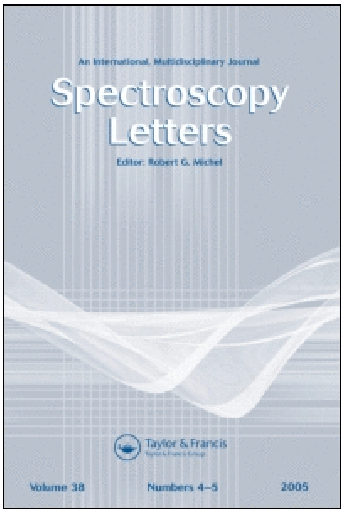

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Fluorescence Quenching of 2,2″-dimethyl-*p*-terphenyl by Carbon Tetrachloride in Binary Mixtures

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ABSTRACT The fluorescence quenching of 2,2″-dimethyl-*p*-terphenyl (DMT) by carbon tetrachloride (CCl_4) was investigated in different solvent mixtures of benzene and acetonitrile at room temperature (300 K). A positive deviation from linearity was observed in the Stern-Volmer plots for all the solvent mixtures. This could be explained satisfactorily by static and dynamic quenching models. The nonlinearities in the S-V plots are interpreted in terms of ground state complex model and the sphere of action static quenching model. The results suggest that positive deviations in the S-V plot are due to the presence of both static and dynamic quenching processes. To explain that bimolecular reactions are diffusion limited, we have used finite sink approximation model. Various rate parameters for the quenching process have been determined by static and dynamic quenching models. The dynamic quenching constant depends on the solvent polarity and indicates that quenching reaction is diffusion limited.

KEYWORDS finite sink approximation model, fluorescence quenching, ground-state complex model, sphere of action model, Stern-Volmer plot

INTRODUCTION

Fluorescence quenching has been widely studied both as a fundamental phenomenon and as a source of information about biochemical systems. A variety of processes can lead to quenching of fluorescence intensity. The two most common processes are collisional or dynamic quenching involving collisional interactions of quencher with the excited fluorophore and static or instantaneous quenching due to the formation of a non-fluorescent complex between the quencher and the ground state fluorophore. For static or dynamic quenching to occur, the fluorophore and the quencher must be in contact with each other. Quenching can also occur by various processes such as excited state reactions, molecular rearrangements, energy transfer, intersystem crossing, singlet-to-triplet excitation, and formation of charge transfer complexes both at ground and excited states.[1] In general, the quenching process depends upon the nature of fluorophore and quencher

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molecule. Apart from this, the polarity of the solvent medium and the range of quencher concentration are also expected to play an important role.

In the case of some quenching studies, the experimental results follow the linear Stern–Volmer (SV) equation.[1] However, in other cases, it is observed that the S-V plots become nonlinear showing positive deviation.[1,2] The quenching of fluorescence of organic molecules in solution by various quenchers like haloalkanes,[3–10] aniline,[10–13] metal ions,[14] halide ions,[15–17] and so forth, have been studied by several investigators. The accessibility of fluorophores to such quenchers can be used as a criterion for the determination of the location of probes on macromolecules to quenchers. Such studies aim at understanding the nature of bimolecular reactions taking place both under steady state and transient conditions. The quenching mechanism is important not only in physical science but also in chemical, biological, and medical sciences. Among haloalkanes, carbon tetrachloride (CCl_4) is known to be a good quencher for several fluorescent compounds.[5–10] In almost all cases of CCl_4 quenching, it has been observed that the experimental results show positive deviation from linear S-V plot.

The compound 2,2″-dimethyl-*p*-terphenyl (DMT) is widely investigated due to its importance as a laser dye, as a nonlinear optical chromophore, and as an excellent probe in the study of solvation dynamics in homogeneous solutions as well as organized media. To date, there are no reports in the literature on fluorescence quenching of DMT by CCl_4 in binary mixture solutions. These studies are important for the current dye to understand its photophysical properties in aqueous media. In literature, there are only few reports on fluorescence quenching of a fluorescent compound in a binary mixture of solvents.[5,11,18] This motivated us to carry out the current work.

In the current work, we have investigated the steady-state fluorescence quenching of DMT by CCl_4 in different solvent mixtures of benzene and acetonitrile at room temperature (300 K). The main objective of the current work is to examine the nonlinearity in the S-V plot in greater detail. The various rate constants responsible for fluorescence quenching mechanisms have been determined, and the possible quenching mechanisms are discussed. We have also studied the effect of solvent polarity on the fluorescence quenching and have discussed the effect of solvent polarity on fluorescence quenching up to a quencher concentration of 0.1 M, which includes the nonlinear range of the quenching curve.

THEORETICAL BACKGROUND

The mechanism of fluorescence quenching of organic fluorophore by external quencher is suggested to be a diffusion controlled, collisional process and is described by the Stern–Volmer equation[1]

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

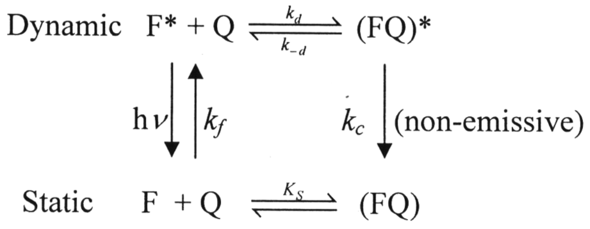
where I_0 and I are the values of fluorescence intensity of fluorophore in the absence and presence of the quencher, K_{SV} is the S-V quenching constant, and Q is the concentration of the quencher. K_{SV} is given as,

$$K_{SV} = k_q \tau_0, \tag{2}$$

where k_q is the bimolecular quenching rate constant and τ_0 is the fluorescence life time of the excited fluorophore in the absence of quencher. Equation (1) is generally for a single class of fluorophores, all equally accessible to quencher. If two fluorophore populations are present, and one is not accessible to quencher, then the S-V plot deviates from linearity, suggesting that quenching mechanism is not purely collisional due to ground-state complex formation but also to the "sphere of action static quenching model."[18]

Groundy-State Complexes

The mechanism of quenching, including both the ground-state complex and exciplex, is summarized in the following scheme [1,2,5]:



where F is the fluorophore (DMT), Q is the quencher, and the symbols k_f, k_d, k_{-d}, and k_c are the rate constants for the radiative decay, diffusion, back diffusion with break up of the exciplex, and nonemissive quenching, respectively. K_S is the equilibrium constant for the ground-state complex formation.

When a ground state complex interacts in a dynamic quenching mechanism, the fractional fluorescence intensity, I_0/I, is given by the product of both static and dynamic quenching[1, 19],

$$\frac{I_0}{I} = (1 + K_{SV}[Q])(1 + k_g[Q]). \tag{3}$$

This modified form of the S-V equation is second-order equation in [Q], which accounts for the upward curvature observed when both static and dynamic quenching occur for the same fluorephore.

Alternatively, $\frac{I_0}{I} = 1 + (K_{SV} + k_g)[Q] + K_{SV}k_g[Q]^2$,

$$\frac{([I_0/I] - 1)}{[Q]} = K_1 + K_2[Q], \tag{4}$$

where $K_1 = K_{SV} + k_g$ and $K_2 = K_{SV} \cdot k_g$, K_{SV} and k_g are the dynamic quenching constant and ground state, association constant of the complex, respectively. Equation (3) is valid for a single species undergoing both dynamic and static quenching.

Sphere of Action Static Quenching Model

In this model,[20–23] any static quenching interaction requires that the fluorophore and the quencher be within a certain distance of one another. In solution, this reaction distance (R) defines an interaction sphere of volume V. On excitation of the fluorophore, a quencher molecule that is already within this volume will be able to quench the fluorescence without the need for a diffusion-controlled collisional interaction.[24] The probability of the quencher being within this volume at the time of excitation depends on the volume (V) and on the quencher concentration [Q]. Assuming the quencher is randomly distributed in solution, the probability of static quenching is given by a Poisson distribution [$e^{V[Q]}$] and the S-V equation is modified to

$$\frac{I_0}{I} = [1 + K_{SV}[Q]]e^{V[Q]}, \tag{5}$$

where V is the static quenching constant and it represents an active volume element surrounding the fluorophore in its excited state

Frank and Wavilow[23] suggested that the static or instantaneous quenching occurs in a randomly distributed system when a quencher happens to reside within a sphere of action surrounding a fluorophore upon its excitation; the volume of such sphere of action is given by

$$V = \frac{4}{3}\pi r^3 \left(\frac{N}{1000}\right), \tag{6}$$

where N is Avogadro's number and r is the radius of sphere of action called kinetic distance.

As $e^{V[Q]}$ is a function of quencher concentration [Q], the S-V plot for a quencher possessing extreme quenching efficiency generally deviate from its linearity character. Therefore, equation (5) can also be expressed in the following form,

$$\frac{[1 - (I/I_0)]}{[Q]} = K_{SV}\left(\frac{I}{I_0}\right) + \frac{[1 - e^{-V[Q]}]}{[Q]}, \tag{7}$$

when $V[Q] \leq 1$; $e^{V[Q]} \approx (1 - V[Q])$; then, equation (7) takes the following form

$$\frac{[1 - (I/I_0)]}{[Q]} = K_{SV}\left(\frac{I}{I_0}\right) + V. \tag{8}$$

The Finite Sink Approximation Model

According to this model,[25–26] the following modified S-V relationship is obtained:

$$K_{\mathrm{SV}}^{-1} = K_{SV}^{0-1} - \frac{(2\pi N')^{1/3}}{4\pi N' D\tau_0}[Q]^{1/3}, \tag{9}$$

where $K_{sv} = [(I_0/I)–1]/[Q]$[1], $K_{SV}^0 = \frac{4\pi N' DR\tau_0 k_a}{4\pi N' DR + k_a}$ is the S-V constant at $[Q] = 0$, D is the sum of the mutual diffusion coefficients of the reactants, R is the encounter distance, k_a is the activation energy controlled rate constant, and N' is Avogadro's number per millimole.

MATERIALS AND METHODS

Chemicals

The laser dye 2,2″-dimethyl-p-terphenyl (DMT) was obtained from Exciton (Dayton, OH, USA) and was used as received, without further purification. The molecular structure of DMT is shown in Fig. 1. The

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[1] For efficient quenching (concentration dependent) processes, the value K_{sv} is often observed to increase with [Q].

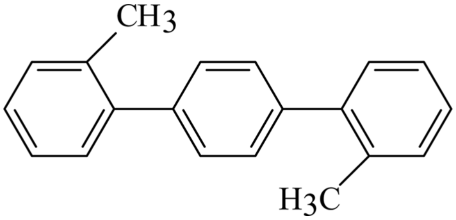

FIGURE 1 The molecular structure of 2,2″-dimethyl-p-terphenyl (DMT).

quencher, CCl_4 was obtained from BDH laboratory (Glaxo, Mumbai, India) and was of HPLC grade. The solvents, benzene and acetonitrile, were obtained from S-D Fine Chemicals Ltd. (Mumbai, India) and were of spectroscopic grade. The quencher and the solvents were used without any further purification. For all the quenching experiments in each solvent mixture, 10^{-4} M stock solution of DMT was used. The CCl_4 concentrations were varied using the respective stock solutions, so as to achieve desirable final concentration. Freshly prepared solutions were used for all experiments.

Spectroscopic Measurements

The absorption spectra were recorded using a Hitachi 150-20 UV-Vis spectrophotometer. The fluorescence spectra were recorded using a Hitachi F-2000 fluorescence spectrophotometer. The excitation wavelength chosen was the absorption maximum of the DMT. The samples were excited at 280 nm and the fluorescence intensity was monitored at 332 nm in all the benzene and acetonitrile (BN-AN) solvent mixtures at various CCl_4 concentrations. The CCl_4 quencher concentration was varied in the range 0.00 M to 0.10 M, with a larger number of observations taken in the linear region at lower concentration of CCl_4 (0.00 M to 0.04 M). All these measurements were carried out at room temperature (300 K).

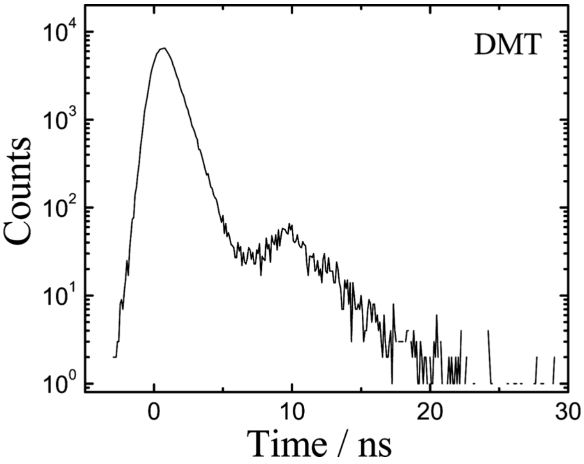

FIGURE 2 Fluorescence decay profiles for DMT in benzene at 300 K.

Fluorescence lifetime measurements were done by using single-photon counting time-domain spectrometer (model EI-199; Edinburgh Instrument, UK). The fluorescence decay measurements were taken with and without quencher using time-correlated single-photon counting (TCSPC) technique (Fig. 2). Fluorescence lifetime of DMT, in benzene,

TABLE 1 Parameters Obtained by Fitting the Experimental Results to Four Different Fluorescence Quenching Equations (Least-Square Fit Procedure)

Solvent mixtures (%v/v)	ε	$K_{SV}^{a}(M^{-1})$	$k_{g}^{b}(M^{-1})$	$k_{q}^{c} \times 10^{10}$ $(M^{-1}s^{-1})$	$k_{q}^{d} \times 10^{10}$ $(M^{-1}s^{-1})$	K_{SV}^{e} (M^{-1})	$k_{q}^{f} \times 10^{10}$ $(M^{-1}s^{-1})$	V^{g} (M^{-1})	r^{h} (Å)
100% BN + 0% AN	2.28	13.24	7.70	1.69	2.87	15.98	2.04	4.84	12.4
80% BN + 20% AN	10.67	18.57	9.34	2.37	4.12	16.33	2.08	6.62	13.8
60% BN + 40% AN	15.18	16.74	8.51	2.14	3.82	17.43	2.22	7.13	14.1
40% BN + 60% AN	24.30	31.34	22.65	4.00	7.74	19.06	2.43	9.62	15.6
20% BN + 80% AN	30.46	42.02	6.89	5.36	7.81	22.81	2.90	11.15	16.4
0% BN + 100% AN	37.12	128.61	16.16	16.40	53.40	25.25	3.22	15.05	18.1

$R_Y = 3.98$ Å, $R_Q = 2.73$ Å, $R\ (= R_Y + R_Q) = 6.71$ Å, $\tau_0 = 0.784$ ns.

[a] S-V quenching constant (dynamic quenching constant) determined from equation (4).

[b] Ground-state association constant of the complex determined from equation (4).

[c] Bimolecular quenching rate constant determined from equation (4).

[d] Bimolecular quenching rate constant obtained from the lower portion of the S-V plot according to equation (1).

[e] S-V quenching constant determined from equation (7).

[f] Bimolecular quenching rate constant determined from equation (7).

[g] Static quenching constant determined from equation (7).

[h] Radius of sphere of action called *kinetic distance* determined from equation (6).

in the absence of the quencher (τ_0) is given at the bottom of Table 1. Here it is assumed that τ_0 value of solute is the same for all solvent mixtures (i.e., independent of solvent polarity).[27,13] The experimental values are reproducible within 5% of the experimental error.

RESULTS AND DISCUSSION

Fluorescence and Absorption Spectra

The absorption and fluorescence spectra of DMT were taken in the absence and in the presence of CCl_4 in different solvent mixtures of BN-AN at room temperature (Figs. 3 and 4). From the spectra, the following observations were made: (i) the absorption spectra do not show any observable differences in shape or maxima. Although there is appreciable quenching in the presence of CCl_4, the shape of the fluorescence spectra also remains the same with no change in the position of the maxima. (ii) No new fluorescence peak is observed at longer wavelengths. (iii) Excitation spectra of the compound are similar in form to their respective absorption spectra. (IV) Absorption spectra of the fluorcphore were found to be unaltered during the course of the experiment.

The above observations suggest that (i) the fluorescence-quencher interaction does not change the absorption and fluorescence spectral properties, because the ground-state complex formed between DMT and CCl_4 is not sufficiently stable owing to weak interaction: (ii) the formation of any emissive exciplex may be discarded.

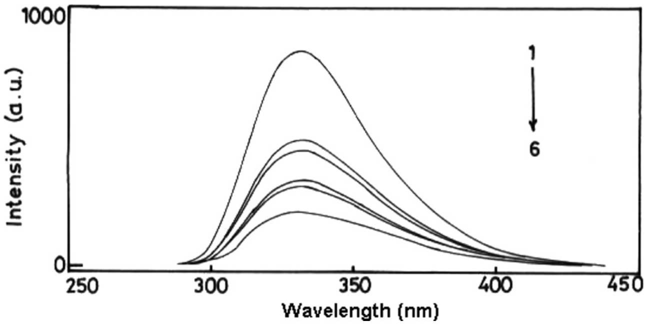

FIGURE 4 Fluorescence emission spectra of DMT ($C = 1 \times 10^{-4}$ M, $\lambda_{ex} = 280$ nm) in the presence of CCl_4 in 40% BN + 60% AN at 300 K. Concentrations of CCl_4 (in M): (1) 0.00, (2) 0.02, (3) 0.04, (4) 0.06, (5) 0.08, and (6) 0.10.

Fluorescence intensity of DMT decreases with the increase in CCl_4 concentration. The S-V plots for different solvent mixtures are given in Fig. 5. From the figure, it can be observed that (i) the quenching of fluorescence is appreciable at low concentrations of CCl_4. The curves are linear (correlation: 0.93) at a low concentration of CCl_4 (less than 0.04 M) and show a positive deviation from linearity for higher concentrations of CCl_4 for all the solvent mixtures. This suggests that dynamic quenching process operates at low concentration of the quencher only. (ii) The positive deviation from linearity indicates that the quenching is not purely dynamic. (iii) The initial slope of the quenching curves increases with increasing dielectric constant (ε) of the solvent mixture.

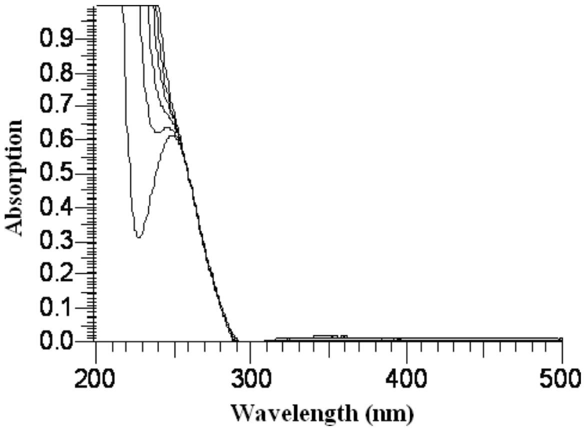

FIGURE 3 Absorption spectra of DMT ($C = 1 \times 10^{-4}$ M, $\lambda_{ex} = 280$ nm) in the presence of CCl_4 in 40% BN + 60% AN at 300 K. Concentrations of CCl_4 (in M): (1) 0.00, (2) 0.02, (3) 0.04, (4) 0.06, (5) 0.08, and (6) 0.10.

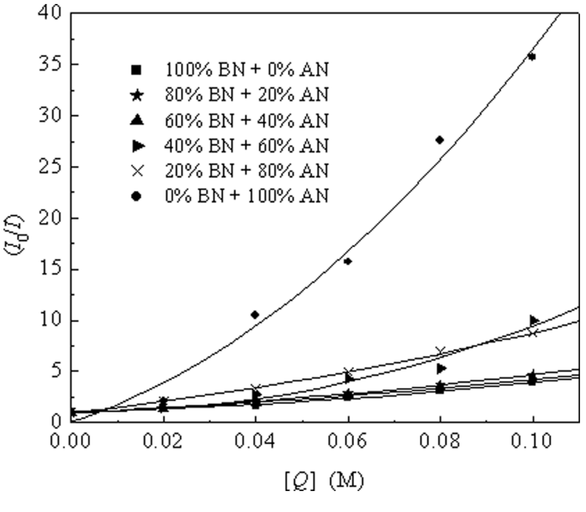

FIGURE 5 The S-V plots of (I_0/I) versus [Q] (nonlinear curves are fitted) for DMT in different solvent mixtures of benzene and acetonitrile (BN + AN).

Mechanism of Quenching

The observed positive deviations in the S-V plots can be due to two reasons: (i) static quenching, due to ground-state complex formation; (ii) transient component of the dynamic quenching, due to the presence of the quencher molecule within the quenching sphere of action, and is discussed using the ground-state complex/the sphere of action static quenching models.

In order to find whether ground state complex is formed, we have invoked groundy state complex model. Our experimental data is fitted to equation (4), and using least-square fit procedure K_{SV} and k_g have been sorted out. Figure 6 shows the plots of $(I_0/I - 1)/[Q]$ versus $[Q]$, which are straight lines with intercept of $(K_{SV} + k_g)$ and slope of $K_{SV} \cdot k_g$. These plots are linear with correlation coefficients greater than 0.90. The individual values of K_{SV} and k_g calculated from these values of intercepts and slopes are given in Table 1. The table shows that the ground-state association constant (k_g) is much smaller in magnitude compared with K_{SV}. No clear trend of its variation with solvent polarity is observed. The quenching constant k_q $(= K_{SV}/\tau_0)$ obtained from these K_{SV} values does not agrees well with that obtained from the lower portion of the S-V plot according to equation (1), that is, in the low concentration region in the plot of I_0/I versus $[Q]$, which is nearly linear. So, in the current case, static quenching is very low. Apart from this, there is no change in the absorption and fluorescence spectra even at higher concentrations of quencher. Hence deviation due to ground-state complex formation is discarded. Thus, the analysis of the data was carried out by employing the sphere of action static quenching model.

In order to see the role of static quenching process, we have used the sphere of action static quenching model. The experimental data is fitted to equation (7), and K_{SV} and V have been sorted out using least-square fit procedure. The plots of $[1 - (I/I_0)]/[Q]$ versus I/I_0 (Fig. 7) are linear with correlation coefficients greater than 0.95. The slope gives the value of K_{sv} and the value of V is calculated from the intercept. The values of K_{sv} and V for DMT in different solvent mixtures of BN-AN are tabulated in Table 1. There is no clear trend of their variation with solvent polarity. The bimolecular quenching rate constants k_q $(= K_{SV}/\tau)$ were determined from these K_{SV}, and the higher values of k_q suggest the efficient quenching of fluorescence (Table 1). From Table 1, it can be seen that the static quenching constant (V) is much smaller in magnitude compared with K_{SV} and also as the values of these parameters increases with increase in the percentage of acetonitrile. The value of static quenching constant (V) is largest in a solution with 100% AN, which is responsible for the larger deviation from the straight line in the S-V plots of Fig. 5. This indicates the solvent polarity effect on the fluorescence quenching. The values of r are calculated by use of equation (6) for all the solvent mixtures (Table 1). The magnitudes of the static quenching constant V and radii r of

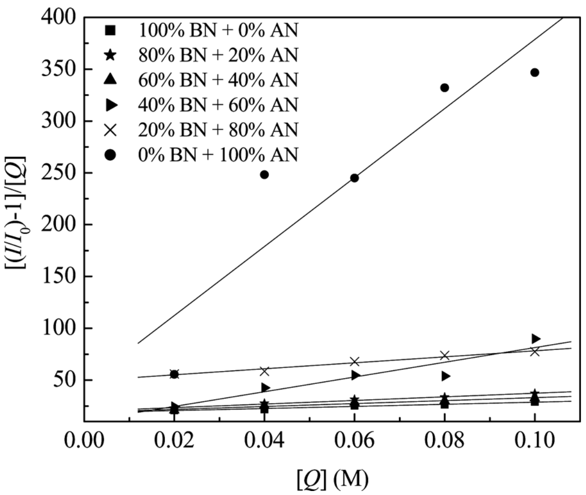

FIGURE 6 **The plots of $[(I_0/I) - 1]/[Q]$ versus $[Q]$ (least-square fit) for DMT in different (BN + AN) solvent mixtures.**

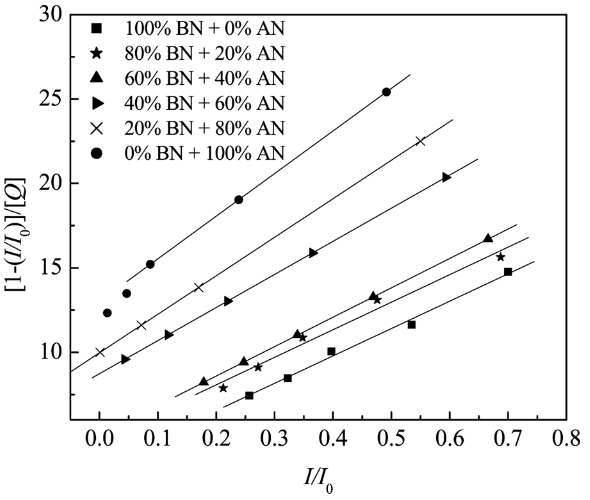

FIGURE 7 **The plots of $[1 - (I_0/I)]/[Q]$ versus (I_0/I) (least-square fit) for DMT in different (BN + AN) solvent mixtures.**

the sphere of action (kinetic distance) support static and dynamic effects. For these reasons, it seems most reasonable in case of DMT to discuss the static quenching phenomena in terms of sphere of action.

The radii of the fluorophore (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[28] and are given at the bottom of Table 1. From these values of R_Y and R_Q, the sum of the molecular radii R, of DMT and CCl_4, is determined. This sum of the molecular radii is referred to as encounter distance. This value is then compared with the values of r to verify whether the reaction is due to sphere of action model. From Table 1, it can be seen that the values of kinetic distance r are greater than the encounter distance R (given at the bottom of Table 1) in all solvent mixtures. Therefore, according to Andre et al.,[29] if the distance between the quencher molecule and excited molecule lies between the encounter distance R and the kinetic distance r, 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. From Table 1, we see that the values of r are greater than the value of encounter distance R in all the solvent mixtures indicating that the sphere of action model holds good very well. Further, it may also be noted that a positive deviation in S-V plot is expected when both static and dynamic quenching occurs simultaneously.[11]

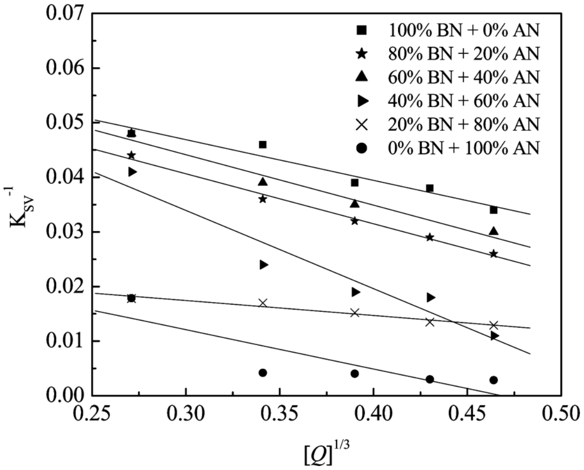

FIGURE 8 The plots of K_{SV}^{-1} against $[Q]^{1/3}$ (least-square fit) for DMT in different (BN + AN) solvent mixtures.

In order to find whether the reactions are diffusion limited, we have used finite sink approximation model. This model helps us to estimate independently the mutual diffusion coefficient D and distance parameter R'. Figure 8 shows the plots of K_{SV}^{-1} against $[Q]^{1/3}$, which are linear with negative slope, and deviations observed may be attributed to experimental uncertainties. This indicates the presence of a transient quenching component.[25 – 26]

The plots are linear with good correlation coefficients (greater than 0.93) for all solvent mixtures. The mutual diffusion coefficient (D) becomes directly accessible from the slope of the graph exemplified in equation (9). K_{SV}^{0} is obtained from the intercept regardless of the relative magnitudes of k_a and k_d ($= 4\pi N'DR$), irrespective of whether quenching is diffusion limited or not (Table 2). From K_{SV}^{0}, it is possible to find the distance parameter (R') through $K_{SV}^{0} = 4\pi NDR'\tau_0$, where R' has the same meaning as in the long-time SCK model.[29, 30] In our investigation, $R' > R$ (Table 2) for all the solvent mixtures and hence the values of k_a cannot be determined. The values of $4\pi N'DR'$ are calculated using the experimentally determined values of R' and D.

TABLE 2 The Values of K_{sv}^{0} (Steady-State Quenching Constant at $[Q] = 0$), Mutual Diffusion Coefficient D, Distance Parameter R', and $4\pi N'DR'$ for DMT + CCl_4 System in Different Solvent Mixtures of Benzene and Acetonitrile at 300 K

Solvent mixtures (%v/v)	K_{SV}^{0} (M^{-1})	D ($10^5 cm^2 s^{-1}$)	R' (Å)	$4\pi N'DR'$ (10^{10} M^{-1} s^{-1})
100% BN + 0% AN	12.99	2.82	7.76	1.66
80% BN + 20% AN	14.71	2.84	8.72	1.87
60% BN + 40% AN	13.89	2.90	8.07	1.77
40% BN + 60% AN	12.20	1.60	12.85	1.56
20% BN + 80% AN	37.71	7.93	8.01	4.81
0% BN + 100% AN	29.47	3.60	13.70	3.73

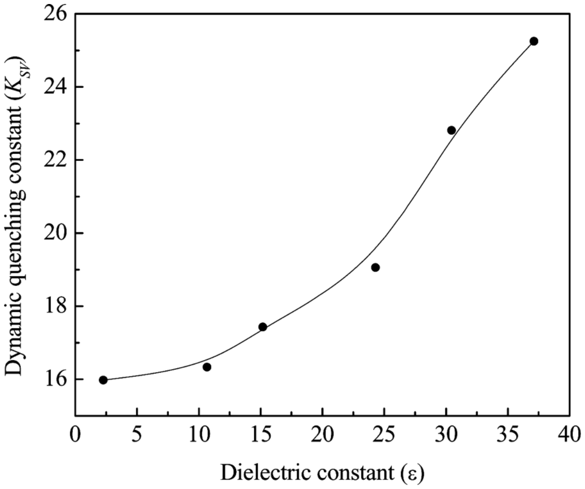

FIGURE 9 Variation of K_{sv} as a function of dielectric constant (ε) for DMT in (BN + AN) solvent mixtures.

According to Joshi et al., [30] the bimolecular reactions are said to be diffusion limited, if the values of k_q determined from equation (7) are greater than $4\pi N'DR'$. From Table 2, it can be seen that, for all the solvent mixtures (except 20% BN + 80% AN, and 100% AN), the values of k_q are greater than $4\pi N'DR'$, which is an expected result for diffusion-limited reaction.[26].

Effect of Solvent

Figure 1 shows a regular but slightly nonlinear increase in quenching with increasing solvent polarity, the nonlinearity being a maximum in acetonitrile. The effect observed is a combined effect of the static and the dynamic quenching. We have used the literature values of dielectric constants for all the solvent mixtures.[31] The variation in K_{SV} with dielectric constant (ε) has been plotted in Fig. 9. From figure, it can be noted that K_{SV} increases with increasing dielectric constant (ε) in a nonlinear way and almost flattens out at low dielectric constants, which can be explained by the greater charge transfer character of the exciplex in the polar solvent.[1] The non-linearity in the S-V plots of Fig. 5 and nonlinear variations in K_{SV} with dielectric constant (Fig. 9) are due to the combined effect of the static quenching constant (V) and the S-V quenching constant (K_{SV}). It is seen from Table 1 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.[5]

CONCLUSIONS

From the above discussion and magnitudes of the rate parameters determined, we may conclude that:

1. Fluorescence quenching of DMT by CCl_4 in different solvent mixtures is due to both dynamic quenching and sphere of action static quenching. The S-V plots show positive deviation leading to high values of k_q, indicating efficient fluorescence quenching. In the systems that we studied, ground-state complex is not formed.
2. The value of bimolecular quenching rate parameter (k_q^f) increases with increase in dielectric constant of the solvent mixture suggesting the charge transfer character of the excited complex.
3. All the rate constants are dependent on the solvent polarity, and thus the reactions are diffusion limited in all the solvent mixtures.

These facts suggest that positive deviations in the S-V plot are due to the presence of both static and dynamic quenching processes.

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