Hydrogen Bonding Effect on the Fluorescence of π-Electron System

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Introduction

In recent years many interesting papers[1–5] have been published about the hydrogen bonding effect upon the visible or ultraviolet spectra of π-electron systems, and especially the beautiful work by S. Nagakura and H. Baba[1,2,3] has demonstrated that in suitable cases the quantitative studies on the equilibrium of the hydrogen bond formation is possible through such spectral investigations. There are, however, scarcely any quantitative studies for the hydrogen bonding effect upon the fluorescence of π-electron system, that is the effect of the addition of hydrogen acceptor (or donor) to the solution of fluorescent hydrogen donor (or acceptor). Such studies would be interesting from the following three points of view.

Firstly, it is expected that the fluorescence spectra would be affected by the hydrogen bond formation as was the case for absorption spectra. The shift of absorption spectra due to the hydrogen bond formation gives of course the difference of the produced energy change of π-electronic system between the ground state and excited Franck-Condon state[6], while for the fluorescence, the shift is to be attributed to the analogous difference

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1) S. Nagakura, *J. Chem. Soc. Japan*, **74**, 153 (1953). S. Nagakura and H. Baba, *J. Am. Chem. Soc.*, **74**, 5693 (1952); S. Nagakura, *J. Am. Chem. Soc.*, **76**, 3070 (1954).

2) S. Nagakura, *J. Chem. Soc. Japan*, **75**, 734 (1954).

3) H. Baba, *Monograph Ser. Research Inst. Applied Electricity*, Hokkaido, No. **4**, 61 (1954).

4) R. Miyasaka, *Busseiron Kenkyū*, No. **62**, 94 (1951).

5) H. Tsubomura, *J. Chem. Soc. Japan*, **73**, 841, 920 (1952).

6) N.S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

between the equilibrium excited state and Franck-Condon state of the ground level.

Secondly, the formation of hydrogen bond would affect the fluorescence yield of the mother substance, and this effect would give valuable information for the mechanism of fluorescence quenching or in general the mechanism of inter-or intra-molecular energy transference.

Lastly, there is a possibility that a new and different equilibrium of the hydrogen bond formation is reached during the lifetime of the excited state and this possibility would be examined through the studies of the fluorescence. The situations are probably somewhat analogous to the ionic dissociation of naphthols and other substances studied by Th. Förster and A. Weller[7,8], who confirmed that the tendency of dissociation is remarkably greater in the excited state than in the ground state.

In this paper the effects of the addition of various hydrogen acceptors to the solutions of α- and β-naphthol used as fluorescer, have been examined from the above mentioned viewpoints; particularly as to the third problem, i. e., the shift of equilibrium in the excited state. A quantitative treatment has been given with the result that β-naphthol in the excited state has a greater tendency toward hydrogen bonding, a new equilibrium being attained during its lifetime.

The main object of the present paper is to report this fact with some discussion on the interaction of the hydrogen bond and π-electron system.

Experimental

Reagent.—Chemical pure grade n-hexane was shaken with fuming sulfuric acid diluted with conc. sulfuric acid and distilled carefully. n-hexane thus purified was completely transparent throughout the whole spectral range measurable by the Beckman spectrophotometer.

Merck's analytical grade α-naphthol was used without any further purification.

β-naphthol was of commercial supply, and purified by repeated distillation in an atmosphere of dry nitrogen.

Purified β-naphthyl-methyl-ether was kindly supplied by Shionokôryô Co., Ltd.

Extra pure grade dioxane was purified according to the method of Weissberger[9].

Methylacetate was washed with the saline solution several times and fractionated after being dried over anhydrous potassium carbonate.

Ethyl and butyl acetate was dried over potassium carbonate and fractionated. Ethyl chloroacetate was kindly supplied by Mr. M. Nakazaki of this Institute. Carbon tetrachloride was purified by shaking with conc. sulfuric acid.

Apparatus.—Absorption spectra were measured by Beckman Spectrophotometer Model D. U.

Fluorescence spectra were photographed with Hilger E. 2 type quartz spectrograph. High pressure mercury lamp or copper arc filtered with 1 cm. thickness of potassium chromate 0.2 g./l. aqueous solution[10] was used as a light source. Slit width was 0.3 mm.

The relative intensity of fluorescence was measured by a fluorometer kindly constructed by S. Kato. Its circuit is almost the same as that of Beckman spectrophotometer with the usage of the ultraviolet sensitive phototube purchased as a spare for Beckman apparatus. As a light source, a high pressure mercury lamp was used and 3100 Å line was taken out as an exciting light through an aqueous solution of potassium chromate. To secure the constancy of the light source intensity, the beam in the direction oblique to that for excitation was passed through another potassium chromate solution, caught by anohter ultraviolet sensitive photocell, and a galvanometer deflection was kept constant by controlling a variable choke in the electric circuit for the mercury lamp. To eliminate 3100 Å from the fluorescence light, Matsuda colour filters VVI and UVDI were employed. Under such conditions, the phototube receives the light from ca. 3200 Å to 4000 Å, the range being enough to cover the fluorescence spectra of all the samples examined.

Experimental Results

1. Spectral Shift of Absorption and Fluorescence caused by Hydrogen Bonding

When the various proton acceptors are added gradually to the solution of naphthols in n-hexane, the absorption spectra show the characteristic changes due to hydrogen bonding, which are similar to those published in

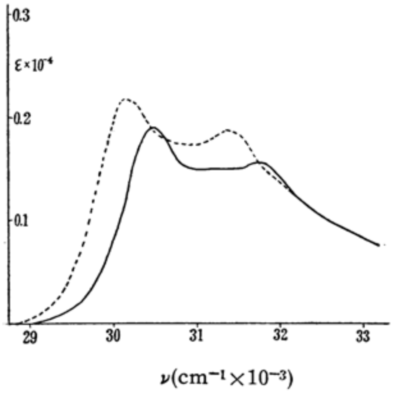

Fig. 1. Absorption spectra of β-naphthol.
——— in n-hexane
- - - - hydrogen bonded with butyl-acetate in n-hexane

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[7] Th. Förster, *Z. Elektrochem.*, 54, 42, 531 (1950).

[8] A. Weller, *Z. Elektrochem.*, 56, 662 (1952).

[9] A. Weissberger and E. Proskaner, "*Org. Solvents*" (1935), p. 110.

[10] M. Kasha, *J. Opt. Soc. Am.*, 38, 929 (1948).

literature[2]; the maximum slightly shifts to the long wave length side with its extinction somewhat strengthened as shown in Figs. 1 and 2. The fluorescence spectra also show the red shift, the magnitude of which is nearly equal or slightly larger than that of the absorption spectra. Some examples of the relative intensity curves which were obtained by the visual observation of the plates, are shown in Figs. 3 and 4. Now it is highly plausible to attribute these spectral changes of fluorescence to the hydrogen bonding, but to confirm it further, the effects of the addition of the same proton acceptors to the n-hexane solution of β-naphthylmethylether were examined.

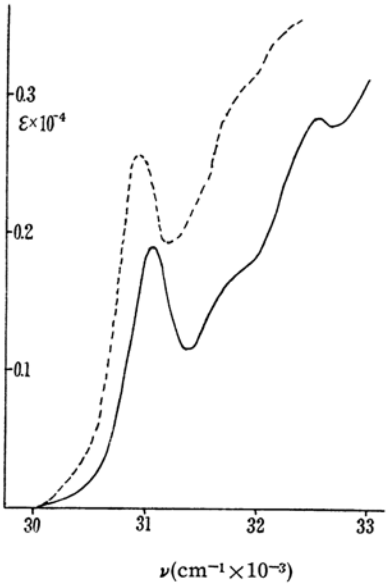

Fig. 2. Absorption spectra of α-naphthol.
——— in n-hexane
- - - - hydrogen bonded with butylacetate in n-hexane

Fig. 3. Fluorescence spectra of β-naphthol.
——— in n-hexane
- - - - hydrogen bonded with butylacetate in n-hexane
(Visually observed blackening of photographic plate)

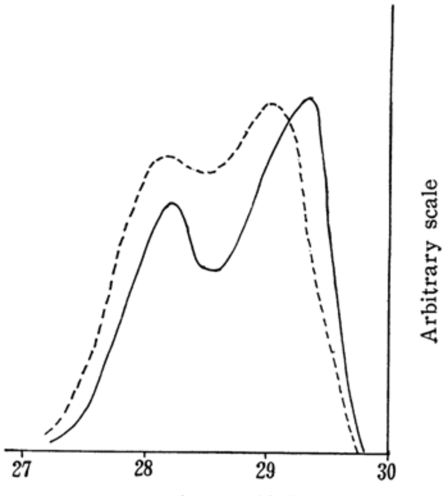

Fig. 4. Fluorescence spectra of α-naphthol.
——— in n-hexane
- - - - hydrogen bonded with butylacetate in n-hexane
(Visually observed blackening of photographic plate)

This substance of which the absorption and fluorescence spectra are quite similar to those of β-naphthol, is unable to form the hydrogen bond, and it was established that the addition of a large quantity of any proton acceptors cannot cause even a slight change either in fluorescence or in absorption. Hence there is no doubt that the above mentioned shifts in fluorescence spectra are due to the hydrogen bonding.

2. Hydrogen Bonding Effect on the Fluorescence Intensity

The fluorescence of both α- and β-naphthol is remarkably quenched by ethylchloroacetate, the magnitude of quenching being somewhat greater in the former case, while in the case of dioxane and acetic acid esters other than ethylchloroacetate, the intensity increases more or less in both naphthols. Some examples of these changes of fluorescence intensity by the added acceptors are shown in Fig. 5, where the ordinate is the relative intensity of fluorescence and the abscissa is the concentration of the proton acceptor. To check the fact that these intensity changes are really due to the hydrogen bond formation, the effect of the addition of similar proton acceptors to the solution of β-naphthylmethylether in n-hexane was examined. Again, as in the case of fluorescence spectra, there was not observed any slight change of fluorescence intensity throughout

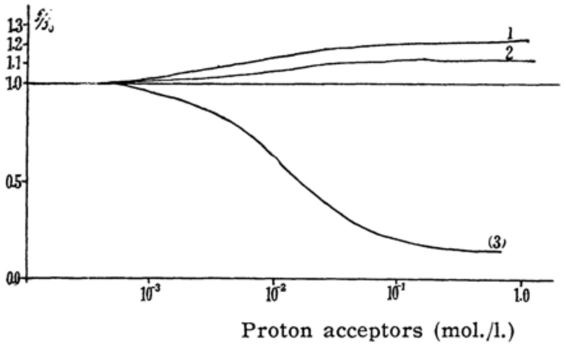

Fig. 5. Change of relative fluorescence intensity of β naphthol by various proton acceptors.
1. Butylacetate at 10°C 2. Methylacetate at 10°C
3. Cl-ethylacetate at 25°C

the whole range of acceptor concentration from ca. 10^{-3} to $\sim 5\times10^{-1}$ mol./l. Further, it was ascertained that the fluorescence of neither β-naphthol nor β-naphthylmethylether was quenched by dichloromethane. Hence the ordinary collisional quenching may be excluded in this case and it is almost certain that the change of fluorescence intensity in the case of β-naphthol is completely due to the hydrogen bond formation.

3. Interpretation of the Variation of Fluorescence Intensity on the Basis of the Hydrogen Bonding Equilibrium

It seems very plausible to attribute the observed changes of fluorescence intensity to the fact that the free naphthol and hydrogen-bonded naphthol have different efficiency of fluorescence and that the concentration of these molecular species are determined from the association equilibrium. But the question whether the situation does really correspond to such an equilibrium state, and further if it really holds, whether the equilibrium in question refers to the ground state or excited state, must be decided from the analysis of the experimental results.

Thus when the equilibrium of the ground state is maintained during the course of fluorescence, then the equilibrium constant deduced from the experimental data of fluorescence intensity must coincide with that obtained from absorption spectra. On the contrary, when the state of association approaches a new equilibrium state during the lifetime of the excited molecule, and until a new equilibrium state is almost completely reached prior to the emission, then the equilibrium constant deduced from the fluorescence data may generally be different from that obtained from absorption spectra. And lastly, if the equilibrium is only partially reached in the excited state, the quantitative relation deduced from the equilibrium consideration would fail to reproduce the experimental results.

Now let us take up first, the case in which the association equilibrium in the ground state be maintained in the excited state. Since the concentration of α- and β-naphthols employed for fluorescence measurement does not exceed 5×10^{-4} mol./l., the phenomenon of self-quenching or concentration quenching can be neglected, and the deduction about the intensity may be made according to the following scheme involving the association equilibrium in the ground state. In this scheme, D and A are respectively proton donor (fluorescer) and proton acceptor, and * denotes the excited state.

	Rate or equilibrium	
$D+A \rightleftharpoons DA$	$K=[DA]/[D][A]$	(1)
$D+h\nu_a \longrightarrow D^*$	$I_{abs}[D]/[D]+[DA]$	(2)
$DA+h\nu_a' \longrightarrow DA^*$	$I_{abs}[DA]/[D]+[DA]$	(3)
$D^* \longrightarrow D+h\nu_f$	$k_f[D^*]$	(4)
$DA^* \longrightarrow DA+h\nu_f'$	$k_f'[DA^*]$	(5)
$D^* \longrightarrow D$	$k_q[D^*]$	(6)
$DA^* \longrightarrow DA$	$k_q'[DA^*]$	(7)

It must be noted that (2) and (3) can express the rate of light absorption of D and DA only under the condition that the extinction of D and DA at the wave length of exciting light are the same; this condition is practically fulfilled in the case of β-naphthol. From the above scheme, the following simple relation can be derived for the relative fluorescence intensity f of the solution in which the concentration of A is [A], f_0 being the intensity of the pure naphthol solution.

$$f/f_0=(1+\alpha K[A])/(1+K[A])$$

or

$$\frac{1-f_0/f}{[A]}=-K+\alpha K(f_0/f) \tag{a}$$

where

$$\alpha=\Phi'/\Phi,\ \ \Phi=k_f/k_f+k_q,\ \ \Phi'=k'_f/k'_f+k'_q,$$

Φ and Φ' are respectively the quantum yields of fluorescence for D and DA. α, the ratio of these two quantities can easily be determined from f_0-value and the f-value of the solution to which A is amply added. To treat the problem more rigorously, it would be necessary to take into account the correction for the difference in the sensitivity of the phototube toward different wave lengths, and for this correction the second term in (a) will have to be multiplied by a certain factor. But in the present case, the spectral shift of AD against D being rather small, the above treatment may be practically exact.

In the case of α-naphthol in which the extinction of the hydrogen bonded naphthol differs to some extent from that of the free naphthol at the wave length of excitation, the relation (a) must be modified as follows.

$$\frac{1-f_0/f}{[\mathrm{A}]}=-K+\frac{\varepsilon'}{\varepsilon}\alpha K(f_0/f) \qquad \text{(b)}$$

In this equation ε and ε' are the extinction coefficients of the free and hydrogen bonded naphthols at the wave length of excitation.

Next let us turn to the case in which a new and different equilibrium is realized during the life time of the excited state. If the extinction of D and AD are the same at the wave length of exciting light, then the sum of the rate of production D* and AD*, that is, the light absorbed per unit time is constant irrespective of the concentration of A, and the following scheme may be used to derive the relative intensity of fluorescence.

$$\begin{array}{lll}
 & \text{Rate or equilibrium constant} & \\
\left.\begin{array}{l}\mathrm{D}+h\nu_a\rightarrow\mathrm{D}^*\\ \mathrm{DA}+h\nu_a'\rightarrow\mathrm{DA}^*\end{array}\right\}\ \text{total} & I_{\mathrm{abs}} & (1')\\
\mathrm{D}^*+\mathrm{A}\rightleftarrows\mathrm{DA}^* & K'=\dfrac{[\mathrm{D}^*][\mathrm{A}]}{[\mathrm{DA}^*]} & (2')\\
\mathrm{D}^*\rightarrow\mathrm{D}+h\nu_f & k_f[\mathrm{D}^*] & (3')\\
\mathrm{DA}^*\rightarrow\mathrm{DA}+h\nu_f' & k_f'[\mathrm{DA}^*] & (4')\\
\mathrm{D}^*\rightarrow\mathrm{D} & k_q[\mathrm{D}^*] & (5')\\
\mathrm{DA}^*\rightarrow\mathrm{DA} & k_q'[\mathrm{DA}^*] & (6')
\end{array}$$

The following relation (a′) analogous to (a) can easily be derived from the above scheme.

$$\frac{1-f_0/f}{[\mathrm{A}]}=-K'+\alpha K'(f_0/f) \qquad \text{(a}'\text{)}$$

In this equation K' is related to the excited state and may generally be different from K in (a).

When the extinction of D and DA is different as in the case of α-naphthol, the matter becomes somewhat complicated but it can easily be verified that the following relation must hold.

$$f/f_0=\left\{\frac{1+\alpha K'[\mathrm{A}]}{1+K'[\mathrm{A}]}\right\}\left\{1+\frac{K[\mathrm{A}]\Delta\varepsilon/\varepsilon}{K[\mathrm{A}]+1}\right\}$$

where $\Delta\varepsilon=\varepsilon'-\varepsilon$.

If the experimentally obtained f_0/f-value be multiplied by a factor $\Delta=\left\{1+\dfrac{K[\mathrm{A}]\Delta\varepsilon/\varepsilon}{K[\mathrm{A}]+1}\right\}^{-1}$,

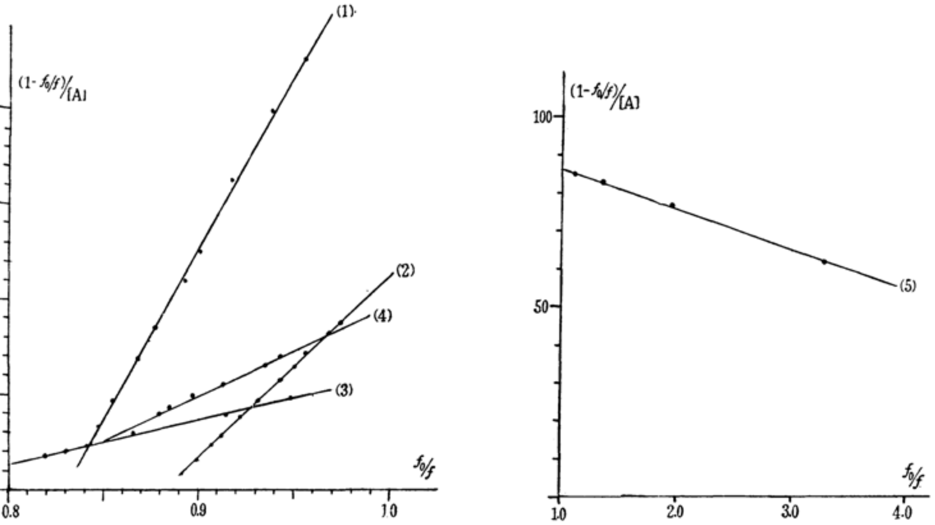

Fig. 6. $\dfrac{(1-f_0/f)}{[\mathrm{A}]}\sim f_0/f$ linear relation of β-naphthol for various proton acceptors.

(1) but. acetate
(2) met. acetate } at 10°C
(3) dioxane

(4) eth. acetate
(5) Cl-eth. acetate } at 25°C

which is easily calculated from the experimental data, then equation analogous to (b) will hold.

$$\frac{1-(f_0/f)\Delta}{[\mathrm{A}]}=-K'+\alpha K'(f_0/f)\Delta \qquad \text{(b}'\text{)}$$

Now the experimental results in the case of β-naphthol can be reproduced very satisfactorily by (b) or (a) as seen from Fig. 6, hence it is very plausible to consider that the equilibrium condition is realized in the excited state. The question whether this equilibrium state is the same or different from that in the ground state can be settled from the comparison of K_f-value obtained from the curves in Fig. 6 and K_a-value obtained from the analysis of the absorption spectra which can simply be calculated by the method of Rosenblatt[11]. Thus if the equilibrium in the ground state is maintained during the emission process, K_f which corresponds to K must coincide with K_a, while in the alternative case K_f which corresponds to K' must be different from K_a. In Table I, the free energy changes of hydrogen bond formation ΔF^f and ΔF^a as calculated from K_f and K_a are tabulated. As seen from Table I, $|\Delta F^f|$ is greater than $|\Delta F^a|$ in the case of β-naphthol; hence it can be concluded that the equilibrium of hydrogen bonding shifts toward the association during the life time of the excited state.

TABLE I

α-Naphthol

Proton acceptor	ΔF^a_{303}	ΔF^f_{303}	$\Delta F^f_{303}-\Delta F^a_{303}$	$\delta\nu_{\mathrm{a,max}}$ (kcal./mol.)	α
Methylacetate	−1.49	−1.8	−0.3	−0.27	1.30
Ethylacetate	−1.57	−2.0	−0.4	−0.27	1.26
Butylacetate	−1.62	−2.0	−0.4	−0.30	1.27
Ethyl-Cl-acetate	−1.08	−2.4	−1.3	−0.27	0.00

β-Naphthol

Proton acceptor	ΔF^a_{283}	ΔF^f_{283}	$\Delta F^f_{283}-\Delta F^a_{283}$	$\delta\nu_{\mathrm{a,max}}$ (kcal./mol.)	α
Dioxane	−1.50	−1.65	−0.15	−0.65	1.33
Methyl-acetate	−1.82	−2.48	−0.66	−0.70	1.13
Butylacetate	−1.80	−2.80	−1.00	−1.00	1.20

	ΔF^a_{298}	ΔF^f_{298}	$\Delta F^f_{298}-\Delta F^a_{298}$	$\delta\nu_{\mathrm{a,max}}$ (kcal./mol.)	α
Ethylacetate	−1.67	−2.04	−0.37	−0.95	1.29
Ethyl-Cl-acetate	−1.29	−1.85	−0.56	−0.80	0.20

As for the case of α-naphthol, we have not yet succeeded in obtaining the data which are reliable enough to test the equation (b) or (b′). The data in Table I are only provisional in nature, but scarcely any doubt remains that $|\Delta F^f|$ values are always greater than $|\Delta F^a|$ values in this case too.

Discussion

a) The Shift of Absorption and Fluorescence Spectra due to Hydrogen Bonding

For the discussion of the solvent effect on the absorption spectrum in general, it is customary to take the shift of absorption maximum as a change of the pure electronic excitation energy. But this is in general, a very crude approximation, because the former corresponds to the difference between the energy change of the Franck-Condon state of excited level and that of the equilibrium state[5] of the ground level. Thus in the case of the hydrogen bonding effect, the shift of the absorption maximum $\Delta\nu^{\mathrm{abs}}$ (positive for the red shift) may be put as follows.

$$\begin{aligned} h\Delta\nu^{\mathrm{abs}} &= \Delta E^{\mathrm{abs}}=(E_{of}'-E_{Hf})-(E_{oe}''-E_{He}'') \\ &= \Delta E_f'-\Delta E_e'' \end{aligned} \qquad (1)$$

where ′ and ″ refers respectively to the excited and the ground state and the suffix o and H denote free and hydrogen-bonded state, while f and e refer to the Franck-Condon state and the equilibrium state. As for the shift of the maximum of fluorescence spectra on the other hand, the following relation must hold.

$$\begin{aligned} h\Delta\nu^{fl} &= \Delta E^{fl}=(E_{oe}'-E_{He}')-(E_{of}''-E_{Hf}'') \\ &= \Delta E_e'-\Delta E_f'' \end{aligned} \qquad (2)$$

From (1) and (2) it is clear that $\dfrac{\Delta\nu^{\mathrm{abs}}+\Delta\nu^{fl}}{2}$ is a better approximation as a change of pure electronic excitation energy; in fact if the potential diagrams are symmetrical around the equilibrium point, then this approximation will give an almost exact value.

In the present case, however, it may be permitted to take $\Delta\nu^{\mathrm{abs}}$ as a change in a pure electronic energy, because $\Delta\nu^{fl}$ does not in general differ much from $\Delta\nu^{\mathrm{ab}}$. Hence such a convention is followed throughout the present discussion, especially in view of such a case as ethylchloroacetate where the fluorescence is so faint that $\Delta\nu^f$ cannot be decided. $\Delta\nu^{\max}$ for various proton acceptors are tabulated in Table I.

From Table I, it is seen that $|\Delta F^f|-|F^a|$ is nearly equal to $\Delta\nu^{\max}$ for every acceptor added to β-naphthol. Of course it is more desirable to compare $\Delta\nu^{\max}$ with the energy of the hydrogen bond, not with the free

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[11] D.H. Rosenblatt, *J. Phys. Chem.*, 58, 40 (1954).

energy; the evaluation of the former, however, necessitates the measurement at different temperatures, which in the present apparatus is extremely difficult. Tentatively neglecting the entropy factor, one may consider that $\Delta\nu^{\max}$ is approximately equal to the difference of the energy of the hydrogen bond between the excited and the ground state.

b) The Intensity of Fluorescence affected by the Hydrogen Bond

In all the cases except ethylchloroacetate, the intensity of fluorescence is increased more or less by the hydrogen bond formation, and the quenching constant k_q may perhaps be reduced by the hydrogen bond formation. This presumption can be further confirmed by the following deduction.

Since the first and the second absorption regions are fairly well separated in the case of β-naphthol, one can easily estimate the spontaneous emission probability from the integrated absorption by the formula of Ladenburg[12)]

$$k_f = 3\times 2.303\times(10^3/N)\times 8\pi c n^2 \tilde{\nu}_0^2 \int \varepsilon_{\tilde{\nu}} d\tilde{\nu}$$

From the k_f-value thus calculated and the α-values tabulated in Table I, the comparison of k_q and k_q' can easily be made on the basis of the following relation,

$$\alpha = \frac{\Phi'}{\Phi} = \frac{k_f'}{k_f'+k_q'} \Big/ \frac{k_f}{k_f+k_q}$$

The result is that k_q' is smaller than k_q in the case of dioxane, acetic acid esters other than ethylchloroacetate, and that $\tau' = \frac{1}{k_f'+k_q'}$ does not differ from $\tau = \frac{1}{k_f+k_q}$ more than 10% in these cases.

The quenching phenomenon observed in the case of ethylchloroacetate may be a very interesting example from the standpoint of the energy transfer. In the case of β-naphthol, this quenching effect can undoubtedly be attributed to the formation of the hydrogen bond on the basis of the already mentioned facts. But in the case of α-naphthol some ambiguity remains since the theoretical relations cannot represent the experimental data so successfully as in the case of β-naphthol, and moreover, no particular experiments using α-naphthyl methyl ether was performed. The collisional quenching might possibly participate in this case making the result very complicated. Though the question still remains to be settled in future, it is quite certain that a large part of quenching in this case may also be due to the hydrogen bond formation. For the system consisting of β-naphthol and ethylchloroacetate, it was established by the above mentioned estimation that k_q' is far greater than k_q and that $\tau > \tau' \approx \frac{\tau}{5}$. In connection with the quenching action of ethylchloroacetate on β-naphthol, it may be worthy to add that we have measured the fluorescence quenching of β-naphthol and β-naphthyl methyl ether caused by the addition of carbon tetrachloride and have found that the change of relative fluorescence yield obeys the Stern-Volmer relation very well with the same quenching constant in both cases. Thus the mechanism for the quenching of fluorescence of β-naphthol by carbon tetrachloride is evidently quite different from that by ethylchloroacetate. The former may parhaps be interpreted as the ordinary collisional quenching though its microscopic mechanism is still open to question, especially in view of such facts as observed by E. J. Bowen and R. J. Cook[13)] that the temperature coefficient of the fluorescence quenching of anthracene and its derivatives caused by chloroform and bromobenzene is negative. In fact, Bowen and Cook insist on the complex formation between the excited molecule and the quencher molecule and suggest that the charge transfer interaction between them induce the excited molecule to go to the triplet state.

Turning to the case of β-naphthol and ethylchloroacetate where the fluorescer and the quencher are certainly combined by the hydrogen bond, an interpretation analogous to that of Bowen and Cook may be plausible, but it is also possible to consider that the excitation energy is efficiently dissipated by Cl-atom, which in this case is closely connected with the fluorescer molecule by the hydrogen bond. At any rate it may be hoped that a key to clarify the microscopic mechanism of the quenching phenomenon in general can be got by further investigations of such systems.

c) The Mechanism of the Hydrogen Bonding Effect

According to our results, it is quite evident that the excited naphthol molecules have a greater tendency to form the hydrogen bond and that at least in the case of β-naphthol a new and different equilibrium state is reached during the lifetime of its excited state. An analogous phenomenon has also been found by Eisenbrand[14)]. He reported

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[12)] R. Ladenburg, *Z. Phys.*, **4**, 451 (1921); R.C. Tolman, *Phys. Rev.*, **23**, 693 (1924); E.J. Bowen and W.S. Metcalf, *Proc. Roy. Soc.*, A **206**, 437 (1951).

[13)] E.J. Bowen and R.J. Cook, *J. Chem. Soc.*, **1953**, 3059.

[14)] J. Eisenbrand, *Z. Elektrochem.*, **55**, 374 (1951).

that 8-quinolinesulfonic acid in the aqueous solution has a greater tendency to form the complex associate with resorcine in the excited state on the basis of the studies of the fluorescence.

The present investigation has afforded another notable example, and this example seems to be particularly valuable since it enables us to make a quite interesting interpretation about the mechanism of the hydrogen bonding effect.

As to the shift of absorption spectra due to the hydrogen bonding, the following plausible interpretation[1-5] has been given on the basis of the electron migration theory developed by Sklar and Herzfeld[15].

Taking phenol as an example, the close approach of the electronegative atom of the proton acceptor causes a decrease in the ionization potential of the non-bonding 2p electron in the OH radical by inductive or direct effect, which eventually makes easier the migration of non-bonding electrons into the vacant orbital of π-electron system. Then the rate of electron migration in the excited state will be greater than in the ground state, since one electron in the highest level of the ground state has been raised to a higher level. From this view point, the values of $\delta\nu_{\mathrm{a,max}}$ tabulated in Table I may be interpreted as the difference of the stabilization due to the electron migration between the excited and the ground state. Now, as already stated, the difference of the hydrogen bonding energy between the excited and the ground states as revealed from $\Delta F^f - \Delta F^a$ roughly coincide with $\Delta\nu_{\mathrm{a,max}}$. Hence it may be concluded that the extra stabilization energy of hydrogen bonding in the excited state is almost exclusively due to the increased electron migration.

The present result is noteworthy for the interpretation of the nature of the hydrogen bond in general and particularly of the interaction between the hydrogen bond and π-electron system.

Further studies on analogous systems are now going on.

Summary

1. The absorption and fluorescence spectra of α-, β- naphthols and related compounds were measured in various mixed solvents in connection with the hydrogen bonding phenomena. The observed spectral shifts of absorption and fluorescence spectra, which were almost the same ($\sim$30 Å), could be solely attributed to the hydrogen bonding effect.

2. It was found that the fluorescence intensity becoms stronger by hydrogen bonding when dioxane and acetic acid esters other than ethylchloroacetate are used as the proton acceptors. In the case of β-naphthol, it was established that the rate of inner quenching is decreased by hydrogen bonding. When ethylchloroacetate was used as a proton acceptor, fluorescence quenching was observed, which is also to be attributed to hydrogen bonding.

3. For β-naphthol, the measurement of the relative intensity established the fact that a new and different equilibrium state of hydrogen bonding, which shifts somewhat toward association, is reached during the life time of the excited state.

4. The mechanism of hydrogen bonding was discussed on the basis of the theory of electron migration, and it was concluded that the observed extra-stabilization of the hydrogen bond in the excited state as compared to the ground state, is mainly due to the increase of electron migration in the former state.

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City University, Osaka

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[15] A.L. Sklar, *J. Chem. Phys.* **7**, 984 (1939); K.F. Herzfeld, *Chem. Rev.*, **41**, 233 (1947).