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Fluorescence Quenching and the Charge Transfer in the Excited State.*[1] II. Dimethylnaphthylamine - Dimethyl Phthalate in Various Solvents

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As an extension of a previous paper (*Bull. Chem. Soc. Japan*, **39**, 2588 (1966)), the quenching action of *p*-methyl toluate, ethyl benzoate, dimethyl esters of *m*-, *o*-, *p*-phthalic acids on the fluorescence of *N, N*-dimethyl-2-naphthylamine has been studied in several solvents. The quenching constants of the above substances (in the above sequence) in cyclohexane and dimethylformamide are respectively (0.5, ~1, 65, 85, 93) and (41, 58, 103, 85, 124). The order, toluate< benzoate<phthalate, is consistent with the charge transfer mechanism of quenching in which fluorescer and quencher act respectively as a donor and an acceptor. In slightly or nonpolar solvents a new emission attributed to an excited CT complex has been found; its intensity has been the strongest in the case of dimethyl *m*-phthalate. Using this substance as a quencher, solvent effect on the quenching efficiency and the CT emissivity has been studied. It has been found that in weakly polar solvents, these two quantities decrease similarly with the increasing solvent polarity, whereas in highly polar solvents the former is large and the latter is negligible. The results in less polar solvents suggest that the reorientation of the solvated molecules is an essential process for both the quenching and the CT emission. Another evidence for this view has been found in the experiments with mixed solvents. In highly polar solvents, the production of free radical ions is most plausible but the possibility of the formation of a solvated ion pair with no emissivity, cannot be ruled out.

Since Weller[1] has succeeded in presenting the experimental evidence for the charge transfer (CT) and the electron transfer mechanism of fluorescence quenching by a flash technique, interest seems to have increased in the studies of these quenching mechanisms. It is interesting in particular, to study how the formation of the excited CT (ex-CT) complex or of the two separate radical ions, is related with the solvent polarity and to study further the dependence of the CT emissivity upon the solvent polarity. Mataga *et al.*[2] have contributed much along this line.

Miwa and one of the present authors (M. K.)[3] also have reported that the quenching action of methyl benzoate on the fluorescence of dimethylnaphthylamine can be interpreted either in terms of the formation of the CT complex or the electron transfer, depending on the polarity of the solvent. In this system a general tendency was observed that the quenching efficiency becomes larger with the increasing polarity of the solvent. But this tendency was distinct only in polar solvents from ethyl acetate to dimethylformamide (DMF) (we classified these solvents as group 2); in less polar solvents from cyclohexane to ether type compounds (group 1), the quenching constant was very small (less than 10), and the quenching efficiency was not so clearly related with the solvent polarity. Charge transfer emission on the other hand, was prominent in the solvents of group 1, but was scarcely observable in the solvents of group 2. Although this is another strong support for the CT mechanism in less polar solvents, the relation between the emissivity of the ex-CT complex and the solvent polarity was not very clear again.

It is interesting therefore, to find a suitable quencher which has a large quenching constant in weakly polar solvents and which forms a stable ex-CT complex with high emissivity. The present paper reports that phthalic acid esters are the quenchers of this type. Choosing dimethyl *m*-phthalate as a quencher, solvent effects on the quenching constant as well as on the emissivity were studied. In addition, studies were made with mixed solvents.

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*[1] Hereafter, the paper by Miwa and Koizumi (Ref. 3) will be referred as the first paper of this series.

[1] H. Leonhardt and A. Weller, *Ber. Bunsges. Physik. Chem.*, **61**, 791 (1963).

[2] a) N. Mataga *et al., Z. Physik. Chem., N. F.*, **44**, 250 (1965); b) This Bulletin, **39**, 2562 (1966); c) *Mol. Phys.*, **10**, 203 (1966); d) *ibid.*, **10**, 201 (1966).

[3] T. Miwa and M. Koizumi, This Bulletin, **39**, 2588 (1966).

Experimental

Materials. Cyclohexane, *n*-hexane, benzene, isopropyl ether, ethyl ether, acetone, *N*, *N*-dimethylformamide, *N*, *N*-dimethyl-2-napthaylamine and methyl benzoate were purified in the same way as in a previous paper.[3]

Toluene of Wako Junyaku, G. R. grade, was dried over sodium and then distilled.

Carbon tetrachloride of Wako Junyaku, G. R. grade, was dried with phosphorus pentoxide and distilled.

n-Buthyl ether of Wako Junyaku, E. P. grade, was shaken with a 10% solution of sodium carbonate and then dehydrated with anhydrous calcium chloride and finally with sodium until no hydrogen evolved. It was then distilled.

All the acetates were shaken with a concentrated aqueous solution of sodium carbonate or potassium carbonate, and of sodium chloride or calcium chloride. They were then dried with anhydrous magnesium sulfate and distilled.

Methyl ethyl ketone of Kanto Kagaku, G. R. grade, was stored over potassium permanganate for a week, refluxed for 2 hr, and then distilled.

Methyl 4-methyl benzoate of Tokyo Kasei, E. P. grade, was purified by recrystallization from ligroin three times and then from ligroin ethanol mixed solution. It was dried *in vacuo* for 6 hr.

Dimethyl phthalate, G. R. grade of Tokyo Kasei, was treated with a 10% aqueous solution of sodium carbonate. It was stored over anhydrous potassium carbonate for two weeks and distilled under reduced pressure in a nitrogen atmosphere.

Dimethyl isophthalate, E. P. grade of Tokyo Kasei, was purified by recrystallization from E. P. grade ethanol, G. R. grade ethanol, G. R. carbon tetrachloride and finally from G. R. grade ethanol. It was then dried *in vacuo* for one day.

Dimethyl telephthalate, E. P. grade of Tokyo Kasei was recrystallized from ethanol three times and then dried *in vacuo*.

Ethyl benzoate, E. P. grade of Tokyo Kasei, was stored over anhydrous magnesium sulfate for half a year and then distilled under reduced pressure.

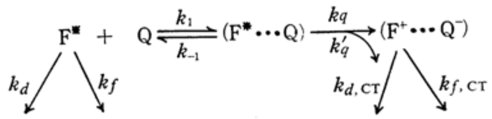
Quinine sulfate of Sanko Seiyaku was purified by recrystallization from ethanol-benzene mixed solution two times and then from distilled water.

Procedures. A Hitachi EPS-3 spectrophotometer was used for the measurement of the absorption spectra. An Aminco-Bowman Spectrofluorimeter was used for the measurement of the fluorescence spectra and the fluorescence intensity. The intensity determination was made by three sets of measurements, each one set consisting of measurements of reference, sample, reference in succession. Since the shape of the intrinsic fluorescence spectra of dimethylnaphthylamine was not essentially affected by the presence of a quencher, the height at the fluorescence peak was used to compare the intensities. Correction was made on the wavelength dependence of sensitivity of a photomultiplier, by calibrating the instrument with a quinine sulfate solution.[4] Aminco Bowman fluorimeter has a defect of being difficult in setting at a desired wavelength, but this was not so serious in the present experiment. It was checked that the fluorescence of anthracene after sensitivity correction, agreed satisfactorily with that reported in the literature. The intensities of the fluorescence are the values thus corrected throughout the present paper. The measurement was made usually at 25°C.

Basis of the Analysis of the Experimental Data

It is convenient to describe here the basis for analyzing the experimental data, anticipating the results to be consistent with the proposed mechanism.

Scheme A. In weakly polar solvents, an excited fluorescer F* forms an encounter complex (F*···Q), where Q is a quencher molecule. Some of the encounter complex then turns into an ex-CT complex ($F^+\cdots Q^-$), which returns to the ground state with or without radiation.



Scheme B. In highly polar solvents an encounter complex which may be a different type from that in less polar solvents, separates into two free radical ions.

$$F^* + Q \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (F^*\cdots Q) \xrightarrow{k_q} F^+ + Q^-$$

In either case the fluorescence intensities in the absence and in the presence of a quencher, denoted respectively as F_0 and F, are related with each other by a Stern-Volmer equation.

$$F_0/F = 1 + \gamma k_1 \tau_0 [Q] = 1 + K[Q] \qquad (1)$$

$$K = \gamma k_1 \tau_0 \qquad (2)$$

where K and γ are respectively a quenching constant and a quenching efficiency and further,

$$\gamma = (k_q + k_q')/(k_q + k_{-1} + k_q') \qquad (3)$$

$$\tau_0 = \frac{1}{k_d + k_f + k_{O_2}[O_2]} \qquad (4)$$

Besides, k_1 is calculated from a well-known relation

$$k_1 = 4\pi a D N' \qquad (5)$$

Since most of the measurements were made in the aerated solution, the quenching action of oxygen

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[4] H. Kokubun and M. Kobayashi, Report of the Inst. Applied Electricity (Hokkaido), **18**, 117 (1965).

was taken into account.*2 This complicating factor can be eliminated by using the following relation

$$\tau_0 = \Phi_0/k_f \tag{6}$$

where Φ_0 is a quantum yield of fluorescence in the absence of a quencher. Since k_f is almost insensitive to solvent and since the relative values of Φ_0 in reference to a certain standard solvent, can easily be obtained, one can evaluate the relative values of γ for each solvent by introducing (5) into (2). Using suffix i and s for solvent i and for a reference solvent,

$$K_i/K_s = \frac{(a\gamma)_i}{(a\gamma)_s}\left(\frac{D_i}{D_s}\right)\left(\frac{\Phi_{0i}}{\Phi_{0s}}\right) \tag{7}$$

As for the CT emission, relations (9), (10) and (11) can easily be derived if a factor Φ_{CT} which gives a ratio of the acts of an emitting process to those of the effective quenching processes, is introduced formally as follows,

$$\Phi_{\mathrm{CT}} = \frac{k_{f,\mathrm{CT}}}{k_{d,\mathrm{CT}} + k_{f,\mathrm{CT}}} \times \frac{k_q}{k_q + k_q'} \tag{8}$$

$$F/F_{\mathrm{CT}} = \frac{k_f}{k_1[\mathrm{Q}]\gamma\phi_{\mathrm{CT}}} = \frac{k_f\tau_0}{K[\mathrm{Q}]\phi_{\mathrm{CT}}} = \frac{\Phi_0}{K[\mathrm{Q}]\phi_{\mathrm{CT}}} \tag{9}$$

$$(F_0 - F)/F_{\mathrm{CT}} = \frac{k_f\tau_0}{\phi_{\mathrm{CT}}} = \frac{\Phi_0}{\phi_{\mathrm{CT}}} \tag{10}$$

$$F_0/F_{\mathrm{CT}} = \frac{k_f}{k_1\gamma[\mathrm{Q}]\phi_{\mathrm{CT}}} + \frac{k_f\tau_0}{\phi_{\mathrm{CT}}} \tag{11}$$

(9), (10) or (11) enables us to evaluate the relative values of ϕ_{CT} from the experimental data.

Results and Discussion

Effect of the Addition of Some Related Substances of Methyl Benzoate on the Fluorescent Behavior of 2-Dimethylnaphthylamine. In order to find a suitable quencher which is efficient in slightly polar solvents and which at the same time exhibits a strong CT emission, the following systems were investigated.

fluorescer: 2-dimethylnaphthylamine (2DMNA)
quencher: methyl 4-methylbenzoate (*p*-MT)

TABLE 1.

Solvent	Quencher	Concentration of quencher (M)	K	CT-Emission	λ_{max} of CT-Emission
Cyclohexane	*p*-MT	4.3×10^{-1}	0.5		
	EB	up to pure quencher	1	+	$<\lambda_{m\text{-DMP}}$
	o-DMP	1.6×10^{-1}	85	++	~530 mμ
	p-DMP	10^{-2}	93	++	$\gtrsim\lambda_{o\text{-DMP}}$
	m-DMP	9×10^{-2}	65	+++	470 mμ
Benzene	*o*-DMP	1.6×10^{-1}	81	Weak	
	p-DMP	1.6×10^{-1}	113	Weak	
	m-DMP	1.6×10^{-1}	80	+	~522 mμ
Dioxane	*o*-DMP	1.6×10^{-1}	79	?	
	p-DMP	1.6×10^{-1}	146	?	
	m-DMP	1.6×10^{-1}	89	Weak	~550 mμ
DMF	*p*-MT	8.87×10^{-3}	41	No	
	EB	up to pure quencher	58	No	
	o-DMP	8.7×10^{-3}	85*	No	
	p-DMP	6.6×10^{-3}	124*	No	
	m-DMP	1.05×10^{-2}	103*	No	

* Larger than the value for methyl benzoate reported in the previous paper. It was supposed in the previous paper that the quenching action of MB may be diffusion controlled. But this is not correct.

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*2 Throughout the present investigation, it was assumed, as is usually the case, that the quenching action of oxygen occurs in an additive manner. This was checked experimentally only in the case of the quenching of the fluorescence of DMNA by dimethyl *o*-, *m*-, and *p*-phthalates in cyclohexane. In the following table K_{Q} and $K_{\mathrm{Q,O_2}}$ are respectively, the quenching constants in the degassed and in the aerated solution. $K_{\mathrm{Q,O_2}}$ was calculated from

$$K_{\mathrm{cal,Q,O_2}} = \frac{K_{\mathrm{Q}}}{1 + K_{\mathrm{O_2}}[\mathrm{O_2}]}$$

where $K_{\mathrm{O_2}}$ is a quenching constant of oxygen which was found to be 322. Since the above relation is based on the additive action of the two quenchers, it can be said that the agreement between $K_{\mathrm{Q,O_2}}$ and $K_{\mathrm{cal,Q,O_2}}$ verifies the present assumption.

	K_{Q}	$K_{\mathrm{Q,O_2}}$	$K_{\mathrm{cal,Q,O_2}}$
dimethyl *o*-phthalate	138	84	83
dimethyl *m*-phthalate	120	78	72
dimethyl *p*-phthalate	150	98	90

ethyl benzoate (EB)
dimethyl *o*-phthalate (*o*-DMP)
dimethyl *m*-phthalate (*m*-DMP)
dimethyl *p*-phthalate (*p*-DMP)
solvent: cyclohexane
benzene
dioxane
dimethyl formamide (DMF)

The results are summarised in Table 1.

As Table 1 shows, all the three isomers of DMP show a remarkable quenching action both in slightly polar and in highly polar solvents. Besides, they all give quite a strong CT emission in cyclohexane. Figure 1 gives a comparison of the fluorescence spectra of 2-DMNA in the cyclohexane solution containing *m*-DMP, with those in the same solvent containing EB.

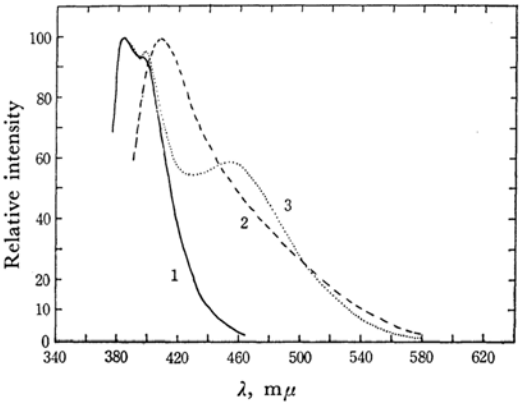

Fig. 1. Influence of the addition of dimethyl *m*-phthalate and ethyl benzoate on the fluorescence spectra of 2-dimethylnaphthylamine in cyclohexane.
—— 2-dimethylnaphthylamine (1×10^{-4} M)
---- 2-dimethylnaphthylamine - ethyl benzoate (1×10^{-4}, 4.89 M)
...... 2-dimethylnaphthylamine - dimethyl *m*-phthalate (1×10^{-4}, 8.62×10^{-2} M)

A new peak is clearly seen at 8.62×10^{-2} M of *m*-DMP. It is also apparent that the intrinsic fluorescence spectra of 2-DMNA is scarcely affected by the addition of a quencher apart from a small shift to the longer wavelength. Such is usually true in all the systems. The absorption spectra also, are not affected by the addition of a quencher in most cases. In a few cases, more or less red shift occurred.

In cyclohexane, the magnitude of the quenching constant is in the following order,

$$p\text{-MT} < \text{EB} \ll m\text{-DMP} < o\text{-} \lesssim p\text{-DMP}$$

while in DMF

$$p\text{-MT} < \text{EB} < o\text{-DMP} < m\text{-DMO} < p\text{-DMP}.$$

Although the quenching efficiency should be discussed on the basis of γ values, the above order may be interpreted if one assumes that a quencher becomes more efficient with the increasing accepting power. It seems reasonable to consider that a CT interaction in less polar solvents occurs between the naphthalene ring of a fluorescer and the benzene ring of a quencher.[*3] This view is supported by the finding that two carboxyl groups enhance the quenching efficiency for more than one carboxyl group; if the direct interaction between the electron deficient amino group in a fluorescer molecule and the electron rich carboxyl group of a quencher molecule, is a principal cause for quenching, such a great enhancement may not be expected. The results in the fifth column suggest that *m*-DMP is the most suitable quencher for our purpose. Figure 2 which gives $F/F_{\rm CT}$ - [quencher] plots for the case of *m*- and *o*-DMP, demonstrates the above deduction quantitatively. Another point worth while to mention is that there is a large difference in the *K*-values of various quenchers in cyclohexane, while they differ little in DMF. Although this may partly be due to the fact that the quenching process in the latter solvent approaches diffusion controlled, it suggests to some extent, difference in mechanism in the two solvents.

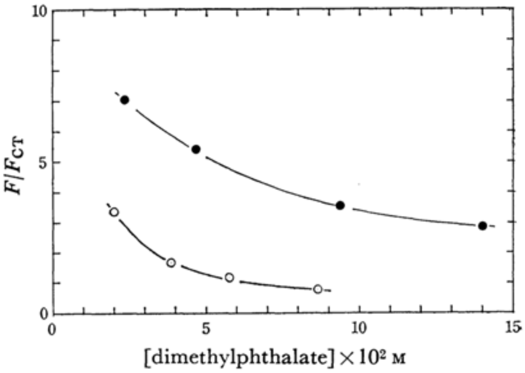

Fig. 2. ($F/F_{\rm CT}$) *vs.* [*m*-DMP] plot for
-○- 2-dimethylnaphthylamine - dimethyl *m*-phthalate
-●- 2-dimethylnaphthylamine - dimethyl *o*-phthalate

Solvent Effects on γ and $\varphi_{\rm CT}$ of *m*-DMP. Seventeen solvents were investigated. For each solvent, measurements were made at several

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[*3] In general CT interaction is expected to become larger, the larger the electron affinity of an acceptor and the smaller the ionization potential of a donor. Although the exact data on the electron affinity of the above substances are unknown, it is quite reasonable that the electron affinity of the above quenchers is in the above order. If one assumes that the electron affinity is in parallel with the lowest vacant level, the order in the former may be estimated from a simple LCAO calculation of the latter. Our calculation has led to the following order

$$p\text{-MT} < \text{MB} < m < o < p$$

which is just the same as above.

TABLE 2. THE DATA FOR ABSORPTION SPECTRA OF 2-DMNA IN VARIOUS SOLVENTS AND SOME PHYSICAL CONSTANTS OF THE SOLVENTS [2-DMNA]$=1\times10^{-4}$ M

No.	Solvent	^1L_b λ_{max} mμ	Optical density at 355 mμ	ε (25°C)	μ	n_D (25°C)	$\eta_{c.poise}$ (25°C)
1	*n*-Hexane	351	0.255	0.890(20°C)	0.08	1.372	0.2923
2	Cyclohexane	351	0.276	2.020	0	1.427	0.898
3	Carbon tetrachloride	355	0.273	—	—	—	—
4	Benzene	356	0.291	2.273	0	1.497	0.6028
5	Toluene	356	0.323	2.379	0.39	1.494	0.5516
6	Dioxane		—	2.280	0.45	1.420	1.16
7	*n*-Butyl ether	352	0.278	3.06	1.22	1.396	0.695
8	Isopropyl ether	352	0.263	3.88	1.22	1.366(20°C)	0.379
9	Ethyl ether	352	0.291	4.265	1.15	1.35(20°C)	0.233
10	Isoamyl acetate	354	0.272	4.63(30°C)	1.8	1.405(20°C)	0.810
11	*n*-Butyl acetate	354	0.272	5.01(20°C)	1.841	1.394(20°C)	0.688
12	Isopropyl acetate	353.6	0.278			1.377	0.535
13	Ethyl acetate	354	0.281	6.02	1.81	1.369	0.426
14	Methyl acetate	354	0.283	6.68	1.75	1.361	0.362
15	Methyl ethyl ketone	355	0.276	18.51	2.747		0.407
16	Dimethyl ketone	355	0.276	20.7	2.72	1.356	0.305
17	*N*, *N*-Dimethyl formamide	357	0.277	36.71	3.86	1.426	0.908

TABLE 3. DATA RELATED TO THE FLUORESCENCE OF (2-DNA - *m*-DMP) [2-DNA] $=1\times10^{-4}$ M

No.	In the absence of a quencher		In the presence of a quencher	
	Peak of the fluorescence spectra mμ	$\alpha_i\equiv\left(\frac{F_{0i}}{F_{02}}\right)$	Concn. of a quencher, M	Max. wavelength of CT emission mμ
1	383	0.67	6.82×10^{-2}	468±2
2	383	1.00	8.62×10^{-2}	471±2
4	401	1.49	1.65×10^{-1}	522±6
5	401.3	1.13	1.68×10^{-1}	526±6
6	403		1.68×10^{-1}	550±6
7	391	0.93	1.67×10^{-1}	510±6
8	393	0.74	1.67×10^{-1}	520±6
9	397.8	1.33	1.65×10^{-1}	530±6
10	403.4	1.20	1.64×10^{-1}	?
11	405.5	1.19	1.64×10^{-1}	?
12	406.7	1.07	1.64×10^{-1}	550±6
13	407.1	1.07	1.64×10^{-1}	?
14	409.7	1.27		
15	412	1.10		
16	414	1.21		
17	420	2.06		

?: difficult to decide

quencher concentrations up to 1.6×10^{-1} M. The data refering to the absorption spectra are listed in Table 2, with some physical constants which will be useful in the later discussion. As is seen from the table, the absorption spectra show a slight shift to the longer wavelength as solvents become more polar. The optical densities at the peaks are usually within several percent from the average; they were taken into account for the evaluation of the fluorescence intensities.

Table 3 gives the data related with the fluorescence. The fluorescence spectra show somewhat larger red shift as compared with that of the absorption spectra. CT emission which is observed in solvents from 1 to 9, exhibits a pronounced red shift in consistence with its polar structure.[2b] As Fig. 3 shows, the wavelength of the peak position is approximately linear against the dielectric constant of the solvent; exceptions are benzene, toluene and dioxane which are anomalous in other

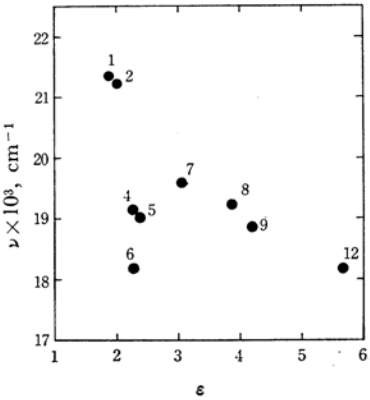

Fig. 3. Solvent effect upon the peak position of an ex-CT emission band of 2-dimethylnaphthylamine - dimethyl *m*-phthalate system.

Solvent: 1) *n*-hexane,* 2) cyclohexane, 4) benzene, 5) toluene, 6) dioxane, 7) *n*-butyl ether 8) isopropyl ether, 9) ethyl ether, 12) isopropyl acetate*

* ε: at 20°C

properties. CT emission is not observed in methyl acetate, ketones and DMF. Three typical examples of the fluorescence spectra are shown in Figs. 4a, b and c. The exciting light was always 355 mμ. It was checked that the excitation spectra agree moderately well with the absorption spectra.

As for the quenching constants, they were evaluated from the Stern-Volmer plots which satisfactorily hold in most solvents. There is scarcely any doubt that the present quenching action is dynamic in nature, since the addition of a quencher scarcely affects the absorption spectra of the fluorescer. The dynamic nature is also supported by a certain relationship holding between the quenching constant and the viscosity of the solvent at least in a series of homologous compounds. This is shown in Fig. 5. The data related with the quenching phenomena are given in Table 4. As a reference standard solvent, cyclohexane was chosen since the CT emission in this solvent is the strongest (see below). Although there is no good relationship between the relative $(a\gamma)_i$ values and the solvent polarity, a general tendency seems to exist that in less polar solvents $(a\gamma)_i$ decreases with the increasing polarity of the solvent and that it increases again in highly polar solvent.[*4] The lack of regularity may be due partly to other structural factors of the solvent which are related with

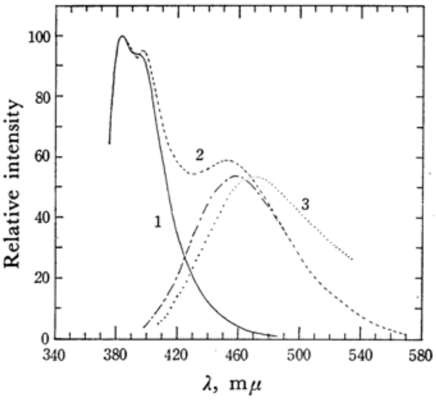

Fig. 4a. Fluorescence spectra of 2-dimethylnaphthylamine - dimethyl *m*-phthalate in cyclohexane.

1) 2-dimethylnaphthylamine (1.024×10^{-4} M)
2) 2-dimethylnaphthylamine (1.024×10^{-4} M) + dimethyl *m*-phthalate (8.62×10^{-2} M)
3) ex-CT emission (corrected for the spectral sensitivity of the instrument).

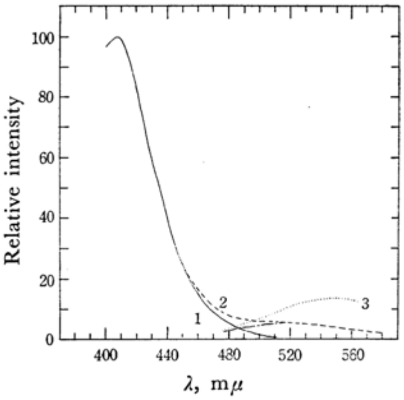

Fig. 4b. Fluorescence spectra of 2-dimethylnaphthylamine - dimethyl *m*-phthalate in isopropyl acetate.

1) 2-dimethylnaphthylamine (1.0040×10^{-4} M)
2) dimethylnaphthylamine (1.0040×10^{-4} M) + dimethyl *m*-phthalate (1.643×10^{-1} M)
3) ex-CT emission (corrected for the spectral sensitivity of the instrument).

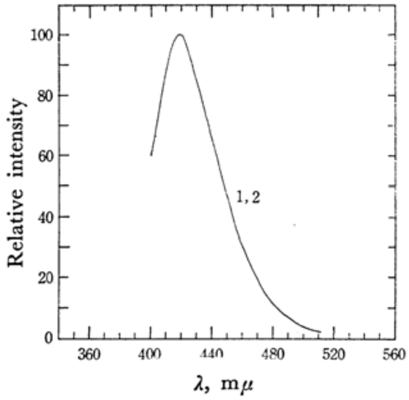

Fig. 4c. Fluorescence spectra of 2-dimethylnaphthylamine - dimethyl *m*-phthalate in dimethylformamide.

1) 2-dimethylnaphthylamine (0.9979×10^{-4} M)
2) 2-dimethylnaphthylamine (0.9979×10^{-4} M) + dimethyl *m*-phthalate (1.049×10^{-2} M)

[*4] We feel that the selection of solvents was not suitable.

TABLE 4. QUENCHING DATA FOR 2-DNA - *m*-DMP
[2-DNA] = 1×10^{-4} M

No.	Quenching const. K_i	$(D_2/D_i)\alpha_i$	$\frac{(a\gamma)_i^*}{(a\gamma)_2}\equiv\left(\frac{K_i}{K_2}\right)\left(\frac{1}{\alpha_i}\right)\left(\frac{D_2}{D_i}\right)$
1	98	0.50	0.76
2	65	1.00	1.00
4	80	0.45	0.55
5	86.5	0.54	0.72
7	70	0.75	0.81
8	68.5	0.46	0.48
9	140	0.59	0.41
10	61	0.74	0.69
11	67	0.63	0.65
12	74	0.57	0.65
13	83	0.43	0.55
14	113	0.31	0.64
15	91	0.39	0.55
16	122	0.27	0.51
17	103		0.8< <1.00

* Absolute values of $a\gamma$ for all the solvents lie in the range from 2.5 to 6.9×10^{-8} cm, if one assumes the τ_0-value as 10^{-8} sec. Since the latter value may depend greatly on the solvent, discussion on the basis of the absolute values of $a\gamma$ will be meaningless.

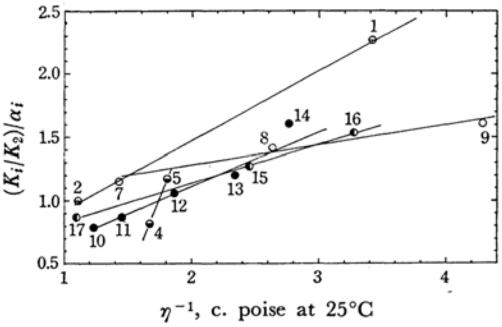

Fig. 5. $(K_i/K_2)/\alpha_i$ *vs.* η^{-1} plot.
1) *n*-hexane, 2) cyclohexane, 4) benzene, 5) toluene, 7) *n*-buthyl ether, 8) isopropyl ether, 9) ethyl ether, 10) isoamyl acetate, 11) *n*-butyl acetate, 12) isopropyl acetate, 13) ethyl acetate, 14) methyl acetate, 15) methyl ethyl ketone, 16) dimethyl ketone, 17) dimethyl formamide

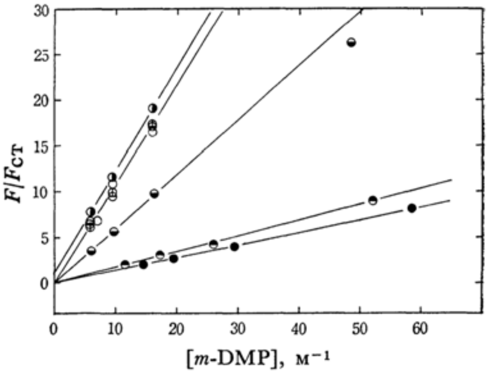

Fig. 6. F/F_{CT} *vs.* [*m*-DMP] plot for ◓; *n*-hexane, ●; cyclohexane, ○; benzene, ◑; toluene, ⊖; *n*-butyl ether, ⦶; isopropyl ether, ◒; ethyl ether.

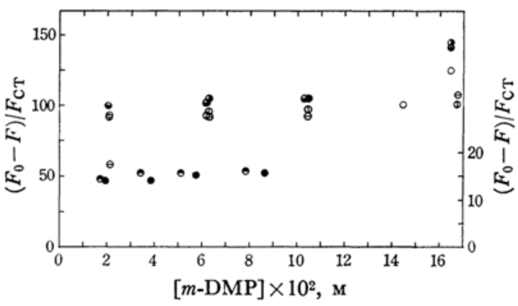

Fig. 7. $(F_0-F)/F_{CT}$ *vs.* *m*-DMP plot for ◓; *n*-hexane, ●; cyclohexane, ○; benzene, ◑; toluene, ⊖; *n*-buthyl ether, ⦶; isopropyl ether, ◐; ethyl ether.
(Right side scale is for *n*-hexane and cyclohexane).

the quenching phenomena. It is worth while to note, for example, that in a series of ether, acetate and ketones, higher homologues have larger quenching efficiencies with a single exception (methyl acetate).

The values of ϕ_{CT} can be evaluated from Eqs. (9), (10) and (11). In Fig. 6, F/F_{CT} is plotted against 1/[Q].

The slopes give $\Phi_0/K\phi_{CT}$ (Method A). In Fig. 7 the values of $(F_0-F)/F_{CT}$ are plotted against [Q]. According to (10), $(F_0-F)/F_{CT}$, is equal to Φ_0/ϕ_{CT} which should be constant if ϕ_{CT} is independent of [Q]. The curves in Fig. 7 suggest that ϕ_{CT} decreases only very little with [Q]. This might be due to an interaction between a quencher molecule and an ex-CT complex. If one assumes

Table 5. Relative efficiency of CT emission

No.	Method A		Method B	
	ϕ_{CT}/Φ_0	$(\phi_{CT})_i/(\phi_{CT})_2$	ϕ_{0CT}/Φ_0	$(\phi_{0CT})_i/(\phi_{0CT})_2$
1	0.19	0.53	0.16	0.56
2	0.24	1.00	0.19	1.00
4	0.051	0.32	0.040	0.31
5	0.048	0.23	0.042	0.25
7	0.056	0.22	0.050	0.24
8	0.064	0.20	0.053	0.20
9	0.065	0.36	0.054	0.38
12			0.012	0.067

the following relation similar to that for the usual quenching process,

$$\phi_{0CT}/\phi_{CT} = 1 + K'[Q]$$

where ϕ_{0CT} is a value of ϕ_{CT} at $[Q]=0$, then Eqs. (9) and (10) yield

$$F/F_{CT} = \Phi_0/\left(\frac{F_0}{F} - 1\right)\phi_{0CT} + \frac{\Phi_0 K'}{\phi_{0CT} K} \qquad (12)$$

$$(F_0 - F)/F_{CT} = \Phi_0/\phi_{0CT}\{1 + K'[Q]\} \qquad (13)$$

The plots of F/F_{CT} against $\{(F_0/F)-1\}$ are given in Fig. 8.

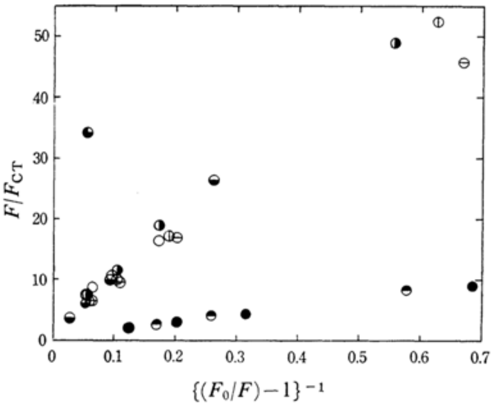

Fig. 8. F/F_{CT} vs. $\{(F_0/F)-1\}^{-1}$ plot for ○; n-hexane, ●; cyclohexane, ○; benzene, ◑; toluene, ⊖; n-butyl ether, ⦶; isopropyl ether, ◒; ethyl ether.

The slopes give Φ_0/ϕ_{0CT} (Method B). The relative values of ϕ_{CTi} in reference to cyclohexane are easily calculated by using the values of $\alpha_i = (\Phi_0)_i/(\Phi_0)_2$. The values obtained by Methods A and B are listed in Table 5.

The agreement of the values for $(\phi_{CT})_i/(\phi_{CT})_2$ with those for $(\phi_{0CT})_i/(\phi_{0CT})_2$ verifies that ϕ_{CT} is really almost independent of the quencher concentration. From the results in Table 5, any quantitative relation between ϕ_{CT} and the polarity of solvent can not be deduced but it is certain that ϕ_{CT} decreases with the increasing polarity.

A plot of $(a\gamma)_i/(a\gamma)_2$ against $(\phi_{CT})_i/(\phi_{CT})_2$ is shown in Fig. 9. It is seen that in less polar solvents, the two quantities change in a parallel way. Although the data in highly polar solvents are scanty, there is scarcely any doubt that $a\gamma$ increases and ϕ_{CT} decreases with the polarity of the solvent. The parallel behavior of $a\gamma$ and ϕ_{CT} in less polar solvents strongly suggests that one common act is essentially affecting both the CT emission and the quenching process. It is quite reasonable to consider that this is the process of formation of the ex-CT complex and that the process requires some activation energy necessary to reorientate the solvent molecules. Then the larger the polarity of the solvent, the greater will be the activation energy. This is perhaps the main reason why ϕ_{CT} and $(a\gamma)$ decreases with the solvent polarity. Of course, once the ex-CT complex is formed, its stability will be greater with the increasing polarity of the solvent,[*5] and it may be possible that with

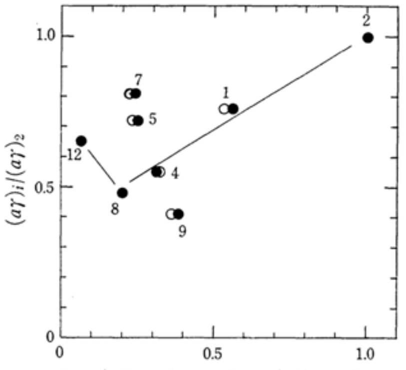

Fig. 9. $(a\gamma)_i/(a\gamma)_2$ vs. $(\phi_{0CT})_i/(\phi_{0CT})_2$ plot for 2-dimethylnaphthylamine - dimethyl m - phthalate system.

●; by method B ○; by method A

Solvent: 1) n-hexane, 2) cyclohexane, 4) benzene, 5) toluene, 7) n-butyl ether, 8) isopropyl ether, 9) ethyl ether, 12) isopropyl acetate.

[*5] This is quite certain from the finding that CT emission shifts to longer wavelength with the increasing polarity of the solvent. But the stability of ex-CT complex relative to the free radical ions is another problem, and stability in this sense will be reduced with the increasing polarity of the solvent.

the stability of ex-CT complex and hence, with the larger solvation in more polar solvents, the emissivity of ex-CT complex is weakened. But if such a situation is the only cause for the decrease of ϕ_{CT} with the solvent polarity and if no activation energy is necessary for the formation of ex-CT complex, $a\gamma$ and ϕ_{CT} will not change in a parallel manner. In highly polar solvents electron transfer may perhaps occur, but it may alternatively be possible that the potential energy relations change in such a way that an ex-CT complex quite resembling the solvated ion pair, can be formed without any appreciable activation energy.

Mixed Solvents. The experiments in mixed solvent were undertaken in order to study in more detail the quenching phenomenon and CT emission in less polar solvents. If the quenching process in less polar solvents, requires the reorientation of the solvent molecules as stated above, then it is expected that the addition of a small quantity of a highly polar component to a nonpolar or slightly polar solvent, will reduce the quenching efficiency.

a) 2-DNA - m-DMP in the Mixed Solvent of Ether and Isoamyl Acetate. This system was studied at first to know the behavior of the system in which two components are not so different in polarity. Fixing the concentration of the quencher at 1.47×10^{-1} M, the volume percent of isoamyl acetate was changed by a step of 20%. Figure 10 shows a plot of $\{(F_0/F)-1\}/\alpha_i$ against the volume percent of isopropyl ether. The plot is almost linear. The intensity of CT emission which is quite appreciable in pure ethyl ether decreases with the increasing amyl acetate concentration, and the magnitude of the decrease is larger at lower concentrations.*6

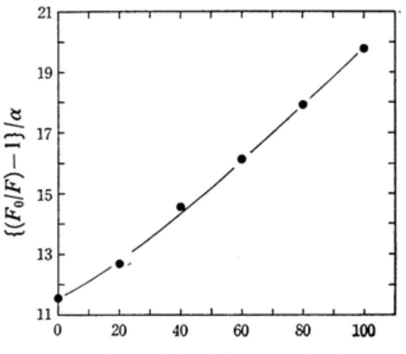

Fig. 10. Dependence of $\{(F_0/F)-1\}/\alpha$ upon the solvent composition (isopropyl ether - isoamyl acetate) for 2-dimethylnaphthylamine (0.99×10^{-4} M) - *m*-DMP (1.37×10^{-1} M).

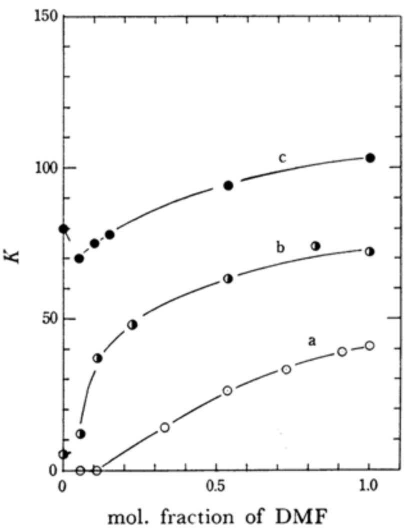

Fig. 11. Dependence of the quenching constant of three quenchers for the fluorescence of 2-dimethylnaphthylamine, upon the solvent composition (benzene-DMF).
quencher; -○- methyl 4-methyl benzoate
-◑- methyl benzoate
-●- dimethyl *m*-phthalate

b) 2-DMNA - p-MT in Benzene-DMF. Quenching constants in the mixed solvents were determined by measuring the fluorescence intensities at two quencher concentrations, 3.63×10^{-3} and 7.26×10^{-3} M. In Fig. 11, Curve a gives a plot of K against the molar fraction of DMF. It is seen that up to 0.1 molar fraction of the quencher, K is practically null and then increases rather rapidly and at high concentrations of DMF, the increase becomes more gradual.

c) 2-DMNA - MB in Benzene-DMF. Measurements were made at 0.2, 0.4 and 2.4 M of the quencher. The plot of K against the molar fraction of DMF is b in Fig. 11. This is similar to that of the previous system. CT emission which is prominent at 2.4 M of the quencher in 5% of DMF, decreases quite rapidly with the increase in the DMF concentration.

d) 2-DMNA - m-DMP in Benzene - DMF. K-Values were obtained from the measurement of the fluorescence intensities at 4.94×10^{-3} and 9.88×10^{-3} M of the quencher. It is apparent from Curve c in Fig. 11 that the K-value which is quite large in pure benzene and in pure DMF, displays a minimum around 0.05 molar fraction of DMF.

e) 2-DMNA in DMF - EB. Figure 12 gives a plot of F_0/F against the concentration of EB. The curve shows a maximum around 5 M of EB. CT emission becomes observable near 3 M of EB and is quite large at 6 M. In pure EB (6.99 M) a clear shoulder of CT emission becomes apparent.

Although the results in mixed solvents are still rather preliminary, it is interesting that some examples have been found in which the quenching process in a nonpolar solvent is suppressed

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*6 Since the peak position of CT emission is very sensitive to the addition of a polar component, quantitative investigation on the intensity of CT emission is very difficult.

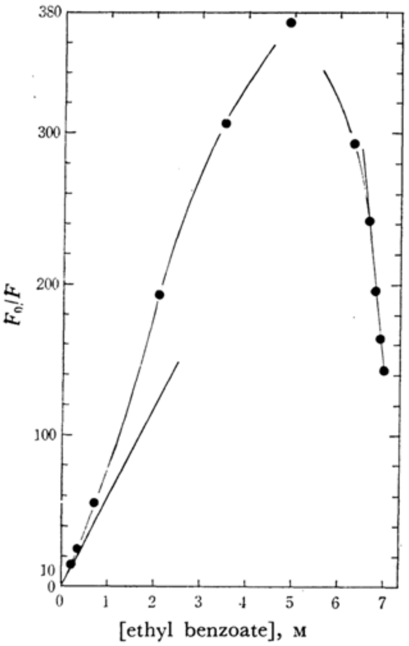

Fig. 12. F_0/F *vs.* [ethyl benzoate] plot for 2-dimethylnaphthylamine - ethyl benzoate.

(ex. d) or is scarcely affected (ex. b and ex. c) by the addition of a small quantity of a highly polar substance. This can be comprehended, if the reorientation of solvent molecules is required for an ex-CT complex to be formed and if the process is accompanied with a potential energy barrier. Large decrease of CT emission caused by a very small quantity of polar compound, also supports this view. The finding in system e, *i. e.* that the addition of a small quantity of DMF causes a great increase in the quenching constant seems to be contradictory to the above view point. But since EB is moderately polar, the formation of separated radical ions might be possible already in EB and this might be greatly enhanced by the addition of DMF. Such systems seem to be worth further studies.

Concluding Remarks

The quenching action of some compounds related with benzoate, on the fluorescence of 2-dimethylnaphthylamine, is intimately connected with a charge transfer interaction. It is most probable that this interaction is a π-π interaction between the naphthalene ring of a fluorescer and the benzene ring of a quencher and that the former acts as a donor and the latter, an acceptor. The spectra of CT emission shift to the longer wavelength with the increasing polarity of the solvent. This implies that an excited CT complex is more stable in more polar solvents. Dimethyl *m*-phthalate was a quencher which gives the most strong CT emission. Choosing this compound as a quencher, solvent effect on the quenching efficiency and the emissivity of CT complex was studied. It was found that in slightly polar solvents from cyclohexane to ether-type compounds, the two quantities depend on the solvent polarity in a similar manner and they both seem to decrease with the increasing polarity of the solvent. This suggests that the reorientation of the solvated molecules is accompanied with the formation of an ex-CT complex. An example in support of this view was found in the experiments involving mixed solvent; the quenching constant of dimethyl *m*-phthalate in a benzene solution is reduced by the addition of a small quantity of dimethylformamide. In highly polar solvents, the quenching efficiency of dimethyl *m*-phthalate increases but the emissivity of CT emission decreases with the polarity. The formation of free radical ions in a highly polar solvent is plausible but not conclusive. Because it is also possible that the interaction between fluorescer and quencher on one hand, and the surrounding solvent molecules on the other, might be in such status that the excited CT complex similar to the solvated ion pair is easily formed which has no emissivity. It must be noted, from the general standpoint, that not only in highly polar but also in slightly polar solvents, the quenching efficiency and the CT emissivity are not necessarily related with each other; because the latter depends not only on the probability of the formation of CT complex but also on the nature of the complex itself. Further studies along the line of the present research will be furitful for the chemistry of excited states and for the study on the solvent effect in general.