Fluorescence Quenching of Bis-msb by Carbon Tetrachloride in Different Solvents

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Fluorescence quenching of 1,4-bis [2-(2-methylphenyl) ethenyl]-benzene (Bis-MSB) by carbon tetrachloride in five different solvents namely hexane, cyclohexane, toluene, benzene and dioxane has been carried out at room temperature with a view to understand the quenching mechanisms. The Stern-Volmer plot has been found to be non-linear with a positive deviation for all the solvents studied. In order to interpret these results we have invoked the Ground state complex and Sphere of action static quenching models. Using these models various rate parameters have been determined. The magnitudes of these parameters imply that sphere of action static quenching model agrees well with the experimental results. Hence the positive deviation in the Stern-Volmer plots is attributed to the static and dynamic quenching. Further, with the use of Finite Sink approximation model, it was possible to check whether these bimolecular reactions as diffusion limited and to estimate independently distance parameter R' and mutual diffusion coefficient D. Finally an effort has been made to correlate the values of R' and D with the values of the encounter distance R and the mutual diffusion coefficient D determined using the Edwardís empirical relation and Stokes-Einstein relation.

key words: Fluorescence quenching, BIS-MSB, solvent effect, Finite sink approximation, model, Sphere of action static quenching model

INTRODUCTION

Fluorescence quenching of organic molecules in solution by various quenchers like aniline, bromobenzene, carbon tetra chloride, eththyltrithiocarbonate, halide ions, metal ions etc. has been studied by several investigators[1-11]. The study has been mainly to understand the nature of bimolecular reactions taking place both under steady state and transient conditions. This study has not only been of importance in physical sciences but also in chemical, biological and medical sciences[12-18]. The fluorescence yield in bimolecular liquid systems is hindered due to several mechanisms such as static and dynamic quenching, excimer and exciplex formation, charge transfer processes, etc. One of the well known experimental techniques used to study the role of fluorescence quenching is to determine the quenching rate parameter using Stern-Volmer (S-V) plots. If the quenching mechanism is mainly due to dynamic process, then it will be largely due to diffusion in which case diffusion rate parameter k_d equals the quenching rate parameter $k_q(=K_{sv}/\tau)$ where K_{sv} is the slope of the linear S-V plot and τ is the decay time of the solute in the absence of the quencher. On the other hand, if the experimental

results do not simulate with the simple linear S-V equation, then it may be due to one of the above processes other than or along with diffusion processes.

In the present study we have used steady state experimental setup to investigate the quenching of 1,4-bis [2-(2-methylphenyl) ethenyl]-benzene (Bis-MSB) by carbon tetra chloride (CCl₄) in five different organic solvents with a view to understand the nature of quenching mechanism involved in these systems.

THEORY

The dynamic process in which quenching mechanism is mainly due to collision is governed by the linear S-V equation

$$\frac{I_0}{I} = 1 + K_{sv}[Q] \tag{1}$$

where I_0 is the fluorescence intensity of the solute in the absence of quencher, I is the fluorescence intensity in the presence of quencher, K_{sv} (= $k_q\tau$, k_q is quenching rate parameter) is the S-V constant and τ is the life time of the solute molecule in the absence of quencher. Equation (1) is applicable as long as the experimental results show linear variation. The departure from linearity in S-V plot, suggests that quenching mechanism is not purely collisional and this may be attributed either to the ground state complex formation or to the sphere of action static quenching model[7].

In order to see whether the ground state complex formation is partly playing a role, one can use extended S-V equation [19, 20] given by

$$[(I_o/I) - 1]/[Q] = (K_{sv} + k_g) + (K_{sv}k_g)[Q] \tag{2}$$

where K_{sv} and k_g are S-V and ground state association constants respectively. From equation (2), the values of K_{sv} and k_g can easily be determined by least square fit method.

The ground state complex formation takes place if quenching constant k_q (= K_{sv}/τ) obtained from equation (2) agrees well with that obtained from the lower portions of the plot according to equation (1) i.e in the low concentration region in the plot of I_o/I against [Q], which is linear. In that case static quenching is very low. Apart from this the ground state complex formation may be noticed if there is a change in the absorption and fluorescence spectra even at higher concentrations of quencher.

In order to see whether static quenching process is playing a role, one can use "Sphere of action static quenching model". According to this model 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 it happens to be excited. This 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 de-activated 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. Several models were employed (Smoluchowski model)[21, 22] to describe this static quenching process, all leading to the following modified form of the S-V equation.

$$(I_o/I) = \frac{1 + K_{sv}[Q]}{W} \tag{3}$$

where K_{sv} has its usual meaning as explained earlier and [Q] is the quencher concentration. The Smoluchowski's diffusion controlled equation containing transient term is given by

$$K_d = 4\pi N'RD + 4R^2N'(\pi D)^{1/2}t^{-1/2} \tag{4}$$

where N' is the Avogadroís number per millimole, R is the encounter distance i.e. the sum of the radii of the solute and quencher molecules and t is the time. The retention of the later term of Eq. (4) leads to an additional factor, W in Eq. (3). This additional factor W is given by

$$W = e^{-V[Q]} \tag{5}$$
$$\ln(1/W) = V[Q]$$

where V is the static quenching constant and it represents an active volume element surrounding the excited solute

molecule.

Instantaneous (static) quenching occurs in a randomly distributed system when a quencher happens to reside within a sphere of action with a volume 'V/N' and radius 'r' i.e

$$V/N' = (4\pi r^3)/3 \tag{6}$$

surrounding a solute molecule at the time of excitation.

As W depends on the quencher concentration [Q] the S-V plots for a quencher with a high quenching ability generally deviate from linearity. Thus it is worth rewriting Eq. (3) as

$$[1 - (I/I_o)]/[Q] = K_{sv}(I/I_o) + (1 - W)[Q] \tag{7}$$

From equation (7) one can easily calculate K_{sv} and the values of W by least square fit method. The static quenching constant V and the values of 'r' of sphere of action can also be calculated using equations (5), (6) and (7). According to Andre et al. and Zeng et al.[20, 24], if the distance between the quencher molecule and the excited molecule lies between the encounter distance and the kinetic distance, the static effect takes place especially in the case of steady state experiments irrespective of ground state complex formation provided reactions are limited by diffusion. In order to find whether the reactions are diffusion limited one can invoke the Finite Sink Approximation Model.

Finite Sink Approximation Model

Keizer[25-27] has proposed a nonequilibrium statistical modification of the Smoluchowski-Collins-Kimball (SCK) expression to fit the I_o/I ratio in fluorescence quenching.

In the case of SCK model time dependent rate coefficient k(t) for diffusion-limited reactions is given by[28]

$$k(t) = a + b\exp(c^2t)erfc(ct^{1/2}) \tag{8}$$

where

$$a = k_a\left[1 + \frac{k_a}{4\pi N'RD}\right]^{-1} \tag{9}$$

$$b = k_a\left[1 + \frac{4\pi N'RD}{k_a}\right]^{-1} \tag{10}$$

$$c = \left[1 + \frac{k_a}{4\pi N'RD}\right]\frac{D^{1/2}}{R} \tag{11}$$

Integration of Eq. (8) between the limits [Q] (8) at r → ∞ and [Q] [R] at r = R provides the well known expression

$$1/k_d = (1/k_q) + (1/k_a) \tag{12}$$

where $k_d = 4\pi N'DR$ and k_a is the activation energy controlled rate constant describing the reaction of encountered pairs at a

reactive distance R and D is the sum of the diffusion coefficients of the solute and quencher molecules. Following this expression, k_q is independent of [Q]. But for efficient quenching process in liquids, k_q is often observed to increase with [Q]. This might be attributed as discussed above to static quenching of solute molecule, in the vicinity of [Q], transient effects arising from an initial time dependence of the concentration gradient or combination of them[20].

But if one assumes that only the first encounter is of interest in the case of efficient fluorescence quenching an initial average separation distance r_0 can be defined (sink radius) so that the diffusive region of interest for a first encounter is in the range $R \leq r \leq r_0$ such that all subsequent encounters are eliminated. Integration of the flux equation between the limits $[Q](r_0)$ at r_0 and [Q] (R) at R leads to modification of expression (12) as

$$\frac{1}{k_q} = \frac{1 - (R/r_o)}{k_d} + \frac{1}{k_a} \tag{13}$$

This equation reduces to the reaction limited form ($k_q = k_a$) both for inefficient quenching ($k_a \ll k_d$) and for quenching in pure quenching solvents where $R = r_0$. In the diffusion controlled limit ($k_a \gg k_d$) Eq. (13) reduces to

$$k_q = \frac{k_d}{1 - R/r_o} \tag{14}$$

and k_q depends on the quenching concentration through r_0. Since the sink radius (r_0) is identified to the most probable nearest neighbour initial separation, the appropriate distribution requires that[26] $r_o = (2\pi N'[Q])^{-1/3}$. Replacing r_0 in Eq. (13) and k_d by its value ($4\pi N'DR$) and dividing everywhere by the fluorescence lifetime of solute in the absence of quencher (τ) one obtains the modified S-V relationship as[20].

$$K_{sv}^{-1} = (K_{sv}^{o}) - \frac{(2\pi N')^{1/3}}{4\pi N'D\tau}[Q]^{1/3} \tag{15}$$

where A plot of $K_{sv}^{-1} = \frac{4\pi N'DR\tau k_a}{4\pi N'DR + k_a}$ against $[Q]^{1/3}$ becomes

linear with negative slope. Mutual diffusion coefficient D becomes directly accessible from the slope of the graph exemplified in Eq. (15) and K_{sv} is obtained at [Q] = 0 regardless of the relative magnitudes of k_a and k_d ($=4\pi N'DR$), irrespective of quenching is diffusion limited or not. From K_{sv} we only have access to R' which is a composite of R and k_a through Eq. (16).

$$K_{sv} = 4\pi N'DR'\tau \tag{16}$$

where R' is the distance parameter and has the same meaning as in the long-time SCK model[20, 28] and is given as

$$R' = R[1 + 4\pi RDN'/k_a]^{-1} \tag{17}$$

Then according to the theory discussed above if k_a is greater than k_d (i.e Eq.12) then the reactions are said to be diffusion limited[20] (i.e. for R'<R). But for R'>R, the bimolecular reactions of fluorescence quenching are said to be diffusion limited[28] if the values of k_q determined from Eq.(7) are greater than 4π N'R'D.

MATERIALS AND METHODS

The solute 1,4-bis[2-(2-methylphenyl) ethenyl]-benzene (Bis-MSB) was obtained from Sigma –Aldrich, USA and is of scintillation grade. The quencher CCl_4 and all solvents were of spectroscopic grade and were used without any further purification. The solutions were prepared keeping the concentration of Bis-MSB fixed ($5 \times 10^{-6} M/L$) and varying the quencher concentration ($0.02M$ to $0.10M$) in all the solvents. Fluorescence spectrophotometer F-2000 was used for fluorescence intensity measurements, with perpendicular geometry. Description of the experimental setup is discussed elsewhere[11]. Fluorescence measurements were made by taking fresh solution each time in a rectangular quartz cell having an airtight stopper. The solute has maximum absorption at 350 nm. The solute was excited at 350 nm and the fluorescence spectrum was recorded. The maximum fluorescence corresponds to 420 nm. 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. The experimental values are reproducible within 5% of the experimental error.

RESULTS AND DISCUSSION

The S-V plots obtained by using the experimentally determined values of I_0 and I are found to be nonlinear in all the solvents showing positive deviation and are shown in Fig. 1. Similar experimental results were also observed by others[1,6]. Thus, positive deviation from linearity suggests that quenching is not purely collisional and this may be attributed either to the ground state complex formation or to the sphere of action static quenching model[7].

The values of K_{sv} from equation (2) were found to be imaginary in all the solvents. Therefore the role of ground state complex formation is ruled out in the present case. This is also confirmed by the fact that there is no shift in the peak position in the emission spectrum of Bis-MSB in cyclohexane with different quencher concentrations and is shown in Fig. 2. These facts show that Eq. (2) is not applicable for the analysis of the data corresponding to the observed positive deviation in the S-V plots. Thus the analysis of the data for positive deviation in the S-V plot was made using "Sphere of action static quenching model". Fig. 3 shows the plots of $[1-(I/I_0)]/[Q]$ against I/I_0 for Bis-MSB with CCl_4 as quencher for different solvents which are linear according to equation (7).

The dynamic quenching constant K_{sv} is determined in all the cases by least square fit method using Eq.7 and the values
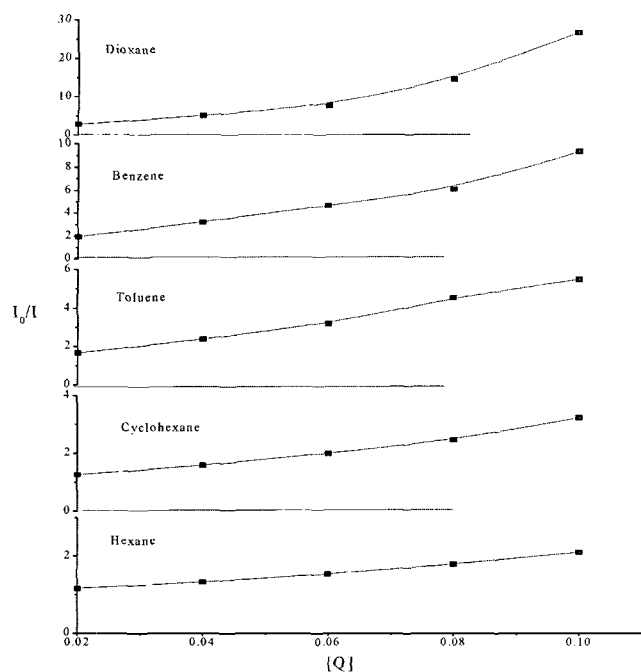
Fig. 1. Stern-Volmer plots of I_0/I against [Q] in different solvents.
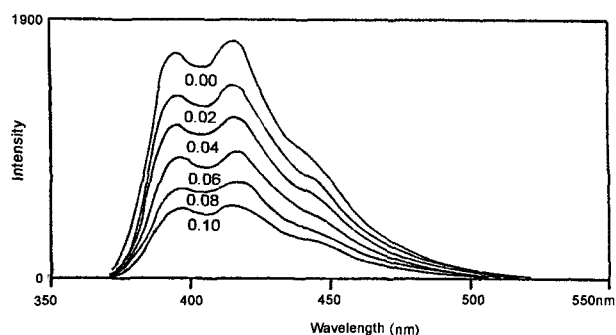

Fig. 2. Emission spectra of Bis-MSB in cyclohexane with different quencher concentrations of CCl_4

Fig. 3. Plots of $[1-(I/I_0)]/[Q]$ against I/I_0 in different solvents.

Table 1. The values of Stern-Volmer constant K_{sv}, Bimolecular quenching rate parameter k_q, Static quenching constant V and kinetic distance r for different solvents.

Solvent	K_{sv} (M^{-1})	$k_q \times 10^{-10}$ $(M^{-1}s^{-1})$	V $(mol^{-1}dm^3)$	r (Å)
Hexane	3.26	0.251	4.62	12.23
Cyclohexane	7.55	0.581	5.97	13.33
Toluene	27.07	2.083	4.00	11.66
Benzene	40.59	3.122	5.28	12.79
Dioxane	73.91	5.685	9.94	15.79

Molecule: 1,4-bis [2-(2-methylphenyl) ethenyl]-benzene Quencher: Carbon Tetra Chloride (CCl_4)
$R_Y = 4.24\ \text{Å}$, $R_Q = 2.79\ \text{Å}$, $\tau = 1.3$ ns

are given in the Table 1. Fluorescence lifetime τ of the solute studied is obtained from the catalogue of the Koch-Light laboratories limited, England and is given at the bottom of the Table 1. Bimolecular quenching rate parameter k_q was determined from the experimentally determined values of K_{sv} and literature value of τ according to the relation $k_q = K_{sv}/\tau$ and the values are given in the Table 1. Here high values of k_q indicate efficient quenching of fluorescence.

In order to support static and dynamic effects, we have determined the magnitudes of static quenching constant V and radii r of sphere of action (or kinetic distance) using the above mentioned theory for sphere of action model. With the use of Eq. (5), (6) and (7) the values of V and r are determined by least square fit method in all the solvents and are given in Table 1. Similar results were also obtained by others[7, 12, 29].

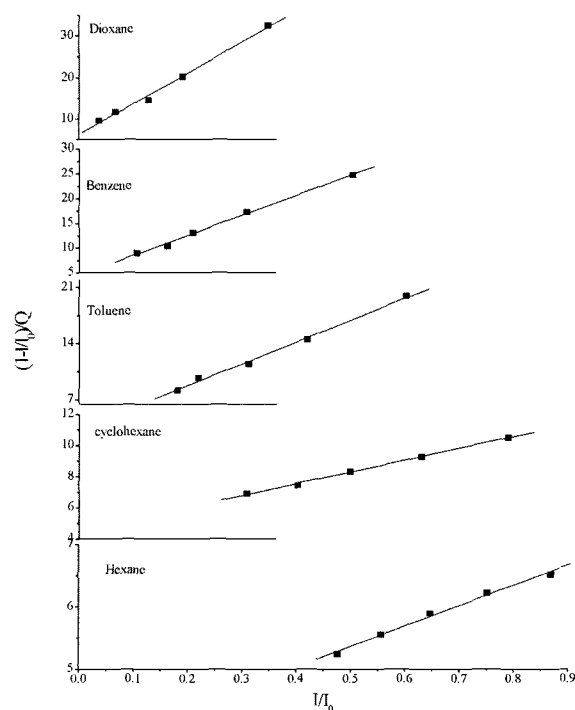The radii of the solute (R_Y) and the quencher (R_Q) molecules

were determined by adding the atomic volumes of all the atoms constituting the molecule as suggested by Edward[23] and are given at the bottom of the Table 1. From these values of R_Y and R_Q the sum of the molecular radii [R] of the solute Bis-MSB and the quencher CCl_4 is determined. This sum of the molecular radii R is referred to as encounter distance or contact distance or reactive distance. This value of R is then compared with the values of 'r' to verify whether the reaction is due to sphere of action model. From Table 1 we see that the values of kinetic distance 'r' are greater than the encounter distance R. Therefore according to Andre et al. and Zeng et al.[20, 24] the static effect takes place irrespective of ground state complex formation provided reactions are limited by diffusion indicating the sphere of action model holds well in our case also. Further it may also be noted that a positive

deviation in S-V plot is expected when both static and dynamic quenching occurs simultaneously[19].

In order to find whether the reactions are diffusion limited we have invoked the Finite Sink Approximation Model. To apply this model according to Eq.(15) we need to determine the values of K_{sv}^{-1} and $[Q]^{1/3}$. Where $K_{sv} = [(I_o/I)-1]/[Q]$ and [Q] the quencher concentration from $0.02M$ to $0.10M$. For efficient quenching processes (concentration dependent) the value K_{sv} is often observed to increase with [Q]. Hence the values of K_{sv} were determined at each quencher concentration in all the solvents and the values of K_{sv}^{-1} are also determined. Fig. 4 shows the plots of K_{sv}^{-1} against $[Q]^{1/3}$. From these figures we see that all the plots in different solvents are almost linear and small deviation may be due to experimental uncertainties. Hence, the linear dependence of K_{sv}^{-1} on the one-third power of quencher concentration within the error limits is confirmed[20]. Then the least square fit value of K_{sv}^0
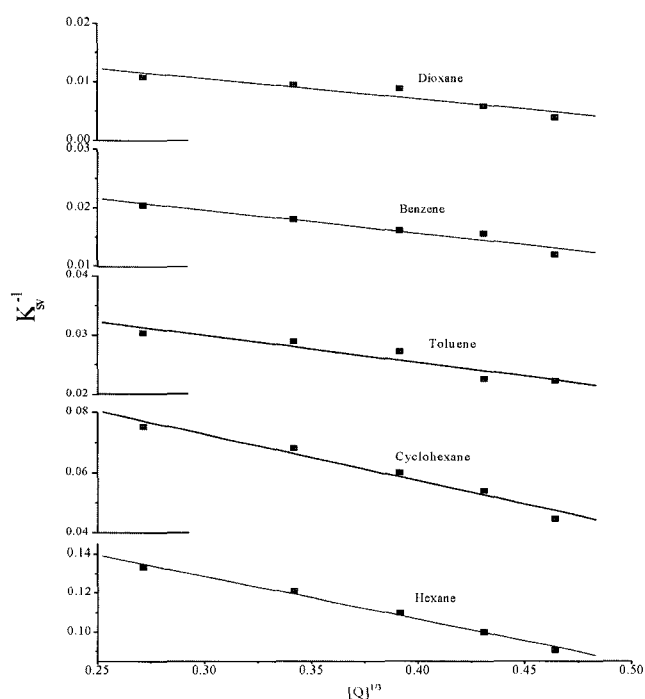

Fig. 4. Plots of K_{sv}^{-1} versus $[Q]^{1/3}$ in different solvents.

(Stern-Volmer constant at [Q] = 0) was obtained from the intercept of the plot of K_{sv}^{-1} against $[Q]^{1/3}$ according to Eq. 15. Similarly, mutual diffusion coefficients D were determined from the slope of the Eq.15 by least square fit method and the values of K_{sv}^0 and D are given in Table 2. Using these values of K_{sv}^0 and D, the distance parameter R' was determined according to Eq.16 and the values are given in the Table 2. According to Joshi et al.[28] the bimolecular reactions are said to be diffusion limited if the values of k_q (determined from Eq. (7)) are greater than 4πN'R'D. Hence the values of 4π N'R'D are calculated using the experimentally determined values of R' and D of Eq. (15) and are given in the Table 2. We see from the Table that in three solvents the values of k_q are greater than 4πN'R'D, which is an expected result for diffusion limited reaction[27].

It is important to note that, when an attempt was made to correlate the experimentally determined values of mutual diffusion coefficient D and distance parameter R' using finite sink approximation model with the corresponding values of D and R calculated from Stokes-Einstein relation and Edward's empirical relations respectively in all the systems, the values of D and R' (or R) determined from the two methods are quite comparable only in some solvents. From the Table 3 it is clear that correlation fails in some other solvents. Similar discrepancies have also been observed by others[20, 28] in some bimolecular quenching reactions. This may be due to the uncertainties in

Table 3. The values of Mutual diffusion coefficients D^a and D^b, Distance parameter R' and encounter distance R.

Solvent	$D^a \times 10^5$ (cm²s⁻¹)	$D^b \times 10^5$ (cm²s⁻¹)	R'(Å)
Hexane	6.97	0.70	7.46
Cyclohexane	2.122	1.00	8.53
Toluene	3.762	3.42	6.77
Benzene	3.446	3.99	8.10
Dioxane	1.745	4.54	10.65

Molecule: 1,4-bis [2-(2-methylphenyl) ethenyl]-benzene
Quencher: Carbon Tetra Chloride (CCl₄) R(=R_Y + R_Q) = 7.03Å
ᵃDiffusion coefficients determined from Stoke's Einstein relation.
ᵇDiffusion coefficients determined from Finite Sink Approximation Model.

Table 2. The values of K_{sv}^0 (steady state quenching constant at [Q] = 0), Mutual diffusion coefficient D, Distance parameter R', 4πN'DR' and Quenching rate parameter k_q.

Solvent	K_{sv}^0 (dm³mol⁻¹)	D × 10⁵ (cm²s⁻¹)	R' (Å)	4πNR'D × 10⁻¹⁰ (M⁻¹s⁻¹)	k_q × 10⁻¹⁰ (M⁻¹s⁻¹)
Hexane	5.141	0.70	7.46	0.39	0.251
Cyclohexane	8.402	1.00	8.53	0.64	0.581
Toluene	22.81	3.42	6.77	1.75	2.083
Benzene	31.80	3.99	8.10	2.44	3.122
Dioxane	47.62	4.54	10.65	3.66	5.685

Molecule: 1,4-bis [2-(2-methylphenyl) ethenyl]-benzene Quencher: Carbon Tetra Chloride (CCl₄)
R(=R_Y + R_Q) = 7.03Å

the values of adjustable parameter 'a' in the Stokes's –Einstein relation and the approximation in the values of atomic volume in the Edwardís relation. Hence we may conclude that finite sink approximation model is valid in recovering the parameters D and R' (or R).

CONCLUSION

From the above discussion we observe that: (1) the S-V plots show positive deviation leading to high values of k_q, indicating efficient fluorescence quenching. (2) Static quenching constant 'V' and kinetic distance 'r' are in agreement with the corresponding literature values. (3) The value of k_q is greater than $4\pi N'R'D$ in three solvents. (4) Further the values of R' and D determined from the finite sink approximation model are close to the values determined from Edwardís and Stokes-Einstein empirical relations respectively. In view of the above facts we may conclude that quenching reaction is diffusion limited and both static and dynamic quenching processes are partly playing a role in these systems.

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