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Pulse radiolysis study of redox reactions of safranine T in sodium dodecylsulphate (SDS) micellar medium

S N GUHA and J P MITTAL*
Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400085, India

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Abstract. Reaction of hydrated electrons with safranine T (SF^+), a phenazine dye useful as sensitizer in photogalvanic cell and the transient semireduced species formed by this reaction have been studied in SDS micellar medium using the technique of pulse radiolysis. The e_{aq}^- reaction with SF^+ in the micellar environment was only marginally slower ($5{\cdot}1 \times 10^9\,dm^3\,mol^{-1}\,s^{-1}$) as compared to that in homogeneous aqueous medium ($2{\cdot}2 \times 10^{10}\,dm^3\,mol^{-1}\,s^{-1}$) explicable on the basis of our finding that although a large fraction of the dye gets localized near the micelle Stern layer where the molecule experiences a dielectric constant of ≈ 40, a small but significant concentration of the dye exists in the aqueous bulk as charge pair complex with the anionic surfactant monomer (association constant for the formation of the complex being $2{\cdot}8 \times 10^4\,dm^3\,mol^{-1}$). The transient semireduced absorption band observed in the micellar medium showed a red shift of ≈ 50 nm and also the decay of the transient, which was very fast with $2k = 1 \times 10^9\,dm^3\,mol^{-1}\,s^{-1}$ in aqueous medium, was stable in the SDS micellar medium over a few tens of milliseconds suggesting that the radical is incorporated deeper than the parent molecule in the SDS micelle. The effect of this stability on the photogalvanic conversion needs to be examined.

Keywords. Pulse radiolysis; safranine T; sodium dodecylsulphate; micellar medium.

1. Introduction

Redox reactions of organic dyes have been the subject of many investigations in the past mainly because dyes can serve as model compounds for biological redox systems (Hevesi *et al* 1970; Singhal *et al* 1970). Among the various classes of dyes thiazine (Rabinowitch 1940; Kamat *et al* 1977) and phenazines (Kaneko and Yamada 1977; Jana *et al* 1988) have received particular attention because they are also found to be useful as sensitizers in photogalvanic cells for the conversion of light to electrical energy. As practical systems they suffer from the drawback of very low power conversion efficiency. Thus, in the case of the well known thionine–ferrous photogalvanic system the conversion efficiency has been achieved only to $< \approx 0{\cdot}01\%$ (Kamat *et al* 1977, 1978). One of the factors responsible for the low efficiency has been the slower discharge of the photo-produced reduced thionine species at the photoanode as compared to its homogeneous recombination in the bulk of the solution (Kamat *et al* 1977, 1978). Although the photoproduced species in this system is predominantly leucothionine, it is produced by the fast disproportionation of a precursor, viz.

*For correspondence

semithionine radical (Ferriera and Harriman 1977; Guha *et al* 1979). More recently, safranine T a dye belonging to the phenazine class has attracted considerable attention from the point of view of light energy conversion to electrical energy (Jana *et al* 1988). Studies carried out in the past have indicated that photogalvanic cell employing SF^+-EDTA (ethylene diamine tetraacetic acid) photoredox system can exhibit a photopotential which is higher than that observed in the thionine-ferrous or proflavin-EDTA systems (Kaneko and Yamada 1977). Although safranine T has shown considerable promise as a sensitizer in the photogalvanic cell, its application for the utilization of solar energy on a large scale is not yet realized. The photoproduced species in this system is also the predominantly leuco form of the safranine dye, which is produced by the fast disproportionation of the semireduced species (Baumgartner *et al* 1981; Neumann *et al* 1986). It is obvious that any system parameters that can affect this disproportionation step can have considerable influence on the photogalvanic effect, particularly the power conversion efficiency. Earlier studies (see for example Fendler and Fendler 1975) have brought to light the profound influence micellar media can have on reaction rates. The importance of micelles in controlling the course of chemical reactions particularly those of relevance to the problem of light energy conversion has been well recognized in the past (Kiwi *et al* 1982). The present study was, therefore, undertaken to find out if the above fast disproportionation of the transient semireduced safranine species can be slowed down in such media. Hydrated electrons generated by nanosecond pulse radiolysis as a specific one-electron reductant have been used to generate semireduced species. Since the concomitant oxidation product of e_{aq}^- is water, it is not expected to complicate the decay kinetics. Before studying the transient behaviour in a micellar medium, it was considered worthwhile to study the location and interactions of the parent dye molecule in such systems. Safranine T, which is present as the monocation (SF^+) in aqueous solution of neutral pH, is expected to be micellised by anionic micelles such as those of SDS. Therefore this micellar system was selected for the present study.

2. Experimental

Safranine T chloride (Fluka) (for its structure see, Neumann and Pastre 1991) was purified by the method described earlier (Guha *et al* 1992). Sodium dodecylsulphate (Fluka, puris) was purified by repeated washing with diethyl ether followed by drying over fused calcium chloride in a vacuum desiccator. All other chemicals and reagents were the purest available commercially and were used as such. Solutions were prepared in water free of inorganic and organic impurities obtained by passing demineralized water through a Barnsted Nanopure water system. Nitrogen gas used for purging the solutions was Iolar/Instrument grade from Indian oxygen. A UV-vis double beam recording spectrophotometer (Hitachi model 330) was used employing proper reference to record absorption spectra. Fluorescence measurements were carried out using a Hitachi fluorescence spectrophotometer (Model F-4010). Fluorescence life time measurements were done using a fluorescence time domain spectrometer with a nanosecond hydrogen discharge lamp (EI-199 system from Edinburgh Instruments, UK). A 7 MeV linear electron accelerator (Radiation Dynamics, England) giving single pulses of 25 ns duration was used as the pulsed radiation source. The pulse radiolysis apparatus has been fully described elsewhere (Guha *et al* 1987). The absorbed dose

per pulse as evaluated by the standard thiocyanate dosimeter (Fielden 1982) varied in the range 8–15 Gy depending on the nature of the experiment. Thus low doses of ≈ 8 Gy/pulse were used for evaluating reaction rate constants, whereas for decay kinetics and spectral studies, higher doses upto ≈ 15 Gy/pulse were employed.

3. Results

3.1 *Absorption and fluorescence behaviour of the dye*

The effect of surfactant, sodium dodecylsulphate (SDS) on the absorbance of the dye can be seen in figure 1. Thus as the SDS concentration is increased the absorbance of the dye at 528 nm decreases until around 1×10^{-3} mol dm^{-3} and then on further increase of SDS concentration the absorption steeply rises between 1×10^{-3} and 4×10^{-3} mol dm^{-3} and levels off thereafter (figure 1a). The steep rise of the dye

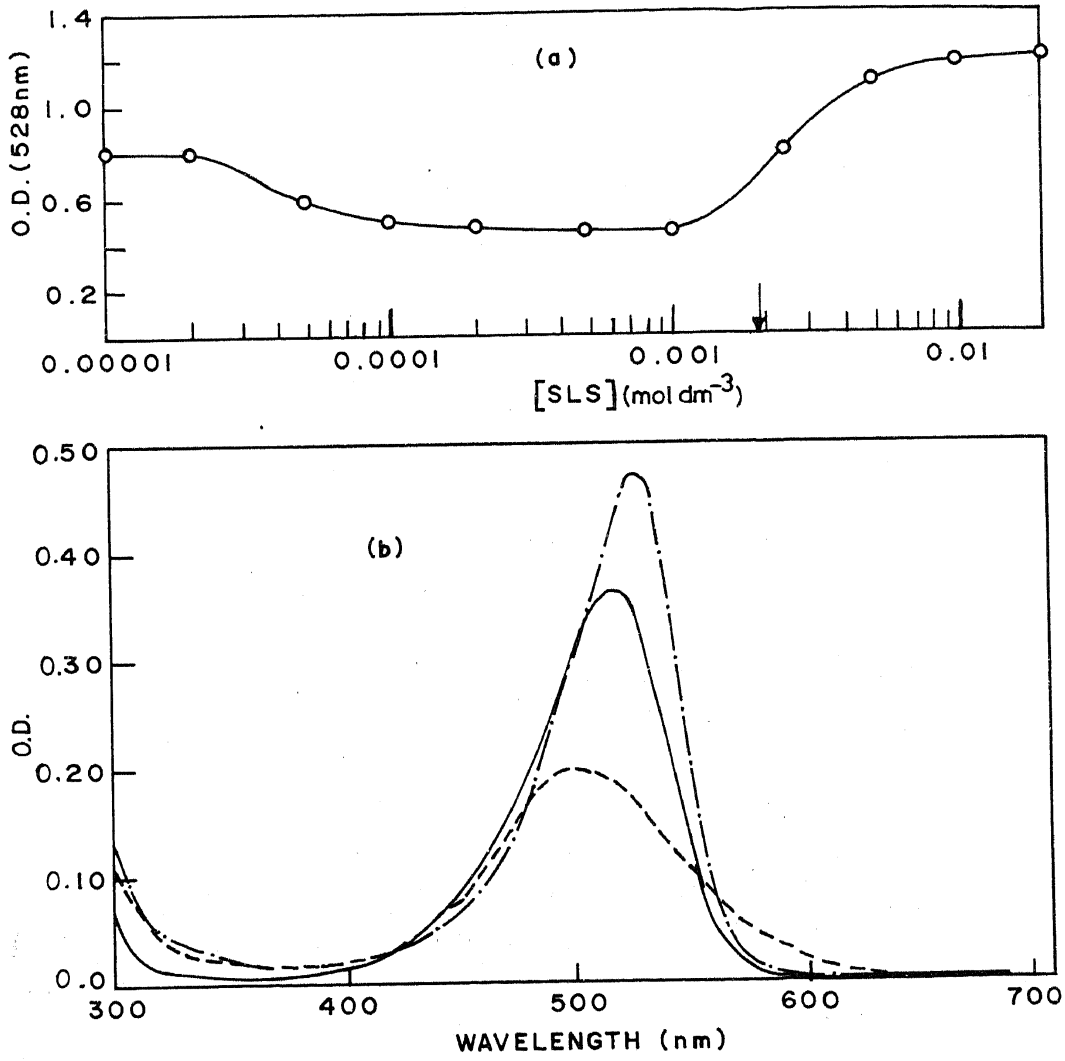

Figure 1. (**a**) Effect of SDS on the absorbance of SF^+ (2×10^{-5} mol dm^{-3}) solutions (**b**) Absorption spectra of SF^+ (1×10^{-5} mol dm^{-3}): (——) in neat aqueous medium; (—·—) in micellar (SDS = 0·01 mol dm^{-3}); and (– – –) in premicellar (SDS = 5×10^{-4} mol dm^{-3}) region.

absorbance in the region 1×10^{-3}–4×10^{-3} mol dm^{-3} SDS is related to the formation of surfactant micelles in which the dye is incorporated. Such sharp changes have been made use of for the determination of CMC (critical micelle concentration) of surfactant in the past (Mukerjee and Mysels 1955: Corrin and Harkins 1974). From the inflexion point of this curve the CMC of SDS is evaluated to be 2×10^{-3} mol dm^{-3}. On the other hand, decrease in absorbance of the dye at 528 nm at the low SDS concentration region (premicellar region) can be attributed to the formation of a dye–surfactant complex. The results obtained in presence of SDS below (premicellar region) and above (micellar region) the CMC are reported below.

3.1a *Premicellar region*: In neat aqueous solution the dye (SF^+) exhibits a pronounced band with $\lambda_{max} = 520$ nm. At SDS concentrations below the CMC, the absorbance of the 520 nm dye band decreases and a new band with $\lambda_{max} = 500$ nm appears which becomes prominent at 5×10^{-4} mol dm^{-3} SDS (figure 1b). Although the new band appears close to the dye band the nature of the two spectra are quite different. Thus the 500 nm band observed at low SDS concentration is broader and absorption extends even beyond 590 nm where the dye in homogeneous aqueous systems ceases to absorb. In figure 2 are shown the fluorescence spectra of the dye in the presence and absence of SDS. The fluorescence intensity of the dye in neat aqueous system is considerably enhanced in SDS micellar medium but it is almost completely diminished in the premicellar region (SDS = 5×10^{-4} mol dm^{-3}). Similar changes in absorption spectra and fluorescence of dyes in presence of oppositely charged surfactant molecules below the CMC have been reported in the past (Mukherjee and Mysels 1955; Corrin and

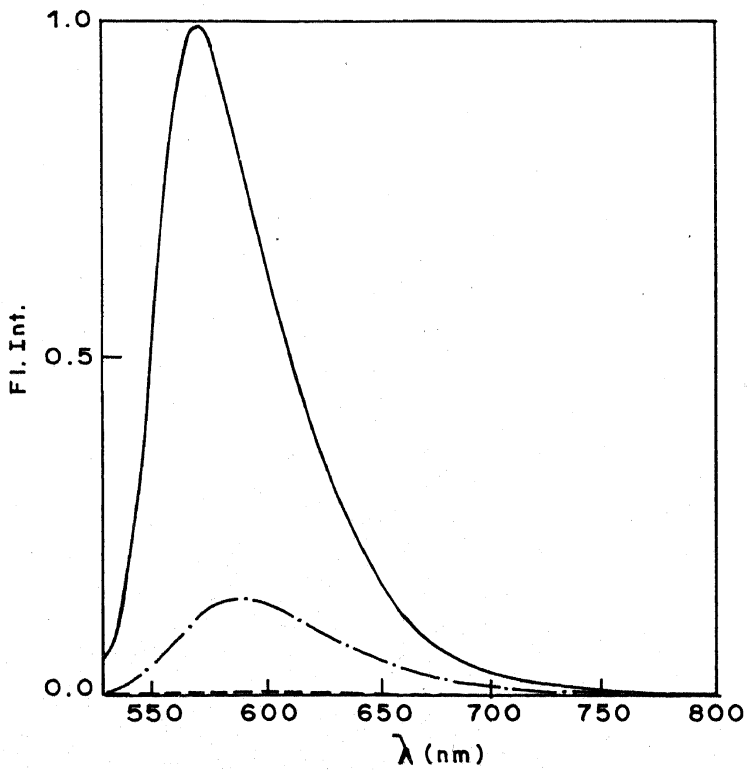

Figure 2. Fluorescence spectra of safranine T (1×10^{-5} mol dm^{-3}) in (—·—) neat aqueous medium; in (——) micellar (SDS = 0·01 mol dm^{-3}) and in (——) premicellar region (SDS = 5×10^{-4} mol dm^{-3}) region ($\lambda_{ex} = 520$ nm).

Harkin 1974). In the case of the cationic dye (Rh 6G, malachite green, roseaniline hydrochloride) and the anionic surfactant dodecane sulphonic acid, shift in the absorption maxima at low surfactant concentration has been assumed to be due to the formation of a dye–surfactant complex (Malik and Chand 1972). The electrostatic interaction between the disodium bromophenolate blue anion and the long chain quaternary cations (CTAB, CTAC etc.) in dilute solutions results in a colour change, which has been attributed to the "ion-pair" association between the surfactant cation and the dye anion (Colichman 1950). Changes in the absorption spectrum and decrease in fluorescence intensity of cationic dye thionine at SDS concentrations below the CMC have been attributed to the formation of a dye–surfactant charge-pair complex (Guha *et al* 1982). Corrin and Harkins (1974), on the other hand, have suggested the possibility of the formation of dye aggregates to account for the observed colour changes in presence of surfactant molecules. The postulation of "ion-pair" or complex formation is characteristic of oppositely charged molecules and appears to be more reasonable than the dye aggregation hypothesis.

In the present system, in the premicellar region the spectral behaviour and also the change in fluorescence intensity can be interpreted as being due to an equilibrium involving association of the dye cation (D^+) and the surfactant anion (S^-).

$$D^+ + S^- \rightleftharpoons DS. \tag{1}$$

From the absorbance data the association constant,

$$K_a = \frac{[DS]}{[D^+][S^-]}, \tag{2}$$

for the safranine–SDS complex (DS) in the premicellar region have been computed following the methodology of Guha *et al* (1982). If the extinction coefficients of the free and the complexed safranine species at a given wavelength are ε_{aq} and ε_c, respectively, the measured absorbance (optical density), OD_{obs} is given by,

$$OD_{obs} = [D]_T l f_{aq} \varepsilon_{aq} + [D]_T f_c \varepsilon_c l, \tag{3}$$

where f_{aq} and f_c are the fraction of the total dye, $[D]_T$, present as free and complexed safranine, respectively, and l is the cell path length. Since $f_{aq} = (1 - f_c)$ and $[S^-] = [S]_T - [DS]$, it can be shown that

$$\frac{1}{\varepsilon_{aq} - (OD_{obs}/[D]_T l)} = \frac{1}{\varepsilon_{aq} - \varepsilon_c} + \frac{1}{(\varepsilon_{aq} - \varepsilon_c) K_a \{[S]_T - f_c[D]_T\}}. \tag{4}$$

Therefore a plot of

$$\frac{1}{\varepsilon_{aq} - (OD_{obs}/[D]_T l)} \text{ vs } \frac{1}{\{[S]_T - f_c[D]_T\}}$$

should be linear and K_a can be calculated from the intercept and slope of such plots. As f_c is not known, first an approximate plot can be constructed using $[S]_T$ instead of $[S]_T - f_c[D]_T$ and the approximate K_a so evaluated can then be used to compute f_c at each surfactant concentration from the following relationship:

$$f_c = \frac{1}{1 + 1/(K_a\{[S]_T - f_c[D]_T\})}. \tag{5}$$

A more accurate plot is now constructed using these f_c values and this successive approximation procedure is continued until the K_a and f_c values become invariant. The K_a so evaluated from the measured absorbances at 520 nm $= 2{\cdot}8 \times 10^4 \text{dm}^3 \text{mol}^{-1}$. From the intercept of the final plot ε_c can be calculated as ε_{aq} is known. The extinction coefficient of the complex computed from the intercept is $1{\cdot}42 \times 10^4 \text{mol dm}^{-3} \text{cm}^{-1}$, which is about a factor 1·4 smaller than that corresponding to the measured absorbance at $5 \times 10^{-4} \text{mol dm}^{-3}$ SDS wherein the absorbance in 520 nm band is at a minimum. The discrepancy is attributed to an appreciable contribution from the micelle bound safranine, which as we shall see later, has an extinction coefficient at 520 nm even higher than the aqueous monomeric safranine species.

As stated before, the fluorescence of the dye in the premicellar region at the SDS concentration of $5 \times 10^{-4} \text{mol dm}^{-3}$ is almost completely diminished (figure 2). At this SDS concentration it is in fact observed that the 500 nm absorption band due to the dye-surfactant complex is at the maximum. Hence it is to be concluded that the SF^+–SDS complex is non-fluorescent. The rapid degradation of excitation energy via internal conversion facilitated by the long hydrocarbon chain in the SDS moiety of the complex must be the reason for the absence of fluorescence.

3.1b *Micellar region*: The CMC of SDS obtained from the inflexion point of the curve in figure 1a is considerably lower than the ones obtained by conductivity, light scattering and viscosity measurements. Such an observation has in the past been made (Mukerjee and Mysels 1955) and could be explained on the basis of dye-induced micellization. At SDS concentration of $5 \times 10^{-4} \text{mol dm}^{-3}$, as mentioned before, the dye is present almost exclusively as the complex. Under this condition the absorbance of the dye at its λ_{max}, 520 nm, is at the minimum. Fluorescences which are absent in the dye-surfactant complex are found to be restored at SDS concentrations well above the CMC (figure 2). This would indicate that the complex is unstable in the micellar environment. At high surfactant concentration ($0{\cdot}05 \text{mol dm}^{-3}$) the absorbance at the 520 nm band as well as fluorescence intensity are appreciably higher than in the absence of the surfactant. The enhancement in fluorescence in other dye-surfactant systems has been interpreted as due to the disaggregation of dye molecules by interaction with surfactant micelles. In the present system, however, comparison of the absorption spectra of the dye (at the concentrations employed) in the absence and presence of SDS revealed no dimer band. The λ_{max} of safranine absorption band also exhibited a small but definite red shift (figure 1b). It is therefore reasonable to assume that the dye in the micellar environment has a different extinction coefficient and radiative lifetime as compared to the pure aqueous environment. It was in fact observed that the fluorescence lifetime of the singlet excited state of the dye ($1 \times 10^{-5} \text{mol dm}^{-3}$) increased from 1·15 ns in neat aqueous medium to 2·88 ns in SDS ($0{\cdot}18 \text{mol dm}^{-3}$) micellar system.

3.1c *Medium polarity effect*: The observed red shift and increase in extinction coefficient both reflect a decrease in the polarity or the dielectric constant of the medium around the probe molecule. Thus, for example, in water–alcohol mixture, the absorbance increases linearly with decreasing dielectric constant (figure 3a). From this plot the dielectric constant experienced by safranine in the SDS micellar system can be read as ≈ 40 against the observed Δ OD at [SDS] $\gg$ CMC. Similarly, as shown in figure 3b, the relative fluorescence intensities also follow linear variations with the

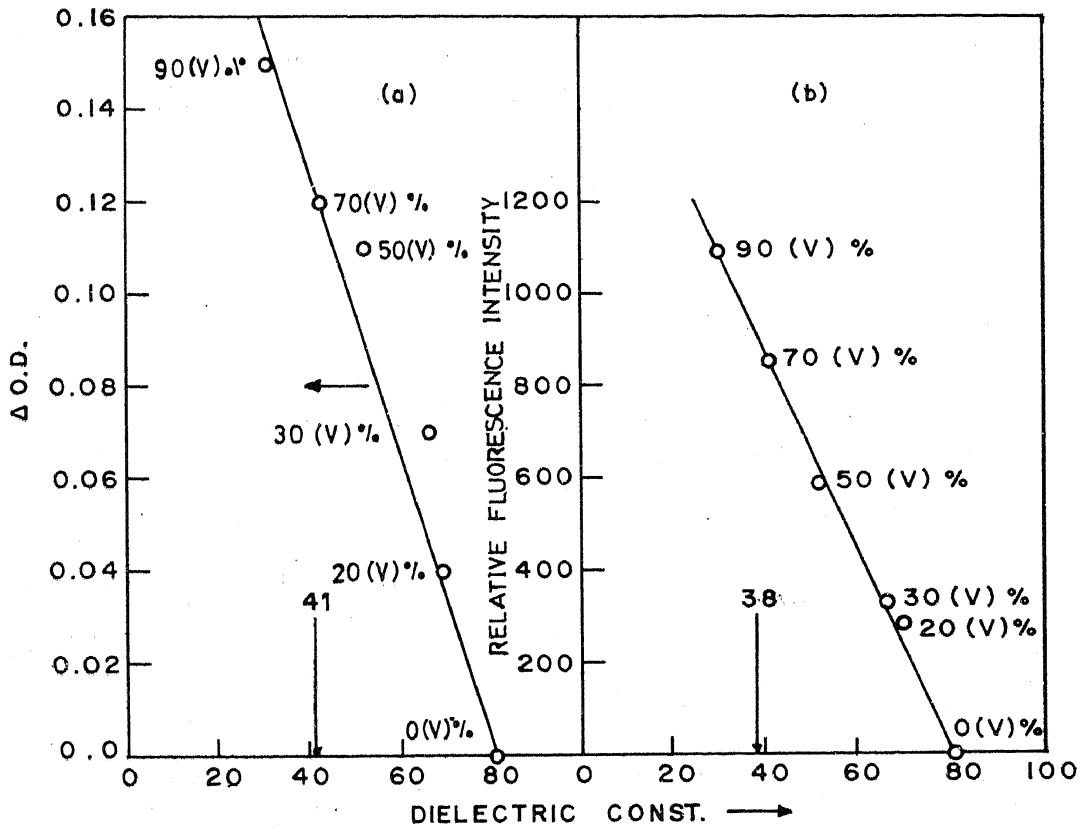

Figure 3. Dependence of safranine absorbance (**a**) and fluorescence (**b**) on the dielectric constant of the medium [composition of water-ethanol mixture employed is indicated inside the figure in % ethanol by volume].

dielectric constant. This plot also gives a value close to the above value. The red shift of the safranine absorption maximum also shows a correlation with the dielectric constant but, as the shifts are rather small, no attempt has been made to evaluate the dielectric constant parameter from this correlation. Similarly, as stated before, the fluorescence lifetime of the singlet excited state of the dye was found to increase from 1·15 ns in homogeneous aqueous medium to 2·88 ns in the SDS micellar system. The lifetime measured in a simulating polar matrix consisting of 75% ethanol (dielectric constant ≈ 38) was found to be 2·55 ns, close to that observed in micellar medium. It should be noted that in the case of thiazine dye, thionine (Guha *et al* 1982), the dielectric constant (≈ 56) experienced by it was considerably higher. A lower value (≈ 40) in the case of safranine molecule is explicable on the basis of hydrophobic groups present in the dye molecule. Thus the two methyl groups and a phenyl ring present in SF^+ make safranine more hydrophobic and hence the molecule experiences a lower dielectric constant.

3.2 *One-electron reduction of safranine T by e_{aq}^- in homogeneous aqueous medium*

One-electron reduction of safranine dye has been studied in the past (Baumgartner *et al* 1981) using the flash photolysis technique. The semireduced safranine species generated flash photolytically was characterized by its absorption spectrum, acid–base equilibrium constant and decay kinetics. The authors have identified two forms of

the semireduced species i.e. the acid radical and the basic radical and have reported their absorption spectra at pH 4·2 and pH 10·65 respectively. Although the spectrum of the acidic form was reported from about 350 nm to 800 nm with two well-defined bands at ≈370 and 650 nm, the spectrum of the basic radical was recorded only up to 500 nm showing a band at around 400 nm. The measurement was not extended beyond 500 nm to establish the nature and the existence of the second absorption band of the basic radical. Moreover, semireduced species cannot exclusively be produced by flash photolysis of the parent dye molecule without the presence of the dye triplet and also the radicals derived from externally added reducing agents such as EDTA, ascorbic acid etc. These radicals and the triplets present in the system could possibly interfere with the absorbance of the semireduced species. In the case where ground state molecule itself has been found to quench its triplet reductively and no external reductant is employed to generate semireduced species, a concomitant semioxidized radical is invariably formed interfering with the absorbance of semireduced species and also with the decay kinetics. Baumgartner *et al* (1981) have infact experienced these difficulties and discussed the uncertainties of decay kinetics arising due to the presence of externally added reducing agents. In a separate study on the photoreduction of safranine by substituted anilinomethanesulphonates, Neumann *et al* (1986) have postulated the formation of a ground state ion-pair complex with an unfavourable configuration for electron transfer. On the other hand, generation of semireduced species by the reaction of hydrated electron, produced on pulse radiolysis of an aqueous solution of a suitable matrix is a clean method, where, as stated before, the concomitant oxidation product of e_{aq}^- is water, which is not expected to complicate either the decay kinetics or the transient absorbance of the semireduced radical. In view of the above a detailed study of the redox reactions of safranine T was undertaken in homogeneous aqueous medium employing pulse radiolysis technique. The first part of the study on one-electron oxidation of this dye has been completed and published recently (Guha *et al* 1992) and the study on one-electron reduction of this dye is being concluded and will be communicated separately. In the present work we shall compare only the relevant results obtained in neat aqueous medium with that observed in SDS micellar medium.

3.3 *Reaction of hydrated electron in SDS micellar medium*

H, OH and e_{aq}^- are the important reactive primary species formed during the pulse radiolysis of aqueous solution. In SDS matrix, H and OH react efficiently with SDS by H-abstraction giving rise to surfactant radicals, which, as has been experimentally confirmed, are unreactive toward SF^+. The reaction of e_{aq}^- with SDS on the other hand is considerably slower (see for example Meisel *et al* 1978) and hence its reaction with SF^+ could be studied in a suitable matrix. For the study of its reaction in neat aqueous medium, OH radicals were scavenged by *t*-butanol and H atoms were converted to e_{aq}^- at neutral pH. For a strict comparison of the results in homogeneous aqueous and in micellar systems, *t*-butanol was invariably added to both the media. The hydrated electron signal monitored at 590 nm in an electron beam pulsed deoxygenated 0·5 mol dm^{-3} *t*-butanol matrix (pH 7) containing 0·5 mol dm^{-3} SDS (well above the CMC) was found to decay faster in presence of safranine T than in its absence. The decay of the hydrated electron absorbance followed pseudo first-order kinetics with respect to safranine concentration from which the bimolecular rate

constant for the reaction of the hydrated electron with the dye was calculated to be $5{\cdot}1 \pm 0{\cdot}5 \times 10^9\,dm^3\,mol^{-1}\,s^{-1}$. Although this is lower than the value ($2{\cdot}2 \pm 0{\cdot}5 \times 10^{10}\,dm^3\,mol^{-1}\,s^{-1}$) obtained for neat aqueous medium, the difference is not so marked as to reflect on the effect of SDS micelles on the cationic dye. There are reports of study available in the literature (see, for example, Thomas 1987) regarding the influence of micelles on the reactions of hydrated electrons. One of the factors influencing reaction rates is the strong electrostatic repulsion or attraction of e_{aq}^- by the anionic or cationic micelles. Thus the rate constant for reaction of e_{aq}^- with pyrene located in the anionic SDS micelle is reduced by several orders of magnitude (from 10^{10} to less than $10^7\,dm^3\,mol^{-1}\,s^{-1}$). In the present case, however, the reduction in rate constant for the reaction of e_{aq}^- with SF^+ in SDS micellar system is not as marked as in the case of pyrene. However, it has also been observed in the past that in SDS micellar medium e_{aq}^- reacts with certain solutes such as biphenyl and naphthalene (both being more soluble in water than pyrene) with rate constant marginally lower than that in homogeneous aqueous medium. It is suggested that e_{aq}^- reacts with these solutes in the aqueous bulk (for discussion, see Thomas 1987). Safranine T is a water soluble dye and hence a small but finite aqueous concentration of it is likely to be present in the system, where it exists in equilibrium with the micellised dye at SDS concentration above CMC. In the study of e_{aq}^- reaction with $Ru(bpy)_3^{2+}$ in SDS micelles, Meisel *et al* (1978) have concluded that the ratio of free to micellized solute is $< 3\%$ (even at the highest solute and lowest SDS concentrations employed) on the basis of the reduction of rate constant (≈ 30 times) in SDS micellar medium. Since, in the present case the specific rate of reaction is about 4 times slower in micellar medium a small but finite concentration of the dye is expected to be present in the aqueous bulk for reaction with e_{aq}^-. It is for this reason that the reaction in micellar medium is also close to diffusion controlled although the major fraction of the dye is incorporated in the Stern layer of SDS micelles. The point that requires to be resolved is whether the dye exists as free SF^+ ion or remains as the complexed species in the aqueous bulk. Since the micelles are in equilibrium with the monomers, a finite concentration of the SDS monomers also present in the bulk aqueous phase would favour formation of the dye-surfactant complex (DS) as in equilibrium 1. Since the association constant for the formation of the complex is $2{\cdot}8 \times 10^4\,dm^3\,mol^{-1}$, presence of free dye molecule in bulk aqueous phase as compared to the complexed species can be considered negligible under the conditions of the present work. It is reasonable to assume that e_{aq}^- reacts predominantly with dye-surfactant complex (DS) in the aqueous bulk in micellar system. However, reaction of e_{aq}^- with the micellized dye can not be completely ignored to account partly for the slowness of this reaction.

The spectrum of the transient in SDS micellar medium formed by reaction of hydrated electron with safranine T in the *e*-beam pulsed $5 \times 10^{-5}\,mol\,dm^{-3}$ SF^+ solution containing $1{\cdot}0\,mol\,dm^{-3}$ *t*-butanol and $0{\cdot}05\,mol\,dm^{-3}$ SDS at neutral pH is shown in figure 4. The transient spectrum recorded in neat aqueous system exhibits two well-defined absorption bands with λ_{max} at 400 and 650 nm attributable to the semi-reduced safranine species. It is observed that the natures of the transient spectra in the two media are the same except that the transient band observed at 650 nm in neat aqueous system is considerably red-shifted in SDS micellar medium. Thus the 650 nm transient band is shifted to 700 nm, a red shift of ≈ 50 nm in the SDS micellar medium. The spectral shift data indicate that the semireduced safranine species get incorporated in the SDS micelles. The incorporation of the semireduced safranine species takes place

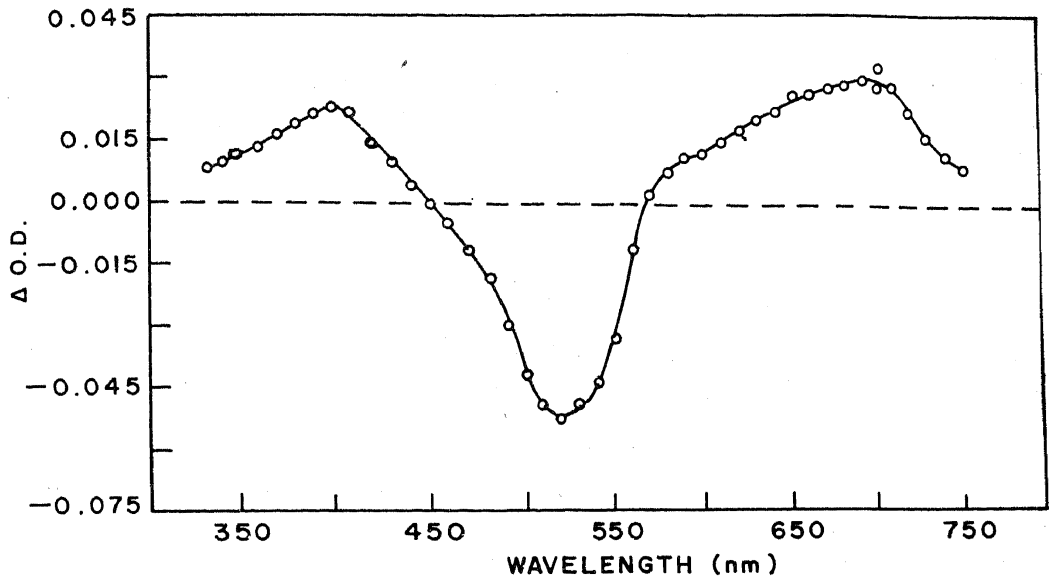

Figure 4. Transient spectrum of semireduced safranine species in SDS micellar medium at pH ≈ 7.

subsequent to its formation by reaction of e_{aq}^- with the dye–SDS complex in the bulk aqueous phase. The localization of semireduced species into the SDS micelles is further evidenced by the nature of its decay in the micellar environment. Thus, the transient semireduced safranine species, which decays very fast following a second-order kinetics attributed to its dismutation, with a rate constant of 1×10^9 dm^3 mol^{-1} s^{-1} in homogeneous aqueous solution, was found to be stable over a period of a few tens of milliseconds in micellar medium at SDS concentration ($\approx 0{\cdot}1$ mol dm^{-3}) well above the CMC. Thus it is seen that second-order dismutation is almost blocked in the micellar medium. At the relative concentrations of SDS and pulse-radiolytically produced semireduced species employed, multiple occupancy of the micelles (i.e., one micelle containing more than one semireduced species) is negligible (Guha *et al* 1985). Therefore second-order reaction between two semireduced species located on two different micelles would depend on the encounter of the micellised radical species. For this to happen two micelles should approach each other. This is expected to be hindered due both to the bulkiness of the micelles, and hence their slower diffusion, and like charge repulsion between the two anionic micelles. These results indicate that the semireduced species are more strongly bound to the SDS micelles as compared to the parent dye molecules. However, a knowledge of the binding constants for the incorporation of the different species into the SDS micelles is necessary in order to draw a more definite conclusion.

The present results demonstrate that decay kinetics can be profoundly altered in suitable micellar media. The stabilization of semireduced radicals in the SDS micellar medium as observed in the present investigation could be of advantage in the power conversion efficiency of a photogalvanic cell. What effect the micellar medium would have on the actual cell performance is yet to be investigated.

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