Fluorescence quenching of BPBD by aniline in benzene–acetonitrile mixtures

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Abstract

The quenching of fluorescence of 2-(4′-*t*-butylphenyl)-5-(4″-biphenylyl)-1,3,4-oxadiazole (BPBD) has been studied by aniline in different solvent mixtures of benzene and acetonitrile at room temperature. The quenching is found to be appreciable and a positive deviation from linearity was observed in the Stern–Volmer plot in all the solvent mixtures. Various rate parameters for the quenching process have been determined by sphere of action static quenching model and finite sink approximation model. The magnitudes of these rate parameters indicate that positive deviation in the Stern–Volmer plot is due to both static and dynamic processes. The dependence of Stern–Volmer constant on dielectric constant of the solvent mixture indicates the possibility of different solvent molecule composition around the fluorescent from that of the bulk.
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Keywords: Fluorescence quenching; BPBD; Finite sink approximation model; Sphere of action static quenching model and charge transfer

1. Introduction

Fluorescence quenching of organic molecules in solution by various quenchers like aniline, bromobenzene, carbon tetra chloride, eththyltrithiocarbonate, halide ions, metal ions, etc. has been studied by several investigators by steady state [1–8] and transient methods [9–12]. In almost all the cases the experimental results follow the linear Stern–Volmer (S–V) relation given by

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

where I_0 and I are the fluorescence intensities in the absence and presence of quencher respectively. K_{SV} is the Stern–Volmer quenching rate parameter and $[Q]$ is the quencher concentration. But in some cases, it has been observed that the experimental results show positive deviation from a linear S–V relation [4–7]. This positive deviation

is attributed to various process like intersystem crossing, formation of charge transfer complexes both at ground and excited states, static and dynamic quenching, etc. Apart from this, the polarity of the solvent medium and the range of quencher concentration are expected to play a role in this mechanism.

In the present study we have used steady state experimental setup to investigate the quenching of 2-(4′-*t*-butylphenyl)-5-(4″-biphenylyl)-1,3,4-oxadiazole (BPBD) by aniline in different solvent mixtures of benzene and acetonitrile with a view to understand the nature of quenching mechanism involved in this system. By choosing two aprotic solvents benzene (BN) and acetonitrile (AN) with widely different dielectric constants ε, a good range of solvent polarity variation (2.28–37.12) was obtained. We have used the literature values [13] of dielectric constants for all the solvent mixtures. The various rate parameters responsible for fluorescence quenching have been determined by sphere of action static quenching model and finite sink approximation model. In light of these rate parameters and dependence of quench-

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ing rate parameter on the polarity of the solvent mixture the possible quenching mechanisms are discussed.

2. Experimental details

The solute 2-(4'-t-butylphenyl)-5-(4''-biphenylyl)-1,3,4-oxadiazole (BPBD) was obtained from Sigma–Aldrich, USA and is of scintillation grade. The quencher aniline was used after double distillation. The solvents benzene and acetonitrile were of spectroscopic grade and were used without any further purification. The solutions were prepared keeping the concentration of BPBD fixed (5×10^{-5} M/L) and varying the quencher concentration (0.002–0.010 M) in all the solvent mixtures. Fluorescence spectrophotometer F-2000 was used for fluorescence intensity measurements, with perpendicular geometry. Fluorescence measurements were made by taking fresh solution each time in a rectangular quartz cell having an airtight stopper. The solute has maximum absorption at 305 nm. The solute was excited at 305 nm and the fluorescence spectrum was recorded. The maximum fluorescence corresponds to 362 nm. First the fluorescence intensity I_0 was measured without the quencher and then the fluorescence intensity I was measured at different quencher concentrations and at a fixed solute concentration. The experimental values are reproducible within 5% of the experimental error.

3. Results and discussion

The S–V plots obtained by using the experimentally determined values of I_0 and I are found to be nonlinear in all the solvents showing positive deviation and are shown in Fig. 1. Similar experimental results were also observed by others [4–7]. Thus, positive deviation from linearity suggests that quenching is not purely collisional and reveals the role of the static quenching process. This was explained by sphere of action static quenching model. According to this model instantaneous or static quenching occurs if the quencher molecule is very near to, or in contact with the fluorescent molecule at the exact moment it happens to be excited. This was explained by the fact that only a certain fraction W of the excited state is actually quenched by the collisional mechanism. Some molecules in the excited state, the fraction of which is $(1 - W)$, are deactivated 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. Several models were employed (Smoluchowski model, Frank and Wawilow model) [2,14] to describe this static quenching process, all leading to the following modified form of the S–V equation

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

where K_{SV} and $[Q]$ have their usual meanings as explained earlier. The Smoluchowski's diffusion controlled equation
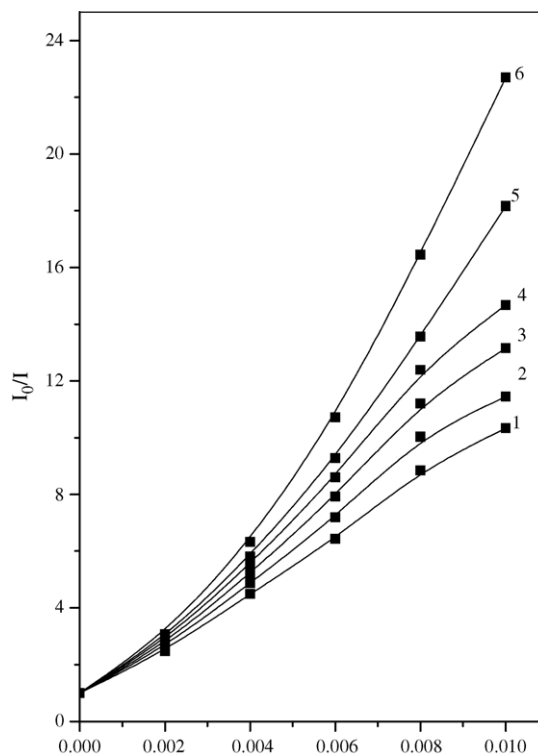

Fig. 1. Stern–Volmer plot of I_0/I against quencher concentration $[Q]$ in different solvent mixtures of benzene and acetonitrile.

containing transient term is given by

$$K_{\mathrm{d}} = 4\pi N' R D + 4R^2 N' (\pi D)^{1/2} t^{-1/2} \tag{3}$$

where N' is the Avogadro's number per millimole, R the encounter distance, i.e. the sum of the radii of the solute and quencher molecules and t is the time. The retention of the latter term of Eq. (3) leads to an additional factor W in Eq. (2), which is given by

$$W = \exp(-V[Q]) \tag{4}$$

where V is the static quenching constant and represents an active volume element surrounding the excited solute molecule.

Instantaneous (static) quenching occurs in a randomly distributed system when a quencher happens to reside within a sphere of action with a volume V/N', and radius 'r' $[V/N' = 4\pi r^3/3]$ surrounding a solute molecule at the time of excitation.

As W depends on the quencher concentration $[Q]$ the S–V plots for a quencher with a high quenching ability generally deviate from linearity. Thus Eq. (2) is rewritten as

$$[1 - I/I_0]/[Q] = K_{\mathrm{SV}}(I/I_0) + (1 - W)/[Q] \tag{5}$$

Fig. 2 shows the plots of $[1 - I/I_0]/[Q]$ against I/I_0 for BPBD with aniline as quencher for different solvent mixtures of benzene and acetonitrile which are linear according to Eq. (5).

The dynamic quenching constant K_{SV} is determined in all the cases by least square fit method using Eq. (5) and the
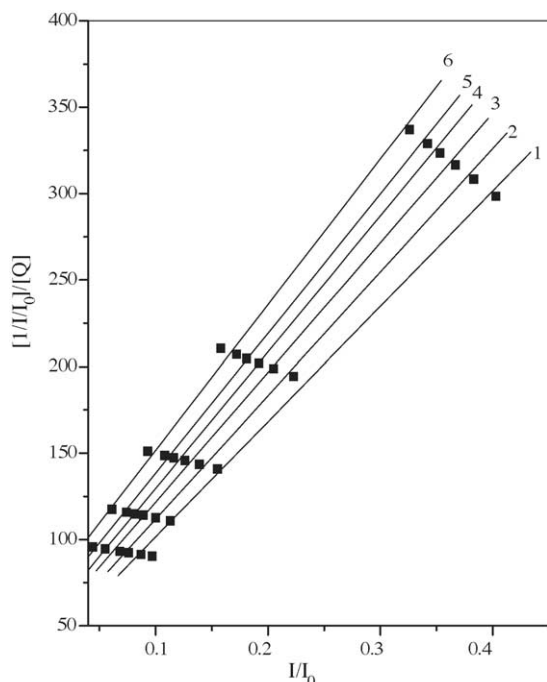
Fig. 2. Plot of $[1 - I/I_0]/[Q]$ against I/I_0 for BPBD in different solvent mixtures of benzene and acetonitrile (1, 100% BN; 2, 20% AN; 3, 40% AN; 4, 60% AN; 5, 80% AN; 6, 100% AN).

values are given in Table 1. Fluorescence lifetime τ of the solute studied is obtained from the catalogue of the Koch-Light laboratories limited, UK and is given at the bottom of Table 1. Bimolecular quenching rate parameter k_q was determined from relation $k_q = K_{SV}/\tau$ (Table 1). Here high values of k_q indicate efficient quenching of fluorescence.

In order to support static and dynamic effects, we have determined the magnitudes of static quenching constant V and radii r of sphere of action (or kinetic distance) using the sphere of action model. With the use of Eqs. (4) and (5) the values of V and r are determined by least square fit method in all the solvent mixtures and are given in Table 1.

The radii of the solute (R_Y) and the quencher (R_Q) molecules were determined by adding the atomic volumes of all the atoms constituting the molecule as suggested by Edward [15] and are given at the bottom of Table 1. From these values of R_Y and R_Q the sum of the molecular radii R of BPBD and aniline is determined. This sum of the molecu-

lar radii is referred to as encounter distance. This value is then compared with the values of 'r' to verify whether the reaction is due to sphere of action model. From Table 1 we see that the values of kinetic distance 'r' are greater than the encounter distance R. Therefore according to Andre et al. [16] and Zeng and Durocher [17] the static effect takes place irrespective of ground state complex formation provided reactions are limited by diffusion indicating the sphere of action model holds well. Further it may also be noted that a positive deviation in S–V plot is expected when both static and dynamic quenching occurs simultaneously [4].

In order to find whether the reactions are diffusion limited we invoked finite sink approximation model. According to this model [18–20] the following modified S–V relationship is obtained

$$K_{SV}^{-1} = (K_{SV}^0)^{-1} - \{(2\pi N')^{1/3}/4\pi N' D\tau\}[Q]^{1/3} \qquad (6)$$

where $K_{SV}^0 = 4\pi N' DR\tau k_a/(4\pi N' DR + k_a)$, N' the Avogadro's number per millimole, D the sum of the diffusion coefficients (mutual diffusion coefficient) of the reactants and R is the reaction distance at which the reaction proceeds, k_a the activation energy controlled rate constant. A plot of K_{SV}^{-1} against $[Q]^{1/3}$ becomes linear with negative slope. Mutual diffusion coefficient D becomes directly accessible from the slope of the plot and K_{SV} is obtained at $[Q] = 0$ regardless of the relative magnitudes of k_a and k_d ($=4\pi N' DR$), irrespective of quenching is diffusion limited or not.

Therefore according to Eq. (6) we need to determine the values of K_{SV}^{-1} and $[Q]^{1/3}$. Where $K_{SV} = [I_0/I - 1]/[Q]$ and $[Q]$ the quencher concentration from 0.002 to 0.010 M. For efficient quenching processes (concentration dependent) the value K_{SV} is often observed to increase with $[Q]$. Hence the values of K_{SV} were determined at each quencher concentration in all the solvent mixtures and the values of K_{SV}^{-1} are also determined. Fig. 3 shows the plots of K_{SV}^{-1} against $[Q]^{1/3}$. From this figure we see that all the plots in different solvent mixtures are almost linear and small deviation may be due to experimental uncertainties. Hence, the linear dependence of K_{SV}^{-1} on the one-third power of quencher concentration within the error limits is confirmed [17]. Then the values of K_{SV}^0 (S–V constant at $[Q] = 0$) and mutual diffusion coefficient D were obtained from the intercept and slope of the plot of K_{SV}^{-1} against $[Q]^{1/3}$, respectively (Table 2). Using the

Table 1
The dielectric constants of the benzene–acetonitrile mixtures, Stern–Volmer quenching constant K_{SV}, quenching rate parameter k_q, static quenching constant V and kinetic distance r values for BPBD + aniline system in different solvent mixtures of benzene (BN) + acetonitrile (AN) at room temperature

Solvent mixture	Dielectric constant, D	K_{SV} (mol^{-1})	k_q ($\times 10^{-10}$ mol^{-1} s^{-1})	V (mol^{-1} dm^3)	r (Å)
100% AN	37.12	841.523	70.10	112.70	35.48
80% AN	30.46	807.313	67.28	86.75	32.52
60% AN	24.30	787.390	65.62	71.33	30.46
40% AN	15.18	749.750	62.48	63.49	29.30
20% AN	10.67	714.690	59.56	51.08	27.25
100% BN	2.28	666.660	55.55	42.77	25.25

$R_Y = 4.31$ Å, $R_Q = 2.84$ Å, $\tau = 1.2$ ns.

Table 2
The values of K_{SV}^0 (steady state quenching constant at $[Q] = 0$), mutual diffusion coefficient D, distance parameter R', $4\pi N'DR'$ for BPBD + aniline system in different solvent mixtures of benzene (BN) + acetonitrile (AN) at room temperature

Solvent mixture	K_{SV}^0 (mol^{-1} dm^3)	D ($\times 10^5$ cm^2 s^{-1})	R' (Å)	$4\pi N'R'D$ ($\times 10^{-10}$ mol^{-1} s^{-1})
100% AN	595.24	29.79	21.99	49.60
80% AN	598.80	33.50	19.68	49.90
60% AN	588.23	33.96	19.07	49.02
40% AN	564.97	34.30	18.13	47.07
20% AN	549.45	36.49	16.57	45.77
100% BN	578.03	51.08	12.46	48.17

$R (= R_Y + R_Q) = 7.15$ Å.

values of K_{SV}^0 and D, the distance parameter R' was determined and is given in Table 2 for all the solvent mixtures. In present case $R' > R$ in all the solvent mixtures and hence the values of k_a cannot be determined. According to Joshi et al. [21] the bimolecular reactions are said to be diffusion limited if the values of k_q are greater than $4\pi N'R'D$. Hence the values of $4\pi N'R'D$ are calculated using the experimentally determined values of R' and D and are given in Table 2. We see from Table 2 that in all the solvent mixtures the values of k_q are greater than $4\pi N'R'D$, which is an expected result for diffusion limited reaction [21]. The possibility of ground state complex formation is ruled out as no shift in absorption spectra of different solvent mixtures of benzene and acetonitrile at room temperature was observed. Further, we observe from Fig. 4 that the value of K_{SV} increases as the dielectric constant of the solvent mixture increases. It is worth to note that the dielectric constant of the mixed solvent is in principle determined as an average, but fluorescence quenching is
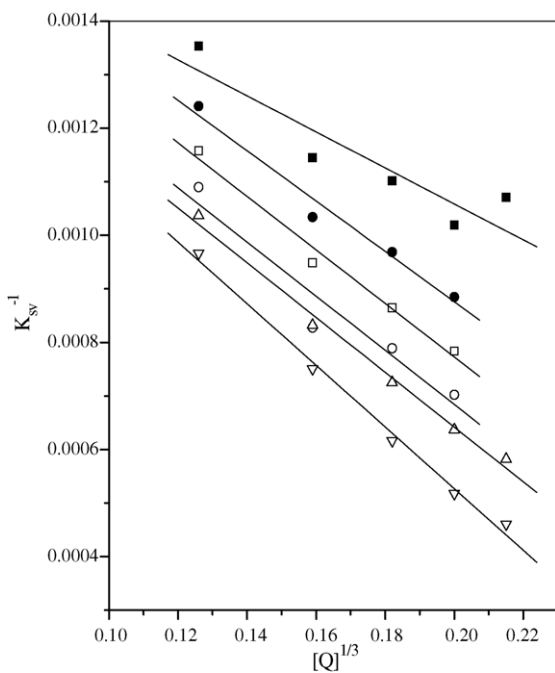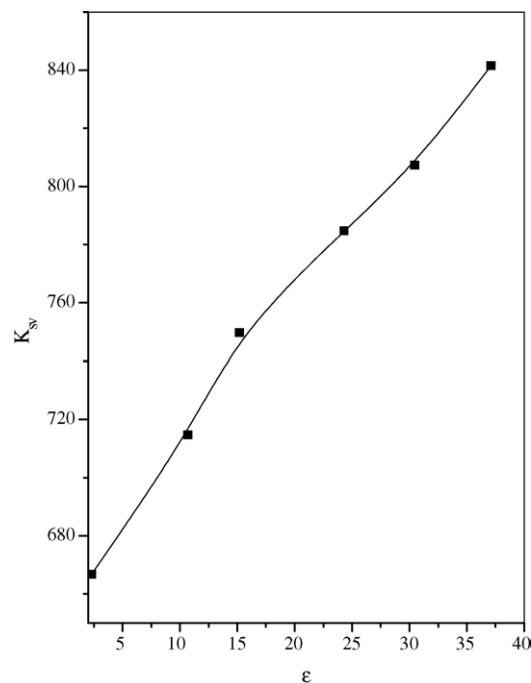

Fig. 4. Variation of K_{SV} as a function of Dielectric constant ε for the solute BPBD.

determined quite locally. This may be attributed to the fact that the solvent molecule composition around the fluorescent is different from that of the bulk in different solvent mixtures. Similar trend was observed by others in some fluorophore-quencher systems [4,22]. This effect of dielectric constant suggests the charge transfer character in the excited complex. The high value of K_{SV} in polar solvent acetonitrile compared to non-polar solvent benzene may also be explained by the greater charge transfer character of the excited complex in the polar solvent [23].

4. Conclusion

From the above discussion we observe that: (1) the S–V plots show positive deviation leading to high values of k_q, indicating efficient fluorescence quenching. (2) The dependence of Stern–Volmer constant on dielectric constant of the solvent mixture indicates the possibility of different solvent

Fig. 3. Plot of K_{SV}^{-1} against $[Q]^{1/3}$ for BPBD in different solvent mixtures of benzene and acetonitrile (($\blacksquare$) 100% BN, ($\bullet$) 20% AN, ($\square$) 40% AN, ($\bigcirc$) 60% AN, ($\triangle$) 80% AN, ($\triangledown$) 100% AN).

molecule composition around the fluorescent and that of the bulk. (3) The value of k_q is greater than $4\pi N'R'D$ in all the solvent mixtures. (4) The value of quenching rate parameter k_q increases with increase in dielectric constant of the solvent mixture suggesting the charge transfer character of the excited complex. In view of the above facts we conclude that quenching reaction is diffusion limited and both static and dynamic quenching processes are partly playing a role in this system.

Acknowledgements

References

[1] R. Roy, S. Mukherjee, Chem. Phys. Lett. 140 (1987) 210.
[2] T. Moriya, Bull. Chem. Soc. Jpn. 57 (1984) 1723.
[3] S.M. Hanagodimath, G.S. Gadaginmath, G.C. Chikkur, Appl. Radiat. Isot. 41 (1990) 817.
[4] P.K. Behera, A.K. Mishra, J. Photochem. Photobiol. A: Chem. 71 (1993) 115.
[5] J.S. Kadadevaramath, T.P. Giraddi, G.C. Chikkur, J. Photosci. 4 (1998) 105.
[6] T.P. Giraddi, J.S. Kadadevaramath, G.H. Malimath, G.C. Chikkur, Appl. Radiat. Isot. 47 (1996) 461.
[7] M.K. Shailaja, S.M. Hanagodimath, J.S. Kadadevaramath, G.C. Chikkur, J. Photosci. 6 (2000) 159.
[8] C. Hariharan, A.K. Mishra, Radiat. Meas. 32 (2000) 113.
[9] Shigeo Murata, Motoi Nishimura, Sanae Y. Matsuzaki, M. Tachiya, Chem. Phys. Lett. 219 (1994) 200.
[10] P.K. Behera, T. Mukherjee, A.K. Mishra, J. Lumin. 65 (1995) 131.
[11] M.S. Mehata, H.B. Tripathi, J. Lumin. 99 (2002) 47.
[12] M. Swaminathan, N. Radha, Spectrochim. Acta, Part A 60 (2004) 1839.
[13] Bilal Acemioglu, Mustafa Arik, Hasan Efeoglu, Yavuz Onganer, J. Mol. Struct. (Theochem.) 548 (2001) 165.
[14] J.M. Frank, S.J. Wawilow, Z. Phys. 69 (1931) 100.
[15] J.T. Edward, Chem. Ind. (London) (1956) 774.
[16] J.C. Andre, M. Niclause, W.R. Ware, Chem. Phys. 28 (1978) 371.
[17] H. Zeng, G. Durocher, J. Lumin. 63 (1995) 75.
[18] J. Keizer, J. Phys. Chem. 86 (1982) 5052.
[19] J. Keizer, J. Am. Soc. Chem. 105 (1983) 1494;
J. Keizer, J. Am. Chem. Soc. 107 (1985) 5319.
[20] J. Keizer, Chem. Rev. 87 (1987) 167.
[21] G.C. Joshi, R. Bhatnagar, S. Doraiswamy, N. Periasamy, J. Phys. Chem. 94 (1990) 2908.
[22] C.C. Leiten, K. Razi Naqvi, Chem. Phys. Lett. 4 (1969) 35.
[23] J.R. Lakowicz, Principles of Fluorescence Spectroscopy, Plenum Press, New York, 1986, p. 266.