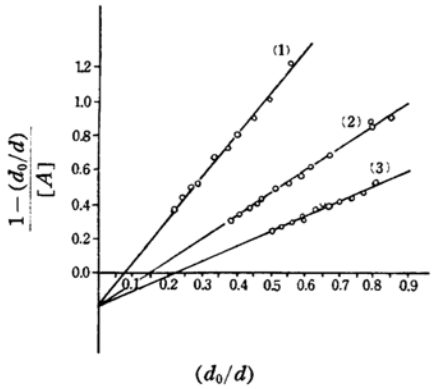

Fig. 3. $\frac{1-(d_0/d)}{[A]}$ vs. (d_0/d) relation for β-naphthylamine-pyridine-benzene system at several wave lengths: (1) 370 mμ, (2) 365 mμ, (3) 362 mμ.

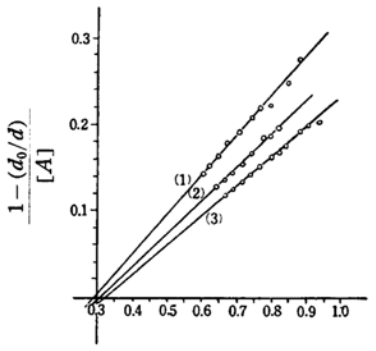

Fig. 4. $\frac{1-(d_0/d)}{[A]}$ vs. (d_0/d) relation for α-naphthylamine-butyl acetate-benzene system at several wave lengths: (1) 365mμ, (2) 354 mμ, (3) 352 mμ.

in Figs. 1 and 2. The change of optical density at a definite wave length is well reproduced by Eq. 1[3]

$$\frac{(1-d_0/d)}{[A]} = -K^{(g)} + (\varepsilon'/\varepsilon)\cdot K^{(g)}\cdot(d_0/d) \quad (1)$$

The equilibrium constants $K^{(g)}$'s of hydrogen bond formation obtained by means of this formula, at several wave lengths, nearly coincide with each other. Some examples of these analyses are shown in Figs. 3 and 4.

B. Change of Relative Fluorescence Intensity Caused by Addition of Proton Acceptor.—Some examples of the enhancement or quenching of fluorescence of β-naphthylamine in benzene caused by the addition of proton acceptors are shown in Fig. 5. The features of these changes are also the same in the case of α-naphthylamine and of β-naphthol. If we use for these cases the following Eqs. 2[3] and 3*,

$$\frac{1-(f_0/f_m)(d_m/d_0)}{[A]} = -K^{(e)} + \alpha(d_m/d_0)K^{(e)}(f_0/f_m) \quad (2)$$

$$(f_m/f_0)(d_0/d_m) = \frac{1}{1+K^{(e)}[A]} \quad (3)$$

the experimental results are well satisfied by these equations, and the equilibrium constants $K^{(e)}$'s of hydrogen bond formation in the excited state are evaluated**. Some examples of these analyses are shown in Figs. 6 and 7. The equilibrium constants $K^{(e)}$'s obtained in this way are remarkably large compared with those evaluated from absorption spectra, as shown in Table I.

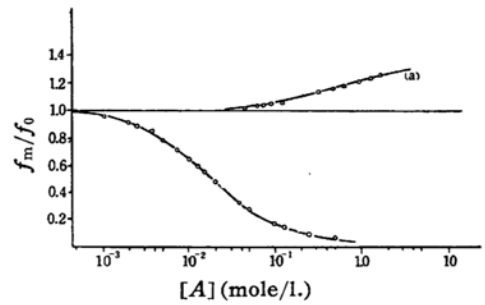

Fig. 5. Change of relative fluorescence intensity, f_m/f_0, of β-naphthylamine produced by added proton acceptors. Acceptors: (a) butyl acetate, (b) pyridine.

* Eq. 3 is obtained putting $\alpha=0$ in Eq. 2 which is the case for naphthylamines or naphthol-pyridine-benzene systems.

** Shifts of fluorescnce spectra of naphthylamines produced by the addition of acetic acid esters is very small in benzene, therefore we may be allowed to neglect the difference of phototube sensitivity for the fluorescence of free and hydrogen bonded naphthylamines.

TABLE I

acceptor	donor		
	α-naphthylamine	β-naphthylamine	β-naphthol
pyridine	$K^{(g)}_{285}:0.15K^{(e)}_{286}:53$	$K^{(g)}_{286}:\ 0.2\ K^{(e)}_{286}:60$	$K^{(g)}_{287}:41K^{(e)}_{287}:\sim84$
$CH_3CO_2C_4H_9$	$K^{(g)}_{283}:0.13K^{(e)}_{285}:\sim1$	$K^{(g)}_{287}:\ 0.1\ K^{(e)}_{287}:\sim1.8$	
$CH_3CO_2C_2H_5$	$K^{(g)}_{287}:0.26K^{(e)}_{285}:\sim1$	$K^{(g)}_{287}:\sim0.26K^{(e)}_{287}:\sim1.8$	

$K^{(g)}_T$ or $K^{(e)}_T$: T is the temperature (in unit of °K) at which the measurement was made.

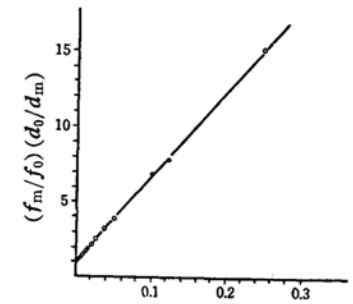

Fig. 6. $(f_0/f_m)(d_m/d_0)$ vs. $[A]$ relation for β-naphthylamine-pyridine-benzene system.

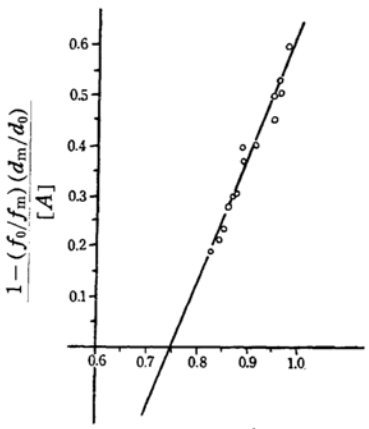

Fig. 7. $\frac{1-(f_0/f_m)(d_m/d_0)}{[A]}$ vs. $(f_0/f_m)(d_m/d_0)$ relation for β-naphthylamine-butyl acetate-benzene system.

When pyridine and acetic acid esters are added to the solutions of *N,N*-dimethyl-α-naphthylamine and β-naphthylmethyl ether in benzene, not even a slight change of fluorescence intensity has been observed throughout the whole range of acceptor concentration from ca. 10^{-3} to 1 mole/l.

Therefore, in the present case, the fluorescence quenching or enhancement may probably be wholly attributable to the hydrogen bond formation, and the equilibrium somewhat shifts to the side of association during the lifetime of the excited molecule. We can confirm further, whether the hydrogen bonding equilibrium in the excited state is really concerned with the fluorescence quenching or enhancement, as follows.

Let us examine the case in which the association equilibrium in the ground state is maintained in the excited state, the naphthylamines hydrogen-bonded with pyridine being completely non-fluorescent, and in which there is superposed the ordinary collisional quenching by pyridine. This is equivalent to assuming that, at the time of collision, pyridine affects specially the fluorescence of naphthylamines but not *N, N*-dimethylnaphthlamines. Then the deduction about the fluorescence intensity may be made according to the following scheme, were D and A are proton donor (fluorescer) and proton acceptor (quencher), respectively, and * denotes the excited state.

	rate or equilibrium
$D+A\rightleftarrows DA$	$K^{(g)}=[DA]/[D][A]$
$D+h\nu_a\rightarrow D^*$	$I_0\varepsilon[D]$
	$[D]=[D]_0/(1+K[A])$
$DA+h\nu_a\rightarrow DA^*$	$I_0\varepsilon'[DA]$
	$[DA]=K[A][D]_0/(1+K[A])$
$D^*\rightarrow D+h\nu_f$	$k_f[D^*]$
$D^*\rightarrow D$	$k_i[D^*]$
$DA^*\rightarrow DA$	$k_i'[DA^*]$
$D^*+A\rightarrow D+A$	$k_q[A][D^*]$

I_0: intensity of exciting light.

ε, ε': extinction coefficients of D and DA, respectively, at the wave length of exciting light.

By means of this scheme, the following formula for the relative fluorescence intensity is easily derived.

$$f_0/f_m = 1+(n_q+K^{(g)})[A]+n_qK^{(g)}[A]^2 \quad (4)$$

$$n_q = k_q/(k_f+k_i)$$

Now, let us assume that $K^{(e)}$ obtained by Eq. 3 is almost entirely contributed by n_q of Eq. 4, and plot f_0/f_m as a function of $[A]$.

As shown in Fig. 8, it is evident that the experimental results can not be reproduced by Eq. 4. Therefore, the possibility of the collisional quenching is rejected, and it is almost certain that the hydrogen

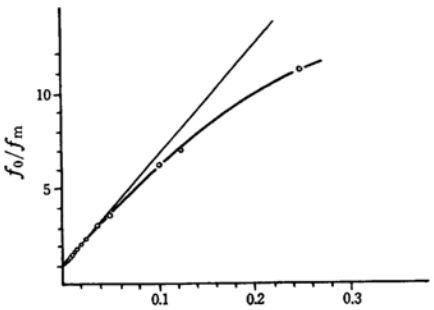

Fig. 8. f_0/f_m vs. [A] relation for β-naphthylamine-pyridine-benzene system.

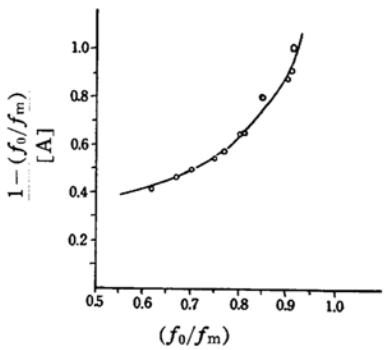

Fig. 9. $\frac{1-(f_0/f_m)}{[A]}$ vs. (f_0/f_m) relationf or β-naphtylamine-butyl acetate-benzene system.

bonding equilibrium shifts remarkably to the side of association during the lifetime of the excited state. For the case of enhancement of fluorescence intensity by acetic acid esters, the shift of equilibrium may be almost certain because Eq. 2 is satisfactorily reproduced by experimental results and the fluorescence of *N,N*-dimethyl-α-naphthylamine solution is not affected by the addition of the esters. If we use Eq. 5[3] which assumes that the equilibrium in the ground state is maintained in the course of fluorescence, instead of Eq. 2, we can see no agreement with experimental results, as shown in Fig. 9.

$$\frac{1-(f_0/f_m)}{[A]} = -K^{(g)} + \alpha(\varepsilon'/\varepsilon)K^{(g)}(f_0/f_m) \quad (5)$$

Further, let us examine, for this case, another possibility that the excited naphthylamine molecule is stabilized specifically by collision with acetic acid ester molecule, provoking the increase in fluorescence yield, though such an effect is very improbable in solution*. Now, let us assume the following scheme involving the equilibrium in the ground state, where the notations are the same as described above and s refers to the fluorescer molecule stabilized by collision.

	rate or equilibrium
$D+A \rightleftarrows DA$	$K^{(g)}=[DA]/[D][A]$
$D+h\nu_a \rightarrow D^*$	$I_0\varepsilon[D]$
$DA+h\nu_a \rightarrow DA^*$	$I_0\varepsilon'[DA]$
$D^* \rightarrow D+h\nu_f$	$k_f[D^*]$
$DA^* \rightarrow DA+h\nu_f'$	$k_f'[DA^*]$
$D^*+A \rightarrow D^{*s}+A$	$k_c[D^*][A]$
$D^{*s} \rightarrow D+h\nu_f$	$k_f^s[D^{*s}]$
$DA^* \rightarrow DA$	$k_i'[DA^*]$
$D^{*s} \rightarrow D$	$k_i^s[D^{*s}]$
$D^* \rightarrow D$	$k_i[D^*]$

According to this scheme, Eq. 6 is easily derived.

$$\frac{1-(f_0/f_m)}{[A]} = -(n_c+K^{(g)}+n_cK^{(g)}[A]) + \frac{(\Phi_0^s\varepsilon n_c+\Phi_0'\varepsilon'K^{(g)}+\Phi_0'\varepsilon'n_cK^{(g)}[A])}{\Phi_0\varepsilon} \times (f_0/f_m), \quad (6)$$

where

$$n_c=k_c/(k_f+k_i), \quad \Phi_0=k_f/(k_f+k_i),$$
$$\Phi_0'=k_f'/(k_f'+k_i'), \quad \Phi_0^s=k_f^s/(k_f^s+k_i^s)$$

Comparing this formula with Fig. 9, it is clear that the former is in essential disagreement with the latter. The possibility of collisional stabilization is thus completely neglected. The rather large difference of observed $K^{(g)}$ and $K^{(e)}$ of naphthylamines compared with that of naphthols may be partially comprehended as due to the difference of ionization potential of non-bonding electrons in the substituent (—OH: 10.95 eV., —NH_2: 9.41 eV.**,[9]). The degree of electron migration from the substituent and accordingly, also the difference of stabilization energy

* The increase in fluorescence yield of β-naphthylamine vapor in the presence of foreign gases was reported by Neporent[a]. Some aspects of his work on this molecule were confirmed by Curme and Rollefson[b] and detailed kinetical study was made by Boudart and Dubois[c].

a) B. S. Neporent, *Zhur. Fiz. Khim.*, **21**, 111 (1947); **24**, 1219 (1950). b) H. G. Curme and G. K. Rollefson, *J. Am. Chem. Soc.*, **74**, 28 (1952). c) M. Boudart and J. T. Dubois, *J. Chem. Phys.*, **23**, 223 (1955).

** These values are the ionization potentials of methanol and methylamine, respectively.

9) J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952).

in the excited and ground state become larger, as the ionization potential of the substituent[10] becomes smaller.

Therefore, in the case of naphthylamines, the difference of the proton donating power in the excited and the ground state may be rather great, although the absolute value of proton donating power in the ground state may be small. In this respect, we have measured the solvent shifts of fluorescence and absorption spectra of naphthylamines in various organic solvents, and the results have been analyzed by Eq. 7[1,11]

$$-hc(\sigma_f^m-\sigma_a^m)\cong\text{Const.}+\left[\frac{2(D-1)}{2D+1}-\frac{2(n^2-1)}{2n^2+1}\right]\frac{(\vec{\mu}_e-\vec{\mu}_g)^2}{a^3} \quad (7)$$

where, σ_f^m and σ_a^m are wave numbers of peaks of fluorescence and absorption spectra, respectively, D and n dielectric constant and refractive index of the solvent, $\vec{\mu}_e$ and $\vec{\mu}_g$ dipole moment of solute molecule in the excited and the ground state, respectively and a is the cavity radius in Onsager's theory of reaction field.

Although we can not make a quantitative discussion because of the broadness of the spectra, it may be certain that the increments of dipole moments of naphthylamines in the excited state are not smaller than those of naphthols in the order of magnitude. In addition we refer to the fact that, Förster has estimated the difference of pK value in the excited and ground states of β-naphthylamine, in the case of the dissociation of the type, $-NH_2 \rightarrow -NH^- + H^+$, to be about 8 units[12], the excited state being very acidic compared with the ground state.

Now, as pointed out in the earlier part of this paragraph, the fluorescence quenching caused by hydrogen bonding with pyridine is analogous to the quenching phenomenon in the case of nitrogen heterocycles hydrogen bonded with phenols and aniline[5]. Accordingly, we may be allowed to say that the quenching in the present case also originates from the interaction between the π-electron systems via the hydrogen bond, in the excited state, although the fluorescer and quencher have reversed their roles as the proton acceptor and donor.

10) A. L. Sklar, ibid., **7**, 984 (1939); K. F. Herzfeld, *Chem. Revs.*, **41**, 233 (1947).
11) E. Lippert, *Z. Naturforsch.*, **109**, 541 (1955); *Z. physik. Chem.*, N. F., **6**, 125 (1956).
12) Th. Förster, *Z. Elektrochem.*, **54**, 531 (1950).

Summary

The enhancement or quenching of fluorescence intensity of naphthylamines and naphthol caused by hydrogen bonding with acetic acid esters or pyridine has been measured. By means of detailed analyses of the experimental results, it has been established that the shift of hydrogen bonding equilbrium toward the side of association is realized during the lifetime of excited state.

The cause of the shift has been interpreted on the basis of the theory of electron migration, and an evidence supporting the interpretation has been provided by measuring the solvent shift of fluorescence spectra. The mechanism of the fluorescence quenching has been discussed as due to the delocalization of π-electrons through the hydrogen bond.

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