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Luminescence behaviour of phenosafranin in reverse micelles of AOT in *n*-heptane

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Abstract

The absorption and fluorescence properties of the cationic dye phenosafranin (PSF) solubilised in the reverse micelles of the surfactant aerosol OT (AOT) in *n*-heptane were studied as a function of water content, $w_0 = ([H_2O]/[AOT])$. The room temperature emission of PSF in reverse micelles at $w_0 = 0$ show a significantly blue shifted maximum as compared with that in pure water. A plot of fluorescence polarisation anisotropy (r) against increasing w_0 shows an increase in the rigidity of the dye environment up to $w_0 \approx 10$, where it maximises and then falls off to attain a steady value between $w_0 = 25$–30. Even at this high w_0 the anisotropy of the embedded dye molecule is appreciably higher than that of the dye in bulk water. Lifetime measurements at different w_0 values showed single exponential decay character. Relevant absorption and luminescence data in representative homogeneous solvents and in low temperature (77 K) glass are also reported. The observations have been interpreted in terms of the location of the dye molecule and changes in its environment with changes in w_0, in the AOT reverse micelles.

Keywords: Phenosafranin; Luminescence behavior; Aerosol OT reverse micelles

1. Introduction

Phenosafranin (PSF, 3,7-diamino-5 phenyl phenazinium chloride) and other azine dyes of the safranin group, namely safranin, tolusafranin etc. absorb very strongly in the green region of the visible spectrum. Reversible electrochemical reduction and long-lived excited states make the dye PSF a potentially useful sensitiser in energy and electron-transfer processes [1]. Application of PSF in photoelectrochemical devices have been reported [2]. PSF can also efficiently inject an electron into the conduction band of TiO_2 semiconductor. The photophysical and photochemical behaviour of the dye in aqueous and non aqueous systems have already been studied [3]. Control over the course of chemical reactions involving conversion and storage of light energy can be achieved with the aid of organised molecular assemblies such as micelles, reversed micelles bilayers and membranes. PSF–ethylene diamine tetra acetic acid system has been studied in storage solar cells in presence of various surfactant assemblies [4]. The performance of the cell depends on the surfactant used.

In the present study we have attempted to characterise PSF in reverse micelles of aerosol OT (AOT, sodium bis [2 ethyl hexyl] sulfosuccinate). Reverse micelles represent useful model systems mimicking water pockets in biological aggregates. Amphiphilic molecules like aerosol OT when dissolved in certain solvents of the *n*-alkane series e.g. heptane, octane, form spheroidal aggregates called "reverse micelles" [5–8]. Their outer sheath is made up of the amphiphile and the inner core is formed by the negatively charged headgroups or counterions. Minute quantities of water are solubilised in the inner core formed by the sulphonate head groups and sodium counterions. The water enclosed in reverse micelles exhibit typical solvation properties which are markedly different from that of bulk water. The average size of reverse micelles is governed by the amount of solubilised water, expressed by the water to surfactant molar ratio, $w_0 = [H_2O]/[AOT]$. The properties of the aqueous core vary continuously with w_0. The water pool can be subdivided into two broad classes; the "bound" water region consisting mainly of water molecules associated with the hydration of the sodium counterions and the "bulk" water region developing in the micellar core after completion of the hydration of the sodium ions. With increasing w_0 the bound and bulk water regions coexist with rapid exchange of water molecules between the two

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regions. Dyes have often been used as fluorescent probes to explore the water/surfactant interface of the AOT reverse micelles in *n*-alkanes [9]. Our present work is devoted to a study of the photophysical properties of the dye PSF in AOT reverse micelles.

2. Experimental

The dye phenosafranin (PSF) was purchased from Sigma and used as received. Its purity was checked from its spectral characteristics. Aerosol OT (AOT) was purchased from Sigma and used without further purification. A 50 mM solution of AOT reverse micelles was prepared in *n*-heptane (Spectrograde, E. Merck, Germany) for all analyses. In order to prepare the sample solution of the dye solubilised in the reverse micelles, a 100 μl aliquot of an ethanolic solution of the dye (5×10^{-5} M) was allowed to evaporate completely in the sample cuvette. Then 2 ml aliquot of a freshly prepared AOT solution was added to the dye in the cuvette and the contents shaken until a steady optical density was obtained at the absorption maxima of the dye. At this stage it was assumed that the given fluorophore species was totally solubilised in the micellar phase. Assuming that a given fluorophore species is totally solubilised in the micellar phase, and distributes itself among the micelles according to the Poisson statistics the average number of fluorophore molecules per micelle is given by $n=[F]/[M_T]$ where [F] is the macroscopic fluorophore concentration and $[M_T]$ is the average concentration of reverse micelles in solution. $[M_T]$ is estimated to be about 0.002 M, for a 50 mM solution of AOT in *n*-heptane assuming that AOT molecules are in complete association in uniformly sized assemblies consisting of about 23 AOT molecules in each assembly as shown by Kalyansundaram [10]. The average number of PSF molecules per micelle would then be 0.001. This ensures that upon solubilisation not more than one molecule of PSF occupy a single micelle. Under such conditions solubilisation of PSF molecules should cause negligible perturbation of the structure and related properties of the micelles. The plot of the difference in absorption and emission maxima of the dye in wavenumbers ($\bar{\nu}_a-\bar{\nu}_f$) against solvent dielectric constant (ϵ) is obtained by determining the absorption and emission maxima of the dye in solvents of known standard dielectric constant.

Steady state absorption and fluorescence spectra were recorded with a Hitachi model U 2000 spectrophotometer and model F 4010 spectrofluorometer respectively. Low temperature emission measurements were carried out using cylindrical Suprasil quartz cells of 5 mm outer diameter. For measurements at 77 K the sample cell was directly immersed in liquid nitrogen contained in a quartz Dewar. Polarisation studies were carried out with the above spectrofluorometer with polarisation accessories and a thermostatted cell holder. For all polarisation measurements the temperature was maintained at 25 ± 0.5 °C. The fluorescence spectra in general were not corrected for wavelength dependence of the instrument. Fluorescence lifetime measurements were carried out using a nanosecond single-photon counting apparatus as described in a previous work [11]. Data analyses were performed by a reconvolution method using a non-linear least squares fitting programme. The goodness of the fit was estimated by χ^2 and standard deviation. All measurements were carried out at ambient temperature (298 K).

3. Results and discussion

Fig. 1 displays the absorption spectra of PSF in reverse micelles of AOT in *n*-heptane at different w_0 values. The absorption maximum (λ_{max}) of PSF in aqueous solution is at 520 nm [12]. Upon incorporation into reverse micelles of AOT/*n*-heptane at $w_0=0$, the lowest energy absorption band of the dye is found to have two closely spaced peaks, with λ_{max} at 508 nm and 531 nm respectively, (difference $\Delta\bar{\nu}\approx 850\ cm^{-1}$). On gradual addition of water, at $w_0=1$ the 508 nm peak is reduced to a shoulder and the 531 nm peak becomes prominent in intensity. The increase in dye absorption in going from $w_0=0$ to $w_0=1$ is significant but on further addition of water the rate of increase of absorption gradually falls off. The isosbestic point in the absorption spectra sug-

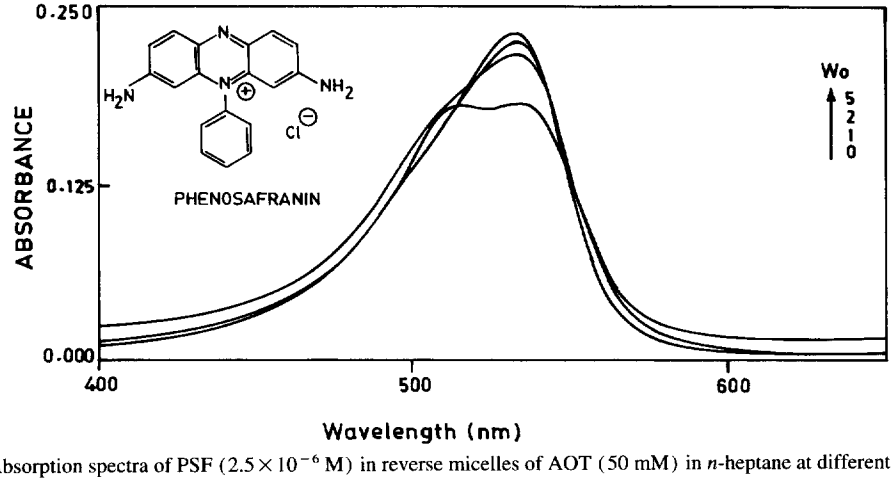

Fig. 1. Absorption spectra of PSF (2.5×10^{-6} M) in reverse micelles of AOT (50 mM) in *n*-heptane at different w_0 values.

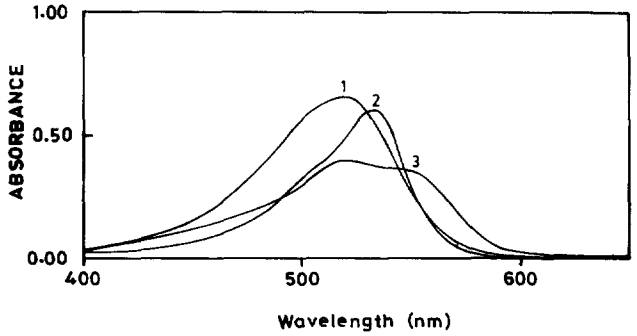

Fig. 2. Absorption spectra of PSF in different homogeneous solvents, namely: 1, water; 2, ethanol; 3, dioxane.

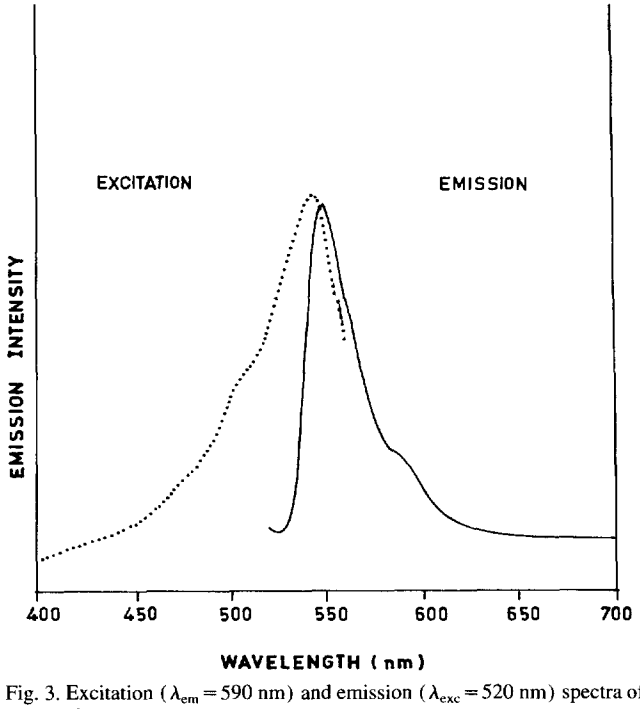

Fig. 3. Excitation ($\lambda_{em}=590$ nm) and emission ($\lambda_{exc}=520$ nm) spectra of 1×10^{-5} M PSF in 1:1 ethanol, methanol glass at 77 K.

gests a possibility of association or a complex formation between the positively charged PSF ions and the negatively charged AOT head groups. Similar observation had been reported earlier for PSF in presence of the surfactant TritonX 100 in aqueous media [12].

Absorption spectra of PSF in some representative homogeneous solvents are presented in Fig. 2. In water a broad absorption spectrum with the characteristic $\lambda_{max}\approx520$ nm is obtained in agreement with previous data. In polar protic solvents like ethanol λ_{max} shifts to 531 nm, which is accompanied by a weak shoulder at $\approx$490–500 nm. In dioxane the presence of twin peaks ($\lambda_{max}\approx520$ nm, 545 nm) in the absorption spectrum (Fig. 2) bears a close similarity to the situation in AOT/*n*-heptane at $w_0=0$. The ratio of optical densities at the two maxima remains unchanged even upon ten fold dilution of the dye in dioxane, thus ruling out the possibility of aggregation as a plausible cause for the twin peaks. Fig. 3 displays the excitation and emission profiles of PSF in 1:1 ethanol:methanol glass at 77 K. The excitation

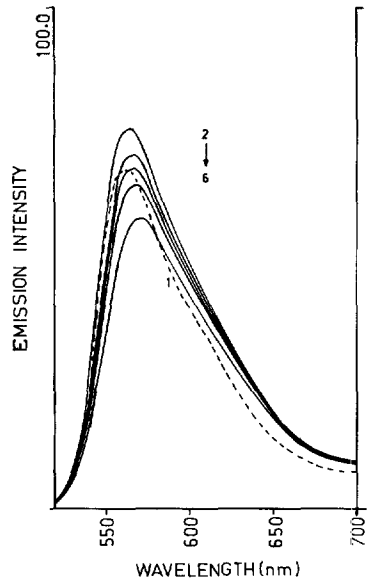

Fig. 4. Effect of increasing water content on the fluorescence spectrum of PSF in reverse micelles of AOT/*n*-heptane: [AOT] = 50 mM and [PSF] = 2.5×10^{-5} M at $w_0=0$ (- - -) and at other w_0 values: 1, 4, 6, 10 and 30 for plots 2–6 of the figure.

spectrum with a $\lambda_{max}\approx541$ nm and a shoulder at 500–510 nm, bears a close mirror image symmetry with the emission spectrum, which maximises at 546 nm with a shoulder around 580–590 nm. Interestingly the twin peaks in the relevant spectral bands appear in media of low polarity and in compact matrices like low temperature glass or microemulsions.

Fig. 4 presents the emission spectra of PSF in reverse micelles of AOT in *n*-heptane at various w_0 values. At $w_0=0$ the emission maximum of PSF occurs at 556 nm which is significantly blue shifted (19 nm) compared with the emission maximum of PSF in water, 575 nm. At $w_0=1$, the emission intensity of PSF increases with respect to the intensity at $w_0=1$. For subsequent additions of water, after $w_0=1$ the emission intensity starts decreasing. Beyond $w_0=6$ the intensity of dye emission is lower than that at $w_0=0$ and decreases further with increasing w_0 till at $w_0=30$ the emission intensity is 15% below that at $w_0=0$. Even at $w_0=30$ where the bulk water region of the inner water pool of the reverse micelles attain considerable dimensions, a red shift of only 3 nm from that at $w_0=0$ is obtained showing that changes in the dye environment are not significant enough to attain the bulk water values.

Fig. 5 shows a plot of $\bar{\nu}_a-\bar{\nu}_f$ for the dye PSF in homogeneous solvents of different dielectric constant. The straight line plot shows that the spectral properties of the dye are guided by the macro dielectric constant (ϵ) of its environment. The emission maximum of PSF which shifts from 575 nm in aqueous solution to 556 nm in reverse micelles at $w_0=0$ shows that in the latter case the dye environment has become significantly less polar in character. The dye retains this environment closely as is seen from the fact that only a slight red shift of 3 nm occurs on going from $w_0=0$ to $w_0=30$

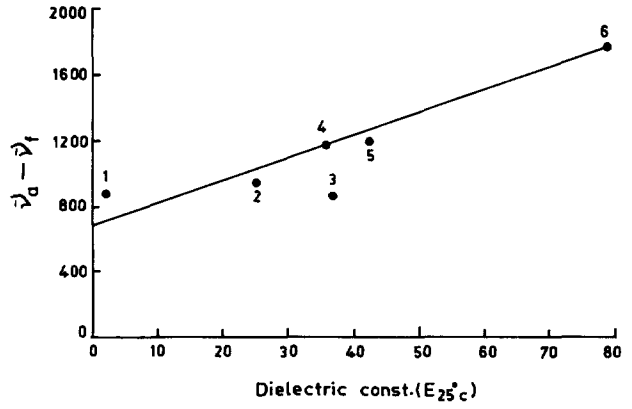

Fig. 5. A plot of the difference in the absorption and fluorescence maxima ($\bar{\nu}_a - \bar{\nu}_f$) in pure solvents of varying dielectric constants.

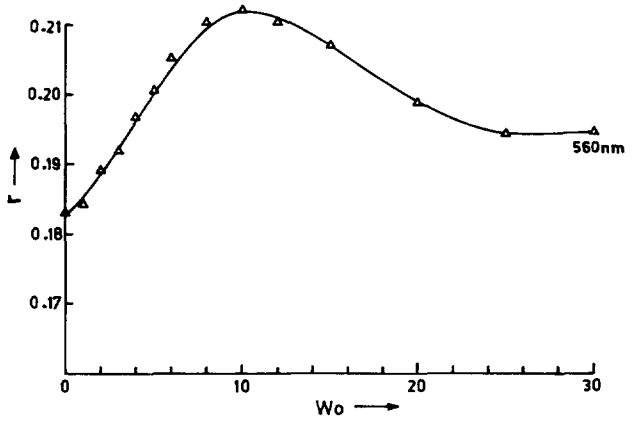

Fig. 6. A plot of fluorescence polarisation anisotropy (r) of PSF in reverse micelles of 50 mM AOT/n-heptane at varying w_0 values.

indicating that the change in the average dielectric constant of the dye environment is not very significant. Up to $w_0 = 1$–8 water clusters of reverse micelles are mainly involved in hydration of the sodium counterions [7]. The hydration of the counterions is completed by $w_0 = 8$, after which free, unbound water is available. From the variation in emission intensity of PSF with w_0 (Fig. 4) it appears that in this range of w_0 (= 8–30) the excess water that is available might be instrumental in lowering of dye emission intensity.

In order to estimate the rigidity of the dye environment, polarisation anisotropy studies were carried out. Fig. 6 shows the plot of anisotropy (r) of PSF at varying w_0 values. Plots of similar nature have previously been reported for other fluorophores, e.g. perylene, cresyl violet etc. [10,13]. From the figure it can be seen that the dye environment attains maximum rigidity at $w_0 = 10$ after which r falls off to attain a steady value around $w_0 = 25$–30. It is significant that even at high w_0 values the anisotropy of PSF in AOT reverse micelles is considerably higher than the value in aqueous solution. Since the dye is cationic in nature it is conceivable that Coulombic interaction will restrict the location of the dye molecule to the micelle–water interface.

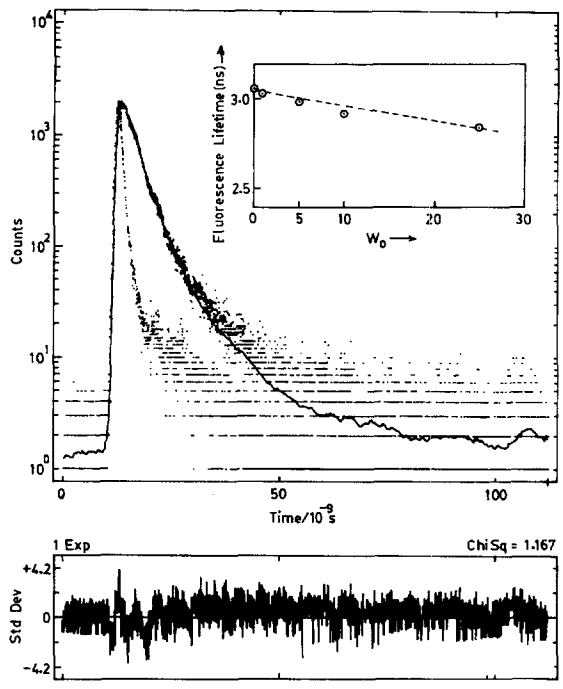

Fig. 7. A typical fluorescence decay profile of PSF in AOT/n-heptane reverse micelles at $w_0 = 1$. The solid curve represents the computer best fit of the experimental points. The unconnected points represent the lamp profile. Inset: variation of the single exponential decay times with w_0 value.

Table 1
Steady state absorption and fluorescence emission characteristics and single exponential decay times of PSF in homogeneous solvents and in AOT/n-heptane reverse micelles at various w_0 values

Medium	Absorption maximum (nm)	Emission maximum (nm)	Lifetime (ns)
Water	520	575	0.93
Ethanol	531	565	3.0
Dioxane	520, 545	577	–
AOT/n-heptane			
$w_0 =$ 0	508, 536	556	3.25
1	534	556	3.18
5	534	557	3.09
10	534	557	2.99
25	531	558	2.80

Fluorescence lifetime measurements show a single exponential decay at all w_0 values. A representative decay curve for $w_0 = 1$ is shown in Fig. 7. There is a slight but monotonic decrease of lifetime of PSF with increasing size of the water pool as can be seen from Table 1, where a complete summary of all the data has been presented. The nature of decay and the changes thus observed with increasing w_0 are commensurate with the location of the probe at a single site towards the micelle water interface of the reverse micelle where water penetration cannot significantly influence probe microenvironment and its emission decay characteristics. From Table 1 it is clear that the fluorescence characteristics of PSF in

reverse micelles are very similar to that of PSF in ethanol and significantly different from the bulk water values. It appears that the PSF embedded in the reverse micelles of AOT/*n*-heptane do not reach the bulk water characteristics even at very high w_0 values.

4. Conclusion

The cationic dye PSF when solubilized in reverse micelles of AOT, is likely to interact preferably with the head groups due to Coulombic forces of attraction between the opposite charges which is evident from the absorption characteristics of PSF in AOT/*n*-heptane reverse micelles. From the emission characteristics it can be inferred that in the reverse micelles the dye molecules are embedded at a comparatively less polar site while maintaining their proximity to the negatively charged surfactant head groups. A single distribution site for the dye molecules is inferred from the single exponential decay characteristics of PSF at all w_0 values in the reverse micelles. Anisotropy data show that water structure around the fluorophore at the water–surfactant interface attains a state of maximum rigidity at $w_0 = 10$, and then falls off to attain a steady value between $w_0 = 25$–30. This steady value is much higher than the bulk water anisotropy of PSF (0.032) which shows that the water–surfactant structure at the micelle–water interface where the fluorophore is located maintains a fair degree of rigidity even at high values of w_0.

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