Fluorescence quenching of DMB by aniline in benzene–acetonitrile mixture

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Abstract. The fluorescence quenching of coumarin dye namely 4-(2, 6-dibromo-4-methyl-phenoxymethyl)-benzo[h]chromen-2-one [DMB] has been studied by aniline, in a different solvent mixture of benzene (BN) and acetonitrile (AN) at room temperature. The quenching is found to be appreciable and shows positive deviation from linearity in the Stern-Volmer (S-V) plots for all the solvent mixtures. The various rate parameters responsible for fluorescence quenching have been determined using a sphere of action static quenching model and finite sink approximation model. The magnitudes of these rate parameters indicate that positive deviation in the S-V plot is due to both static and dynamic quenching processes.

1. Introduction

Derivatives of coumarin are well-known for their photochemical and photophysical properties, as well as for their interesting second-order nonlinearities [1]. They are extensively studied due to their widespread industrial use as dye lasers [2]. Now a day, there has been drive to synthesize coumarin-based organic dyes for use in high-efficiency dye-sensitized solar cells (DSCs) [3-4]. Coumarin and its derivatives have attracted significant interest in pharmaceutical research areas such as anti-inflammatory, hepatoprotective, antiviral, anticarcinogenic and anticoagulant activities [5-6].

The fluorescence quenching of organic molecules in solution by various quenchers like aniline, carbon tetrachloride, halides ions, ethyltriocarbonate, CdSe nanoparticles, oxygen etc has been studied by several investigators [7-12]. In all most all cases the experimental results follow the linear Stern-Volmer equation given by

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

$K_{SV} = k_q \tau_0$ called S-V constant. Where I_0, I, k_q, τ_0 and $[Q]$ are the fluorescence intensities in the absence and presence of the quencher, bimolecular quenching rate parameter, lifetime of the excited solute molecule in the absence of quencher and quencher concentration respectively. But in few cases, it has been observed that the experimental results show positive deviation from a linear S-V relation [13-15]. This positive deviation was attribute to various processes like singlet to triplet excitation, static and dynamic quenching, the formation of charge transfer complexes both at the ground and excited states. Apart from this, the polarity of the solvent medium and the range of quencher concentration are also except to play a part in this mechanism.

In the present work, we have studied the steady state fluorescence quenching of the newly synthesised coumarin derivative DMB using aniline as a quencher in a different mixture of benzene and acetonitrile at room temperature. The various rate constants responsible for fluorescence quenching mechanisms have been estimated using a sphere of action static quenching model and a finite sink approximation model.

2. Materials and methods

The coumarin dye DMB was synthesized according to the literature [16] and its molecular structure is shown in **Fig. 1**. The solvents were obtained from the SD-fine chemical limited Indian. The quencher aniline was double distilled and tested for its purity before use. The solutions were prepared using benzene and acetonitrile in different proportions by volume with a fixed solute concentration of 1×10^{-5} M/L and quencher concentrations were varied from 0.02 - 0.10 M/L. The absorption spectra, fluorescence spectra and fluorescence lifetime were recorded using UV/visible spectrophotometer [model: Hitachi U-3310, Japan], fluorescence spectrophotometer [model: Hitachi F-7000, Japan] and time-correlated single photon counting technique (TCSPC) [model: ISS-90021] respectively. All these spectroscopic measurements were carried out at room temperature [300 K].
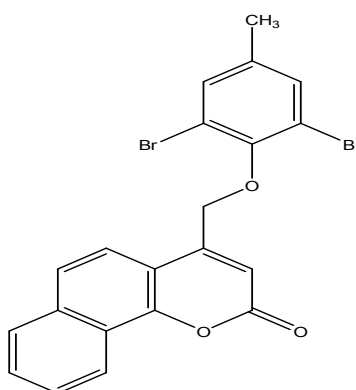
Fig. 1 Molecular structure of DMB.

3. Results and discussion

Initially, the fluorescence intensity I_0 was measured without quencher concentration and then the fluorescence intensity I was measured at different quencher concentrations in a fixed solute concentration. Practical values were reproducible within 5% of the experimental errors. The S-V plots I_0/I versus [Q] for DMB are shown in **Fig. 2** were found to be non-linear, shows positive deviation, it may be concluded that the quenching is not purely collisional in other word's it may be due to either the ground state complex formation or static quenching process.
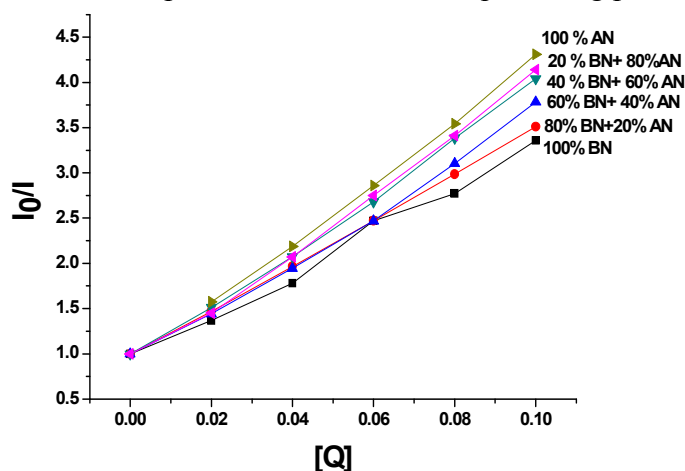

Fig. 2 S-V plots for DMB.

The deviations from the linearity of S-V plots were explained using the sphere of action static quenching model. According to this, the static quenching was explained by introducing an additional factor *W* in the linear S-V plots and the fraction W depends on the quencher concentration [Q].

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

The graph of $[1-(I/I_0)]/[Q]$ versus (I/I_0) for DMB are shown in **Fig. 3**, from these graphs we can easily estimate the values of K_{sv} and W by least-square fit method.

Frank and Wawilow [17] 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 volume of $\frac{V}{N'}$ and kinetic distance r.

i.e. $\quad \frac{V}{N'} = \frac{4}{3}\pi\, r^3 \tag{3}$
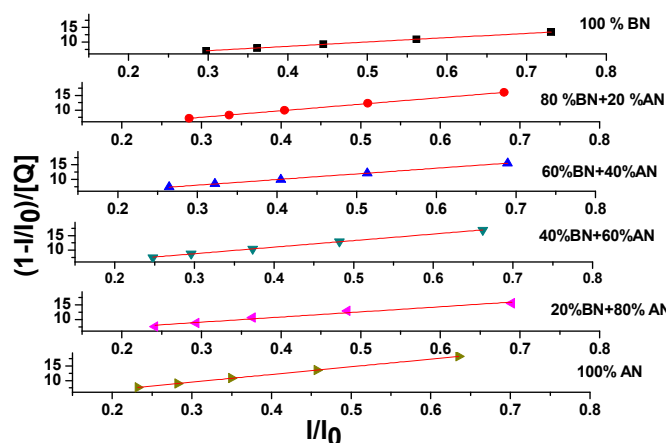
Fig. 3 The plots of $[1-(I/I_0)]/[Q]$ versus (I/I_0) in different solvent mixtures (BN+AN).

The dielectric constant of solvent mixtures and various quenching rate parameters calculated from sphere of action static quenching models namely S-V constant (K_{sv}) bimolecular quenching rate parameters (k_q), range (W), static quenching constant (V) and kinetic distance (r) for DMB in different solvent mixtures are shown in **Table 1**. The radii of the solute (R_S) and a quencher (R_Q) were estimated by Edward method [18] and are given at the bottom of **Table 1**, from these values the sum of the molecular radii R ($R_S + R_Q$) is determined, and it is referred as encounter distance. These values are compared with the values of 'r' in order to verify whether the reaction is due to sphere of action static quenching model. From **Table 1** we observed that values of kinetic distances r are greater than the encounter distances R. Therefore, according to Andre et al. [19] and Zeng et al. [20] the static effect takes place irrespective of ground state complex formation, provided reactions are limited by diffusion indicating the sphere of action static models holds good.

Table 1. The dielectric constant of solvent mixture and various fluorescence quenching rate parameters calculated from the sphere of action static quenching model.

Molecule	Solvent mixture		Dielectric constant	K_{SV} (m^{-1})	k_q $(m^{-1}s^{-1})$	Range W	V $(mol^{-1}dm^3)$	r (A°)
	BN%	AN%						
	100	00	2.284	14.599	1.339	0.726-0.945	3.253	10.88
	80	20	10.67	18.309	1.679	0.769-0.953	2.689	10.20
DMB	60	40	15.18	21.008	1.927	0.776-0.955	2.588	10.08
	40	60	24.30	22.415	2.056	0.792-0.958	2.488	9.95
	20	80	30.46	24.684	2.264	0.846-0.964	1.688	8.74
	00	100	37.12	26.273	2.410	0.841-0.968	1.748	8.84

$R_S = 4.2819$ A$^\circ$, $R_Q = 2.840$ A$^\circ$, $\tau_0 = 1.09$ ns.

In order to find out whether the reactions are diffusion limited, we need to use the finite sink approximation model [21].

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

This model helps us to estimate independently the mutual diffusion coefficient (*D*) and distance parameter *R′*. **Fig. 4** shows the graph of K_{SV}^{-1} versus $[Q]^{1/3}$, which are linear with a negative slope for all the solvent mixtures. The mutual diffusion coefficient (D) becomes directly

accessible from the slope and K_{sv}^0 is obtained from the intercept of the graph of K_{SV}^{-1} V/s $[Q]^{1/3}$ and these values are given in **Table 2**. From K_{sv}^0, it is possible to find out the distance parameter R'. The value of 4πN'DR' are estimated using the experimentally determined values of R' and D are shown in **Table 2.** According to Joshi et al. [22] the bimolecular reactions are said to be diffusion limited if the values of k_q are greater than 4πN'DR'. From the **Table 2**, it can be seen that for all the solvent mixtures the values of k_q are greater than 4πN'DR', which is an excepted result for diffusion limited reaction.
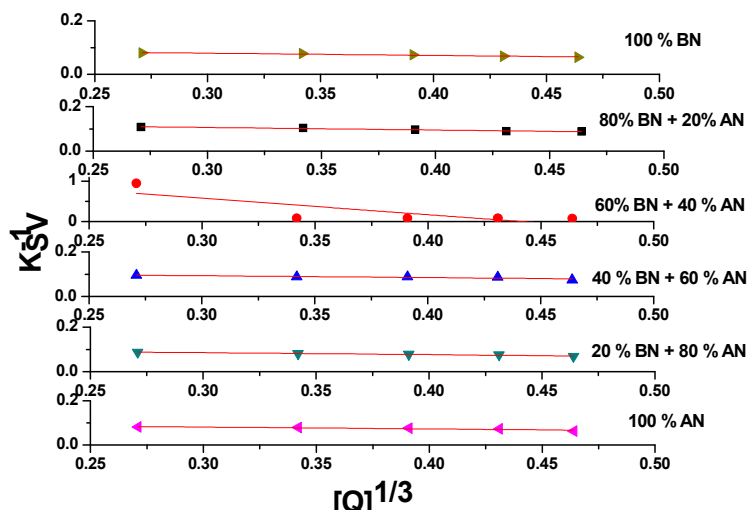
Fig. 4 The plots of K_{SV}^{-1} versus $[Q]^{1/3}$ in different solvent mixtures (BN+AN).

Table 2. The various quenching rate parameters calculated from finite sink approximation model.

Molecule	Solvent mixture		K_{sv}^o (dm^{3}mol^{-1})	$Dx10^5$ (cm^{2}s^{-1})	R' (Å)	$4\pi N'R'D$ x 10^{-10} (m^{-1}s^{-1})	k_qx10^{-10} (m^{-1}s^{-1})
	BN (%)	AN (%)					
DMB	100	00	8.4033	1.9328	5.040	0.07521	0.5421
	80	20	8.5540	2.1842	4.538	0.07503	0.6979
	60	40	8.1830	1.8310	5.177	0.07170	0.7063
	40	60	8.9440	2.0638	5.022	0.07844	0.7546
	20	80	10.619	3.8770	3.173	0.09313	0.8583
	00	100	10.245	2.8860	4.115	0.08990	0.8991

4. Conclusions

From the above discussion we observed that
(1) The S-V plots show the positive deviation leading to high value of k_q it indicates the efficiency of fluorescence quenching.
(2) The dependence of S-V constant on dielectric constant of the solvent mixture indicates the possibility of solvent molecule composition around the fluorescent.
(3) The value of quenching rate parameter k_q increases with increase in dielectric constant of the solvent mixture and it is suggesting the charge transfer character of the excited state complex.
(4) Finite sink approximation model helps to recover R' and D directly from the plots of K_{SV}^{-1} versus $[Q]^{1/3}$.
(5) The value of k_q is greater than 4πN'R'D in all the solvent mixtures.
From the above facts, we conclued that quenching phenomenon in DMB is diffusion limited and both static and dynamic quenching processes are playing a role.

Acknowledgements

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