

STEADY STATE FLUORESCENCE QUENCHING OF INDOLE DERIVATIVE BY CARBON TETRACHLORIDE

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Abstract

The fluorescence quenching of 2-[2-(1H-indol-3-yl)-4-oxo-thiazolidin-3-ylamino]-5-oxo-5,6-dihydro-4H-[1,3,4]thiadiazine-6-carboxylic acid ethyl ester by carbon tetrachloride in different solvents viz. benzene, toluene, butanol, methanol and acetonitrile, and time dependent study in toluene 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 magnitude of various rate parameters determined 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, it is concluded that these bimolecular quenching reactions are diffusion limited by using the finite sink approximation model, and also the dependence of Stern-Volmer constant on dielectric constant of the solvents suggest the charge transfer character of the excited complex.

Keywords: Fluorescence, Stern-Volmer plot, Static and dynamic quenching, Charge transfer, Indole.

1. 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 excited-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 (CCl₄), aniline, bromobenzene and halide ions etc., have been studied by several investigators^[1-10]. This study has not only been of importance in physical sciences but also in chemical, biological and medical sciences^[10,11]. 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:

$$I_0/I = 1 + K [Q] \quad (1)$$

$$\tau_0/\tau = 1 + K'_{sv} [Q] \quad (2)$$

where I_0 and τ_0 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 Stern-Volmer Constant. In some cases^[5-7] 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^[1-4], 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 2-[2-(1H-indol-3-yl)-4-

oxo-thiazolidin-3-ylamino]-5-oxo-5,6-dihydro-4H-[1,3,4]thiadiazine-6-carboxylic acid ethyl ester (IDCE) by carbon tetrachloride at room temperature in different organic solvents viz. benzene, toluene, butanol, methanol and acetonitrile. The time dependent fluorescence quenching has also been studied in toluene 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.

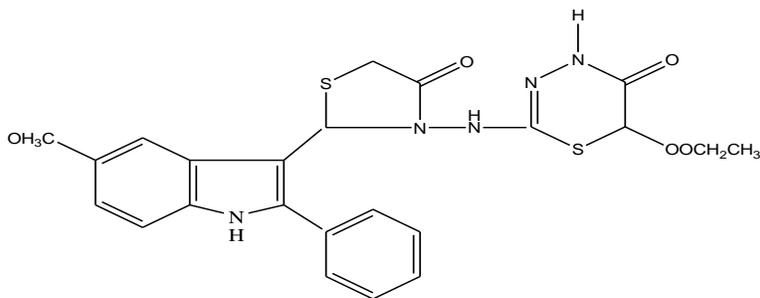


Figure 1. Molecular structure of 2-[2-(1H-indol-3-yl)-4-oxo-thiazolidin-3-ylamino]-5-oxo-5,6-dihydro-4H-[1,3,4]thiadiazine-6-carboxylic acid ethyl ester

II. Experimental

The molecule, Indole derivative has been synthesized in our laboratory and characterized by using IR, NMR, and Massbauer techniques for its purity, and its molecular structure is shown in figure 1. The spectroscopic grade solvents viz., 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 $1 \times 10^{-5} \text{ M/L}$ and varying the concentration of quencher from 0.00 to 0.10 M/L. The absorption spectra of the solute at the concentration of $1 \times 10^{-5} \text{ M/L}$ 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 320 nm 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. 370 nm at room temperature in the absence and presence of quencher CCl_4 in dioxane solvent using Nano-second Spectrometer Model SP-70 of Applied Photophysics, England. The fluorescence life-time data were analysed by considering the reduced chi-square (χ^2) values.

III. Results and Discussion

The fluorescence intensities I_0 and I were measured in the absence and presence of quencher, respectively, in benzene, toluene, butanol, methanol and acetonitrile solvents at fixed solute concentration. The typical fluorescence spectra in benzene solvent with different quencher concentration are shown in figure 2. Further, the fluorescence lifetimes τ and τ representing without and with CCl_4 were measured in dioxane solvent. The typical fluorescence decay profile in toluene solvent is shown in Figure 3. It is observed that the fluorescence decay was fitted to be single exponential. The lifetime value of IDCE agrees closely with the lifetime values of other indole derivatives^[1,4]. The experimental values are reproducible within 5% of the experimental error.

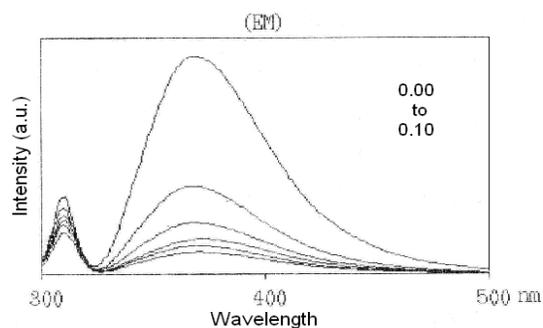


Figure 2. Fluorescence spectra of the molecule in benzene for different quencher concentrations of CCl_4

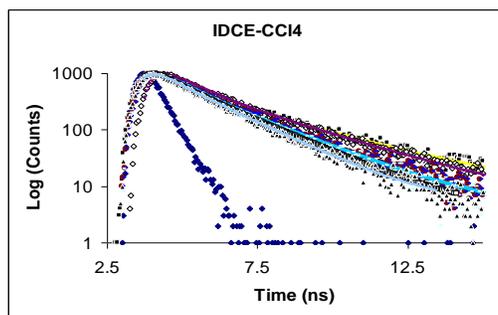


Figure 3. Fluorescence decay of the molecule in Toluene with CCl₄

The S-V plots of I_0/I versus $[Q]$ in different solvents and τ/τ_0 versus $[Q]$ in different solvents, with CCl₄ as quencher are respectively shown in figure 4. It is observed that, the S-V plots are non-linear, showing positive deviation. Similar experimental results for other indole derivatives were also observed^[1,4,10]. 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.

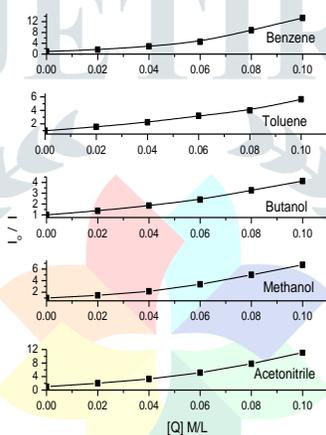


Figure 4. Stern-Volmer plot of I_0/I against $[Q]$ in different solvents for IDCE with CCl₄.

In order to see whether the ground state complex formation is partly playing a role, we have used extended S-V equation^[2,11] given by

$$I_0/I = 1 + K_g [Q] (1 + K_{sv} [Q]) \quad (3)$$

$$\text{i.e. } [(I_0/I) - 1]/[Q] = (K_{sv} + k_g) + (K_{sv} k_g) [Q] \quad (4)$$

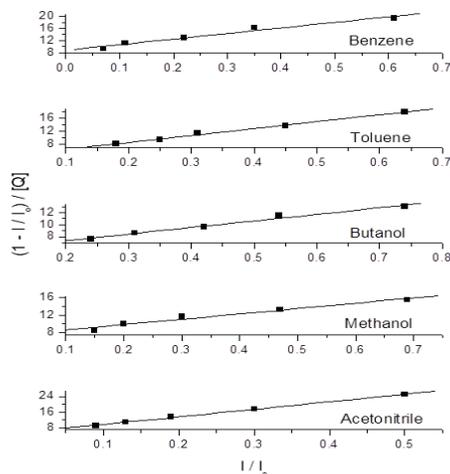
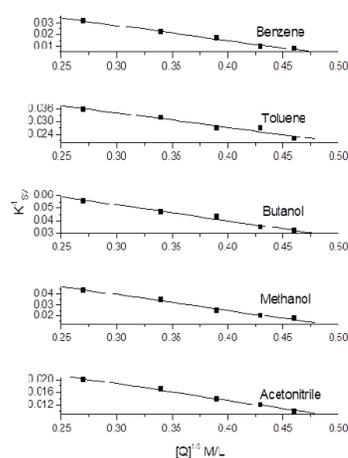
where K_{sv} and k_g are S-V and ground state association constants, respectively and $[Q]$ is the quencher concentration. The plots $[(I_0/I) - 1]/[Q]$ versus $[Q]$ were drawn and found to be linear. The intercept $(K_{sv} + k_g)$ and slope $K_{sv} \cdot k_g$ were obtained using least square fit method. 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^[10].

$$I_0/I = (1 + K_{sv} [Q]) / W \quad (5)$$

$$\tau/\tau_0 = (1 + K' [Q]) / W' \quad (6)$$

The factor W in the modified S-V equation (5) 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^[12] 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 concentration [Q].

Figure 5. Plot of $(1-I/I_0)/[Q]$ v/s $[Q]^{1/3}$ in different solvents with CCl_4 Figure 6. Plot of K_{SV}^{-1} against $[Q]^{1/3}$ in different solvents with CCl_4

Hence, it is meaningful to rewrite equation (5) and (6) as

$$[1-(I/I_0)]/[Q]=K_{sv}(I/I_0)+(1-W)/[Q] \quad (7)$$

$$[1-(\tau/\tau_0)]/[Q]=K'_{sv}(\tau/\tau_0)+(1-W)/[Q] \quad (8)$$

The modified S-V plot $[1-(I/I_0)]/[Q]$ versus I/I_0 for steady state in different solvents 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 ($=K_{SV}/\tau_0$) is calculated using experimentally determined K_{SV} and τ_0 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_0 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^[13] 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^[11] and Andre et al.^[14], 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 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^[3].

Table 1. The dynamic quenching constant K_{SV} , quenching rate parameter k_q , intercept, range of W , static quenching constant V and radii of the sphere of action (kinetic distance) r of with CCl_4 .

$\tau_0 =$ 1.27	Solvent	Dielectric Constant (ϵ)	K_{SV} m^{-1}	$k_q \times 10^{-9}$ $m^{-1}s^{-1}$	Intercept	Range of W	V mol dm^{-3}	r \AA
	Benzene	2.28	18.41	1.66	8.83	0.12-0.82	23.25	20.96
	Toluene	2.38	21.23 23.80*	16.72 18.74*	4.40 2.73*	0.56-0.91 0.73-0.95*	6.08 3.28*	13.41 10.9*
	Butanol	17.10	10.91	8.59	5.17	0.48-0.90	7.70	14.51
	Methanol	32.60	12.02	9.46	7.37	0.26-0.85	14.48	17.91
	Acetonitrile	37.12	39.64	17.40	4.22	0.58-0.92	5.75	13.16

$$R_S = 4.10 \text{ \AA} \quad R_Q = 2.79 \text{ \AA} \quad R = R_S + R_Q = 6.89 \text{ \AA}$$

* Data from lifetime measurements

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].

$$K_{sv}^{-1} = (K_{sv}^0)^{-1} - [(2\pi N')^{1/3} / (4\pi N' D \tau_0)] [Q]^{1/3} \quad (9)$$

Where,

$$(K_{sv}^0) = (4\pi N' DR \tau_0 K_a) / (4\pi N' DR + K_a) \quad (10)$$

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 $[Q]$ [11]. Hence, the values of K_{SV} were determined at each quencher concentration in all the solvents. According to equation (8) the graph k_{sv}^{-1} , 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_{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 $K_{sv}^0 = 4\pi N' D r' \tau_0$ and these values are given in Table 2. The activation energy controlled rate constant k_a $[=4\pi N' D r' / (R/R' - 1)]$ can be determined only when $R' \gg 4\pi N' D R'$, 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 [12].

Table 2. The values of K_{sv}^0 (steady state quenching constant at $[Q]=0$), mutual diffusion co-efficient D , distance parameter R' , $4\pi N' D R'$, activation energy controlled rate constant k_a and quenching rate constant for diffusion controlled reaction k_d for IDCE with CCl_4 .

Solvent	K_{SV}^0 m ⁻¹	Dx10 ⁵ cm ² s ⁻¹	R' Å	$4\pi N' D$ $R' \times 10^9$ m ⁻¹ s ⁻¹	k_a D x 10 ¹⁵ m ⁻¹ s ⁻¹
Benzene	15.15	2.07	7.58	1.19	-
Toluene	18.18	1.12	3.10	0.26	4.26
	*4.17	*7.21	*0.17	*0.94	*1.33
Butanol	10.99	2.06	5.55	0.86	2.17
Methanol	11.90	2.39	4.45	0.80	9.52
Acetonitrile	33.33	3.06	11.33	2.62	-

*Data from lifetime measurements

IV. Conclusion:

Following are the 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 .

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