

EFFECT OF SOLVENT POLARITY ON THE FLUORESCENCE QUENCHING OF ORGANIC LIQUID SCINTILLATORS BY ANILINE

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Abstract – The fluorescence quenching of 2-phenyl-5-(4-biphenyl)-1,3,4-oxadiazole (PBD) and 1,4-di-[2-(5-phenyloxazolyl)]-benzene (POPOP) by aniline has been carried out in different solvent mixtures of dioxane and acetonitrile at room temperature. The quenching is found to be appreciable and a positive deviation from linearity was observed in the Stern-Volmer plot in all the solvent mixtures. Various rate constants for the quenching processes have been determined using a modified Stern-Volmer equation. From the positive deviations of linear Stern-Volmer plots and the dependence of rate constants on the polarity of the solvents, it has been concluded that both static and dynamic quenching processes are responsible for the observed positive deviation in the Stern -Volmer plot.

Introduction

Fluorescence quenching of organic molecules in solution by various quenchers like aniline, bromobenzene, carbon tetrachloride, ethylenetrithiocarbonate, halide ions, *etc.* has been studied by several investigators.¹⁻⁶ In almost all the cases the experimental results follow the linear Stern-Volmer equation given by:

$$I_0/I = 1 + K_{sv}[Q] \quad (1)$$

Where I_0 and I are the fluorescence intensities in the absence and presence of the quencher, respectively, K_{sv} is the quenching constant equal to $k_q\tau$ in which k_q is the Stern-Volmer quenching rate parameter and τ is the fluorescence lifetime of solute in the absence of the quencher and Q is the quencher concentration. But in a few cases, it has been observed that the experimental results show positive deviation^{1,2,6} from a linear Stern-Volmer relation. This positive deviation was attributed to various processes like singlet-to-triplet excitation, formation of charge transfer complexes both at ground and excited states, static and dynamic quenching, *etc.* Apart from this, the polarity of the solvent medium and the range of quencher concentration are also expected to play a part in this mechanism.

In the present work we have studied the steady state fluorescence quenching of 2-phenyl-5-(4-biphenyl)-1,3,4-oxadiazole (hereafter referred to as PBD) and 1,4-di-[2-(5-phenyloxazolyl)]-benzene (hereafter referred to as POPOP) by aniline at room temperature in different mixtures of dioxane + acetonitrile. The various rate constants responsible for fluorescence quenching mechanisms have been determined using a modified Stern-Volmer equation and in the light of these rate constants the possible quenching mechanisms are discussed.

EXPERIMENTAL DETAILS

PBD and POPOP were obtained from Koch-Light Laboratories Ltd., England. Both are of scintillation grade and thus are used as received. The quencher aniline was obtained from BDH Laboratories, England and was tested for purity before use. The solvents dioxane and acetonitrile (MeCN) were procured from BDH, India and were double distilled before use. The solutions were prepared taking dioxane and MeCN in different proportions by volume with a fixed solute concentration of 0.25 g/L and quencher concentrations were varied from 0.02 to 0.1 mol/L for both the solvents and in each mixture as a particular proportion of solvent. Fluorescence spectrophotometer F-2000 was used for fluorescence intensity measure-

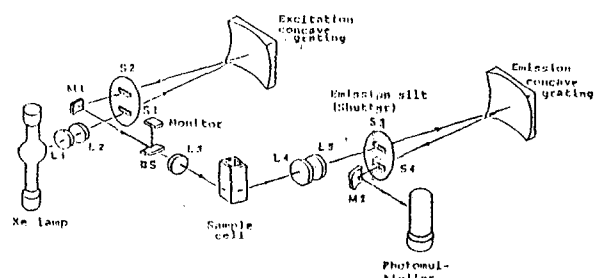


Fig. 1. Optical system configuration of the fluorescence spectrophotometer of the Model F-2000.

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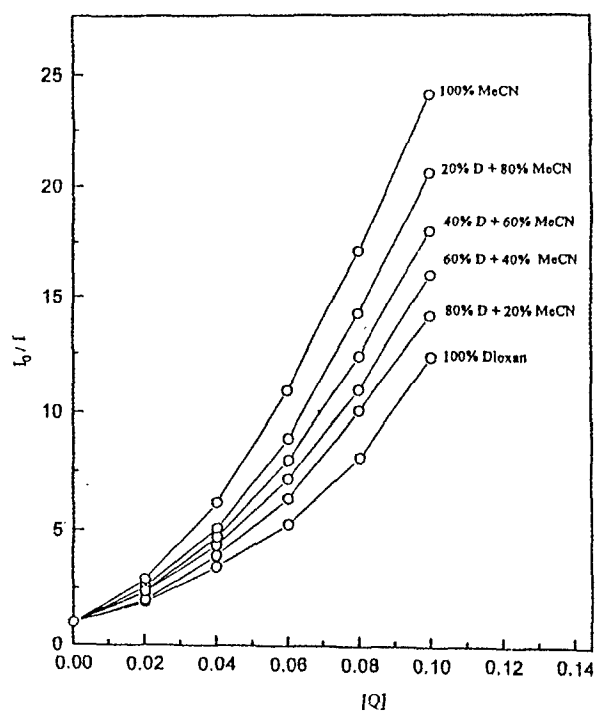


Fig. 2. Stern-Volmer plot of I_0/I against $[Q]$ for PBD in different solvent mixtures of dioxan + MeCN.

ments, with perpendicular geometry as shown in Fig.1 in which two monochromators were used. The radiation coming from the Xe lamp is converged at entrance slit S1 of the excitation monochromator through lenses L1 and L2. Only the light dispersed by the excitation concave grating (excitation beam) enters exit slit S2. The excitation beam from exit slit S2 is reflected by concave mirror M1 and split into two by the beam splitter BS. The one of two excitation beam goes to the monitor detector for its measurement. And, the other beam (most of excitation) passing through BS is converged to the sample cell through lens L3. The fluorescence coming out of the sample is restricted into entrance slit S3 of the emission monochromator through lenses L4 and L5. The fluorescence dispersed by the emission concave grating passes through exit slit S4 and is converged at the photomultiplier *via* concave mirror M2 for intensity measurement. Since no shift in the peak position of the emission spectrum was observed with addition of the quencher in both the cases studied, the fluorescence intensity was determined by measurement of relative intensity at the emission maxima which are found at 361nm and 417 nm for PBD and POPOP, respectively.

RESULTS AND DISCUSSION

First the fluorescence intensity I_0 was measured without the quencher and then the fluorescence intensity I was measured at different quencher concentrations and at a fixed solute concentration in both the compounds. The experimental val-

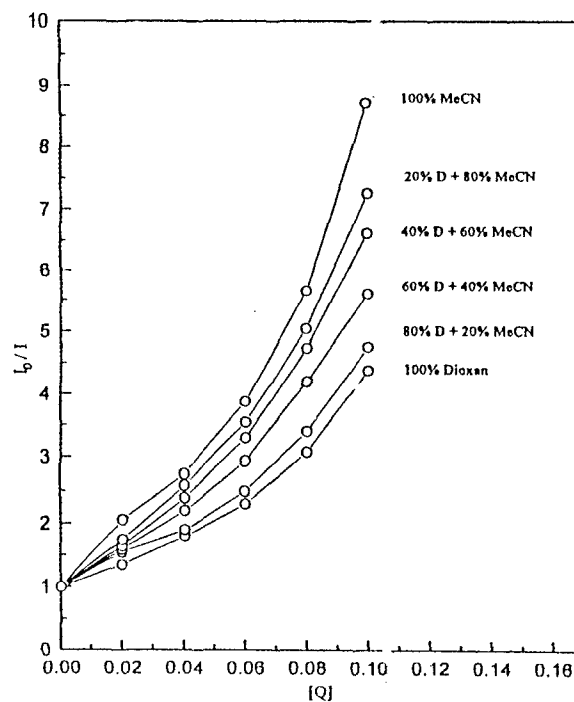


Fig. 3. Stern-Volmer plot of I_0/I against $[Q]$ for POPOP in different solvent mixtures of dioxan + MeCN.

ues are reproducible within 5% of the experimental errors. Then the Stern-Volmer plots were obtained using the experimentally measured values of I_0 and I and were found to be non-linear showing positive curvature for both solutes and are shown in Figs. 2 and 3. Similar experimental results were also observed by others.^{1,7,8} This positive deviation from S-V plots reveals the role of the static quenching process and was explained by the fact that only a certain fraction W of the excited state is actually quenched by the collisional mechanism. Some molecules in the excited state, the fraction of which is $1-W$, are deactivated almost instantaneously after being formed because a quencher molecule happens to be randomly positioned in the proximity at the time the molecules are excited and interacts very strongly with them. Thus the instantaneous or static quenching occurs if the quencher molecule is very near to, or in contact with the fluorescent molecule at the exact moment that it happens to be excited. Several models were employed (Smoluchowski model, Frank and Wawilow model) to describe this static quenching process, all leading to the following modified form of the Stern-Volmer equation²

$$I_0 / I = (1 + K_{sv}[Q]) / W \quad (2)$$

Where K_{sv} is the Stern-Volmer quenching constant or steady state quenching constant, Q is quencher concentration and all other terms have their usual meanings.

The equation for the diffusion controlled quenching reac-

Table 1. The Stern-Volmer quenching constant K_{sv} , fluorescence lifetime τ_0 of solutes and the quenching rate parameter k_q for different solute-quencher systems in different solvent mixtures of dioxan + acetonitrile at room temperature.

Solute	Quencher	Solvent Mixture (%v/v)	Dielectric Constant D	K_{sv} (m^{-1})	$k_q \times 10^{-10}$ ($m^{-1}s^{-1}$)
PBD	Aniline	100% MeCN	36.0	74.75	6.23
		80% MeCN	28.6	62.54	5.21
		60% MeCN	22.0	52.02	4.34
		40% MeCN	15.3	42.50	4.38
		20% MeCN	8.1	36.06	3.01
		100% Dioxan	2.1	32.57	2.71
POPOP	Aniline	100% MeCN	36.0	44.30	2.95
		80% MeCN	28.6	30.19	2.01
		60% MeCN	22.0	24.32	1.62
		40% MeCN	15.3	18.35	1.54
		20% MeCN	8.1	21.00	1.40
		100% Dioxan	2.1	10.43	0.70

τ_0 of PBD = 1.2 ns

τ_0 of POPOP = 1.5 ns

tion, formulated by Smoluchowski, contains an often neglected transient term:

$$K = \frac{4\pi N'RD}{(\text{Steady state term})} + \frac{4R^2(\pi D)^{1/2} t^{-1/2}}{(\text{transient term})} \quad (3)$$

Where N' is Avogadro's number per millimole, R is the encounter distance, *i.e.*, the sum of the radii of the solute and the quencher molecules, D is the sum of the diffusion coefficients of the solute and quencher molecules and t is the time. An additional factor W appears in the Stern-Volmer equation [equation (2) above] due to the retention of transient term and W is approximately equal to $\exp[-V(Q)]$, where V is the static quenching constant.

According to Frank and Wavilov² instantaneous quenching occurs at these instances in a randomly distributed system when a quencher happens to reside within a "sphere of action" with a volume of V/N' and radius r , *i.e.*, $V/N' = 4\pi r^3/3$ surrounding a solute molecule at the time of excitation. In this case also W is given by $\exp[-V(Q)]$.

Because the fraction W depends on the quencher concentration Q in both the cases as mentioned above, the Stern-Volmer plots for a quencher with high quenching ability generally deviate from a linear plot. Thus it is worth rewriting equation (2) as:

$$[1-(I/I_0)]/Q = K_{sv} (I/I_0) + (1-W)/Q \quad (4)$$

It is meaningful to calculate the value of $[1-(I/I_0)]/Q$ from equation (4) to gather more information because the plot of $[1-(I/I_0)]/Q$ against I/I_0 becomes linear, the slope of which is K_{sv} , and the intercept is $(1-W)/Q$ and this in turn equals V .

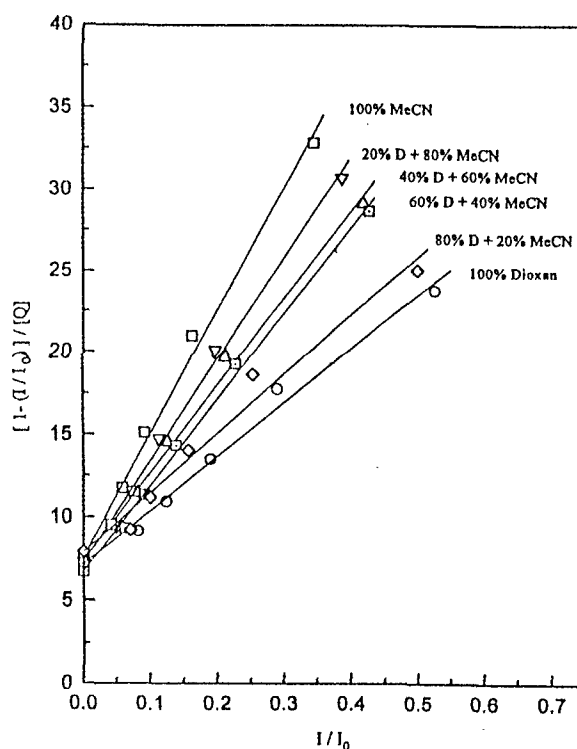


Fig. 4. Stern-Volmer plot of $[1-(I/I_0)]/Q$ against I/I_0 for PBD in different solvent mixtures of dioxan + MeCN.

Figs. 4 and 5 show plots of $[1-(I/I_0)]/Q$ against I/I_0 for PBD and POPOP, respectively, with aniline as quencher. The Stern-Volmer quenching constant (or steady-state quenching constant) K_{sv} is determined in both cases by the least square fit method using equation (4) and the values are tabulated in Table 1. Fluorescence lifetimes (τ) of both the solutes studied were taken from literature and are given in Table 1. The quenching rate parameter k_q was determined from the experimentally determined values of K_{sv} and τ according to the relation $k_q = K_{sv}/\tau$ and the values are given in Table 1.

As is evident from Figs 4 and 5 the intercepts are large and their values increase with an increase in dielectric constant of the medium. This intercept being equal to $(1-W)/Q$, the values of W were determined and the range of W values are given in Table 2. The static quenching constant V was determined by the least square fit method using the equation:

$$W = e^{-V(Q)} \quad (5)$$

and the kinetic distance, *i.e.*, the radius r of the "sphere of action" was determined using the calculated values of V according to the equation:

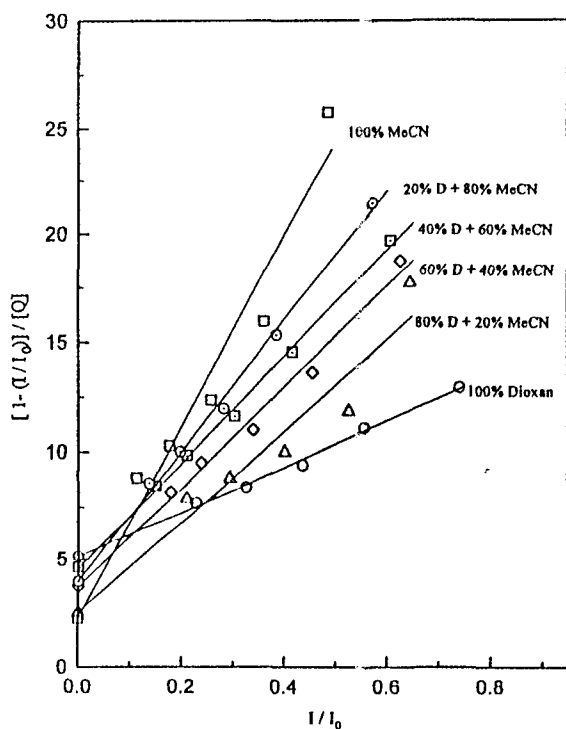
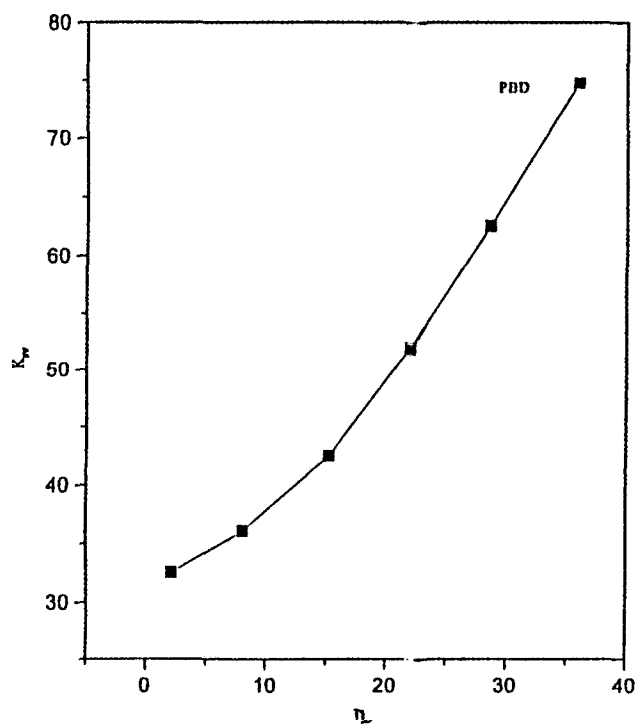
$$V/N' = 4\pi r^3/3 \quad (6)$$

From Fig. 2 it is observed that there is a regular but slightly non-linear increase in quenching with increasing solvent

Table 2. Intercept, range of W, static quenching constant V and kinetic distance r of different solvent mixtures of dioxan + acetonitrile at room temperature.

Solute	Quencher	Solvent mixture	Intercept	Range of W	V(mol ⁻¹ dm ³)	r (Å)
PBD	Aniline	100% MeCN	7.69	0.231 - 0.846	15.92	18.50
		80% MeCN	7.22	0.278 - 0.856	13.85	17.64
		60% MeCN	7.62	0.238 - 0.848	15.65	18.37
		40% MeCN	6.71	0.329 - 0.866	11.99	16.81
		20% MeCN	7.92	0.208 - 0.842	17.07	18.91
		100% Dioxan	7.19	0.281 - 0.856	13.65	17.56
POPOP	Aniline	100% MeCN	2.26	0.773 - 0.955	2.60	10.10
		80% MeCN	3.97	0.603 - 0.921	5.25	12.77
		60% MeCN	4.64	0.536 - 0.907	6.50	13.71
		40% MeCN	3.75	0.625 - 0.925	4.92	12.49
		20% MeCN	2.55	0.745 - 0.949	8.00	14.69
		100% Dioxan	5.16	0.484 - 0.897	7.72	14.52

$$R_y(\text{PBD}) = 4.06 \text{ \AA}, \quad R_y(\text{POPOP}) = 4.32 \text{ \AA}, \quad R_Q(\text{Aniline}) = 2.84 \text{ \AA}$$

Fig. 5. Stern-Volmer plot of $[1-I/I_0]/[Q]$ against I/I_0 for POPOP in different solvent mixtures of Dioxan + MeCNFig. 6. Variation of K_{sv} as a function of Dielectric constant D for the solute PBD.

polarity, *i.e.*, dielectric constant and the non-linearity is maximum in 100% MeCN [the literature values⁷ (Behera and Mishra, 1993) of the dielectric constant for various mixtures of the solvents at different proportions by volume are given in Table 1]. Further, from Figs. 6 and 7 we see that the variation in K_{sv} with dielectric constant is non-linear. The non-linear variations in K_{sv} with dielectric constant in Figs. 6 and 7 are due to the combined effect of the static quenching constant V and the Stern-Volmer quenching constant K_{sv} . It is

seen from Tables 1 and 2 that the values of K_{sv} are rather large compared with V in all the solvent mixtures, which explains the lack of absorption spectral change on addition of the quencher.⁷

The radii of the solute and quencher molecules were determined by adding the atomic volumes of all the atoms constituting the molecule as suggested by Edward (1956)⁹ and are given at the bottom of Table 2. From Table 2 we see that the sum of the radii of the solute and quencher for PBD is 6.9 Å

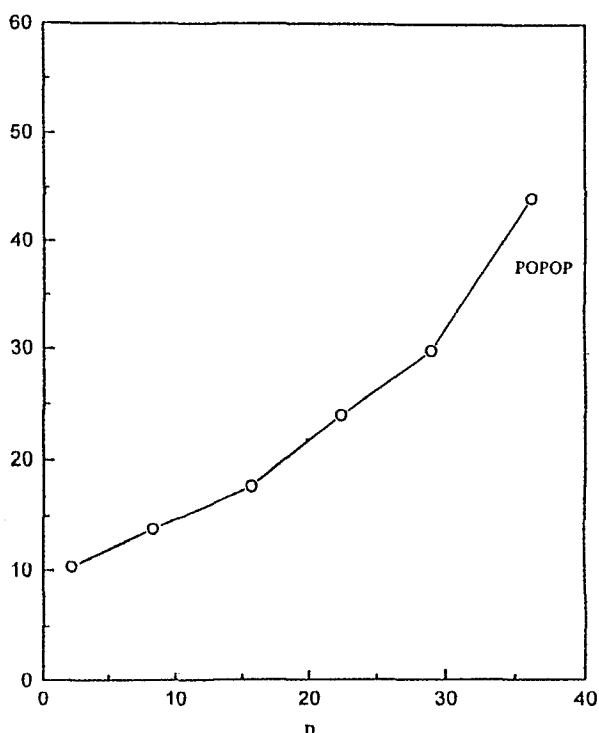


Fig. 7. Variation of K_{sv} as a function of Dielectric constant D for the solute POPOP.

and for POPOP is 7.16 \AA and the values of r are 1.5 to 2.5 times greater than the sum of the radii of the solute and the quencher. Similar results were obtained by others.¹⁰⁻¹² Further, we see from Tables 1 and 2 that the values of kinetic distance r are dependent on the polarity of the solvent medium and their values increase in polarity.

According to Andre *et al.*⁸ if the distance between the quencher molecule and excited molecule lies between the encounter distance (*i.e.* the sum of radii of the solute and quencher) and the kinetic distance, the static effect takes place especially in the case of steady state experiments, irrespective of ground state complex formation provided the reactions are limited by diffusion. Further, it may also be noted that a positive deviation in the S-V plot is expected when both static and dynamic quenching occurs simultaneously.^{2,7}

From the foregoing discussion we see that all the rate constants are dependent on the solvent polarity and thus the reactions are limited by diffusion. Further a positive deviation in the S-V plot is likely when both static and dynamic quenching occur simultaneously. In the light of these facts we may conclude that both static and dynamic quenching processes are responsible for observed positive deviation in the S-V plots leading to the high k_q values presented in Table 1.

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