Fluorescence quenching of 5-methyl-3-phenyl-2-[s-oxadiazol-2'-thione- 5'-yl] indole by CCl₄ and aniline in different solvents

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The fluorescence quenching of 5-methyl-3-phenyl-2-[s-oxadiazol-2'-thioneñ5'-yl] indole by carbon tetrachloride (CCl₄) and aniline in different solvents viz., dioxane, benzene, toluene, methanol, propanol has been carried out at room temperature to understand the role of quenching mechanisms. The Stern-Volmer plots have been found to be linear. As probability of quenching per encounter 'p' is less than unity, and the activation energy for quenching 'E_a' is greater than the activation energy of diffusion 'E_d', it is inferred that the fluorescence of quenching mechanism is not due to material diffusion alone.

key words : Indole, Fluorescence, Quenching, Stern-Volmer plot, Activation energy, Material diffusion

INTRODUCTION

Fluorescence quenching is a process, which decreases the fluorescence intensity of a sample by a variety of molecular interactions such as excited-state reactions, molecular rearrangements, energy transfer, ground-state complex formation, and collisional quenching. Fluorescence quenching of organic molecules including indole and its derivatives in solution by various quenchers like carbon tetrachloride (CCl₄), aniline, bromo benzene, halide ions, etc., has been studied by several investigators.[1-12] In many cases the experimental results show the linear Stern-Volmer equation and it is given by [5]

$$\frac{F_0}{F} = 1 + k_q \tau_0 [Q] \tag{1}$$

and $$\frac{\tau_0}{\tau} = 1 + k_q' \tau_0 [Q] \tag{2}$$

where F_0 and τ_0 are the fluorescence intensity and fluorescence lifetime, F and τ are the fluorescence intensity and fluorescence lifetime respectively in the absence and presence of the quencher at a concentration [Q], and $k_q(k_q')$ is the quenching rate parameter. The term $k_q \tau_0$ ($k_q' \tau_0$) is called the Stern-Volmer constant K_{SV}, which is obtained from the slope of Stern-Volmer plot.

The quenching phenomena can be understood due to short-range collision between the excited and the quencher molecules [5,6]. If the close collision between the excited molecule and quencher molecule to occur, the two reactants should occupy the contiguous position in the solution and separated due to diffusion after the collisional encounter. In solutions, the reactants before separating due to diffusion undergo numerous mutual collisions of which each series represents an encounter. The probability of quenching per encounter is symbolically represented by 'p', which is less than unity and the frequency of encounter is represented by K_0. The quenching rate parameter k_q is then given by

$$k_q = K_0 p \tag{3}$$

The theoretical equation for the bimolecular reactions controlled by material diffusion is given by

$$K_0 = \frac{4\pi NDR}{1000}\left\{1 + R(2D\tau_0)^{\frac{1}{2}}\right\} \tag{4}$$

where N is the Avogadro's number, D ($=D_S+D_Q$) and R ($=R_S+R_Q$) represents the sum of the diffusion coefficients and the sum of the molecular radii of the solute and the quencher respectively. The degree to which material diffusion controls the quenching and also efficiency of quenching can be determined by comparing the values of K_0 with k_q. If dynamic quenching alone is operative without any static quenching, then K_{SV} values (slope of the S-V plot) obtained from equations (1) and (2) should be identical.

In the present work, we have studied the steady state fluorescence quenching of newly synthesized indole derivative 5-methyl-3-phenyl-2-[s-oxadiazol-2'-thione-5'-yl] indole at room temperature using CCl₄ and aniline as quenchers in dioxane, benzene, toluene, methanol, propanol solvents; and by transient method in toluene solvent with both quenchers to understand the nature of quenching mechanism.

EXPERIMENTAL

The solute, 5-methyl-3-phenyl-2-[s-oxadiazol-2'-thione-5'-yl] indole was synthesized in our laboratory using standard methods and its molecular structure is shown in Fig. 1. The spectroscopic grade solvents (s.d. Fine Chemicals Ltd.) were used without further purification to prepare the solutions. However, the purity of the solvents was checked by the background fluorescence. Spectroscopic grade CCl_4 and aniline solvents were used as quenchers. The steady state fluorescence spectra were recorded at a fixed solute concentration in different solvents by varying the quencher concentration from 0.00 to 0.10 mol dm^{-3} with fluorescence spectrophotometer of Hitachi Model F-2000.

The fluorescence decay measurement of the solute were recorded in the absence and presence of quenchers in Toluene solvent using time correlated single photon counting technique (TCSPC) Model 5000U, IBH, UK with micro channel plate photo multiplier tube (MCP-PMT) as detector and pico-second laser as the excitation source.
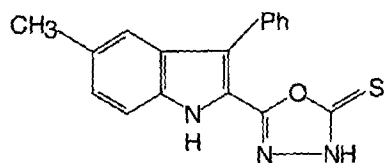
RESULTS AND DISCUSSION

The fluorescence intensities F_0 and F were measured without and with quencher respectively at different quencher concentrations and at a fixed solute concentration for both quenchers. The Stern-Volmer plots F_0/F versus [Q] in different solvents are shown in Fig. 2 and 3 for CCl_4 and aniline respectively, and they are found to be linear with intercept equal to unity. Further, the fluorescence lifetimes τ_0 and τ were measured without and with quencher for the solute in toluene solvent. The total fluorescence decay was bi-exponential and it is observed that τ_1 is less than τ_2. However, τ_1 value cannot be neglected in view of its relative amplitude contribution. Hence, we considered the average values for studying the quenching phenomena. The measured lifetime values are comparable with the lifetime values of the other indole derivatives.[6] The typical fluorescence decay profiles in toluene solvent with aniline quencher are shown in Fig. 4. The S-V plots τ_0/τ versus [Q] using equation (2) in Toluene

Figure 1. Molecular structure of 5-methyl-3-phenyl-2-[s-oxadiazol-2'-thione-5'-yl] indole.
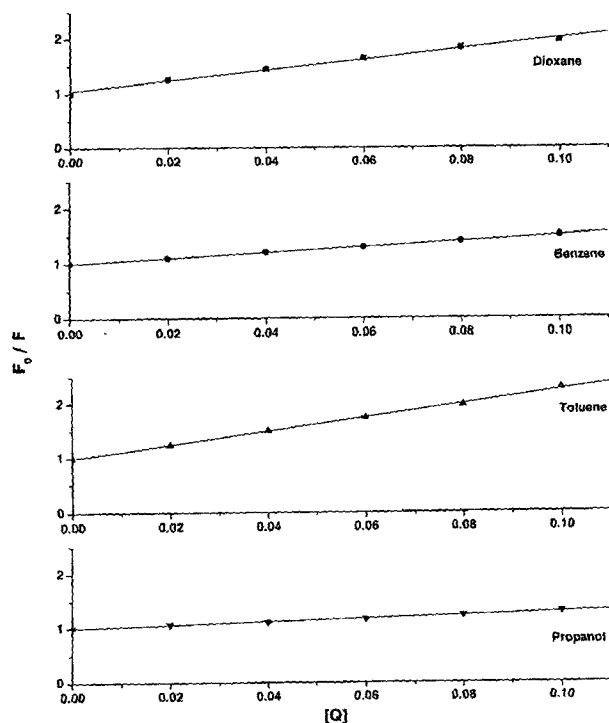
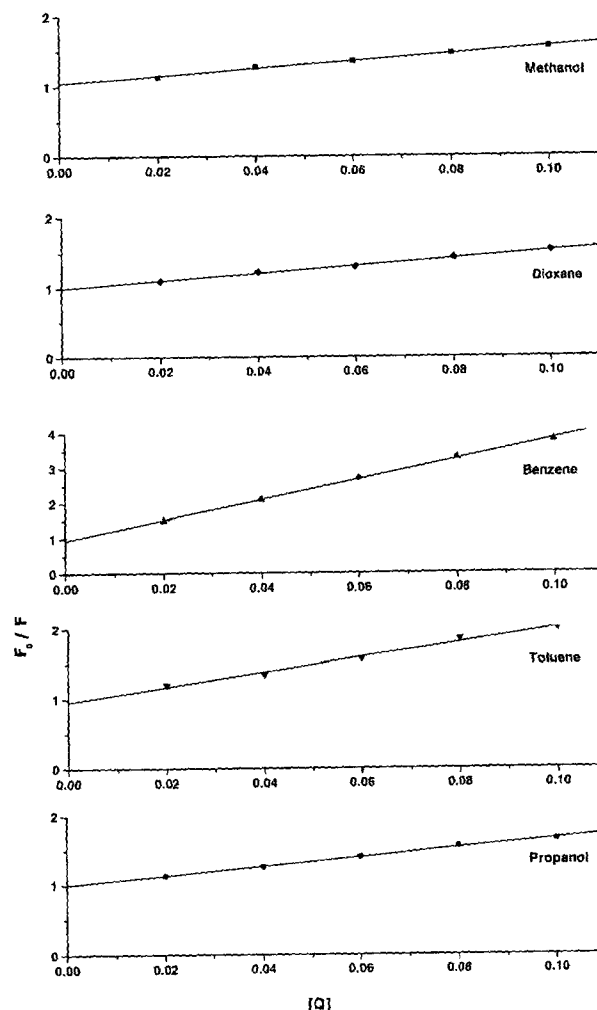Figure 2. Stern - Volmer plots of F_0 / F against [Q] in different solvents with CCl_4.

Figure 3. Stern - Volmer plots of F_0 / F against [Q] in different solvents with Aniline.
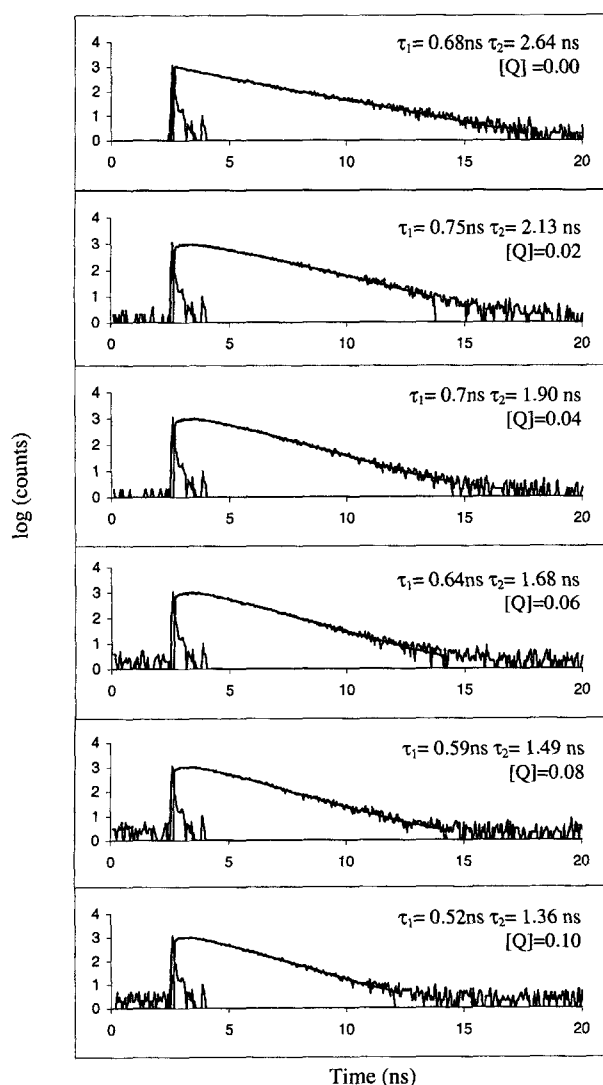
Figure 4. Fluorescence decay in Toluene with Aniline quencher.

Figure 5. Stern ñ Volmer plot of τ_0 / τ against [Q] in Toluene solvent with CCl_4 and Aniline.

solvent were plotted and they are also found to be linear for both quenchers as shown in Fig. 5. This clearly shows that the phenomenon of quenching follows S-V relation. Using least-squares fit method, the slopes, $k_q\tau_0$ ($=K_{SV}$) for steady state

measurements using equation (1) were determined in each solvent medium for both the quenchers. Similarly, for transient method, the slopes from least-squares fit method equal to $k_q'\tau_0$ ($=K_{SV}'$) were determined from equation (2). The quenching rate parameter $k_q(k_q')$ was determined for all the solvents and for both the quenchers using the relation $k_q = K_{SV}/\tau_0$. The values of K_{SV} and $k_q(k_q')$ are presented in Table 1 and 2. (Here we assumed the τ_0 value is same for all the solvents[6]). The rate constant K_0 of the bimolecular reactions controlled purely by material diffusion can be calculated according the equation (4) using the numerical values of the sum of the diffusion coefficients ($=D_S+D_Q$) and the sum of the molecular radii (R_S+R_Q) of the solute and quencher respectively. The diffusion co-efficient of solute D_S and quencher D_Q can be calculated by using Stokes-Einstein equation

$$D = \frac{kT}{a\pi\eta R} \tag{5}$$

Table 1. Values of S-V constant K_{SV}, quenching rate parameter k_q, diffusion rate parameter K_0, probability per encounter p, activation energy for quenching E_a and diffusion E_d in different solvents with CCl_4.

Solvent	$\eta^{-1} \times 10^{-2}$ p^{-1}	K_{SV} M^{-1}	$k_q=K_{SV}/\tau_0\times 10^{-9}$ $M^{-1}s^{-1}$	$K_0\times 10^{-10}$ $M^{-1}s^{-1}$	p	E_d kcal mol^{-1}	E_a kcal mol^{-1}
Dioxane	0.83	8.95	5.39	1.15	0.47	3.06	3.13
Benzene	1.68	4.99	3.00	2.20	0.14	3.00	4.09
Toluene	1.81	12.75 *7.83	7.71 4.72	2.34	0.33 0.20	2.66	3.08 3.58
Propanol	2.25	3.05	1.84	2.54	0.07	--	--

*Data determined from lifetime measurement.

Radius of the Solute R_S = 3.94 Å   Radius of CCl_4 R_Q = 2.80 Å

Table 2. Values of S-V constant K_{SV}, quenching rate parameter k_q, diffusion rate parameter K_0, probability per encounter p, activation energy for quenching E_a and diffusion E_d in different solvents with Aniline

Solvent	$\eta^{-1} \times 10^{-2}$ p^{-1}	K_{SV} M^{-1}	$k_q = K_{SV}/\tau_0 \times 10^{-9}$ $M^{-1}s^{-1}$	$K_0 \times 10^{-10}$ $M^{-1}s^{-1}$	p	E_d kcal mol^{-1}	E_a kcal mol^{-1}
Methanol	0.54	5.15	3.10	0.80	0.39	-	-
Dioxane	0.83	5.22	3.13	1.16	0.27	3.06	3.66
Benzene	1.68	28.74	17.31	2.19	0.79	3.00	2.20
Toluene	1.81	10.22	6.14	2.33	0.26	2.66	3.27
		*5.95	3.58		0.15		3.68
Propanol	2.25	6.65	4.00	2.86	0.14	-	-

Radius of the Solute $R_S = 3.94$ Å   Radius of Aniline $R_Q = 2.84$ Å

where k is the Boltzman's constant, T - the absolute temperature, η - the viscosity of the solvent, R - the radius of the solute or quencher as the case may be, and a - the Stokes-Einstein number. In the present case, the radius of the solute molecule is larger than the solvent molecule, and that of the quencher molecule is close to the solvent molecule. Hence, we have taken a=3 for quencher and a=6 for the solute[6,8,14]. The radius of the solute R_S and quencher R_Q have been calculated as suggested by Edward[13] and the values are given at the bottom of the Table 1 and 2.

Further, the probability of quenching per encounter ëpí has been determined according to equation (3) and the values are tabulated in Tables 1 and 2. Similarly, the experimentally determined values of k_q' from the lifetime measurements for the solute in toluene, the respective value of K_0 and the probability of quenching per encounter $p' = (k_q'/K_o)$ has been determined in both quenchers and are tabulated in Tables 1 and 2. It is observed that the values of p are less than unity for all the solvents confirming that the quenching is only due to close collision between solute and quencher molecules. Therefore, the reactions of quenching is not solely controlled by material diffusion in which p=1.

Further, from Fig. 6 and 7 it is observed that although the frequency of collisional encounter K_0 increases with decrease in viscosity of the solvents, the quenching rate parameter k_q does not depend on the viscosity of the solvent. Hence, it is inferred that the phenomenon of quenching is not solely controlled by material diffusion. If so, the values of k_q would have been equal to K_0 and hence p is equal to unity in all the cases. Therefore, in addition to diffusion it may also depend on the activation process.

The activation energies for quenching reaction E_a in accordance with the equation

$$E_a = E_d + RT \ln \left(\frac{1}{p} - 1 \right) \qquad (6)$$

have been calculated for both the quenchers using experimentally determined values of p along with the literature values of E_d and the gas constant R. The values are shown in the Table1 and 2.
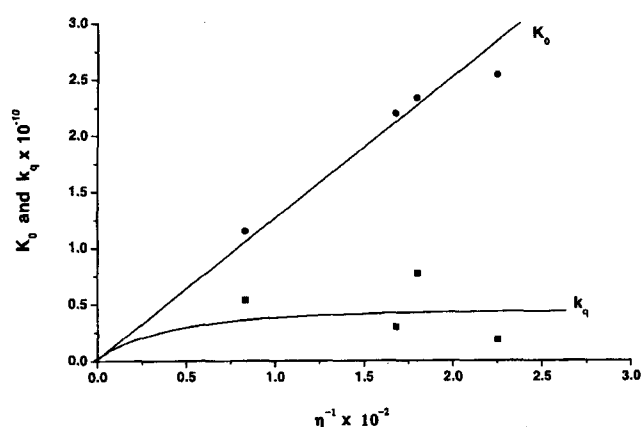
Figure 6. Variation of k_q and K_0 as a function of inverse viscosity $(\eta^{-1} \times 10^{-2})$ of the solvents with CCl_4.
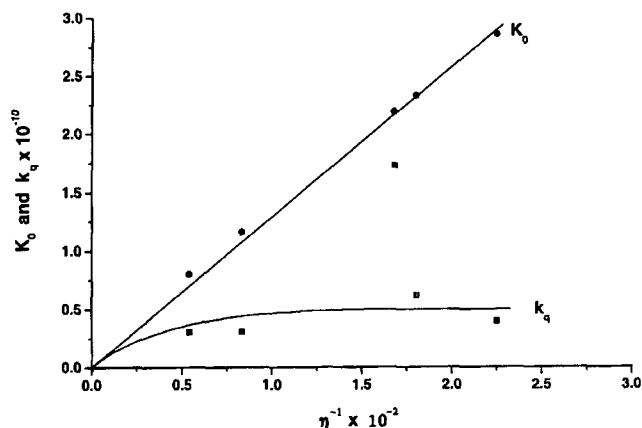
Figure 7. Variation of k_q and K_0 as a function of inverse of viscosity $(\eta^{-1} \times 10^{-2})$ of the solvents with Aniline.

From these data, it is observed that the activation energy (E_a) for quenching is consistently larger than activation energy for diffusion (E_d). But, the value of E_d is greater than E_a in benzene with aniline quencher, a fact that was observed by others for different organic molecules[6-8]. This is due to the role played by p in equation (6), i.e. the value of E_a turns out to be smaller than E_d for values of p > 0.5. Therefore, even if

the values of p are less than unity, we cannot ignore the role played by material diffusion if p is greater than 0.5. But for the remaining solvents, E_a values are greater than E_d. This proves that the quenching reaction is not controlled by material diffusion alone and may also be governed by activation process. Further, this molecule has shown positive deviation in methanol solvent with CCl_4 and the detailed study is in progress.

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