December 2007 Volume 3 Issue 4

Trade Science Inc.

Macromolecules

An Indian Journal

Full Paper

MMAIJ, 3(4), 2007 [163-168]

Fluorescence quenching of 5-methyl-2-phenylindole by carbon tetrachloride

S.V.Nishti[1], R.S.Kunabenchi[1]*, O.V.Mangalgi[1], H.M.Suresh Kumar[1], S.M.Praveen[2], J.S.Biradar[2]
[1]Department of Physics, Gulbarga University, Gulbarga- 585 106, Karnataka, (INDIA)
[2]Department of Chemistry, Gulbarga University, Gulbarga-585 106, Karnataka, (INDIA)
Tel: +91-8472-245512, Fax: +91-8472-245927
E-mail: kunabenchi@yahoo.co.in

Received: 2nd October, 2007 ; Accepted: 7th October, 2007

ABSTRACT

The steady state fluorescence quenching of 5-methyl-2-phenylindole by carbon tetrachloride in different solvents viz. dioxane, benzene, toluene, butanol, methanol and acetonitrile, and time dependent study in butanol solvent 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 plot in all the solvents. The quencher concentration dependence data were analyzed using ground state complex formation and sphere of action static quenching models in order to interpret the results. The various rate parameters have been determined and the magnitudes of these rate parameters suggest that the ground state complex formation model is not applicable in this case but the sphere of action static quenching model agrees well with the experimental results. Hence, both the static and dynamic quenching processes are responsible for the observed positive deviation in the Stern-Volmer plots. Further, with the use of finite sink approximation model, it is concluded that these bimolecular quenching reactions are diffusion limited, and also the dependence of Stern-Volmer constant on dielectric constant of the solvents suggest the charge transfer character of the excited complex.

© 2007 Trade Science Inc. - INDIA

KEYWORDS

Indole;
Fluorescence;
Stern-Volmer plot;
Static and dynamic quenching;
Charge transfer.

INTRODUCTION

The phenomena of quenching is the one which competes with the spontaneous emission and causes reduction in the fluorescence intensity and lifetime of the molecule by a variety of molecular interactions such as exited-state reactions, molecular re-arrangements, energy transfer, ground-state complex formation, collisional quenching etc. Fluorescence quenching of organic molecules in solution by various quenchers like carbon tetrachloride (CCl_4), aniline, bromobenzene, halide ions etc., have been studied by several investigators[1-14]. This study has not only been of importance in physical sciences but also in chemical, biological and medical sciences[15,16]. The role of fluorescence quenching can be studied experimentally by determining the quenching rate parameters using Stern-Volmer (S-V) plots that are in accordance with the S-V equation:

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

$$\tau o/\tau=1+K'_{sv}[Q] \qquad (2)$$

where I_o and τ_o are the fluorescence intensity and fluorescence lifetime, I and τ are the fluorescence intensity and fluorescence lifetime in the absence and presence of quencher concentration[Q], respectively, and K_{SV} (K'_{SV}) is the S-V constant. In some cases[6-8] of quenching, the S-V plots were found to be linear, in which, the quenching mechanism is mainly due to dynamic process, where diffusion process is a dominant one and in a few cases[2-5], the experimental results show positive deviation from linear S-V relation. This positive deviation was attributed to various processes like singlet-to-triplet excitation, formation of charge transfer complexes both at ground and excited states. Also, the polarity of the solvent medium and the range of quencher concentration are expected to play a role in this mechanism.

In the present work, we have studied the steady state fluorescence quenching of 5-methyle-2-phenylindole by carbon tetrachloride at room temperature in different organic solvents viz. dioxane, benzene, toluene, butanol, methanol and acetonitrile. The time dependent fluorescence quenching has also been studied in butanol solvent at room temperature. The various rate constants responsible for fluorescence quenching mechanisms have been determined using modified S-V equation and in the light of these rate constants the possible quenching mechanisms are discussed.

EXPERIMENTAL

The indole derivative 5-methyle-2-phenylindole has been synthesized in our laboratory and characterized by using IR, NMR, and Massbaur techniques for its purity, and its molecular structure is shown in figure 1. The spectroscopic grade solvents viz., dioxane, benzene, toluene, butanol, methanol and acetonitrile (s.d. Fine Chemicals Ltd.) were used without further purification. However, the purity of the solvents was checked by the background fluorescence. Spectroscopic grade CCl_4 solvent has been used as a quencher and it was double distilled before use. The solutions were prepared keeping the concentration of solute fixed at 1×10^{-5}M/L and varying the concentration of quencher from 0.00 to 0.10M/L. The absorption spectra of the solute at the concentration of 1×10^{-5}M/L in different solvents were recorded using UV-visible absorption spectrophotometer (Hitachi Model 150-20). For the same concentration, the steady-state fluorescence intensities were recorded by exciting the solute at 320nm corresponding to longer wavelength absorption band by varying the quencher concentration from 0.00 to 0.10 M/L using fluorescence spectrophotometer (Hitachi Model F-2000) in different solvents. The fluorescence decays were recorded corresponding to fluorescence maxima i.e. 370nm at room temperature in the absence and presence of quencher CCl_4 in butanol solvent using Nano-second Spectrometer Model SP-70 of Applied Photophysics, England. The fluorescence lifetime data were analysed by considering the reduced chi-square (χ^2) values.

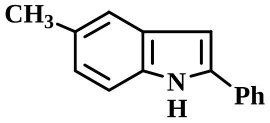

Figure 1: Molecular structure of 5-methyl-2-phenylindole.

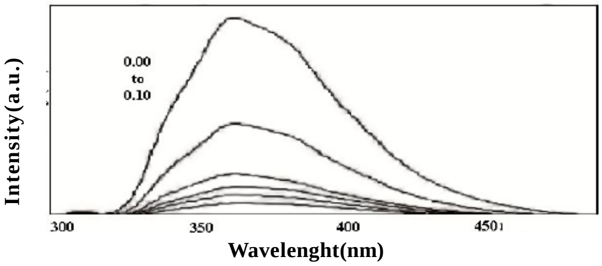

Figure 2 : Fluorescence spectra of 5-methyl-2-phenylindole in butanol at concentration of 1×10^{-5}M/L with quencher concentration of CCl_4 from 0.00 to 0.10M/L

RESULTS AND DISCUSSION

The steady state fluorescence intensities I_o and I were measured in the absence and presence of quencher, respectively, in dioxane, benzene, toluene, butanol, methanol and acetonitrile solvents at fixed solute concentration. The typical fluorescence spectra in butanol solvent with different quencher concentration are shown in figure 2. Further, the fluorescence lifetimes τ_o and τ representing without and with CCl_4 were measured in butanol solvent. The typical fluorescence decay profile in butanol solvent without quencher is shown in figure 3. It is observed that the fluorescence decay was fitted to be single exponential. The lifetime value of 5-methyle-2-phenylindole. Agrees closely with the lifetime values of other indole derivatives[2,5]. The experimental values are reproducible within 5% of the experimental error.

The S-V plots of I_o/I versus[Q] in different solvents and τ_0/τ versus [Q] in butanol solvent, with CCl_4 as quencher are respectively shown in figure 4. It is observed that in both the cases, the S-V plots are non-linear, showing positive deviation. Similar experimental results for other indole derivatives were also observed[2,5,17]. From the S-V plot, it may be concluded that the quenching is not purely collisional but also due to the formation of either the ground state complex or static quenching process.

In order to see whether the ground state complex formation is partly playing a role, we have used extended S-V equation[3,18] given by

$$I_0/I=1+K_g[Q](1+K_{sv}[Q])$$

$$\text{i.e.}[(I_0/I)-1]/[Q]=(K_{sv}+k_g)+(K_{sv}k_g)[Q] \qquad (3)$$

where K_{SV} and k_g are S-V and ground state association constants, respectively and [Q] is the quencher concentration. The plots $[(I_0/I)-1]/[Q]$ versus [Q] were drawn and found to be linear. The intercept($K_{SV}+k_g$) and slope $K_{SV}\cdot k_g$ were obtained using least square fit method. However, in all the cases, $K_{SV}+k_g$ values were found to be imaginary. Further, the appreciable shift in the absorption and emission peaks without and with the quencher is not observed. These facts show that equation (3) is not applicable for the analysis of data corresponding to the observed positive deviation in the S-V 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 of excitation. And this was explained by the fact that only a certain fraction W (in case of steady state) and W′(for transient case) of the excited state is actually quenched by the collisional mechanism. Some molecules in the excited state, the fraction of which is 1-W or (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. This static quenching can be explained by introducing an additional factor W(W′) in linear S-V equation[16].

$$I_0/I=(1+K_{sv}[Q])/W \qquad (4)$$

$$\tau_0/\tau=(1+K'_{sv}[Q])/W' \qquad (5)$$

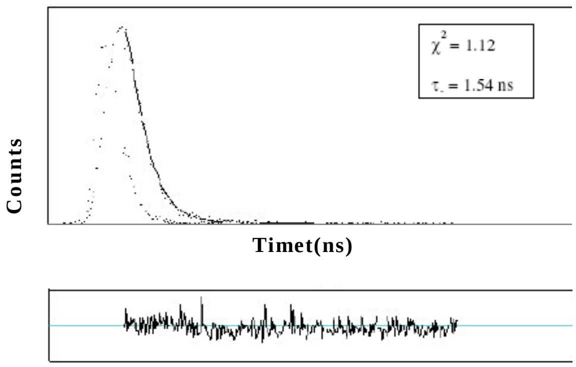

Figure 3: Fluorescence decay profile of 5-methyl-2-phenylindole in butanol at the concentration of 1×10^{-5}M/L

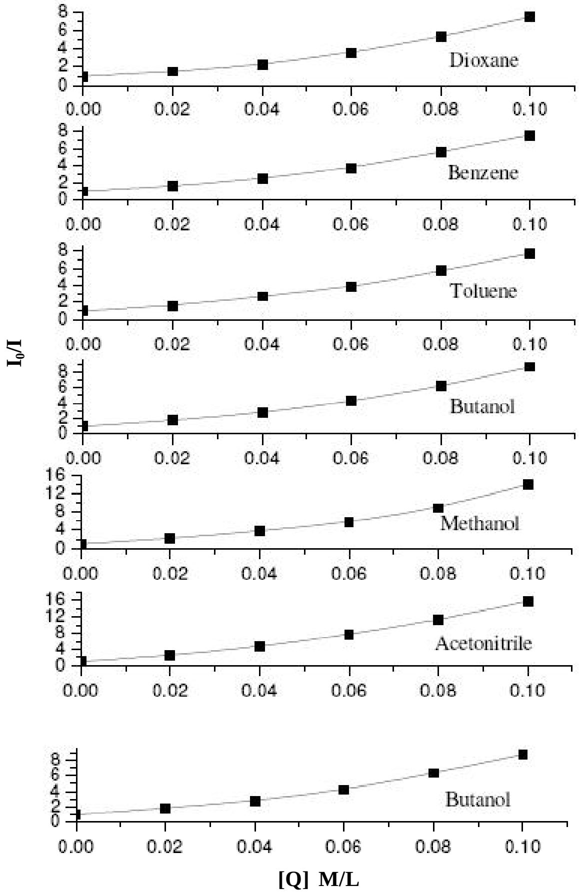

Figure 4 : S-V plots of I_0/I versus [Q] in different solvents and τ_0/τ versus [Q] in butanol solvent with CCl_4

The factor W in the modified S-V equation (4) is approximately equal to exp (-V [Q]) where V is the static quenching constant and it represents an active volume element surrounding the excited solute molecule.

Frank and Wawilow[19] have suggested that the instantaneous quenching results at the instances in a randomly distributed system, when a quencher happens to reside within a "sphere of action" with a volume of

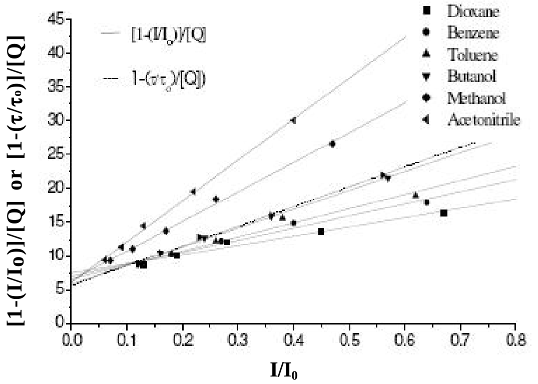

Figure 5 : Plots of $[1-(I/I_0)]/[Q]$ versus I/I_0 in different solvents and $[1–(\tau/\tau_0)]/[Q]$ versus τ/τ_0 in butanol with CCl_4

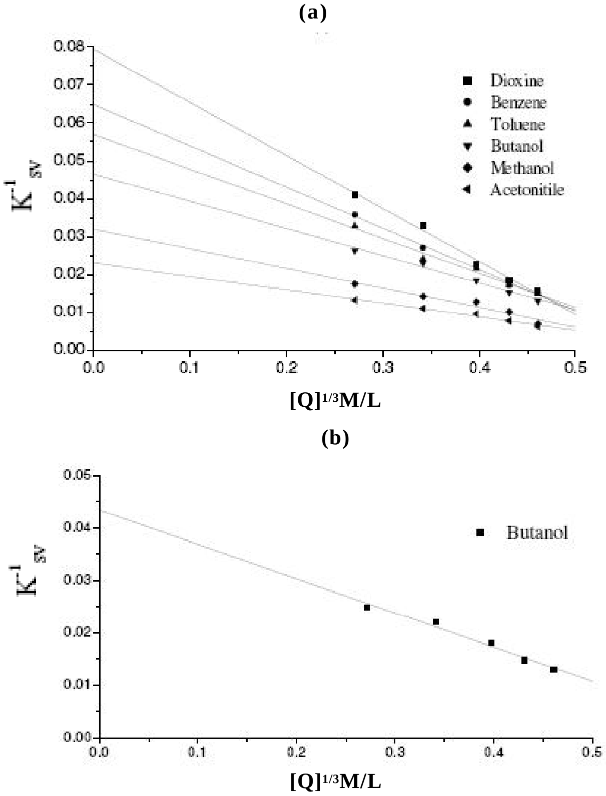

Figure 6 : Plot of K^{-1}_{sv} versus $[Q]^{1/3}$ determined from (a) fluorescence intensities in different solvents with CCl_4 and (b) fluorescence lifetimes in butanol with CCl_4

V/N′ and radius r (kinetic distance), i.e. $V/N'= 4\pi r^3/3$ surrounding a solute molecule at the time of excitation. On excitation of the solute molecule, a quencher molecule, which is already within this volume, will be able to quench the fluorescence without the need for a diffusion controlled collisional interaction. The probability of quencher being within this volume at the time of excitation depends on the volume V and on the quencher concentration[Q]. Hence, it is meaningful to rewrite equation (4) and (5) as

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

$$[1-(\tau/\tau_0)/=[Q]\,K'_{sv}(\tau/\tau_0)+(1-W')/[Q] \qquad (7)$$

The modified S-V plot $[1-(I/I_o)]/[Q]$ versus I/I_o for steady state in different solvents and $[1-(\tau/\tau_o)]/[Q]$ versus τ/τ_o in butanol are found to be linear and are shown in figure 5. The S-V quenching constant K_{SV} is obtained using least square fit method by determining the slope. The quenching rate parameter $k_q(=K_{SV}/\tau_o)$ is calculated using experimentally determined K_{SV} and τ_o values. The intercepts of least-square fit of figure 5 are equal to (1-W)/[Q]. From these intercepts, the values of W were calculated for each quencher concentration. Using the values of W, the static quenching constant V was obtained by the least-square fit method using the equation W=exp(-V[Q]) and in turn the kinetic distance r, i.e. "radius of sphere of action" was determined by the equation $V/N'= 4\pi r^3/3$. All these data are collated in TABLE 1. The value of τ_o is given at the bottom of the TABLE 1. It is observed from TABLE 1 that the values of K_{SV} are rather large in comparison with V in all the solvents, which explains the lack of appreciable change in absorption or fluorescence on addition of the quencher[3]. The radii of the solute, R_S and that of the quencher, R_Q were determined by adding the atomic volumes of all the atoms constituting the molecule by the method suggested by Edward[20] and are given at the bottom of the TABLE 1. The sum of the molecular radii R of the solute and quencher is determined and is called as encounter distance or contact distance or reactive distance which is also given at the bottom of TABLE 1. This value of R is then compared with the value of kinetic distance (r) to verify whether the reaction is due to sphere of action or not. According to Zeng and Durocher[18] and Andre et al.[21], if the distance between the quencher molecule and the excited molecule lies between the encounter distance R and the kinetic distance r, the static effect takes place especially in case of steady-state experiments irrespective of ground state complex formations, provided the reactions are diffusion limited. From TABLE 1 it is observed that the values of kinetic distance r are higher than the encounter distance R in all the solvents indicating the sphere of action static quenching model agrees

TABLE 1: The values of dynamic quenching constant K_{SV}, quenching rate parameter k_q, static quenching constant V and radius of the sphere of action r (kinetic distance)

Solvent	Dielectric constant ε	K_{SV} M^{-1}	$k_q \times 10^{-10}$ $M^{-1} s^{-1}$	V M^{-1}	r Å
Dioxane	2.21	13.71	0.89	12.04	16.82
Benzene	2.27	17.86	1.16	10.64	16.23
Toluene	2.38	20.84	1.35	9.74	16.21
Butanol	17.1	27.74	1.80	8.12	14.80
		*29.18	*1.89	*9.35	*15.47
Methanol	32.6	43.64	2.83	9.20	15.40
Acetonitrile	36.0	60.35	3.92	8.57	15.03

***Data from lifetime measurements: R_S = 3.64 Å R_Q = 2.79 Å $R = R_S + R_Q$=6.43 Å τ_0=1.54 ns**

TABLE 2: The values of mutual diffusion co-efficient D, distance parameter R′ and 4π N′DR′

Solvent	$D \times 10^{5}$ $cm^{2} s^{-1}$	R′ Å	$4\pi N'DR' \times 10^{-10}$ $M^{-1} s^{-1}$
Dioxane	0.98	11.05	0.82
Benzene	1.19	11.40	1.02
Toluene	1.42	10.88	1.17
Butanol	1.81	10.47	1.43
	1.99	10.22	1.54
Methanol	2.54	10.91	2.10
Acetonitrile	3.79	10.02	2.81

well in this case. Further, it may also be noted that a positive deviation in the S-V plot is expected when both static and dynamic quenching occurs simultaneously[1,3].

Further, it is investigated whether the reactions are diffusion limited or not, for that we have invoked the finite sink approximation model for steady-state, and from this model the values of mutual diffusion coefficient D, distance parameter R' are estimated independently. The modified S-V equation[18].

$$K_{sv}^{-1} = (K_{sv}^{0})^{-1} - \frac{(2\pi N')^{1/3}}{4\pi N' D\tau_0}[Q]^{1/3} \qquad (8)$$

where

$$(K_{sv}^{0}) = \frac{4\pi N' DR\tau_0 k_\alpha}{4\pi N' DR + k_\alpha} \qquad (9)$$

of finite sink approximation model is used to determine the values of D, R′ and k_a. For an efficient quenching process, the value of K_{SV} often observed to increase with [Q][18]. Hence, the values of K_{SV} were determined at each quencher concentration in all the solvents. According to equation (8) the graph k^{-1}_{sv}, versus$[Q]^{1/3}$ were plotted as shown in figure 6 and found to be linear in all the cases. Using least square fit method, the values of mutual diffusion coefficient D, and k^0_{sv},(S-V constant at [Q] = 0) were determined by measuring the slopes and intercepts. The distance parameter R′ was calculated by using these values according to the equation $k^0_{sv} = 4\pi N' D r' \tau_0$ and these values are given in TABLE 2. The activation energy controlled rate constant k_a [$=4\pi N'Dr/(R/R'-1)$] can be determined only when R′<R. But in this case, it is found that R′ is greater than R in all the solvents and hence k_a cannot be determined. But according to Joshi et al.[17], the bimolecular quenching reactions are said to be diffusion limited if $k_q > 4\pi N'DR'$, and it is found to be true in the present case for all the solvents, which confirms that the reactions are diffusion limited.

Further, it can be observed from TABLE 1 that, K_{SV} increases with increase in dielectric constants ε of the solvents. This effect of dielectric constant suggest the charge transfer character in the excited complex. The high value of K_{SV} in polar solvents (butanol, methanol and acetonitrile) and low value in non-polar solvents (dioxane, benzene and toluene) can be explained by the greater charge transfer character of the exciplex in the polar solvents[17].

CONCLUSIONS

The specific conclusions emerged from the present work are: 1) The Stern-Volmer plots show positive deviations leading to high values of k_q, 2) Both static and dynamic quenching processes are partly playing a role in the quenching mechanism, and from finite sink approximation model it is concluded that the reactions are diffusion limited and 3) The charge transfer nature of the excited complex is observed by the increase in K_{SV} with ε.

ACKNOWLEDGEMENT

The authors wish to thank Dr. S.R.Inamdar, Department of Physics, Karnatak University, Dharwad for extending the laboratory facilities to carryout the experiments.

REFERENCES

[1] T.Moriya; Bull.Chem.Soc.Japan, **57**, 1723 **(1984)**.

[2] R.Roy, S.Mukherjee; Chem.Phys.Lett., **140**, 210 **(1987)**.

[3] P.K.Behera, A.K.Mishra; J.Photochem.Photobiol. A: Chem., **71**, 115 **(1993)**.

[4] J.S.Kadadevarmath, T.P.Giraddi, G.C.Chikkur; J. Photoscience, **4**, 105 **(1997)**.

[5] H.M.Suresh Kumar, R.S.Kunabenchi, J.S.Biradar, N.N.Math, J.S.Kadadevarmath, S.R.Inamdar; J. Lumin., **116**, 35 **(2006)**.

[6] S.V.Nishti, R.S.Kunabenchi, H.M.Suresh Kumar, S.M.Hanagodimath, J.S.Biradar; Indian J.Phys., **81**, 53 **(2007)**.

[7] H.M.Suresh Kumar, R.S.Kunabenchi, J.S.Biradar, N.N.Math, J.S.Kadadevaramath; J.Photoscience, **10**, 225 **(2003)**.

[8] T.P.Giraddi, J.S.Kadadevarmath, G.H.Malimath, G.C.Chikkur; Indian J.Pure & Appl.Phys., **34**, 244 **(1996)**.

[9] W.R.Ware, C.Lewis; J.Chem.Phys., **57**, 3546 **(1972)**.

[10] P.K.Behera, T.Mukherjee, A.K.Mishra; J.Lumin., **65**, 131 **(1995)**.

[11] P.K.Behera, T.Mukherjee, A.K.Mishra; J.Lumin., **65**, 137 **(1995)**.

[12] C.Hariharan, A.K.Mishra; Radiation Measurements, **32**, 113 **(2000)**.

[13] S.Nigam, M.Belletete, R.S.Sarpal, G.Durocher; J.Chem.Soc.Faraday Trans., **91**, 2133 **(1995)**.

[14] J.Sujatha, A.K.Mishra; J.Lumin., **75**, 135 **(1997)**.

[15] Guo-Dong Liu, Xin Yang, Zeng-Ping Chen, Guo-Li Shen, Ru-Qin Yu; Analytical Sciences, **16**, 1225 **(2000)**.

[16] J.Keizer; Chem.Rev., **87**, 167 **(1987)**.

[17] G.C.Joshi, R.Bhatnagar, S.Doraiswamy, N. Periasamy; J.Phys.Chem., **94**, 2908 **(1990)**.

[18] H.Zeng, G.Durocher; J.Lumin., **63**, 75 **(1995)**.

[19] J.M.Frank, S.J.Wawilow; Z.Phys., **69**, 100 **(1931)**.

[20] J.T.Edward; ‘Molecular Volumes and Parachor’ Chem.Ind., London, **(1956)**.

[21] J.C.Andre, M.Niclause, W.R.Ware; Chem.Phys., **28**, 371 **(1978)**.