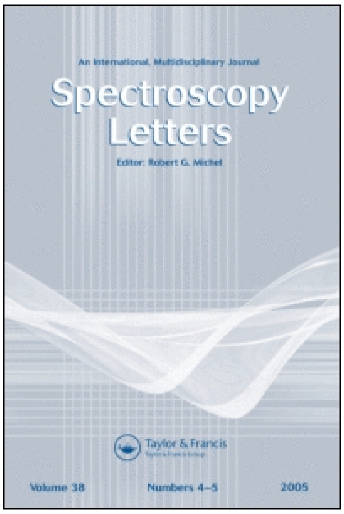

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Effect of Solvent Polarity on Fluorescence Quenching of New Indole Derivatives by CCl_4

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ABSTRACT The fluorescence quenching of solutes 3-[5′-methyl-3′-phenylindol-2′-yl]-s-triazolo [3,4-b] [1,3,4] thiadiazol-6(5H)-thione (MPITTT) and 3-phenyl-2,5-bis-[thiosemicarbazido] indole (PbisTI) by carbon tetrachloride (CCl_4) in dioxane and acetonitrile mixtures has been studied at room temperature by steady-state fluorescence measurements. The positive deviation from linearity has been observed in the Stern–Volmer (S-V) plots for both fluorophores in different composition of mixed solvents even at moderate CCl_4 concentration ($0.10\,\mathrm{mol\,dm^{-3}}$). Various quenching parameters of the quenching processes have been determined using the extended S-V equation and have been found to be dependent on the solvent polarity. Further, with the use of the finite sink approximation model, it is concluded that the bimolecular quenching reactions are diffusion limited, and the distance parameter R' and mutual diffusion coefficient D are estimated independently.

KEYWORDS fluorescence, indole, solvent polarity, static and dynamic quenching, Stern–Volmer plot

INTRODUCTION

The quenching of fluorescence of organic molecules by carbon tetrachloride (CCl_4) has been a subject of continued investigation for the past couple of decades to understand the nature of bimolecular reactions taking place both under steady state and transient conditions.[1–9] Carbon tetrachloride is known to be a good quencher for several fluorescent molecules. The role of fluorescence quenching can be studied experimentally by determining quenching parameters using Stern–Volmer (S–V) plots. In almost all cases of CCl_4 quenching, the S-V plots were found to be linear, in which the quenching mechanism is mainly due to dynamic process, where the diffusion process is a dominant one. In a few cases, the experimental results show positive deviation from linear S-V relation. This positive deviation was attributed to various processes, like singlet–triplet excitation, formation of charge transfer complex both at ground and excited states, static and dynamic quenching, and so faith. For the anthracene–CCl_4

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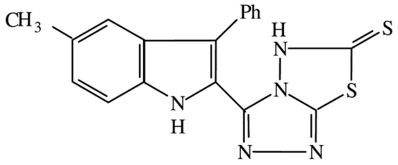
system, Ware and Lewis [1] found a relatively low fluorescence quenching efficiency. Excitation to the S_1 level of anthracene gave a linear S-V plot. However, excitation to the S_3 level showed a positive deviation from linearity. These results were attributed to the formation of ground-state complex. Many reports of the ground-state complex of a charge transfer nature between aromatic molecules and chlorinated alkanes have appeared in the literature.[10,11] If nonemissive exciplex formation is the mechanism for fluorescence quenching by chlorinated methane, polarity of the solvent medium is expected to play a role in the mechanism.[3,7] The fluorescence properties of indole and its derivatives have been extensively studied.[5,6,11] This is in part due to the occurrence of the indole moiety in the majority of protein. The quenching studies are able to provide valuable information concerning the exposure of tryptophanyl residues and dynamics of the proteins matrix surrounding such residues. Further studies using this technique to investigate protein dynamics and ligand-induced changes in the conformation and dynamics of proteins are likely to appear. Also, fluorescence quenching with anisotropy measurements shows much promise in revealing additional dynamic features of proteins (e.g., rotation and segmental mobilites of the fluorescing residues or probes).[12,13]

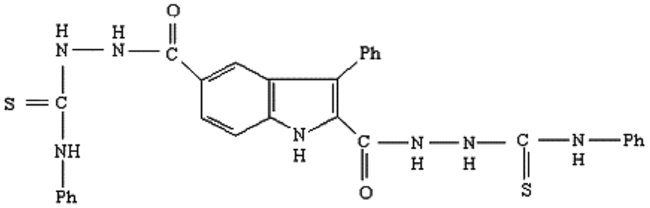
In the current study, the effect of solvent polarity on the fluorescence quenching of newly synthesized indole derivatives has been studied at room temperature using CCl_4 quencher in different mixtures of dioxane and acetonitrile (AN). The change of composition of the current solvents provides a good range of solvent polarity ranging from 2.1 to 36.0 debye. Also, the dependence of fluorescence quenching on solvent polarity at various quencher concentrations that cover the nonlinear range of the quenching curve has been studied.

MATERIALS AND METHODS

The solutes 3-[5′-methyl-3′-phenylindol-2′-yl]-s-triazolo [3,4-b] 1,3,4] thiadiazol-6(5H)-thione (MPITTT) and 3-phenyl-2,5-bis-[thiosemicarbazido] indole (PbisTI) were synthesized in our laboratory using standard methods,[14,15] and the purity was checked by HPLC method. The molecular structures are as shown in Figure 1. The spectroscopic grade solvents (S.D. Fines Chemicals Ltd., Mumbai, India) were used without further purification to prepare the solutions. However, the purity of the solvents was checked by recording the background fluorescence. The spectroscopic-grade CCl_4 solvent was used as a quencher, and it was double distilled before use. Dielectric constants (ε) of the pure solvents were obtained from the literature,[16] and those of the mixed solvents (ε_{MS}) were calculated using the equation $\varepsilon_{MS} = f_A\varepsilon_A + f_B\varepsilon_B$, where the subscripts A and B represent the cosolvents and f represents their volume fraction.[17,18]



3–[5′–methyl–3′–phenylindol–2′–yl] –s–triazolo [3,4-b][1,3,4] thiadiazol – 6(5H) – thione (MPITTT).



3–phenyl–2,5–bis –[thiosemicarbazido] indole (PbisTI).

FIGURE 1 **Molecular structures of the indole derivatives.**

The absorption spectra of the solutes at the concentration of $1 \times 10^{-5}\,\text{mol}\,\text{dm}^{-3}$ in different solvent mixtures were recorded using a UV-visible absorption spectrophotometer (Hitachi model 150–20). For the same concentration, the steady-state fluorescence intensities were recorded by exciting the solute MPITTT at 310 nm and the solute PbisTI at 330 nm corresponding with longer wavelength absorption band by varying the quencher concentration from 0.00 to 0.10 mol dm^{-3} using a fluorescence spectrophotometer (Hitachi model F-2000) in different solvent mixtures. The fluorescence decays of both solutes were recorded in dioxane solvent using picosecond time correlated single photon counting technique (TCSPC) (model 5000U; IBH, UK). The third harmonic picosecond laser pulse of wavelength 310 nm, derived from the mode locked Ti-sapphire laser (model Spectra Physics; Tsunami) pumped by $Nd\text{-}YVO_4$ laser was used as an excitation source. The decays were measured corresponding with the emission maxima. The data analysis was accomplished by the software DAS-6 (IBH) based on the deconvolution technique using iterative nonlinear least square methods. The quality of the fit is identified by the reduced chi-square value, weighted residuals, and the autocorrelation function of the residuals.

RESULTS AND DISCUSSION

The Stern–Volmer plots for the quenching of fluorescence intensities of the solutes by CCl_4 quencher in different solvent mixtures were plotted according to the Stern–Volmer equation[19]

$$\frac{I_0}{I} = 1 + K_{SV}[Q] \qquad (1)$$

where I_0 and I are the fluorescence intensities of the solutes in the absence and presence of the quencher, respectively, K_{SV} is the S-V quenching constant and $[Q]$ is the quencher concentration. The S-V plots (I_0/I against $[Q]$) as shown in Figures 2 and 3 were found to be nonlinear and showing positive deviation. It may be concluded that the quenching is not purely collisional and may be due to the formation of either the ground state complex or static quenching process.

The formation of ground-state complex has been analyzed by using the extended S-V equation,[20]

$$\frac{I_0}{I} = (1 + K_g[Q])(1 + K_{SV}[Q])$$

That is,

$$[(I_0/I) - 1]/[Q] = (K_{SV} + K_g) + K_{SV}K_g[Q] \qquad (2)$$

where K_{SV} and K_g are S-V and ground-state association constants, respectively. The plots $[(I_0/I)–1]/[Q]$ against $[Q]$ were drawn and found to be linear. The intercept $(K_{SV}+K_g)$ and slope K_{SV}. K_g were found using the least squares fit method. However, in all the cases, the K_{SV} and K_g values were found to be imaginary. This shows that equation (2) is not applicable to analyze the positive deviation. The absorption and fluorescence spectra of both solutes in any of the solvent mixtures used in the absence and presence of a quencher do not show any observable difference in the shape or the peak position, and also no new fluorescence band is observed at longer wavelength. This clearly indicates that the fluorescence quenching for these solutes by CCl_4 occurred without involving any ground-state complex or exciplex formation.[2–4,11] In the absence of exciplex formation, the quenching process appears to be due to the electron transfer (ET) interaction, because these solutes are good electron donors[11] in the excited state, and CCl_4 is known be a good electron acceptor.[21,22]

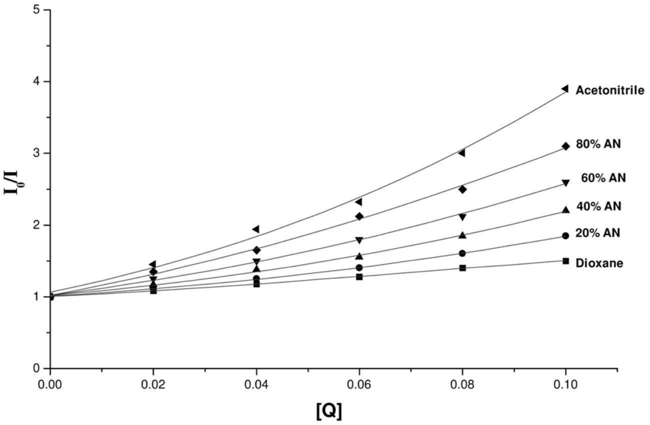


FIGURE 2 Stern–Volmer plot of I_0/I against $[Q]$ for solute MPITTT.

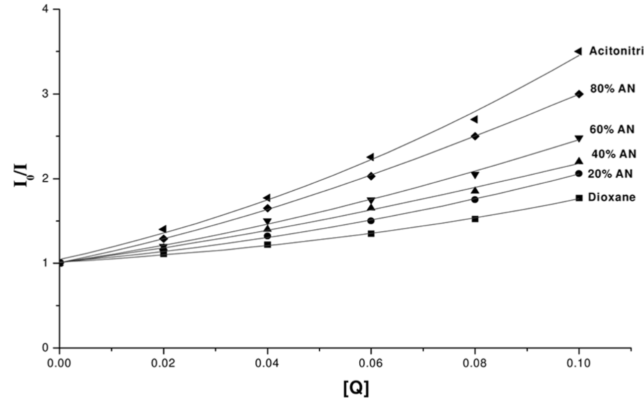


FIGURE 3 Stern–Volmer plot of I_0/I against $[Q]$ for solute PbisTI.

The analysis of data for the positive deviation in S-V plots was made using "sphere of action" static quenching model. According to the static quenching model, the instantaneous or static quenching occurs only when the quencher molecule is very near to or in contact with the fluorescent molecule, just at the moment of its excitation. This model can be explained by the fact that only a certain fraction W of the excited state is quenched by the collisional mechanism. Some molecules in the excited state, the fraction of which is $(1 - W)$, are deactivated almost instantaneously after being excited because a quencher molecule happens to be randomly positioned in the proximity at the time when the molecules are excited and interacts very strongly with them. Thus, the fraction W decreases from unity in contrast with the linear S-V equation. Several models were employed to describe this static quenching process, all leading to the modified form of the S-V equation[19]

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

Smoluchowski's diffusion-controlled equation containing a transient term is written as[23]

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

where N' is Avogadro's number per millimole, R is the encounter distance, that is, the sum of the radii of the solute (R_S) and quencher (R_Q) molecules, D is the sum of the diffusion coefficient of solute (D_S) and quencher (D_Q) molecules, and t is the time. The retention of the second term in equation (4) leads to an additional factor W in equation (3). This additional factor is given by

$$W = \exp(-V[Q])$$

That is,

$$\ln W = -V[Q] \tag{5}$$

where $V\,(\mathrm{dm^3\,mol^{-1}})$ is the static quenching constant and represents the active volume element surrounding the excited molecules.

According to Frank and Wawilow,[24] instantaneous quenching occurs in a randomly distributed system, when a quencher happens to reside within a "sphere of action" with volume of $V/N'\,(\mathrm{dm^3})$ and is given by

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

where r is the radius of the sphere of action and also called kinetic distance.

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, equation (3) can be rewritten as[5,7,11]

$$[1-(I/I_0)]/[Q] = K_{SV}(I/I_0) + (1-W)/[Q]. \tag{7}$$

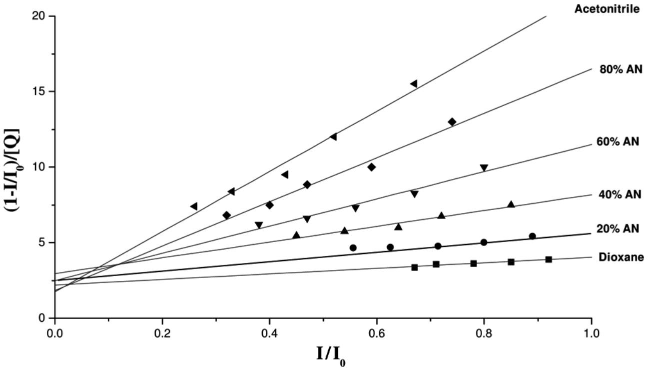


FIGURE 4 Modified Stern–Volmer plot of $(1-I/I_0)/[Q]$ against I/I_0 for solute MPITTT.

The modified S-V plots of $[1–(I/I_0)]/[Q]$ against I/I_0 for both solutes are shown in Figures 4 and 5 and were found to be linear. From these graphs, it is evident that the intercepts are non-zero and are large. The S-V quenching constant K_{SV} was determined in all the cases by least squares fit method, and the quenching rate parameter k_q was calculated using the equation $k_q = K_{SV}/\tau_0$, where τ_0 is the fluorescence lifetime in the absence of quencher. The fluorescence decay profile for both solutes in dioxane solvent without quencher is shown in Figure 6. It is observed that the fluorescence decay for MPITTT was fitted to biexponential with time constants $\tau_1 = 0.53\,\mathrm{nm}$ (amplitude $a_1 = 0.6$) and $\tau_2 = 1.96\,\mathrm{ns}$ (amplitude $a_2 = 0.4$). However, the average lifetime, $<\tau_0> = 1.10\,\mathrm{ns}$ (calculated using the relation $<\tau_0> = \tau_1 a_1 + \tau_2 a_2$) is considered in estimating the quenching parameters, whereas the decay profile for solute PbisTI was fitted to monoexponential and its value is 1.60 ns. The determined lifetime values agree closely with the lifetime values of the other indole derivatives.[5,11] The values of K_{SV} and

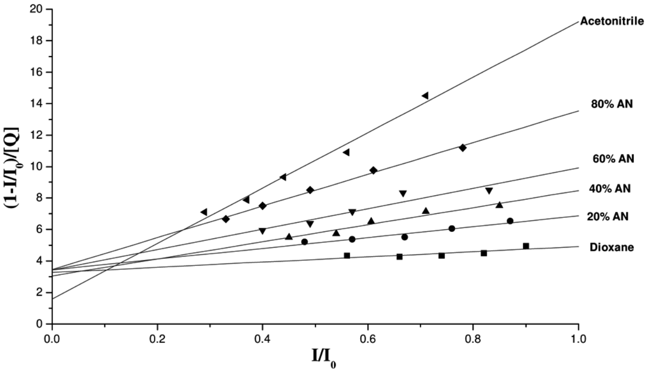
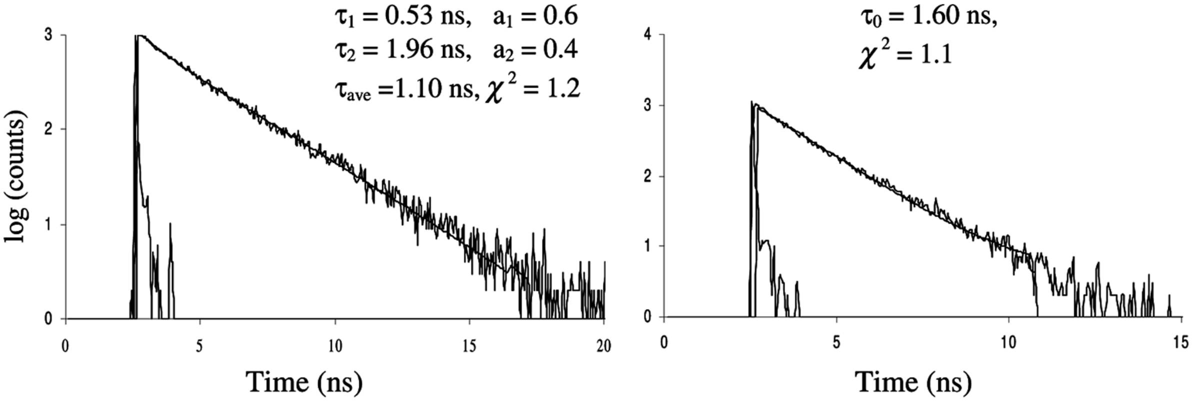


FIGURE 5 Modified Stern–Volmer plot of $(1-I/I_0)/[Q]$ against I/I_0 for solute PbisTI.



(a) (b)

FIGURE 6 **Fluorescence decay profiles of (a) MPITTT and (b) PbisTI in dioxane solvent at the concentration of 1×10^{-5} mol dm^{-3}.**

k_q are collected in Tables 1 and 2. The intercepts of least squares fit lines of Figures 4 and 5 are equal to $(1-W)/[Q]$. From these intercepts, the values of W were determined for each concentration, and the range of W is given in Tables 1 and 2. Using the values of W, the static quenching constant V and the kinetic distance or radius of sphere of action r were determined according to equations (5) and (6) for both solutes. All these data are collected in Tables 1 and 2. It is observed that the values of K_{SV} are rather larger relative to the V value in almost all the mixtures, which explains the lack of the absorption change on addition of the quencher.[2] Also, from Tables 1 and 2, it is seen that the static quenching constant V for both solutes is approximately around 3 and 4 mol^{-1} dm^3 in different mixtures, respectively. This indicates that the static quenching constant V is independent of solvent polarity, which was also observed by others.[2,5,20]

From the graph of K_{SV} against dielectric constant (ε) (Fig. 7), it is observed that there is a regular but slightly nonlinear increase in quenching with increasing solvent polarity (i.e., dielectric constant and nonlinearity is maximum in acetonitrile solvent). The nonlinearity in the S-V plots of Figures 2 and 3 and nonlinear variation in K_{SV} with dielectric constant in Figure 7 are due to the combined effect of the static quenching V and S-V quenching constant K_{SV}.[2,3,5,11]

In order to compare the radius r of sphere of action with encounter distance or reactive distance R, that is, the sum of the radii of the solute (R_S) and quencher molecules (R_Q), the radii of the solutes and quenchers were determined and are given at the bottom of Tables 1 and 2. The radii of the molecules were obtained by using the software PCMODEL version 4 (Serena Software, Bloomington, IN, USA). After drawing the structure of the molecule, the software is able to calculate total surface area (TSA) occupied by the molecule by optimizing the bond length and bond angles. This calculation was done by assuming the molecules as sphere. The TSA in square angstrom was obtained, from which the

TABLE 1 **The Stern–Volmer Constant K_{SV}, Quenching Rate Parameter k_q, Range of W, Static Quenching Constant V, and Kinetic Distance r for Solute MPITTT**

Solvent mixture (% v/v)	Dielectric constant ε	K_{SV} (dm^3 mol^{-1})	$k_q \times 10^{-9}$ (dm^3 mol^{-1} s^{-1})	Range of W	V (dm^3 mol^{-1})	r (Å)
Dioxane	2.10	1.83	1.66	0.78–0.96	2.55	10.02
20% AN	8.10	3.12	2.84	0.74–0.95	3.14	10.78
40% AN	15.3	5.31	4.82	0.72–0.94	3.38	11.80
60% AN	22.0	9.02	8.18	0.75–0.95	2.92	10.52
80% AN	28.6	14.53	13.21	0.81–0.96	2.62	10.08
Acetonitrile (AN)	36.0	19.14	17.40	0.80–0.96	2.31	9.71

$R_S = 4.18$ Å; $R_{CCl4} = 2.80$ Å; $<\tau_0> = 1.10$ ns.

TABLE 2 **The Stern–Volmer Constant K_{SV}, Quenching Rate Parameter k_q, Range of W, Static Quenching Constant V, and Kinetic Distance r for Solute PbisTI**

Solvent mixture (% v/v)	Dielectric constant ε	K_{SV} ($dm^3\,mol^{-1}$)	$k_q \times 10^{-9}$ ($dm^3\,mol^{-1}s^{-1}$)	Range of W	V ($dm^3\,mol^{-1}$)	r (Å)
Dioxane	2.10	1.64	1.02	0.67–0.94	4.02	11.68
20% AN	8.10	3.56	2.23	0.66–0.93	4.22	17.12
40% AN	15.3	5.43	3.39	0.71–0.94	4.12	11.78
60% AN	22.0	6.48	4.28	0.66–0.93	4.37	12.01
80% AN	28.6	10.22	6.81	0.70–0.94	3.72	11.40
Acetonitrile (AN)	36.0	17.31	10.82	0.84–0.97	1.95	9.18

$R_S = 4.94$ Å; $R_{CCl4} = 2.80$ Å; $\tau_0 = 1.60$ ns.

radius of the molecule could be found using the relation

$$r = \left(\frac{TSA}{4\pi}\right)^{1/2}. \tag{8}$$

From Tables 1 and 2, it is evident that the values of r are greater than the encounter distance R. Similar results were also obtained for other molecules.[5,25,26]

According to Andre et al.[27] 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. To find out whether the reactions are diffusion limited, we considered the finite sink approximation model, which helps to estimate independently the mutual diffusion coefficient D, distance parameter R', and the activation energy controlled rate constant k_a.

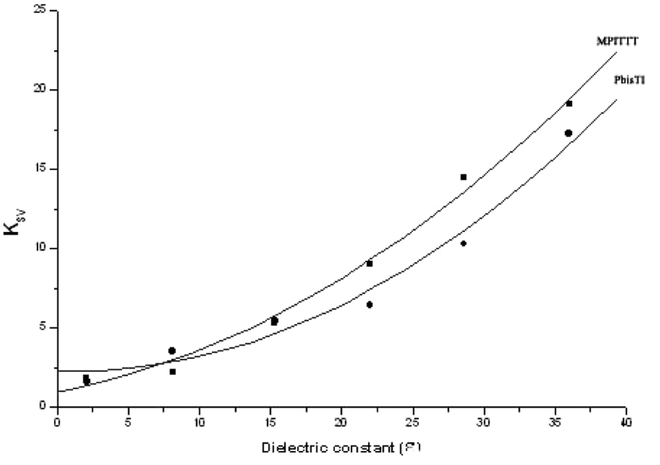


FIGURE 7 **Plot of K_{SV} against dielectric constant (ε) for solutes MPITTT and PbisTI.**

Finite Sink Approximation Model

Keizer[28] has proposed a nonequilibrium statistical modification of the Smoluchowski–Collins–Kimball (SCK) expression to fit the I_0/I ratio in fluorescence quenching. The modified Smoluchowski model, known as the SCK, model has been found to be adequate to explain the experimental data for several fluorescence quenching reactions. In this model, time-dependent rate coefficient $k(t)$ for diffusion-limited reaction of initially randomly distributed reactants is given by[23,29]

$$k(t) = a + b\exp(c^2 t)\mathrm{erfc}(ct^{1/2}) \tag{9}$$

where

$$a = k_a\left[1 + \frac{k_a}{4\pi NRD}\right]^{-1} \tag{10}$$

$$b = k_a\left[1 + \frac{4\pi NRD}{k_a}\right]^{-1} \tag{11}$$

$$c = \left[1 + \frac{k_a}{4\pi NRD}\right]\frac{D^{1/2}}{R}. \tag{12}$$

Integration of equation (10) between the limits [Q] (∞) at $r \to \infty$ and [Q] (R) at $r = R$ provides the well-known expression

$$\frac{1}{k_q} = \frac{1}{k_d} + \frac{1}{k_a} \tag{13}$$

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 coefficient of solute and quencher molecules. In equation (13), 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 a combination of these.[23]

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 (13) as

$$\frac{1}{k_q} = \frac{1 - (R/r_0)}{k_d} + \frac{1}{k_a}. \tag{14}$$

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 ($k_a \gg k_d$), equation (14) reduces to

$$k_q = \frac{k_d}{1 - R/r_0} \tag{15}$$

and k_q depends on the quenching concentration through r_0.

Because the sink radius (r_0) is identified with the most probable nearest-neighbor initial separation, the appropriate distribution requires that $r_0 = (2\pi N' [Q])^{-1/3}$. Replacing r_0 in equation (14) and k_d by its value ($4\pi N' DR$) and dividing the equation by the fluorescence lifetime of solute in the absence of quencher (τ_0), one obtains the modified Stern–Volmer relationship as[23,29]

$$K_{SV}^{-1} = (K_{SV}^0)^{-1} - \frac{(2\pi N')^{1/3}}{4\pi N' D\tau_0}[Q]^{1/3} \tag{16}$$

where

$$K_{SV}^0 = \frac{4\pi N' DR\tau_0 k_a}{4\pi N' DR + k_a}. \tag{17}$$

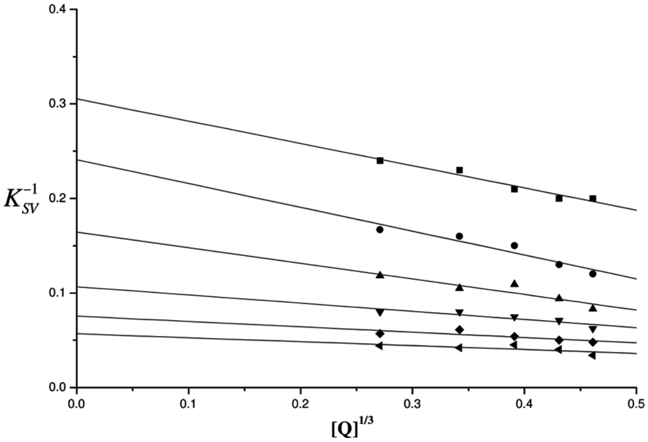


FIGURE 8 Modified Stern–Volmer plot of K_{SV}^{-1} against $[Q]^{1/3}$ for solute MPITTT.

A plot of K_{SV}^{-1} against $[Q]^{1/3}$ becomes linear with negative slope. Mutual diffusion coefficient D is accessible directly from the slope of the graph exemplified in equation (16), and K_{SV}^0 is obtained at $[Q] = 0$ regardless of the relative magnitudes of k_a and k_d ($=4\pi N' DR$), whether quenching is diffusion limited or not. From K_{SV}^0 , R' is estimated using[20]

$$K_{SV}^0 = 4\pi N' DR' \tau_0 \tag{18}$$

where R' has the same meaning as in the long-time SCK model[22,28] and is given as

$$R' = R[1 + 4\pi RDN'/k_a]^{-1}. \tag{19}$$

Then according to the theory discussed above, if $k_a > k_d$, then the reactions are said to be diffusion limited[20,25] (i.e., for $R' < R$). But if $R' > R$, the bimolecular quenching reactions of fluorescence quenching are said to be diffusion limited if the values of k_q

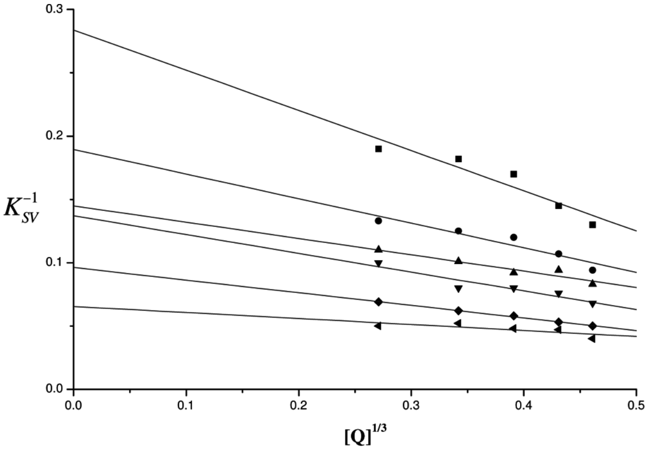


FIGURE 9 Modified Stern–Volmer plot of K_{SV}^{-1} against $[Q]^{1/3}$ for solute PbisTI.

TABLE 3 The Values of K_{SV}^0 (Steady-State Quenching Constant at $[Q]=0$), Mutual Diffusion Coefficient D, Distance Parameter R' , $4\pi N'DR'$, Activation Energy Controlled Rate Constant k_a and Quenching Rate-Constant for Diffusion Controlled Reaction k_d for Solute MPITTT

Solvent mixture (% v/v)	K_{SV}^0 (dm^3 mol^{-1})	$D\times 10^5$ (cm^{2}s^{-1})	R' (Å)	$4\pi N'DR'$, $\times 10^{-9}$ (dm^3 mol^{-1} s^{-1})	$k_a\times 10^{10}$ (dm^3 mol^{-1} s^{-1})	$k_d\times 10^{-10}$ (dm^3 mol^{-1}s^{-1})
Dioxane	3.22	0.82	4.94	3.05	1.06	0.43
20% AN	4.16	0.74	6.76	3.78	12.21	0.39
40% AN	6.10	1.13	6.66	5.96	12.42	0.59
60% AN	9.43	2.18	5.22	8.60	14.35	1.15
80% AN	13.33	3.32	6.46	16.22	21.92	1.75
Acetonitrile (AN)	17.54	4.46	4.72	15.92	4.90	2.35

determined from equation (7) are greater than $4\pi\ N'\ DR'$.[29]

For efficient quenching process, the values of K_{SV} are often observed to increase with $[Q]$. Hence, the values of K_{SV} were determined at each quencher concentrations ranging from 0.02 to 0.10 mol dm^{-3} in different binary mixtures using $K_{SV}=[(I_0/I)-1]/[Q]$. The graphs K_{SV}^{-1} versus $[Q]^{1/3}$ were plotted using equation (16) as shown in Figures 8 and 9, and they were found to be linear in all the mixtures. Using least squares fit method, the values of D and K_{SV}^0 (S-V constant at $[Q]=0$) were determined by measuring the slopes and intercepts. Then, distance parameter R' was determined according to equation (18) using the values of K_{SV}^0 and D. Further, the activation energy controlled rate constant k_a was calculated using equation (18) by considering distance parameter R' and encounter distance R. The determined values (i.e., K_{SV}^0 , D, R', k_a, and k_d) are collected in Tables 3 and 4, and it is observed that k_a is greater than k_d in all the binary mixtures. This suggests that the activation process is more predominant in quenching mechanism than the diffusion process. Hence the reactions are said to be diffusion limited.[20]

CONCLUSIONS

The fluorescence quenching behavior of MPITTT and PbisTI by CCl_4 has been studied in different binary mixtures of dioxane and acetonitrile. The S-V intensity plots of both solutes show positive deviation in all the mixtures. The nonlinearity in the S-V plots is interpreted by the sphere of action static quenching model due to the fact that no specific interactions between the solutes and the quencher were observed both in absorption and fluorescence spectra. The dynamic quenching constant k_q is determined from this model and is found to be quite high. It indicates that the quenching efficiency is large in both the solutes. The mutual diffusion coefficient D and distance parameter R' are accessed independently and, hence, k_a is calculated from the finite sink approximation model. This model is more precise in determining D and R' values due to the fact that all quencher concentrations are used in the calculation and also allows us to discriminate the nature of bimolecular quenching reactions. It is seen that for both the solutes, the activation energy controlled rate for electronic transfer ET (k_a) is greater than diffusion coefficient (k_d) indicating that the bimolecular

TABLE 4 The Values of K_{SV}^0 (Steady-State Quenching Constant at $[Q]=0$), Mutual Diffusion Coefficient D, Distance Parameter R', $4\pi N'DR'$, Activation Energy Controlled Rate Constant k_a, and Quenching Rate Constant for Diffusion Controlled Reaction k_d for Solute PbisTI

Solvent mixture (% v/v)	K_{SV}^0 (dm^3 mol^{-1})	D $\times 10^5$ (cm^{2}s^{-1})	R' (Å)	$4\pi N'DR'$, $\times 10^{-9}$ (dm^3 mol^{-1} s^{-1})	$k_a\times 10^{10}$ (dm^3 mol^{-1} s^{-1})	$k_d\times 10^{-10}$ (dm^3 mol^{-1} s^{-1})
Dioxane	3.53	0.41	7.12	2.18	2.76	0.25
20% AN	5.32	0.64	6.78	3.28	2.64	0.37
40% AN	6.94	1.01	5.68	4.34	1.63	0.59
60% AN	7.30	0.89	6.70	4.51	3.35	0.52
80% AN	10.42	1.32	6.62	6.61	4.57	0.77
Acetonitrile (AN)	15.38	2.58	4.93	9.62	2.65	1.56

quenching reactions are diffusion limited. Therefore, the above facts suggest that the quenching reaction is diffusion limited and that both static and dynamic quenching processes partly play a role in both systems.

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