BININARY 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
1Department of Physics, Government First Grade College, Sedam-585 222, Karnataka.
2Department 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-oxothiazolidin-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 CCl$_4$ 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$^{[9]}$.

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 $I_0$ 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
The 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 $k_q = K_{SV}/\tau_0$.

The calculated values of $K_{SV}$, $k_q$, 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, $K_{SV} = ([I/I_0] - 1)/[Q]$ and $[Q]$ the quencher concentration. The Stern – Volmer quenching constant at $[Q] = 0$ i.e. $K_{SV}^{-1}$ 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 $r$

<table>
<thead>
<tr>
<th>Solvent mixture (% v/v)</th>
<th>Dielectric constant $D$</th>
<th>$K_{SV}$ m$^{-1}$</th>
<th>$k_q \times 10^{-9}$ m$^3$s$^{-1}$</th>
<th>Intercept</th>
<th>Range of $W$</th>
<th>$V$ mol$^{-1}$ dm$^{-3}$</th>
<th>$r$ Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>2.28</td>
<td>18.41</td>
<td>1.66</td>
<td>8.83</td>
<td>0.12-0.82</td>
<td>23.25</td>
<td>20.96</td>
</tr>
</tbody>
</table>
As the values of $R' > R_s$ and hence $k_q$ cannot be determined. But according to Joshi et al.\cite{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\cite{2}. Further, it is also observed that the variation of $K_{SV}$ as a function of dielectric constant $\varepsilon$ is non-linear and it confirms the combined effect of static quenching constant $V$ and the Stern–Volmer quenching constant $K_{SV}$\cite{12}.

\begin{table}
\begin{tabular}{cccc}
Solvent mixture & $K_{SV}^0$ m$^{-1}$ & $D \times 10^{-5}$ cm$^2$s$^{-1}$ & $R'$ Å & $4\pi N'DR'$ x 10$^{-9}$ m$^{-1}$s$^{-1}$
\hline
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 \\
\end{tabular}
\end{table}
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 \( 4\pi N'DR' \) 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:

We are thankful to Dr J S Biradar, Professor (Retd.), Department of Chemistry, Gulbarga University, Kalaburagi for providing the fluorescent molecules-Indole derivatives for the present work.

References:


