BINARY MIXTURE STUDIES ON THE FLUORESCENCE QUENCHING OF PHARMACOLOGICALLY POTENT INDOLE DERIVATIVE BY CCL4

[1] Dr. Sanganna V. Nishti, [2] Dr. S. M. Hanagodimath

[1] Assistant Professor, [2] Professor
[1]Department of Physics, Government First Grade College, Sedam-585 222, Karnataka.
[2]Department of Physics, Gulbarga University, Kalaburagi - 585 106, Karnataka.

Abstract

Indole ring system is found in many natural products, pharmaceuticals agents, and polymer materials. Indole and its derivative have great importance in clinical chemistry. The Indole derivative chosen for the present study is pharmacologically active molecule. The solvent polarity effect on 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 (CCl4) in benzene and acetonitrile mixtures has been studied at room temperature by steady state fluorescence measurements. The positive deviation from linearity in different composition of mixed solvents at different CCl4 concentration was observed from Stern-Volmer plots. The quenching parameters have been determined using extended S-V equation and found to be dependent on the polarity of the solvents. This indicates that both static and dynamic quenching processes are responsible for the observed fluorescence quenching. Further, it is concluded that the bimolecular quenching reactions are diffusion limited (finite sink approximation model), and the distance parameter R' and mutual diffusion co-efficient D are also estimated.

Keywords: Indole, Fluorescence Quenching, Solvent Polarity and Binary Mixtures.

I. Introduction:

The photophysical and photochemical properties are understood by the nature and energy of electronically excited molecules. The surrounding solvent molecules influence the electronic spectra of the probe molecules. The ground and excited states are affected differently by the change in solvent environment. The fate of an excited state can also be determined by quenching phenomena. Several authors [1-8] have studied the mechanism of excitation energy transfer from excited molecules to unexcited molecules either directly or through quenching by adding external quenchers. Fluorescence quenching has been widely studied both as a fundamental phenomenon and as a source of information about biochemical system. There are different models, which differ from each other in principle, to explain the basic mechanisms responsible for excitation energy transfer from solute to quencher molecule. In the present work the fluorescence quenching of Indole derivative 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) has been studied in the binary mixture of benzene and acetonitrile with CCl4 as quencher.

II. Experimental:

Indole dyes and its derivatives have great importance in clinical chemistry and are found in many natural products, pharmaceuticals agents, and polymer materials. The chosen Indole derivative (Fig.1) 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) is found pharmacologically active[9].
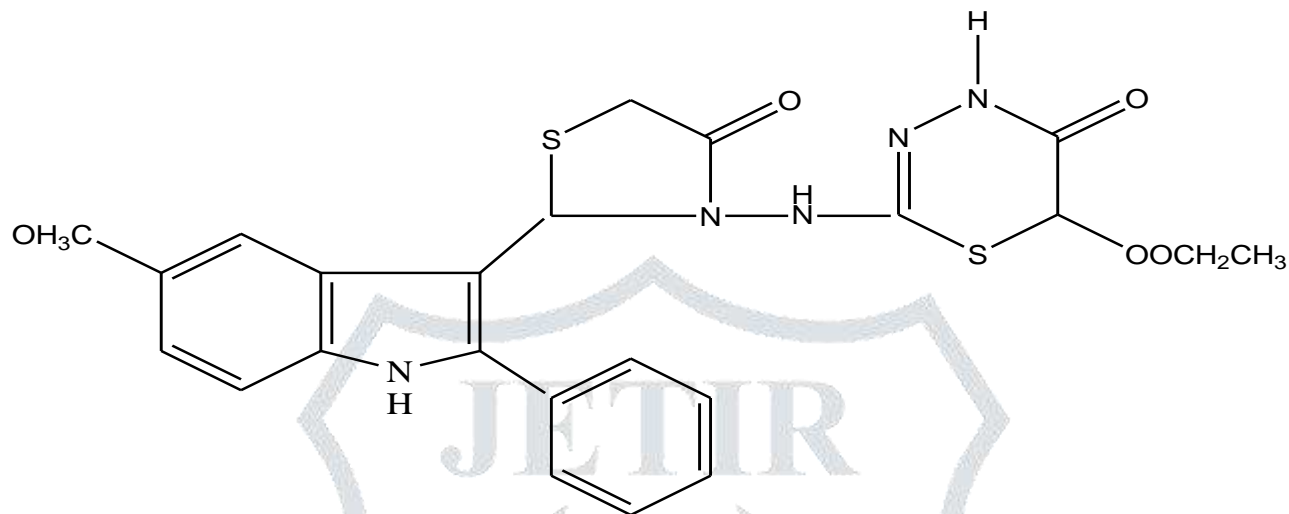

Fig.1. Molecular Structure of 2-[2-(1H-indol-3-yl)-4-oxo-thiazolidin-3-ylamino]-5-oxo-5, 6-dihydro-4H-[1,3,4]thiadiazine-6-carboxylic acid ethyl ester (IDCE)

The fluorescence quenching is studied in the binary mixture of benzene and acetonitrile with CCl_4 as quencher. The solvents are of spectroscopic grade and obtained from s.d-fine Chemicals. The absorption spectra are recorded using UV/VIS Spectrophotometer [Hitachi Model U-3310] and the fluorescence spectra with Fluorescence Spectrophotometer [Hitachi Model F-7000].

III. Results and Discussion:

The fluorescence intensity I_o and I were measured with and without quencher in different solvent mixtures for molecule IDCE with CCl_4 as quencher and the values are given in the Table.1. The Stern-Volmer[10] plots I_0/I against [Q] were plotted and are shown in Fig.2. It is observed that the Stern-Volmer plots are non-linear showing positive deviations. This positive deviation from S-V plots reveals the role of static quenching process, and is explained on the basis of sphere of action static quenching model. The S-V plots of $[1-(I/I_0)]/[Q]$ versus I/I_0 are shown in Fig.3. From these graphs, it is evident that the intercepts are non zero (in case of linear S-V plot, intercept is zero and W=1) and are large. The S-V quenching constant K_{SV} was determined in all the cases by least square fit method and the quenching rate parameter k_q for all the solutes was determined according to the equation $k_q = K_{SV}/\tau_o$.
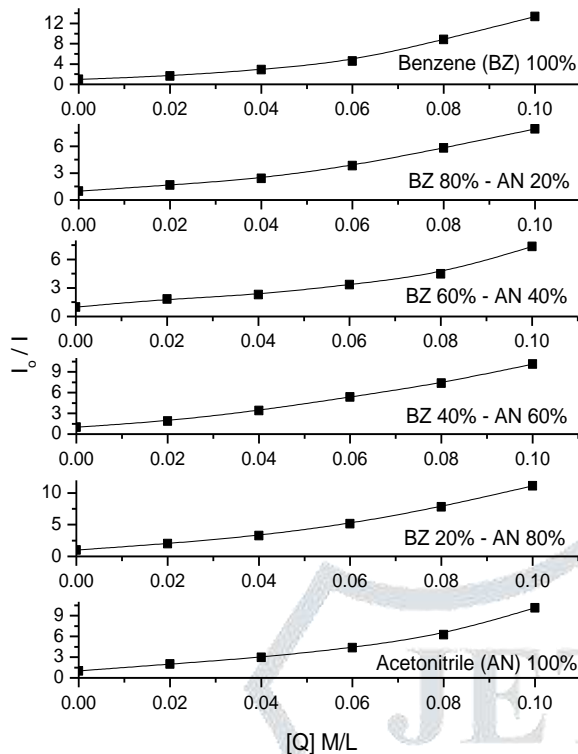
Fig.2. S-V Plots for IDCE
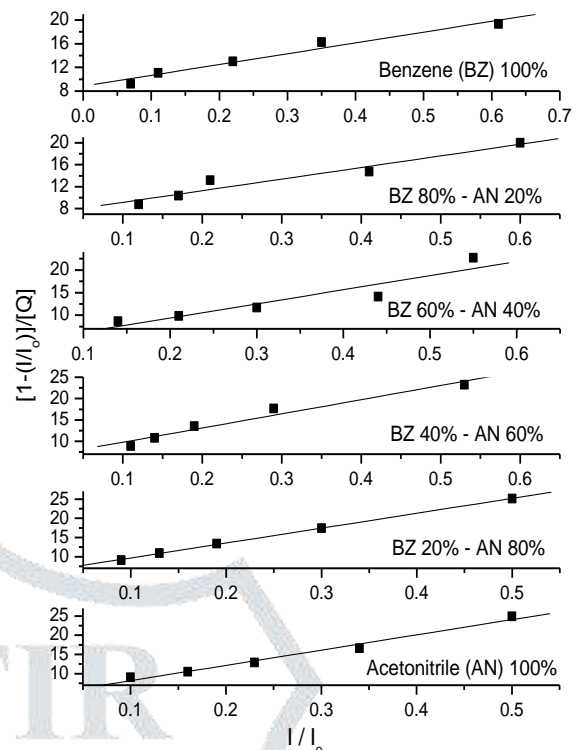
Fig.3. Modified S-V plots of (1- I/I₀)/[Q] against I/I₀ for IDCE

The calculated values of Ksv, kq, range of W, static quenching constant V and the kinetic distance r are collated in Table.1. Further, to find out whether the reactions are diffusion limited, we considered the finite sink approximation model, which helps to estimate independently the diffusion coefficient D, distance parameter R' and the activation energy controlled rate constant k_a. To determine these values, the modified S-V equation of finite sink approximation model is used. To make use of this model we need to determine the values of K_{SV}^{-1} and $[Q]^{1/3}$. Where, $K_{SV} = [(I_o/I)-1]/[Q]$ and [Q] the quencher concentration. The Stern – Volmer quenching constant at [Q] = 0 i.e. K_{SV}^{0} and mutual diffusion coefficient D and R' were determined and are tabulated in Table.2.   For efficient quenching processes, the values of K_{SV} are often observed to increase with $[Q]$[7]. The modified S-V plots i.e. K_{SV}^{-1} against $[Q]^{1/3}$ were plotted and all the plots are almost linear as shown in Fig.4.

Table 1. The Stern-Volmer constant K_SV, quenching rate parameter k_q, intercept,

range of W, static quenching constant V and kinetic distance r

Solvent mixture (% v/v)	Dielectric constant D	K_{SV} m^{-1}	k_q x 10^{-9} m^{-1}s^{-1}	Intercept	Range of W	V mol^{-1} dm^{-3}	r Å
Benzene	2.28	18.41	1.66	8.83	0.12-0.82	23.25	20.96
20% An	10.67	1.13	2.84	7.04	0.30-0.86	12.95	17.25
40% An	15.18	1.26	4.82	3.14	0.69-0.94	3.90	11.56

60% An	24.30	3.17	8.18	6.48	0.35-0.87	11.15	16.41
80% An	30.46	38.43	13.21	5.90	0.41-0.88	9.40	15.50
Acetonitrile	37.12	39.64	17.40	4.22	0.58-0.92	5.75	13.16

$R_S = 4.10$ Å $R_{ccl4} = 2.79$ Å $R_s + R_Q = 6.89$ Å $\tau_o = 1.27$ ns

Table 2. The values of K_{SV}^0 (steady state quenching constant at [Q] = 0), D, R', $4\pi N'DR'$

Solvent mixture (% v/v)	K_{SV}^0 m^{-1}	D x 10^{-5} cm^2s^{-1}	R' Å	$4\pi N'DR'$ x 10^{-9} $m^{-1}s^{-1}$
BZ 100%	15.15	2.07	7.58	1.19
AN 20%	16.67	1.76	9.85	1.31
AN 40%	25.00	2.84	9.16	1.97
AN 60%	33.33	3.60	9.63	2.62
AN 80%	25.00	3.52	7.39	1.97
AN 100%	33.33	3.06	11.33	2.62

As the values of $R' > R_S$ and hence k_a cannot be determined. But according to Joshi et al.[2] the bimolecular reactions of fluorescence quenching are said to be diffusion limited, if the values of k_q are greater than $4\pi N'DR'$. Hence the values of $4\pi N'DR'$ are determined using the experimentally determined values of D and R' and is tabulated in the Table.2. From these tables, it is seen that the values k_q are greater than $4\pi N'DR'$, hence we may infer that fluorescence quenching is diffusion limited[2]. Further, it is also observed that the variation of K_{SV} as a function of dielectric constant ε is non-linear and it confirms the combined effect of static quenching constant V and the Stern–Volmer quenching constant K_{SV} [12].
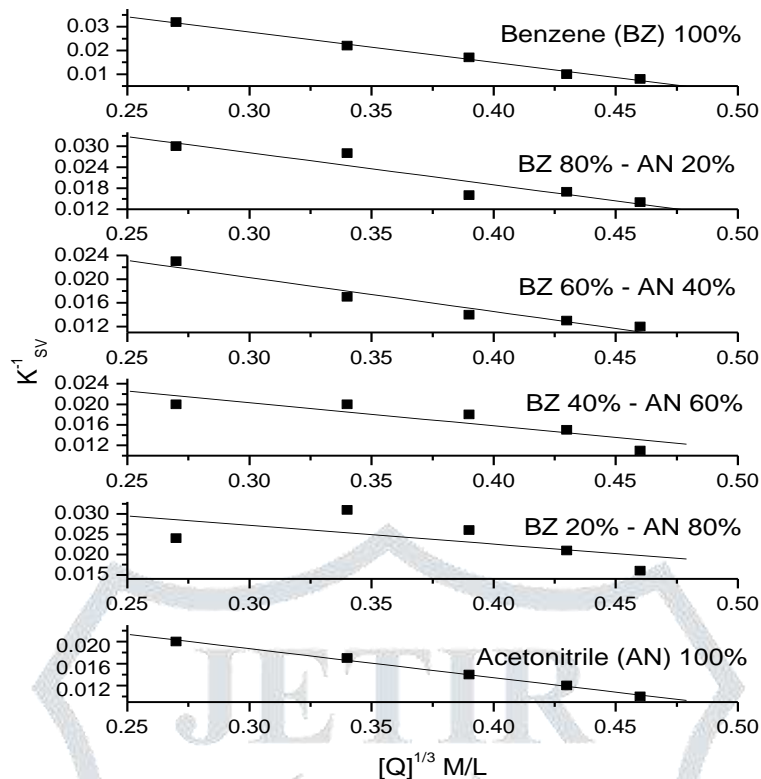
Fig.4. The plots of K_{SV}^{-1} **against [Q]$^{1/3}$**

From the above discussion, we observe that 1) the S–V plots show positive deviation 2) the S–V quenching constant K_{SV} increases with increase in dielectric constant of the mixtures of Benzene - Acetonitrile for IDCE. 3) The determined values of k_q are greater than $4\pi N' D R'$ in all mixtures. Further, a positive deviation in the Stern-Volmer plot is likely when both static and dynamic quenching occur simultaneously. In the light of these facts, we may conclude that both static and dynamic quenching processes are responsible for the observed positive deviations in the S–V plots for this systems.

IV. Acknowledgement:

References:

1. J. C. Andre, M. Niclause and M. R. Ware, Chem. Phys., 28, 371 (1978).

2. G. C. Joshi, R.Bhatnagar, S. Doraiswamy and N. Periasamy, J.Phys.Chem., 94, 2908(1990).

3. P. K. Behra, T. Mukherjee and A. K. Mishra, J. Lumin., 65, 131 (1995).

4. H. M. Suresh Kumar, R. S. Kunabenchi, J. S. Biradar and S. R. Inamdar, J. Lumin,116, 35 (2006).

5. H. M. Suresh Kumar, R. S. Kunabenchi, S. V. Nishti, J. S. Biradar, J. S. Kadadevarmath, Spectroscopy Letters, 42, 226(2009).

6. S. V. Nishti, R. S. Kunabenchi, H. M. Suresh Kumar, S. M. Hanagodimath and J. S. Biradar, Indian J. Phys., 81(2), 53 (2007).

7. S. V. Nishti, R .S. Kunabenchi, O. V. Mangalgi, H. M. Suresh Kumar, S. M. Praveen and J. S. Biradar, Macromolecules: An Indian Journal, 3(4), 63 (2007).

8. S. V. Nishti, R. S. Kunabenchi, B. G. Evale, J. S. Biradar and J. R. Mannekutla, Macromolecules: An Indian Journal, 4 (1), 1 (2009).

9. Dharmendra Kumar, Narendra Kumar, Sandeep Kumar, Tarun singh, and C. P. Singh, Int. J. Engg. Sci. & Tech., 2(7), 2553 (2010).

10. O. Stern and M. Volmer, Physik Z., 20, 183 (1919).

11. H. Zeng and G. Durocher, J. Lumin., 63, 75 (1995).

12. T. P. Giraddi, J. S. Kadadevaramath, G. Malimath and G. C. Chikkur, Ind. J. Pure and Apll. Phys., 34, 244 (1996).