Localization of N-Hexadecyl-4-(p-N, N-dimethyl aminostyryl) Pyridinium Bromide in Anionic SDS Micelle: Fluorescence Quenching Method

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Abstract:
The fluorescence quenching behaviour of N-hexadecyl-4-(p-N, N- dimethyl amino styryl) pyridinium bromide in different solvent and anionic SDS micellar concentration both in presence and absence of the 1-((4-phenylthiazol-2- yl)diazenyl)naphthalen-2-ol azo dye (2) have been studied. Various quenching processes have been analyzed to explain the quenching efficiency. In solvent, the quenching depends both on dielectric constant and viscosity of the medium. In case of SDS micelle localization of probe and quencher plays important role in quenching efficiency.

Keywords: Styryl pyridinium dye, Fluorescence quenching, Micelle, Sten- Volmer constant.
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INTRODUCTION

Fluorescence quenching has been extensively used to probe the structure of the assembly and to understand the dynamics of organization [1-9]. The fundamental nature of micelle-mediated quenching has also been explored [10-19]. In the simplest scenario, quenching is modeled based on the Stern-Volmer [20] equation in which the ratio of fluorescence in the absence of quencher to that in the presence of quencher is a linear function of quencher concentration. Deviations from linearity generally fall into two categories: saturated and superlinear. In certain cases, the saturated behavior is characteristic of an inaccessible fraction of fluorophores [13]. This fraction is typically buried in a hydrophobic region of a macromolecular system, such as a protein. In biology fluorescence quenching was first used to examine the positions of aromatic amino acids within proteins [21]. Moreover, high iodide concentrations have been employed in recent reports of tryotophan quenching for bovine serum albumin in the aqueous phase [22] and immobilized in a sol-gel [23]. Superlinear behavior is more common and usually occurs owing to a strong partitioning of the quencher into a region of space containing the fluorophore. Within micelle solutions, the kinetic equations for such behavior are based on the probabilities of finding the quenchers and fluorophores in the same micelle [24,25]. These probabilities are based on Poissonian micelle occupation statistics. A rarer, but simpler scenario for superlinear behavior is when both static and dynamic quenching occurs

simultaneously. This leads to a quadratic dependence on quencher concentration.

Styryl pyridinium dyes has the following particularly interesting photophysical property: a high molecular hyperpolarizability [26] that plays a key role in second-harmonic generation [27-31] as well as in the sensitivity to the environment, detectable as a solvatochromic effect [32] or as the dependence of the electrical membrane potential [33]. The absorption and emission behaviour of some tailor made styryl pyridinium dyes have been extensively used to investigate the surface behaviour of monolayers on water surface [34, 35] and on solid silica surface [36-39], and solubilization behaviour in micelles [40-47] and reversed micelles [35] by our research school.

In this thesis, fluorescence quenching behaviour of N-hexadecyl-4-(p-N, N-dimethyl amino styryl) pyridinium bromide (1: C16-NMe2) in different solvent and anionic SDS micellar concentration both in presence and absence of the 1-((4-phenylthiazol-2- yl)diazenyl)naphthalen-2-ol azo dye (2) have been studied in order to investigate any effect of localization of probe and quencher on the quenching behavior.

MATERIALS AND METHODS

Acetonitrile (MeCN), Dioxane and Methanol (Merck India) are of spectroscopic grade. Sodium dodecyl sulphate (SDS; Sigma) was crystallized twice from alcohol before use. Millipore water was used throughout the study. N-hexadecyl-4-(p-N, N-dimethyl aminostyryl) pyridinium bromide has been synthesized by the procedure as reported earlier [44].

The absorption spectra of the fluorophore were recorded by a UV-Visible Shimadzu- 2450 Spectrophotometer using the same media as references. The fluorescence spectra were recorded by a Hitachi F-7000 spectrofluorimeter. The excitation wavelength was chosen at around the absorption maximum of the respective fluorophore. Narrow excitation and emission slit widths (half band with = 1.5nm, 3nm) were chosen. The concentration of 1 was maintained at 2 x 10-4 M. The concentration of quencher 2 was varied in the range 0.0 - 0.1 M. Thenconcentration of surfactant (SDS) was varied in the range 0.01-0.03 M which is above the critical micellar concentration (cmc) of SDS (8 mM) [48]. The fluorescence intensities of 2 (?ex = 385 nm, ?em = 490 nm) were monitored at various concentrations of quencher.

RESULT AND DISCUSSION

1.1 Absorption and fluorescence Spectra

The absorption spectra of N-hexadecyl-4-(p-N, N-dimethyl amino styryl) pyridinium bromide (1) in different solvent and anionic SDS micellar concentration both in presence and absence of the 1-((4-phenylthiazol-2-yl)diazenyl)naphthalen-2-ol as quencher (2: phenyl thiazole azo dye) show no observable change in spectral shape and maxima. C16-NMe2 shows the emission peak at 480-500 nm depending on the nature of solvent. In SDS micelle it shows emission peak at 490 nm. Although there is appreciable quenching even at low concentration of quencher 2 (0.005 M), the shape of the fluorescence spectra remains the same with no change in the position of the maxima in all the solvent and SDS micelle. Fluorescence spectra of C16-NMe2 dye (1) in dioxane is given in Fig. 1.

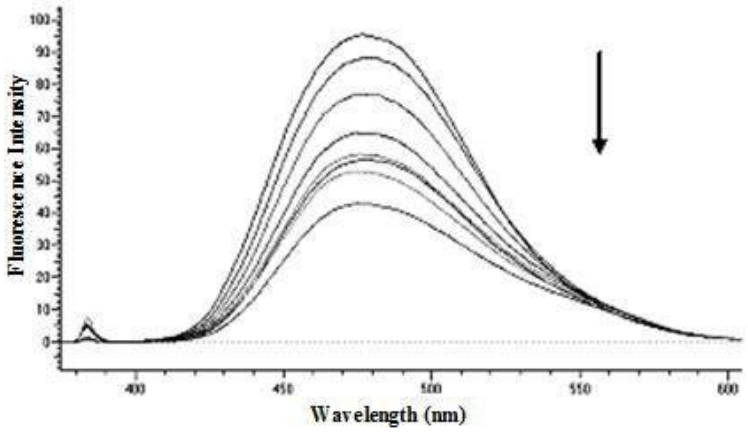

Fig. 1: Fluorescence spectra of C16-NMe2 dye (1) in presence of azo dye (2) in Dioxane.

Similar observation of absorption spectra of a solution containing any concentration of the quencher after carrying out the fluorescence indicates that no detectable photoproduct is formed under the experimental condition. No new fluorescence peak is also observed at longer wavelength. The excitation spectra monitored at different emission wavelengths also remain the same in all the media. These observations indicate that there is no ground state complexation of C16-NMe2 dye (1) and azo dye (2). Decrease in the fluorescence intensity of C16-NMe2 dye (1) without the appearance of any new band in the presence of quencher concentration up to 0.05 M indicates that no emissive exciplex is formed between the fluorophores with the quencher in solvent and SDS micelle.

1.2 Fluorescence quenching of C16-NMe2 dye in solvent

Quenching of C16-NMe2 dye (1) and azo dye (2) is appreciable in case of all solvent used. The Stern-Volmer plots of [(Io/I)-1] versus [Quencher] for 1 in different solvents are shown in Fig. 2. The plots are linear up to a limiting concentration (˜ 0.02 M of quencher concentration. Beyond this limiting concentration of quencher 2, the plots show a upward deviation in all the solvent. This suggests that dynamic quenching process operates at low concentration of quencher only.

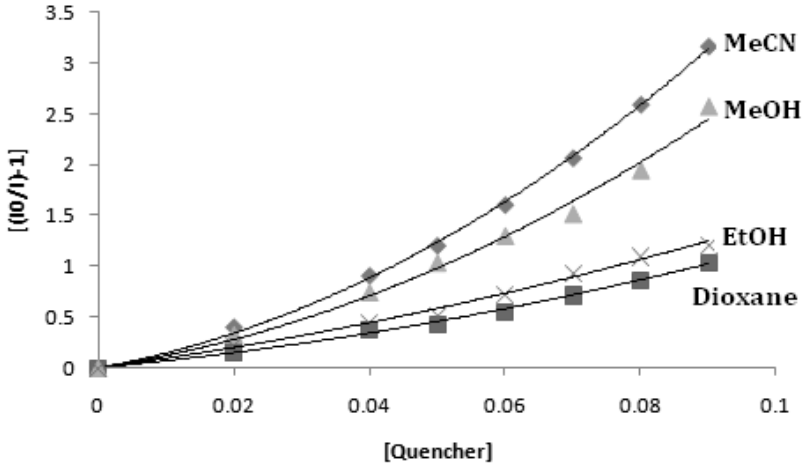

Fig. 2: The Stern-Volmer plots of C16-NMe2 dye (1) in acetonitrile (MeCN), dioxane, methanol (MeOH) and Ethanol (EtOH) at 27 0C.

As discussed earlier that the quenching of fluorescence of C16-NMe2 dye (1) by azo dye 2 is dynamic (collisional) quenching in low concentration of quencher. The Stern- Volmer quenching constants (KSV) determined by the equation (Eq. 1),

$$\left[\left(\frac{I_0}{I}\right) - 1\right] = K_{SV}[Q] \quad (1)$$

where I0 and I are the intensities of the fluorophore in the absence and in the presence of the quencher respectively, KSV is the Stern-Volmer quenching constant and [Q] is the concentration of the quencher. The KSV data in various solvent are reported in Table-1.

Table 1: The Stern-Volmer quenching constants (KSV) and transient quenching constant (KT) of C16-NMe2 dye (1) in acetonitrile (MeCN), dioxane, methanol (MeOH) and ethanol (EtOH) at 27 0C.

It can be seen from Table 1 that as the dielectric constant decreases the KSV value decreases whereas as the viscosity coefficient increases the KSV value decreases. The plot dielectric constant and viscosity coefficient against KSV is found to be non-linear with r2=0.99 (Fig. 3 & 4).

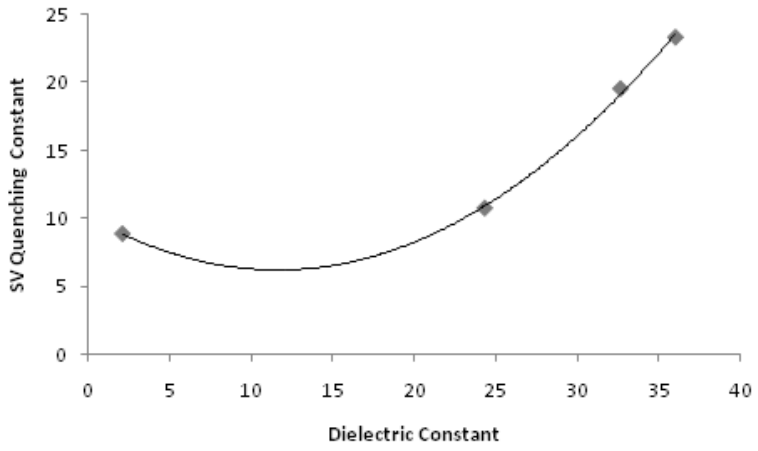

Fig. 3: The plot dielectric constant vs Stern-Volmer quenching constant.

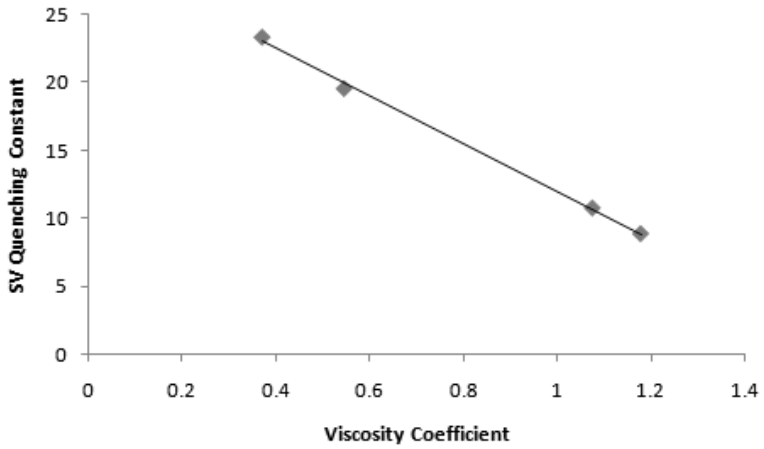

Fig. 4: The plot viscosity coefficient vs Stern-Volmer quenching constant.

In the absence of any chemical reactions of C16-NMe2 dye (1), the deviation from the linearity may be due to (i) ground state complex formation or (ii) quenching sphere of action i.e. transient quenching. But deviation due to ground state complex formation is discarded on the ground that no change is observed in the absorption spectra in presence of quencher. So it is clear that fluorescence quenching at high quencher concentration involves a quenching sphere of action.

While studying the fluorescence quenching of perylene by oxygen molecule, Lakowicz and Weber [49] have shown that for effective quenching, the oxygen molecules do not have to form complex with perylene. As long as it is within a distance of 16 Å from the fluorophore, oxygen molecule is able to quench effectively. From this observation they have proposed a sphere of action within which a molecule can quench the fluorophore effectively.

According to quenching sphere of action model [50, 51],

$$\ln\left(\frac{I_0}{I}\right) K_T[Q] \quad (2)$$

where KT(=vN) is the transient quenching constant, `v' is the volume of the transient quenching sphere and N is Avogadro's number. The plots of In (Io/I) versus [Quencher] for C16-NMe2 dye (1) are found to be linear in all the solvent (Fig. 5). It infers that quenching occurs through sphere of action model. The KT values are reported in Table 1.

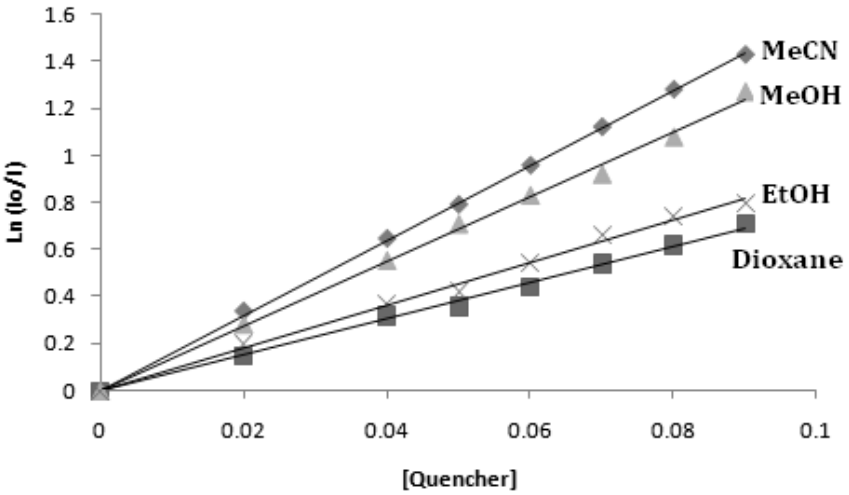

Fig. 5: The plot ln I0/I) vs [Quencher] of C16-NMe2 dye (1) in acetonitrile (MeCN), dioxane, methanol (MeOH) and Ethanol (EtOH) at 27 0C.

It can be seen from Table 2 that as the dielectric constant decreases the KT value decreases whereas as the viscosity coefficient increases the KT value decreases. The plot dielectric constant vs KT is nonlinear with r2=0.99.

1.3 Fluorescence quenching of C16-NMe2 dye in SDS micelle

Quenching of C16-NMe2 dye (1) and azo dye (2) is appreciable in case of all anionic micellar concentrations (0.01 M-0.03M). The Stern-Volmer plots of [(Io/I)-1] versus [Quencher] for 1 in different SDS micelle are shown in Fig. 6. The plots are linear up to a limiting concentration (˜ 0.02 M of quencher concentration. Beyond this limiting concentration of quencher 2, the plots show a upward deviation in all the solvent. This suggests that dynamic quenching process operates at low concentration of quencher only.

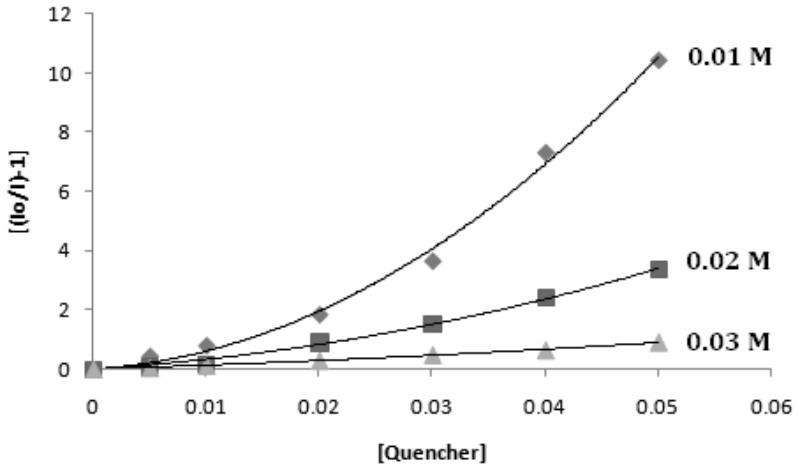

Fig. 6: The Stern-Volmer plots of C16-NMe2 dye (1) in anionic SDS Mice

The linearity in Stern-Volmer plot in the limiting concentration of quencher is dynamic (collisional). The Stern-Volmer quenching constants (KSV) can be determined by the equation (Eq. 1). The KSV data in various SDS micelle are reported in Table 2.

Table 2: The Stern-Volmer quenching constants (KSV) and transient quenching constant (KT) of C16-NMe2 dye (1) in anionic SDS Micelle at 27 0C.

[SDS] in mM	K_{SV} (M^{-1})	K_T (M^{-1})
0.01	82.80	54.41
0.02	16.27	29.90
0.03	12.25	12.62

It can be seen from Table 2 that as the micellar concentration increases the KSV value decreases. As discussed earlier that the quenching of fluorescence of C16-NMe2 dye (1) by azo dye 2 involves a quenching sphere of action or transient quenching. The plots of ln (Io/I) versus [Quencher] for C16-NMe2 dye (1) are found to be linear in all the SDS micelle (Fig. 7). It infers that quenching occurs through sphere of action model. The KT values are reported in Table 2.

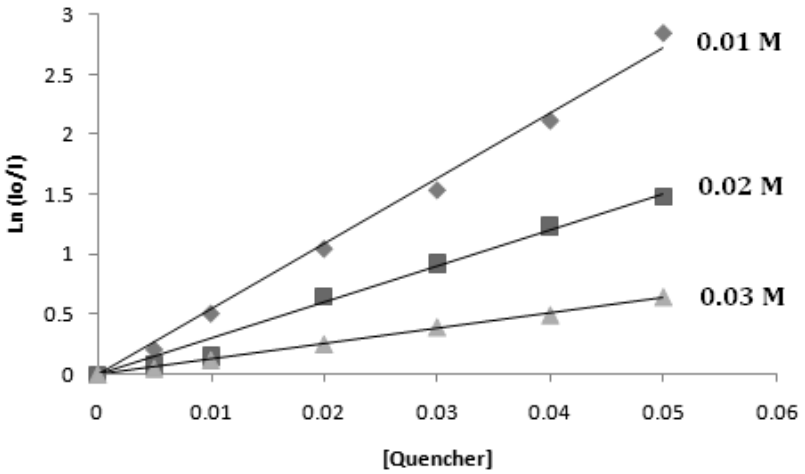

Fig. 7: The plot of ln (Io/I) vs [Quencher] of C16-NMe2 dye (1) in anionic SDS micelle.

The linearity in the plot suggests quenching of fluorescence of C16-NMe2 dye (1) by azo dye 2 involves a quenching sphere of action or transient quenching. The transient quenching constants (KT) can be determined by the equation (Eq. 2). The KT data in various SDS micelle are reported in Table 2. It can be seen from Table 2 that as the micellar concentration increases the KT value decreases. This may be due to as the micellar concentration increases, the size of the micelle increases and C16-NMe2 dye (1) localization site differs due to which extent of quenching decreases. Comparing the KT data from the plot of dielectric constant vs transient quenching constant (Fig. 8) and viscosity coefficient vs [Quencher] (Fig. 9) it infers that as the micellar concentration increases the localization site of C16-NMe2 dye (1) shifts towards the micellar interface.

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