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FLUORESCENCE QUENCHING OF BBOT BY ANILINE IN DIFFERENT ORGANIC SOLVENTS

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Abstract – The fluorescence quenching of 2,5-di-(5-tert-butyl-2-benzoxazolyl)-thiophene (BBOT) by aniline in five different solvents namely heptane, hexane, cyclohexane, dioxane and acetonitrile has been carried out at room temperature with a view to understand the quenching mechanisms. The experimental results show positive deviation in the Stern-Volmer plots in all the solvents. 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 suggest that sphere of action static quenching model agrees well with the experimental results. Hence this positive deviation is attributed to the static and dynamic quenching. Further, with the use of Finite Sink approximation model, it was possible to check these bimolecular reactions as diffusion-limited and to estimate independently distance parameter R' and mutual diffusion coefficient D. Finally an attempt 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 Edward's empirical relation and Stokes-Einstein relation.

INTRODUCTION

Fluorescence quenching of organic molecules using external quenchers, in liquid phase has been a study of intensive investigation over the last nearly four decades.[1-7] 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.[8-15] 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 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}/τ) where K_{sv} is the slope of the linear Stern-Volmer 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 Stern-Volmer relationship, then it may be due to one of the above processes other than or along with diffusion process.

In the present study we have used steady state experimental setup to investigate the quenching of 2,5-di-(5-tert-butyl-2-benzoxazolyl)-thiophene (BBOT) by aniline in five different organic solvents with a view to understand the nature of quenching mechanism involved in these systems.

MATERIALS AND METHODS

The solute 2,5-Di-(5-tert-butyl-2-benzoxazolyl)-thiophene (BBOT) was obtained from Koch-Light Laboratories Ltd., England and is of scintillation grade. The quencher aniline was obtained from BDH Laboratory, England and was tested for its purity before use. The solvents were obtained from BDH, India and were double distilled and tested for their purity before use. The solutions were prepared keeping the concentration of BBOT fixed (0.5 g/L) and varying the quencher concentration (0.02 *M* to 0.1 *M*) in all the solvents.

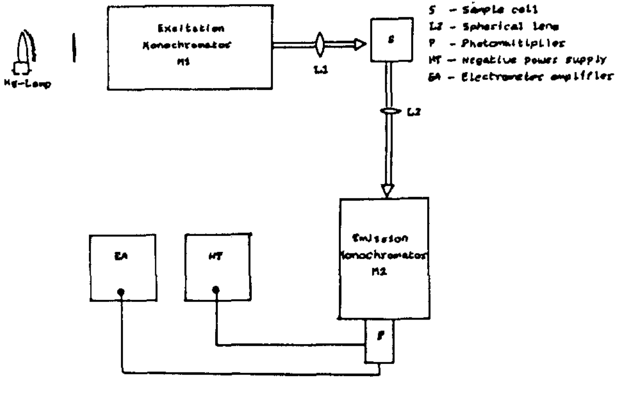

Figure 1. A schematic sketch of the experimental arrangement to measure the intensity of the scintillator solution.

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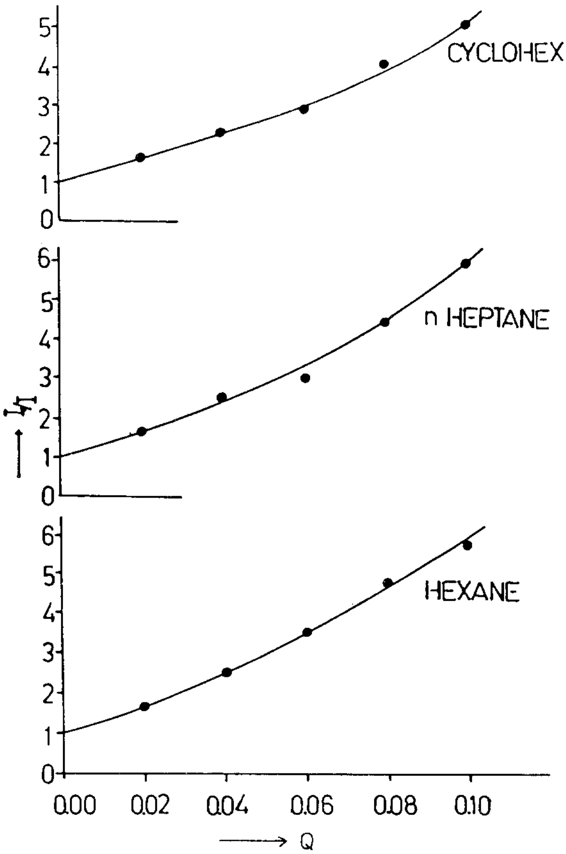

Table 2. Stern-Volmer plot of I_0/I against [Q] in hexane, heptane and cyclohexane.

All the solutions were studied at room temperature.

Fluorescence intensities were measured using perpendicular geometry and the schematic sketch of the experimental arrangement is as shown in Fig. 1 and the experimental details are given elsewhere.[9]

RESULTS AND DISCUSSION

At a fixed solute concentration same quantity of the fresh solution at different quencher concentrations was taken in a rectangular quartz cell having an air tight stopper. First the fluorescence intensity, I_0 was measured without the quencher and then the fluorescence intensity, I was measured at different quencher concentrations at a fixed solute concentration. The experimental values are reproducible within 5% of the experimental error. Using the experimentally determined values of I_0 and I in different solvents, the Stern-Volmer plots were obtained and are given in Figs. 2 and 3, respectively. Figs. 2 and 3 show that the plots are non-linear showing positive deviation. 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.[5]

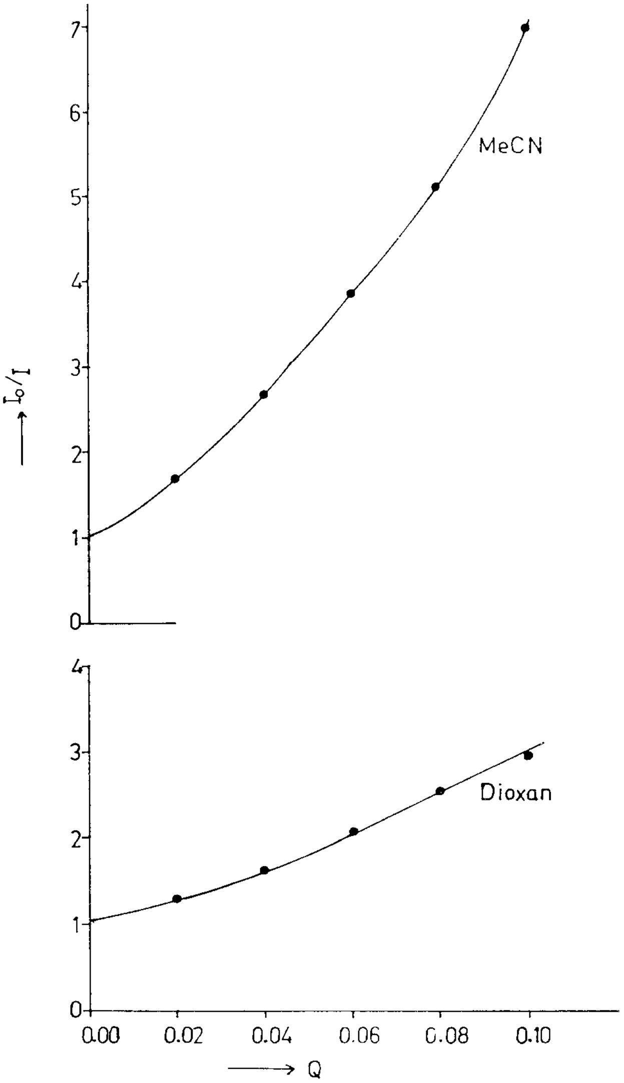

Figure 3. Stern-Volmer plot of I_0/I against [Q] in dioxane and acetonitrile.

In order to see whether the ground state complex formation is partly playing a role, we have used extended Stern-Volmer equation[3,16] given by

$$[(I_0/I) - 1]/[Q] = (K_{sv} + k_g) + (K_{sv}\, k_g)\,[Q] \qquad (1)$$

Where K_{sv} and k_g are Stern-Volmer and ground state association constants, respectively. In accordance with the above equation, the values of K_{sv} and k_g can easily be determined by least square fit method and these values are given in table 1 for all the solvents except in acetonitrile. Since in acetonitrile the values of K_{sv} and k_g are found to be imaginary. From the values of K_{sv}, the bimolecular quenching rate parameters k_q (= K_{sv}/τ) were determined (where τ = 1.2 ns is the life time of the solute BBOT in the absence of quencher taken from Koch-Light Laboratories Ltd., England). The values of k_q thus determined using Eq. (1) are referred as k_q^a in

Table 1. The values of Stern-Volmer constant K_{sv}, ground state association constant of the complex k_g and biomolecular quenching rate parameter k_q.

Solvent	K_{sv} (M^{-1})	k_g (M^{-1})	$k_q^a \times 10^{-10}$ (M^{-1})	$k_q^b \times 10^{-10}$ ($M^{-1}S^{-1}$)	$k_q^c \times 10^{-10}$ ($M^{-1}S^{-1}$)
Hexane	24.60	12.79	2.05	2.31	2.03
Heptane	18.41	10.25	1.53	2.78	2.24
Cyclohexane	25.17	4.20	2.10	2.43	2.42
Dioxan	9.05	5.58	0.75	1.39	1.06
Acetonitrile				2.90	3.18

Molecule: 2,5-di-(5-tert-butyl-2-benzoxazolyl)thiophene
Quencher: Aniline

[a]Bimolecular quenching rate parameter determined from ground state complex model.

[b]Bimolecular quenching rate parameter determined from linear portion (low concentration) of the plots I_0/I against [Q].

[c]Bimolecular quenching rate parameter determined from sphere of action static quenching model.

Table 1. Then from Figs. 2 and 3 the values of k_q were determined from lower portion (lower concentration region) of the curve I_0/I versus [Q]. These values of k_q are referred as k_q^b in Table 1. Then according to the theory,[3,16] if the values of k_q^a and k_q^b determined from these two methods are equal, then there is formation of weak ground state complex. But in our case these values of k_q^a and k_q^b are not equal in all the solvents. However, they may be approximately equal in hexane and cyclohexane. Further, if there is appreciable shift in the absorption and emission peaks of the solute without and with the quencher, then there is ground state complex formation. The fact that there is no shift in the peak position was confirmed by recording emission spectra of BBOT in cyclohexane with different quencher concentrations and is shown in Fig. 4. These facts show that equation (1) is not applicable for the analysis of the data corresponding to the observed positive deviation in the Stern-Volmer plots. Thus the analysis of the data for positive deviation in S — V plots was made using "Sphere of action static quenching 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. And 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)[17,18] to describe this static quenching process, all leading to the following modified form of the Stern-Volmer equation[4].

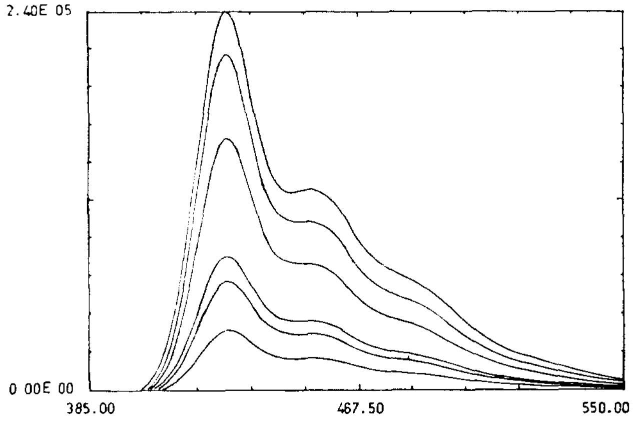

Figure 4. Emission spectra of BBOT in cyclohexane with different quencher concentrations of aniline.

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

where K_{sv} and τ have their usual meanings and explained earlier and [Q] is the quencher concentration. The Smoluchowski's diffusion controlled equation containing transient term is written as

$$K_d = 4\pi N' R D + 4 R^2 N' (\pi D)^{1/2} t^{-1/2} \qquad (3)$$

where N' is the 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 solute and quencher molecules and t is the time. The retention of the latter term of Eq. (3) leads to an additional factor, W in Eq. (2). This additional factor W is given by[4]

$$W = e^{-V[Q]} \qquad (4)$$

$$\ln(1/W) = V[Q]$$

where V is the static quenching constant.

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.

$$V/N' = (4\pi r^3)/3 \qquad (5)$$

surrounding a solute molecule at the time of excitation.

As W depends on the quencher concentration [Q] the Stern-Volmer plots for a quencher with a high quenching ability generally deviate from linearity. Thus it is worth rewritting Eq. (2) as

$$[1 - (I/I_0)]/[Q] = K_{sv}(I/I_0) + (1 - W)/[Q] \qquad (6)$$

In order to extract more information from Eq. (6) it is

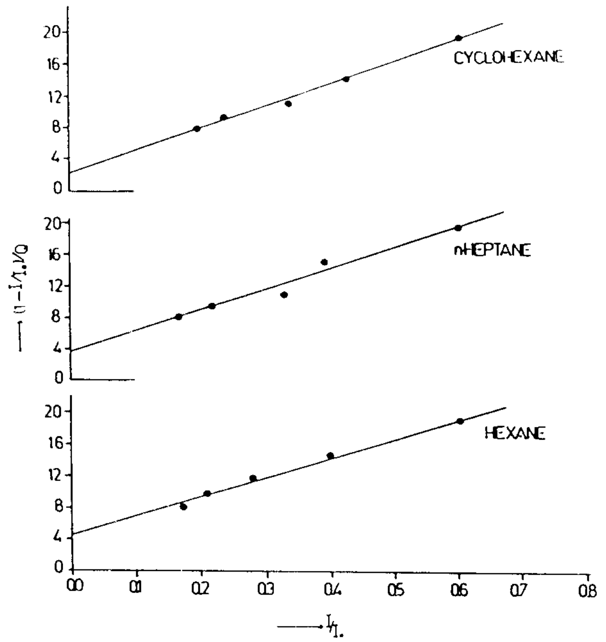

Figure 5. Plots of $[1 - (I/I_0)]/[Q]$ against I/I_0 in hexane, heptane and cyclohexane.

sensible to calculate the value of $[1 - (I/I_0)]/[Q]$, because the plot of $[1 - (I/I_0)]/[Q]$ versus I/I_0 becomes linear the slope of which is K_{sv} and the intercept is $(1 - W)/[Q]$. Hence in Figs. 5 and 6 we give the plots of $[1 - (I/I_0)]/[Q]$ against I/I_0 for BBOT with aniline as quencher for different solvents.

The dynamic quenching constant K_{sv} is determined in all the cases by least square fit method using equation (6) and the values are given in Table 2. Fluorescence lifetime τ of the solute studied is obtained from the catalogue of the Koch-Light Laboratories Ltd., England and is given at the bottom of Table 2. Bimolecular quenching 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 Table 2. These values of k_q are also given in Table 1 and are referred as k_q^c. From the table 1 we see that the values of k_q^b and k_q^c are quite comparable (of course, k_q^b is the value determined from lower portion of the curves of Figs. 2 and 3). i.e. the values of quenching rate parameter k_q determined from these two methods are approximately equal in all the solvents. This shows that the sphere of action model was able to recover the dynamic bimolecular quenching constant (k_q). Further no specific interactions between the solute and the quencher have been identified. Hence we may conclude that sphere of action model is the best model to use if one needs the static quenching mechanism. Therefore the positive deviation in the S-V plots may be attributed to the sphere of action static quenching model.

In order to support static and dynamic (transient) 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 Eqs. (4), (5) and (6) the values of V and r are determined by least square fit method in all the systems and the values of V and r are given in Table 2.

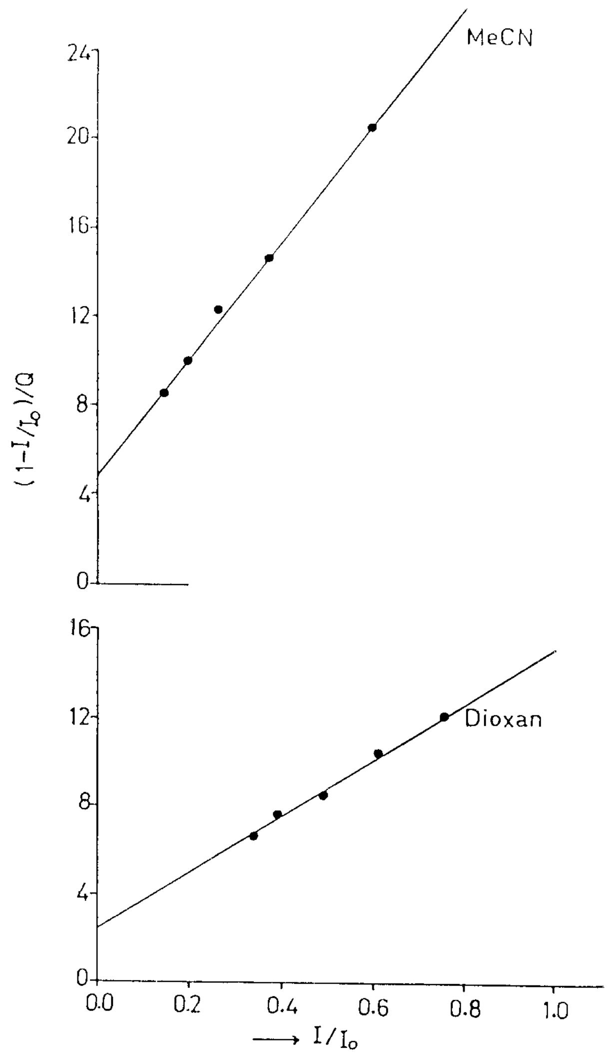

Figure 6. Plots of $[1 - (I/I_0)]/[Q]$ against I/I_0 in dioxane and acetonitrile.

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[19] and are given at the bottom of Table 2. From these values of R_Y and R_Q the sum of the molecular radii (R) of the solute (BBOT) and the quencher (aniline) is determined. This sum of the molecular radii R is reffered as encounter distance or contact distance or reactive distance. This value of R is then compared with the values of 'r' to varify whether the reaction is due to "sphere of action model" or not. Since according to Andre *et al.*[1], and Zeng *et al.*[16], if the

Table 2. The Stern-Volmer constant K_{sv}, 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 ($mole^{-1}dm^3$)	r (Å)
Hexane	24.36	2.03	6.75	13.88
Heptane	26.91	2.24	4.80	12.39
Cyclohexane	29.02	2.42	2.45	9.90
Dioxan	12.70	1.06	2.85	10.41
Acetonitrile	26.53	3.18	7.15	14.15

Molecule: 2,5-Di-(5-tert-butyl-2-benzoxazolyl)thiophene
Quencher: Aniline
$R_Y = 4.57$ Å, $R_Q = 2.84$ Å, $\tau = 1.2$ ns

distance between the quencher molecules and the 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 the ground state complex formation provided the reactions are limited by diffusion. From Table 2 we see that the values of kinetic distance (r) are larger than the encounter distance (R) indicating that the sphere of action model holds good in our case also. Further it may also be noted that a positive deviation in the S-V plot is expected when both static and dynamic quenching occur simultaneously[3,4]. In order to find out whether the reactions are diffusion limited we invoke the finite sink approximation model.

Finite Sink Approximation model

Keizer[22-24] has proposed a nonequilibrium statistical modification of the Smoluchowski-Collins-Kimball (SCK) expression to fit the I_0/I ratio in fluorescence quenching.

In the case of SCK model time-dependent rate coefficient k(t) for diffusion-limited reaction of initially randomly distributed reactants is given by[25]

$$k(t) = a + b \exp(c^2 t) \operatorname{erfc}(ct^{1/2}) \tag{7}$$

where

$$a = k_a \left[1 + \frac{k_a}{4\pi N' RD} \right]^{-1} \tag{8}$$

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

$$c = \left[1 + \frac{k_a}{4\pi N' RD} \right] \frac{D^{1/2}}{R} \tag{10}$$

Integration of Eq. (7) between the limits [Q](∞) at r →∞ and [Q](R) at r = R provides the well known expression

$$1/k_q = (1/k_d) + (1/k_a) \tag{11}$$

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 solute and quencher molecules. Following Eq. (11), 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.[16]

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_o can be defined (sink radius) so that the diffusive region of interest for a first encounter is in the range $R \leq r \leq r_o$ such that all subsequent encounters are eliminated. Integration of the flux equation between the limits $[Q](r_o)$ at r_o and [Q](R) at R leads to modification of Eq. (11) as

$$\frac{1}{k_q} = \frac{1 - (R/r_o)}{k_d} + \frac{1}{k_a} \tag{12}$$

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 $R = r_o$. In the diffusion controlled limit ($k_a \gg k_d$) Eq. (12) reduces to

$$k_q = \frac{k_d}{1 - R/r_o} \tag{13}$$

and k_q depends on the quenching concentration through r_o. Since the sink radius (r_o) is identified with the most probable nearest neighbour initial separation, the appropriate distribution requires that [23] $r_o = (2\pi N'[Q])^{-1/3}$. Replacing r_o in Eq. (12) by $(2\pi N'[Q])^{-1/3}$ and k_d by its value (*i.e.* $4\pi N'DR$) and dividing everywhere by the fluorescence lifetime of solute in the absence of quencher (τ) one obtains the modified Stern-Volmer relationship as[16]

$$K_{sv}^{-1} = (K_{sv}^{o})^{-1} - \frac{(2\pi N')^{1/3}}{4\pi N'D\tau} [Q]^{1/3} \tag{14}$$

where $K_{sv}^{o} = \dfrac{4\pi N'DR\tau k_a}{4\pi N'DR + k_a}$ A plot of K_{sv}^{-1} 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. (14) and K_{sv}^{o} is obtained at [Q] = 0 regardless of the relative magnitudes of k_a and

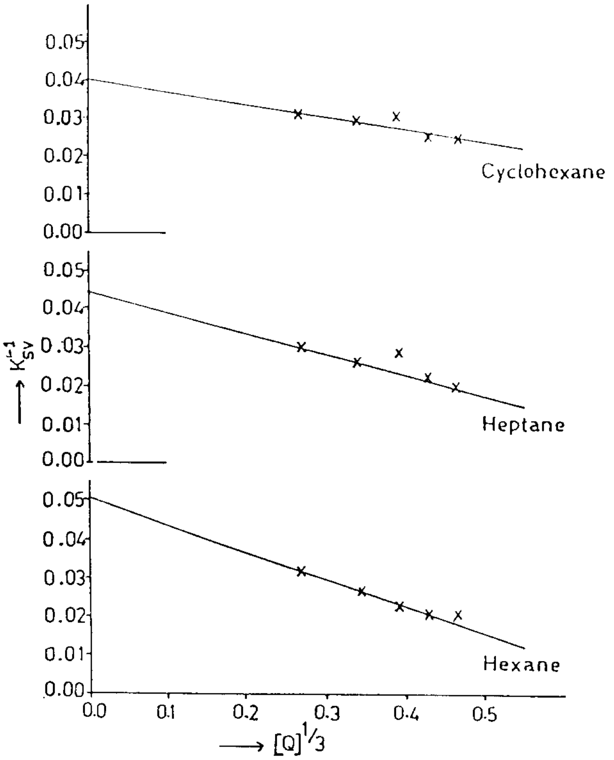

Figure 7. Plots of K_{sv}^{-1} against $[Q]^{1/3}$ in hexane, heptane and cyclohexane.

k_d (= 4 π N'DR), whether quenching is diffusion limited or not. From K_{sv}^0 we only have access to R' which is a composite of R and k_a through Eq. (15)

$$K_{sv}^0 = 4\pi N'DR'\tau \qquad (15)$$

where R' is the distance parameter and has the same meaning as in the long-time SCK model[16,25] and is given as

$$R' = R\left[1 + 4\pi RDN'/k_a\right]^{-1} \qquad (16)$$

Then according to the theory discussed above if k_a is greater than k_d (i.e. Eq. (11)) then the reactions are said to be diffusion limited[16] (i.e.for R'<R). But for R' > R, the bimolecular reactions of fluorescence quenching are said to be diffusion limited[25] if the values of k_q determined from Eq. (6) are greater than 4πN'R'D.

Therefore according to Eq. (14) we need to determine the values of K_{sv}^{-1} (reciprocal of K_{sv}) and $[Q]^{1/3}$. Where $K_{sv} = [(I_0/I) - 1]/[Q]$ and [Q] the quencher concentration from 0.02 to 0.1 *M*. For efficent quenching processes (concentration dependent) the value of 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} (reciprocal of K_{sv}) are also determined. In Figs. 7 and 8 we give the plots of K_{sv}^{-1} against $[Q]^{1/3}$ according to Eq. (14). From these Figures we see that all the plots in different solvents are almost linear and small deviations 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 associated with relative fluorescence intensity measurements was confirmed.[16] Then the least square fit value of K_{sv}^0 (Stern-Volmer constant at [Q] = 0) was obtained from the intercept of the plot of K_{sv}^{-1} against $[Q]^{1/3}$ according to equation (15). Similarly, the mutual diffusion coefficient D was determined from the slope of Eq. (14) by least square fit method and the values of K_{sv}^0 and D are given in Table 3. Using these values of K_{sv}^0 and D, the distance parameter R' was determined according to Eq. (15) and the values are given in Table 3. Using the values of distance parameter R' and encounter distance R activation energy controlled rate constant k_a was also determined according to Eq. (16). (This value of k_a can only be determined for R' less than R)[16]. In the case of dioxan the experimentally determined value of the distance parameter R'(= 5.17 Å) is less than the encounter distance R (= 7.41 Å). Hence the Value of k_a is determined only for dioxan and is given in Table 3. From Table 3, we see that $k_q \approx 4\pi N'R'D$, and $k_a > k_q$ or alternatevily $k_a > k_d$ (since the value of $k_q = 1.06 \times 10^{10}$ $M^{-1}S^{-1}$ is almost equal to the value of $k_d = 0.942 \times 10^{10}$ $M^{-1}S^{-1}$), may suggest that quenching is less efficient in dioxan than in the remaining solvents.[9,16] This may be due to the fact that the activation process is more predominant in the quenching mechanism than the diffusion process. However, according to Zeng *et al.*[16], if k_a is greater than k_d (i.e. Eq. (11)) then the reactions are said to be diffusion limited which is true in our case for

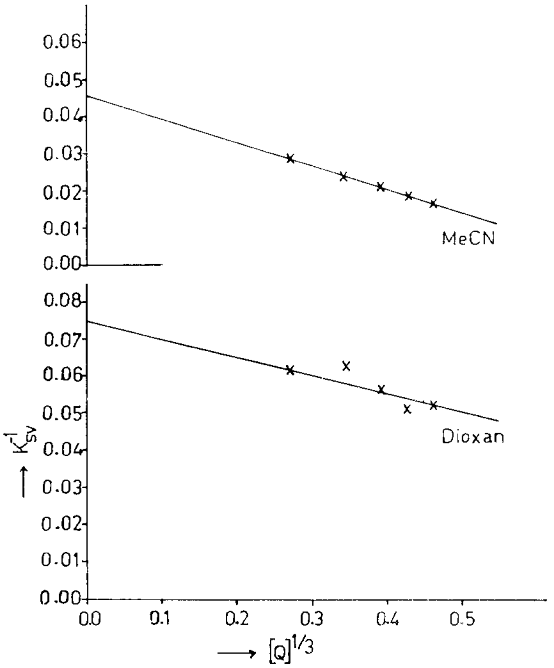

Figure 8. Plots of K_{sv}^{-1} against $[Q]^{1/3}$ in dioxane and acetonitrile.

Table 3. The values of K^{o}_{sv} (Steady state quenching constant at [Q] = 0, Mutual diffusion coefficient D, Distance parameter R', 4 π N'R'D, Quenching rate parameter k_q and Activation energy controlled rate constant k_a.

Solvent	K^{o}_{sv} (M^{-1})	D x 10^5 (cm^2S^{-1})	R' (Å)	$4\pi N'DR' \times 10^{-10}$ ($M^{-1}S^{-1}$)	$k_q \times 10^{-10}$ ($M^{-1}S^{-1}$)	$k_a \times 10^{-10}$ ($M^{-1}S^{-1}$)
Hexane	20.28	2.66	8.39	1.69	2.03	—
Heptane	18.56	2.30	8.88	1.55	2.24	—
Cyclo-hexane	20.83	2.82	8.13	1.74	2.42	—
Dioxan	13.89	2.96	5.17	1.16	1.06	1.56
Aceto-nitrile	23.26	2.73	9.38	1.94	2.21	—

Molecule: 2,5-di-(5-tert-butyl-2-benzoxazolyl)thiophene
Quencher: Aniline
$R(R_Y + R_Q) = 7.41$ Å

dioxan (*i.e.* in the case of dioxane k_a is 1.56×10^{10} and k_d is 0.942×10^{10}). However, for remaining solvents the values of k_a cannot be determined because the values of R' in these solvents are greater than the values of R for BBOT + Aniline system. But according to Joshi *et al.*,[25] the bimolecular reactions of fluorescence quenching are said to be diffusion limited if the values of k_q (determined from Eq. (6)) are greater than $4\pi N'R'D$. Hence the values of $4\pi N'R'D$ are calculated using the experimentally determined values of R' and D of Eq. (14) and are given in Table 3. We see from Table 3 that in four solvents the values of k_q are greater than $4\pi N'R'D$ (*i.e.* $k_q > 4\pi N'R'D$), which is an expected result for diffusion limited reaction[25].

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 Stoke's-Einstein 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 in cyclohexane. (In the case of cyclohexane the value of D from finite sink model is 2.82×10^{-5} cm²/sec, whereas from the Stoke's-Einstein equation the value of D is 2.25×10^{-5} cm²/sec (given in Table 4) and the value of R' from finite sink model is 8.13 Å where as from Edward's empirical formula value of R is 7.41 Å). But from table 4 we see that such correlation fails in the remaining solvents. In fact similar discrepancies have also been observed by others[16,25] in some bimolecular quenching reactions. This may be due to the uncertainties in the values of the adjustable parameter 'a' in the Stoke's-Einstein relation and the approximation in the values of the atomic volume in the Edward's empirical relation. Hence, we may conclude that finite sink approximation model is valid in recovering the parameters D and R'(or R).

Table 4. The values of Mutual diffusion coefficients D^a and D^b, distance parameter R' and encounter distance R are given.

Solvent	$D^a 10^5$ (cm^2S^{-1})	$D^b 10^5$ (cm^2S^{-1})	R' × 10^8 (Å)
Hexane	6.31	2.66	8.39
Heptane	5.11	2.30	8.88
Cyclohexane	2.25	2.82	8.13
Dioxan	1.68	2.96	5.17
Acetonitrile	5.96	2.73	9.38

Molecule: 2,5-di-(5-tert-butyl-2-benzoxazolyl)thiophene
Quencher: Aniline
$R(R_Y+R_Q) = 7.41$ Å
[a]Diffusion coefficients determined from Stoke's Einstein relation.
[b]Diffusion coefficients determined from Finite sink model.

CONCLUSION

From the foregoing discussion we observe that: (1) the Stern-Volmer plots show positive deviation leading to high values of k_q and are almost equal to the values extracted from linear portion of the curve I_o/I versus [Q]. (2) Static quenching constant 'V', and kinetic distance 'r' agree with the corresponding literature values and (3) The value of k_a is greater than k_d in dioxan and the values of k_q are greater than $4\pi N'R'D$ in the remaining solvents. (4) Further the values of R' and D determined from the finite sink approximation model are close to the values determined from Edward's empirical and Stoke-Einstean relations respectively. In view of the above facts we may conclude that quenching reaction is diffusion limited and both static and dynamic (transient) quenching processes are partly playing a role in these systems.

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REFERENCES

1. Andre, J. C., M. Niclause and W. R. Ware (1978) Kinetics of partly diffusion controlled reactions. I. Transient and apparent transient effect in fluorescence quenching. *Chem. Phys.* **28**, 371-375.
2. Roy, R. and S. Mukherjee (1987) Fluorescence quenching of carbozole and indole by ethylenetrithiocarbonate. *Chem. Phys. Lett.*, **140**, 210-214.
3. Behera, P. K. and A. K. Mishra (1993) Static and dynamic model for 1-napthol fluorescence quenching by carbontetracholride in dioxan-acetonitrile mixtures. *J. Photochem. Photobiol. A: Chem.*, **71**, 115-118.

4. Moriya, T. (1984) Excited-state reactions of coumarins in aqueous solutions. II. The fluorescence quenching of 7-ethoxy. *Bull. Chem. Soc. Jpn.*, **57**, 1723-1729.
5. Giraddi, T. P., J. S. Kadadevarmath, G. H. Malimath and G. C. Chikkur (1996) Effect of solvent on the fluorescence quenching of organic liquid scintillators by aniline and carbon tetrachloride. *Appl. Radiat. and Isot.*, **47**, 461-466.
6. Nemzek, T. L. and W. R. Ware (1975) Kinetics of diffusion controlled reactions: Transient effects in fluorescence quenching. *J. Chem. Phys.*, **62**, 477-481.
7. Ware, W. R. and H. P. Richter (1968) Fluorescence quenching via charge transfer: The perylene-N,N-dimethylamiline system. *J. Chem. Phys.*, **48**, 1595-1601.
8. Mathad, R. D. and N. Umakantha (1986) An experimental method of determining the electronic excitation energy migration coefficient in organic liquids. *Chem. Phys. Lett.*, **124**, 31-34.
9. Kadadevarmath, J. S., T. P. Giraddi, G. H. Malimath and G. C. Chikkur (1996) Electronic excitation energy quenching of an organic liquid scintillator by carbon tetrachloride in different solvents. *Radiation Measurements (USA)*, **26**, 117-121.
10. Giraddi, T. P., J. S. Kadadevarmath, G. H. Malimath and G. C. Chikkur (1996) Quenching of 2-Phenylindole by carbon tetrachloride and aniline in different solvents. *Ind. J. Pure. & Appl. Phys.*, **34**, 244-248
11. Mathad, R. D., G. C. Chikkur and N. Umakantha (1986) Electronic excitation energy transfer in organic liquid scintillators. *J. Chem. Phys.*, **84**, 2187-2195.
12. Mathad, R. D. and N. Umakantha (1985) On the mechanism of electronic excitation energy migration in organic liquids. *Phys. Lett.*, **108**A, 167-169.
13. Mathad, R. D. and N. Umakantha (1986) On the mechanism of intermolecular energy transfer encounter in organic liquids. *Phys. Lett A.*, **117**, 97-100.
14. Lissi, E. A., M. V. Encinas, S. G. Birtolotti, J. J. Cosa and C. M. Previtali (1990) Fluorescence quenching of indolic compounds in reverse micells of AOT. *Photochem. Photobiol.*, **51**, 53-58.
15. Nigam, S., M. Belletete, R. S. Sarpal and G. Durocher (1995) Solubilization of two cyano 3H-indole molecular probes in CDS and CTAB micelles; Spectral and photophysical characterization. *J. Chem. Soc. Faraday Trans.*, **91**, 2133-2139
16. Zeng, H. and G. Durocher (1995) Analysis of fluorescence quenching in some antioxidants from nonlinear Stern-Volmer plots. *J. Lumin.*, **63**, 75-84.
17. Frank, J. M. and S. J. Wawilow (1931) Sphere of action of the extinction phenomena in fluorescent liquids. *Z. Phys.*, **69**, 100-110.
18. Moon, A. Y., D. C. Poland and H. A. Scheraga (1965) Thermodynamic data from fluorescnce spectra I. The system phenol-acetate. *J. Phys. Chem.*, **69**, 2960-2966
19. Edward, J. T. (1956) Molecular Volumes and Parachor. *Molecular Volumes and Parachor.*, (Chem. Ind., London) 774.
20. Birks, J. B., M. Salete and S. C. P. Leite (1970) Energy transfer in organic systems VIII. Quenching of naphthalene fluorescence by biacetyl. *Proc. Phys Soc., (London)* **3**, 417-425.
21. Lewis, C. and W. R. Ware (1976) Quenching of toluene fluorescence by oxygen. *J. Chem. Soc. Faraday Trans.*, **1172**, 1851-1855.
22. Keizer, J. (1982) Nonequilibrium stastical thermodynamics and the effect of diffusion on chemical reaction rates. *J. Phy. Chem.*, **86**, 5052-5067.
23. Keizer, J. (1983) Nonlinear fluorescence quenching and the orgin of positive curvature in stern-Volmer plots. *J. Am. Chem. Soc.*, **105**, 1494-1499.:Keiger, J. (1985) Additions and Corrections. *J. Am. Chem. Soc.*, **107**, 5319.
24. Keizer, J. (1987) Diffusion effects on rapid bimolecular chimical reactions. *Chem. Rev.*, **87**, 167-180
25. Joshi, G. C., R. Bhatnagar, S. Doraiswamy and N. Periasamy (1990) Diffusion controlled reactions: Transient effects in the fluorescence quenching of indole and N-acetyltryptophanamide in water. *J. Phy. Chem.*, **94**, 2908-2914.