Kinetic and Redox Characteristics of Semireduced Species Derived from Phenosafranine in Homogeneous Aqueous and Sodium Dodecyl Sulfate Micellar Media

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ABSTRACT: One-electron reduction of phenosafranine (PS^+, 3,7-diamino-5-phenylphenazinium chloride), a phenazinium dye, has been studied in homogeneous aqueous and sodium dodecyl sulfate (SDS) micellar media, using the pulse radiolysis technique. The various reducing radicals employed for the study in homogeneous aqueous medium were e_{aq}^-, $H^\cdot$, $CO_2^{\cdot-}$, and isopropyl ketyl radicals $(CH_3)_2{}^\cdot COH$. Semireduced species generated by these reactions have been characterized by their absorption spectra, decay kinetics, and pK_a. The one-electron reduction potential of PS^+ was determined at pH 7 in homogeneous aqueous solution employing nitrobenzene ($NB/NB^{\cdot-}$) as the standard couple. One-electron reduction in SDS micellar medium and a detailed spectrophotometric investigation of the parent dye in this surfactant system was carried out in order to understand the dye–surfactant interactions in the micellar and premicellar media. © 2001 John Wiley & Sons, Inc. Int J Chem Kinet 34: 56–66, 2002

INTRODUCTION

Phenosafranine, a cationic dye (PS^+, 3,7-diamino-5-phenylphenazinium chloride; Scheme 1) belonging to phenazinium class, finds application in diverse areas [1–3] wherein its redox chemistry plays an important role. Redox reactions of this class of compounds are

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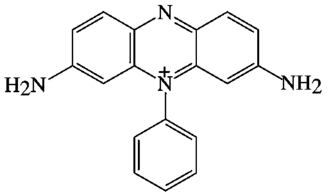


(PS+)

Scheme 1

important in view of their usefulness as sensitizers in photogalvanic cells for the conversion of light to electrical energy [1]. Thus, for example, the phenazine dye, Safranine T (SF^+) has been considered to be a well-known sensitizer and in order to explain the photopotential of a photogalvanic cell employing the SF^+–EDTA system [1], the semireduced safranine radical was postulated as the electroactive species. Formation of semireduced species of phenazinium dyes has been demonstrated in flash photolysis experiments [4–7]. Also, in the case of thiazine dyes the formation of the semireduced species was observed [8–12] in both flash photolysis and pulse radiolysis experiments. Generally in the photoreduction of dyes an intermediate semireduced radical is formed through the excited states of the dye in the presence of a suitable reducing agent [6]. Chlorophyll-sensitized reduction of safranine has been investigated in the past [3], in connection with the elucidation of the mechanism of photosynthesis in the plant. Formation of the excited states species of a simple member of this class vizPS^+ has been demonstrated in laser flash photolysis experiments [13,14]. Similar studies were reported with other members (e.g. Safranine T and Safranine O) using flash photolysis technique [4–7]. The semireduced safranine species cannot exclusively be produced by flash photolysis of the parent dye molecule without the presence of dye triplet and also the radicals derived from externally added reducing agents such as EDTA, ascorbic acid, etc [6]. These radicals and the triplet present in the system might 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 required to generate semireduced species, a concomitant semioxidised radical is invariably formed interfering with the absorbance of semireduced species and also with its decay kinetics. Baumgartner et al. [6] have in fact experienced these difficulties and discussed the uncertainties of decay kinetics arising because of the presence of externally added reducing agent. 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 solution [15] is a clean method where the concomitant oxidation product is water, which is not expected to complicate either the decay kinetics or the transient absorption spectrum of the semireduced species. In their flash photolysis experiments, Gopidas and Kamat [14] have generated semireduced PS^+ by quenching of the dye triplet by amines in acetonitrile solution in which the transient is expected to show a different absorption property as compared to neat aqueous medium. In this paper ,we report pulse radiolytic generation and characterization of semireduced phenosafranine radical in homogeneous aqueous medium. As practical systems thiazines and phenazines suffer from very poor power conversion efficiency. One of the factors has been the slower discharge of the photoproduced reduced dye species at the photoanodes as compared to its homogeneous recombination in the bulk of the solution. In these systems, photoinduced reduction leads primarily to unstable semireduced dye species, which disproportionate to give further reduced leuco dye and the parent molecule. Any system parameters that can affect this disproportionation step can have considerable influence on the photogalvanic effect particularly the power conversion efficiency. The importance of micelles in controlling the course of chemical reaction particularly those of relevance to the problem of high energy conversion has been recognized in the past [16]. The present study was extended to find out if the fast disproportionation of semireduced species can be slowed down in suitable micellar medium. Since phenosafranine is a cationic dye we have employed anionic sodium dodecyl sulphate (SDS) surfactants for detailed pulse radiolysis study to see the behaviour of semireduced species in this micellar medium. Before studying the redox reactions of phenosafranine in this micellar medium, we considered it worthwhile to investigate its location and interaction in this surfactant system. Although some work on the dye–surfactant interaction in premicellar [17a] and micellar [18] media employing this dye has been reported in the literature, no work on the redox reactions of PS^+ is reported so far in this micellar system. Further, we have used an improved iteration method to compute the binding constant, and on the basis of medium polarity effect, we have suggested the location of the dye inside the SDS micelle.

EXPERIMENTAL

Phenosafranine (PS^+, 3,7-diamino-5-phenylphenazinium chloride) was a Sigma product and was recrystallized twice from water–ethanol mixture before use. The pH dependence of the absorption spectrum of PS^+ showed that there is no pK_a of the dye in the pH range of 2–11. Sodium dodecyl sulfate (SDS) was extrapure obtained from Sigma and was used as such. All other chemicals were of the highest available purity. Solutions were prepared in nano pure water obtained by passing demineralized water through a Barnsted Nanopure water system. Nitrogen and N_2O gases used for purging the solutions were Iolar grade from BOC India Ltd, Mumbai. UV–Visible double beam recording spectrophotometer (Hitachi model 330) was used to record absorption spectra. The pHs of the solutions were adjusted using H_2SO_4, $Na_2HPO_4 \cdot 2H_2O$, KH_2PO_4, and NaOH.

For studying the reactions of e_{aq}^- and $H^{\cdot}$ atom, *tert*-butyl alcohol (0.2 mol dm^{-3}) was used as the $^{\cdot}OH$ radical scavenger as shown in Eq. (1).

$$(CH_3)_3COH + {}^{\cdot}OH \rightarrow {}^{\cdot}CH_2(CH_3)_2COH + H_2O \quad (1)$$

A solution containing 2-propanol (1 mol dm^{-3}) was used at all the pHs to study the reactions of isopropyl ketyl radicals, which were generated as follows.

$$(CH_3)_2CHOH + {}^{\cdot}OH({}^{\cdot}H)$$

$$\rightarrow CH_3{}^{\cdot}CH_2CHOH + H_2O(H_2) \quad (2a)$$

β-hydroxy radical(~15%)

$$\rightarrow (CH_3)_2{}^{\cdot}COH + H_2O(H_2) \quad (2b)$$

α-hydroxy radical (~85%)

Sodium formate was added to the N_2O saturated solutions to generate $CO_2^{\cdot-}$ radicals according to Eqs. (3) and (4)

$$e_{aq}^- + N_2O \rightarrow {}^{\cdot}OH + OH^- + N_2 \quad (3)$$

$$HCOO^- + {}^{\cdot}OH(H^{\cdot}) \rightarrow CO_2^{\cdot-} + H_2O(H_2) \quad (4)$$

All the above solutions contained 8×10^{-5} mol dm^{-3} PS^+ and were taken for the pulse radiolysis studies.

Details of the pulse radiolysis set up have been described elsewhere [8]. Single pulses of 7 MeV electrons of 50 ns duration with typical doses of ~10 Gy (1 Gy = 1 J kg^{-1}) were used.

The absorbed dose was determined by monitoring the transient absorbance of $(SCN)_2^{\cdot-}$ formed by pulsing aerated solutions of 0.01 mol dm^{-3} KSCN. $G\ \varepsilon$ for $(SCN)_2^{\cdot-} = 21{,}520$ dm^3 mol^{-1} cm^{-1}/100 eV at 500 nm [19], where G is radiation chemical yield and is defined as the number of molecules formed per 100 eV of energy absorbed ($G = 1$ corresponds to 0.1036 μmol J^{-1}) and ε is the molar extinction coefficient at 500 nm. For evaluation of extinction coefficients, formation rate constants and redox potential values absorbed doses employed were ~8 Gy.

The extinction coefficients of the product transient species (ε_T) were evaluated at any wavelength λ employing corrections for the parent dye absorption using Eq. (5).

$$\varepsilon_T = \varepsilon_P + \frac{[A_T].\left[G_{(SCN)_2^{\cdot-}}\right].\left[\varepsilon_{(SCN)_2^{\cdot-}}\right]}{G_T \cdot \left[A_{(SCN)_2^{\cdot-}}\right]} \quad (5)$$

where ε_p is the extinction coefficient in dm^3 mol^{-1} cm^{-1} for the parent dye molecule at wavelength λ, G_T is the G-value of the product transient species. A_T and $A_{(SCN)_2^{\cdot-}}$ are the observed absorbances of the transient dye at λ and of the $(SCN)_2^{\cdot-}$ radical at 500 nm respectively under isodose conditions.

RESULTS AND DISCUSSION

One-Electron Reduction Studies in Homogeneous Aqueous Medium

One-electron reduction of PS^+ was carried out in aqueous solution employing e_{aq}^-, $H^{\cdot}$, $(CH_3)_2{}^{\cdot}COH$, and $CO_2^{\cdot-}$ radicals, in appropriate solutions using the technique of nano-second pulse radiolysis.

Reactions of Hydrated Electron.e_{aq}^-. The absorption of e_{aq}^-, monitored at its $\lambda_{max} = 720$ nm in N_2 saturated *tert*-butyl alcohol solution, was found to decay faster in the presence of PS^+(8×10^{-5} mol dm^{-3}, Fig. 1a

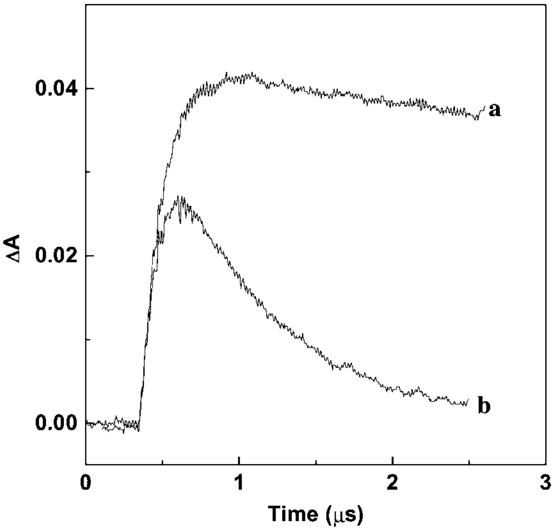
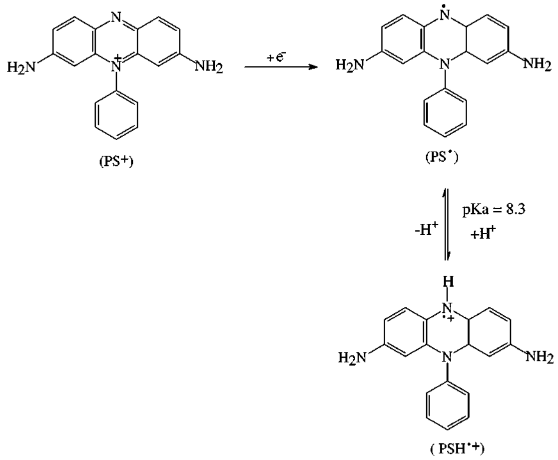


FIGURE 1 Kinetic traces at 720 nm for a N_2-bubbled solution (pH = 10.5) containing *tert*-butyl alcohol (0.05 mol dm^{-3}) and PS^+ (a) 0.0 mol dm^{-3} and (b) 8.0×10^{-5} mol dm^{-3}.

and 1b.). Also considerable bleaching of the dye absorption band at 520 nm was observed (see parent dye absorption spectrum in Fig. 6a). Both these observations clearly indicate the high reactivity of e_{aq}^{-} with the dye. The transient absorption spectrum recorded in the 300–800 nm region is shown in Fig. 2a. Two well defined absorption bands with λ_{max} at 410 and 650 nm were observed. Both the bands were found to grow with time and reached maximum in ~4 μs. The decay of the transient absorbance in the 410 and 650 nm bands followed second order kinetics with $2k$ close to each other and the average value being 9.6×10^{8} dm^{3} mol^{-1} s^{-1}. These two bands can therefore be inferred to be due to a single transient species i.e. semireduced PS^{+} ($PS^{\cdot}$, Scheme 2) formed from the one-electron reduction of the dye. The formation traces were found to fit psuedo-first-order kinetics with PS^{+} concentration. The bimolecular rate constant for the reaction of e_{aq}^{-} with PS^{+} evaluated from these traces at pH 7 was 2.1×10^{10} dm^{3} mol^{-1} s^{-1}. The molar extinction coefficients evaluated using the relationship (Eq. (5)) were $12{,}600 \pm 100$ dm^{3} mol^{-1} cm^{-1} and $11{,}300 \pm 50$ dm^{3} mol^{-1} cm^{-1} at 410 and 650 nm, respectively. The nature of the absorption spectrum recorded at lower pH ~5 was exactly similar to the one observed at neutral pH. However, the transient spectrum observed at alkaline pH ~9.6 was quite different and indicated a distinct pH effect (Fig. 2b). Thus, the 410 nm band exhibited shift in the absorption maxima and the 650 nm band diminished considerably in intensity showing a big change in extinction coefficient. This effect can be attributed to the existence of a pK_a of the semireduced species. Plots of absorbance (ΔA) vs pH recorded at both the wavelengths 410 and 650 nm are shown in inset of Fig. 2. The inflexion points of both the curves revealed pK_a of 8.3 for the semireduced PS^{+} species.



Scheme 2

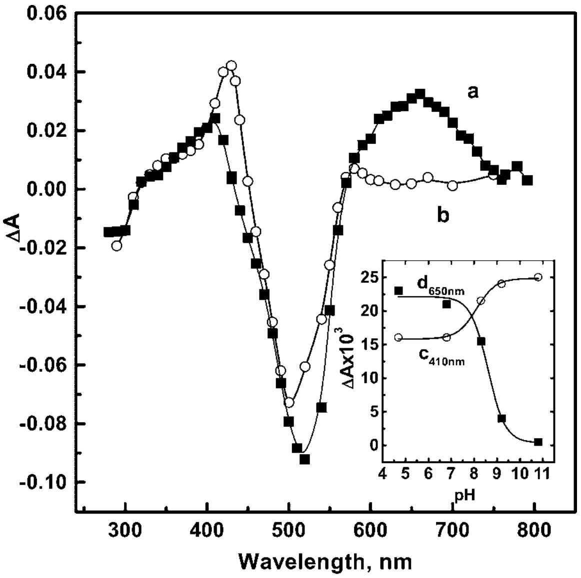


FIGURE 2 Transient optical absorption spectrum (end of 50 ns electron pulse) obtained on reaction of e_{aq}^{-} with PS^{+} at pH (a) 7 and (b) 9.6. Inset shows variation of absorbance vs. pH at wavelength (c) 410 nm and (d) 650 nm. Dose = 11.0 Gy/pulse.

Since the dye exists as PS^{+} over the entire pH, its reduction with e_{aq}^{-} can be represented as

$$e_{aq}^{-} + PS^{+} \rightarrow PS^{\cdot} \qquad (6)$$

and the protolytic equilibrium of the semireduced species can be represented as shown in Eq. (7) and Scheme 2.

$$PSH^{\cdot +} + H_2O \overset{pK_a=8.3}{\rightleftharpoons} PS^{\cdot} + H_3O^{+} \qquad (7)$$

Reactions of Isopropyl Ketyl $(CH_3)_2{}^{\cdot}COH$ Radicals. $(CH_3)_2{}^{\cdot}COH$ is well-known reducing radical and are known to react with many dyes by electron transfer process giving rise to semireduced species. The reaction of this radical was studied in N_2O-saturated aqueous solution containing 8×10^{-5} mol dm^{-3} PS^{+} and 1 mol dm^{-3} 2-propanol at pH 7. Electron pulse irradiation of this solution gave rise to transient absorption spectrum with two well defined bands having λ_{max} at 410 and 650 nm identical to the one obtained by e_{aq}^{-} reaction at this pH. The absorbances at these wavelengths reached maxima at ~11 μs and from the formation traces for different PS^{+} concentrations the bimolecular rate constant for the reaction of isopropyl ketyl radical with PS^{+} was computed to be 3.3×10^{9} dm^{3} mol^{-1} s^{-1}. The transient decayed by second-order kinetics with $2k$ value comparing closely with that obtained in *tert*-butyl alcohol solution. From the spectral similarity and also the closeness of decay kinetics in the two solutions, it is inferred that $(CH_3)_2{}^{\cdot}COH$ also brings about one-electron reduction of PS^+ leading to the formation of semireduced species. The reaction of $(CH_3)_2{}^{\cdot}COH$ was studied over entire pH from 2 to 11, and was observed that while the transient absorption spectrum at lower pH ∼2.5 remained the same as observed in pH 7, the nature of the spectrum observed at pH 10.0 was considerably different, and was exactly similar to the one observed in the case of $e_{aq}{}^-$ reaction at the higher pH. It has been reported in the past [20] that among the radicals formed by reactions (2a) and (2b) ∼15% are unreactive β-hydroxy alkyl radicals $(CH_3)^{\cdot}CH_2\ COH$ and the rest ∼85% are α-hydroxy alkyl radical $(CH_3)_2{}^{\cdot}COH$ which are the strong reducing species. In computing the yield of semireduced PS^+, the G-value has been assumed to be 5.1 i.e. 15% lower than the total radical yield with G-value of 6.0. With this assumption and the corrected band intensity, we computed the yield of semireduced PS^+ to be same as obtained in the reaction of $e_{aq}{}^-$, with experimental uncertainty of ±5%. It may be noted here that although $(CH_3)_2{}^{\cdot}COH$ radicals are reducing in nature and bring about electron transfer reactions, they are known to undergo addition as well as abstraction reactions. Since in the present case isopropyl ketyl radical gives rise to 100% yield of semireduced species, it is apparent that the other modes of reactions such as abstraction and additions are totally absent. In this system also we attempted to determine pK_a using both the bands over the entire pH range from pH 2 to 11. The advantage in this case, in addition to a high G-value, is that a single solution can be employed over the entire pH range. In order to determine pK_a of semireduced PS^+, a single solution consisting of N_2O saturated 8×10^{-5} mol dm^{-3} PS^+ and 1 mol dm^{-3} 2-propanol was employed throughout the pH study. The optical density of transient measured at 410 and 650 nm as a function of pH gave curves (figure not shown) with inflexion points corresponding to pK_a of 8.3 same as in the case of $e_{aq}{}^-$. The spectra recorded at pH 2.5 and 10.0 may be assigned to the two different forms of semireduced species $PSH^{\cdot +}$ and $PS^{\cdot}$ respectively as shown in Scheme 2.

Reaction of $CO_2{}^{\cdot -}$. Reaction of $CO_2{}^{\cdot -}$ radical in N_2O-saturated aqueous solutions containing 8×10^{-5} mol dm^{-3} PS^+ and 0.1 mol dm^{-3} sodium formate were studied at pH 2.8 and 9.6. The radical absorption spectra were similar to those observed in $e_{aq}{}^-$ and $(CH_3)_2{}^{\cdot}COH$ reactions at respective pHs. The transient decay in this case also followed a second order kinetics with $2k$ almost same as in the case of $e_{aq}{}^-$ and $(CH_3)_2{}^{\cdot}COH$. It is inferred that $CO_2{}^{\cdot -}$ also reacts with PS^+ by electron transfer and gives rise to semireduced species. The transient semireduced PS^+ yield was almost 100% and the extinction coefficient was same in this case also. The rate constant for the reaction of $CO_2{}^{\cdot -}$ with PS^+ as evaluated from formation traces was 4.1×10^9 dm^3 mol^{-1} s^{-1}.

Reaction of $H^{\cdot}$ atom. The spectrum of the transient species formed by reaction of $H^{\cdot}$ atoms at pH 2.6 is shown in Fig. 3a. The solution used for the reaction was N_2-saturated 0.5 mol dm^{-3} *tert*-butyl alcohol containing 8×10^{-5} mol dm^{-3} of PS^+. For comparison, the normalized spectrum (normalized to the same dose and G-value) of the semireduced species, formed by reaction of the $(CH_3)_2{}^{\cdot}COH$ radical at this pH, is also given in Fig. 3b. It is seen that the nature of the 650 nm band is the same except that its intensity is lower in the case of $H^{\cdot}$-atom reaction products. The reducing ability of of $H^{\cdot}$ atom is expected to be higher than that of $(CH_3)_2{}^{\cdot}COH$ on the basis of the one-electron reduction potentials of these two species. Moreover, the rate constant for the reaction of $H^{\cdot}$-atom with PS^+, determined from the pseudo-first order rate for build-up of transient absorption was found to be higher (4.5×10^9 dm^3 mol^{-1} s^{-1}) than that for reaction of $(CH_3)_2{}^{\cdot}COH$ with PS^+ (3.3×10^9 dm^3 mol^{-1} s^{-1}). Therefore, the decrease in the intensity is obviously not due to inefficiency of the hydrogen atom reaction with PS^+. Since $H^{\cdot}$ atoms are known to react by different modes, we infer that $H^{\cdot}$ atoms formed in the system react to give other species in addition to semireduced PS^+. Evidence for the formation of such species was obtained from comparison of the shorter wavelength band in the spectra of Fig. 3. It is seen that there is an appreciable shift of the 410-nm band and also a change in intensity. In the resulting spectrum obtained by subtracting the absorbance of the two spectra, we clearly see a new band with λ_{max} at 370 nm (Fig. 3c). This band could be attributed to the new species formed by $H^{\cdot}$-atom reaction. In the pulse radiolysis work on nicotinic acid Solar et al. [21] observed different modes of $^{\cdot}H$-atom reaction including H-adduct with different absorption band. In the case of thionine such a new band has been assigned to H-adduct [12]. It is reasonable to assume in the present case that the new band with λ_{max} at 370 nm is also due to H-adduct. It is supported by the observation that the decay of the transients formed by isopropyl ketyl radical and $H^{\cdot}$-atom reactions at 370 nm are entirely different (inset A of Fig. 3). The decay of 650 nm band generated by $H^{\cdot}$-atom reaction followed second order kinetics with $2k/\varepsilon l$ close to that observed for semireduced dye species. The nature of the decay traces monitored at 650 nm in the case of

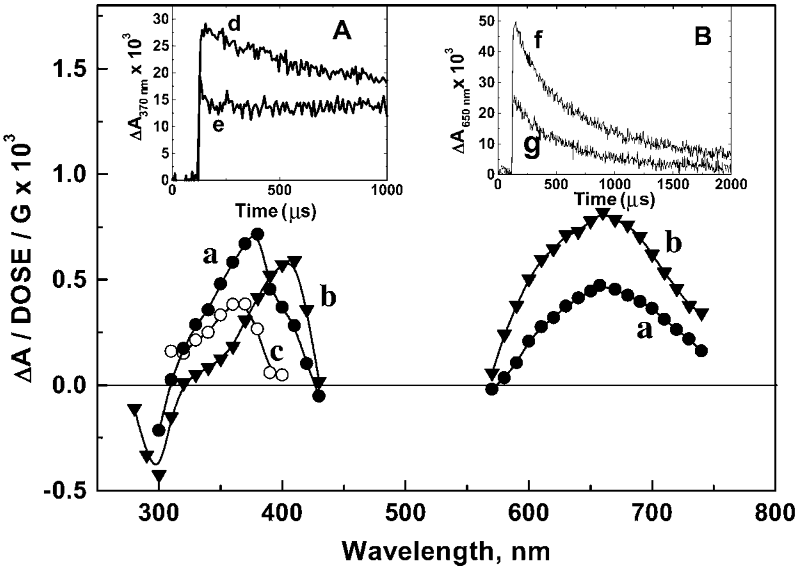
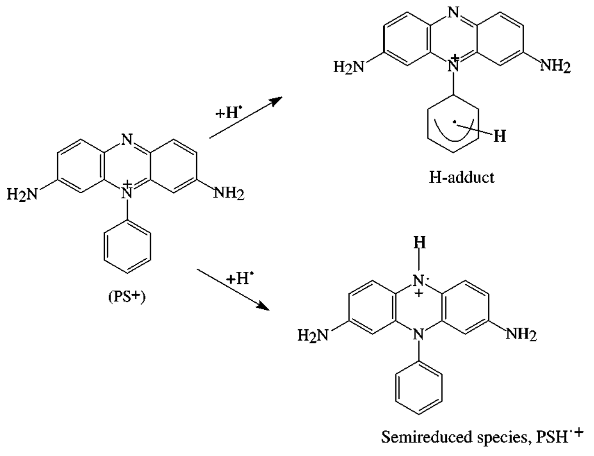


FIGURE 3 Absorption spectra (end of 50 ns electron pulse) of transient semireduced phenosafranine species formed by reaction of PS^+ (a) with $H^\cdot$ atoms at pH 2.6, (b) with isopropyl ketyl radicals at pH 2.5, and (c) difference in the absorption spectra of (b) and (a). Inset (A) shows absorption time profiles of radical decay formed on reaction with isopropyl ketyl radical (d) and with $H^\cdot$-atom (e) at 380 nm. Inset (B) shows absorption time profiles of radical decay formed on reaction with isopropyl ketyl radical (f) and with $H^\cdot$-atom (g) at 650 nm.

isopropyl ketyl radical and $H^\cdot$-atom reactions are seen to be similar in inset B of Fig. 3. It is therefore inferred that the band observed at 650 nm in the $H^\cdot$-atom reaction is exclusively due to semireduced species. Since the isopropyl ketyl radical reacts with PS^+ by electron transfer with 100% efficiency, and using the absorbances of 650 nm band, we compute the yield of semireduced species formed on reaction with $H^\cdot$ atom to be 58% and the remaining 42% is attributed as due to H-adduct. The following Scheme 3 suggests the two different modes of $H^\cdot$ atom reactions with PS^+.



Scheme 3

One-Electron Reduction Potential Of Phenosafranine (PS^+)

Among the various standard couples (Duroquinone, $DQ/DQ^{\cdot -}$; Anthraquinone disulfonate, $AQDS/AQDS^{\cdot -}$; Nitrobenzene, $NB/NB^{\cdot -}$) employed to determine one-electron reduction potential of PS^+, we have found that the $NB/NB^{\cdot -}$ couple establishes an equilibrium as shown below:

$$\mathrm{PS^+(H^+)} + \mathrm{NB}^{\cdot -} \overset{K}{\rightleftharpoons} \mathrm{PSH}^{\cdot +} + \mathrm{NB} \qquad (8)$$

where K is equilibrium constant and was evaluated using both kinetic and yield measurement methods.

Kinetic Method. In this method equilibrium constant K is related to k_f and k_b as $K = k_f/k_b$, where k_f and k_b are the rate constants for the forward and the back reactions respectively. The observed rate constant k_{obs} determined at different NB concentrations can be shown to follow the relationship.

$$k_{obsd} = k_f[PS^+] + k_b[NB] \qquad (9)$$

$$\text{or } \frac{k_{obsd}}{[NB]} = \frac{k_f[PS^+]}{[NB]} + k_b \qquad (10)$$

On plotting $k_{obsd}/[NB]$ vs $[PS^+]/[NB]$ we computed k_f from the slope and k_b from the intercept of the plot of

Fig. 4A and finally we calculated equilibrium constant K as k_f/k_b to be 293. By substituting this value of K in the Nernst's Eq. (11)

$$E^1(PS^+/PS^\cdot) = E^o(NB/NB^{\cdot-}) + 59.16 \log K \quad (11)$$

the one-electron reduction potential E^1 (mV) of PS^+ was computed to be −340 mV vs. NHE (Normal Hydrogen Electrode) at pH 7 by using $E^o(NB/NB^{\cdot-}) = -486$ mV vs. NHE [22].

Yield Measurement Methods. The equilibrium constant K can be shown to be related to ΔA as

$$\frac{1}{\Delta A} = \frac{K[PS^+]}{\in l[R].[NB].} + \frac{1}{\in l[R]} \quad (12)$$

where [R] is the total radical concentration (at given dose and G-value), ε is the molar extinction coefficient of semireduced species and l is the optical path length (1 cm in the present case). Plot of $1/\Delta A$ vs. $[PS^+]/[NB]$ would be linear with slope/intercept = K. From the linear plot [Fig. 4B], slope and intercept was computed to be 41743 and 140, respectively, and the K was evaluated to be 298, close to the value obtained in the previous case. The one-electron reduction potential of PS^+ at pH 7 was then computed by substituting the above value of K in Eq. (11) and was found to be close to the one obtained by kinetic method.

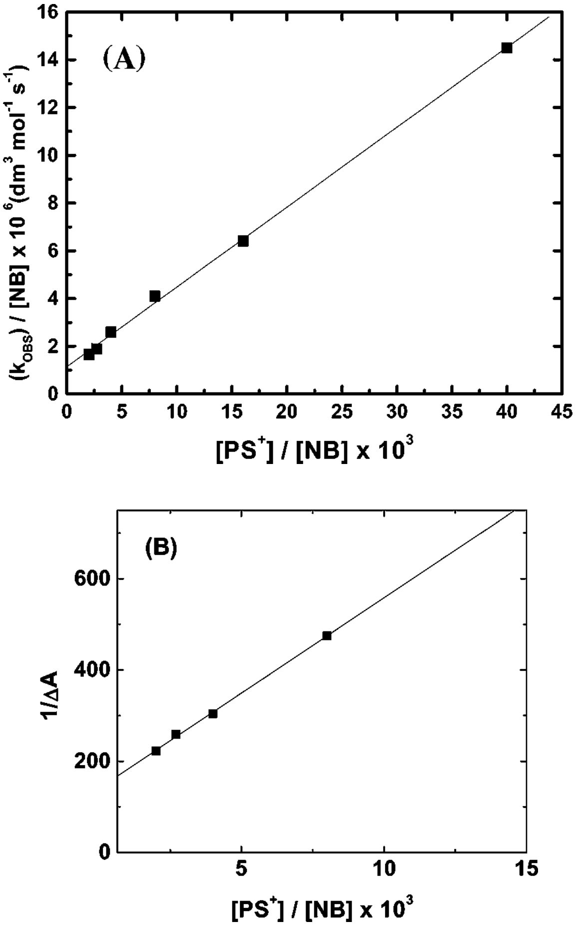


FIGURE 4 Plots of (A) $k_{obs}/[NB]$ vs. $[PS^+]/[NB]$ at pH 7 and (B) $1/\Delta A_{650\ nm}$ vs. $[PS^+]/[NB]$ in N_2-saturated 2 mol dm^{-3} *tert*-butyl alcohol solution containing varying concentrations of NB.

Optical Absorption Studies in Presence of Anionic Surfactant SDS

The effect of surfactant SDS on the absorption properties of the dye can be seen in Fig. 5. It is seen that as the SDS concentration is increased the absorbance of the dye at 520 nm decreases until around 0.8×10^{-3} mold̃m^{-3} and on further increase of SDS concentration the absorption rises between 0.8×10^{-3} and 3×10^{-2} mol dm^{-3}. This rise of dye absorbance in the region $0.8 \times 10^{-3} - 3 \times 10^{-2}$ mol dm^{-3} SDS is related to the formation of surfactant micelles in which the dye is incorporated. From the inflexion point of this curve the CMC (critical micelle concentration) of SDS is evaluated to be 2.6×10^{-3} mol dm^{-3}. The CMC of SDS evaluated from the inflexion point of curve (Fig. 5) is lower than the ones obtained by light scattering and conductivity measurements. Lowering of CMC values in dye–surfactant systems has also been observed in the past by Mukherjee and Mysels [23]. Even in the case of thiazine dye (i.e. the thionine and SDS system) also the CMC of SDS evaluated from the inflexion point of similar curve was lower than the ones obtained by other methods. It is reported in the work [24] that the observed CMC values increased and approached the latter with increasing thionine concentrations. The

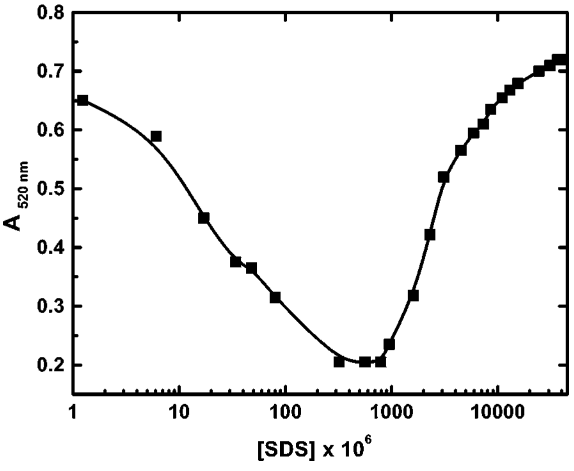


FIGURE 5 Effect of SDS on the absorbance of PS^+ (1.8×10^{-5} mol dm^{-3}) solutions at 520 nm.

present CMC value in fact agree closely with the one reported for the thionine–SDS system for a comparable dye concentration.

The decrease in absorbance of the dye at 520 nm, below the CMC (premicellar region), can be attributed to the formation of a dye–surfactant complex. In neat aqueous solution the dye (PS^+) exhibits a pronounced band with $\lambda_{max} = 520$ nm ($\varepsilon = 36{,}000 \pm 100$ dm^3 mol^{-1} cm^{-1}) (Fig. 6a). At SDS concentrations in the premicellar region the absorbance of the 520 nm dye band decreases and a new band with $\lambda_{max} = 500$ nm appears, which becomes prominent at 8×10^{-4} mol dm^{-3} SDS (Fig. 6b). Although the new band appears close to the dye band, the nature of the two spectra are quite different. The band at 500 nm in the premicellar region is broader and the intensity of the absorption band is reduced considerably for the same dye concentration. Similar changes in absorption spectra of PS^+ in the presence of oppositely charged SDS molecules below the CMC have been reported in the past [17a] and have been attributed to the formation of a dye–surfactant complex. The authors have determined the equilibrium constant for interaction of PS^+ with S^- (SDS) in the premicellar region and concluded that the hydrophobicity of SDS plays an important role in the ion-pair formation. In their review on dye–surfactant interactions, Diaz Garcia and Sanz-Medel [17b] also suggested the existence of ion-association complexes formed at below CMC between ionic surfactants and dyes of opposite charge. In the present case, we infer that the dye–surfactant interaction leads to the formation of ion-pair complex of the following type:

$$PS^+ + S^- \leftrightharpoons PSS \qquad (13)$$

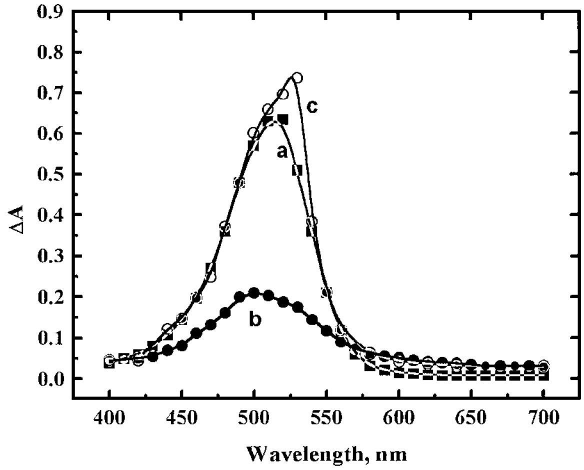


FIGURE 6 Absorption spectra (end of 50 ns electron pulse) of PS^+ (1.8×10^{-5} mol dm^{-3}) (a) in neat aqueous medium, (b) in premicellar (SDS = 8×10^{-4} mol dm^{-3}), and (c) in micellar (SDS = 0.04 mol dm^{-3}) region.

Interactions with Anionic Micelles. As stated before PS^+ is present as complex (PSS) in the premicellar region of the SDS. As the surfactant concentration increases beyond the CMC the main dye band appears and the complex band at 500 nm disappears. This indicates that the dye surfactant complex is unstable in the micellar region, where the surfactant molecules tend to aggregate to form the micelle. The equilibrium for the incorportion of the dye into the micelles (M) can be represented as

$$PSS + M \overset{K_B}{\leftrightharpoons} PSM \qquad (14)$$

PSS, M, and PSM represent dye–surfactant complex, micelle, and micellized dye species respectively. The measured absorbance (A) of the dye at different SDS concentrations can be used to compute the dye–micelle binding constant K_B. Thus, $A_{obs} = f_c\,[PS^+]_T\varepsilon_c\,l + f_m\,[PS^+]_T\,\varepsilon_m\,l$, where ε_c and ε_m are molar absorption coefficients of complexed and micellised dye at a given wavelength, respectively, f_c and f_m are the fractions of the complexed and micellized dye respectively.

[M] is given by $[M] = [M]_T - f_m\,[PS^+]_T$, where $[PS^+]_T$ and $[M]_T$ are the total dye and micelle concentrations respectively. $[M]_T$ is given by

$$[M]_T = \frac{([S]_T - CMC)}{N} \qquad (15)$$

where N is the aggregation number and is defined as the number of surfactant molecules involved in the formation of micelle. For our calculation N for SDS has been taken to be 62 [25]. The binding constant, K_B, can be shown to be related to measured absorbance of the dye as

$$\{A/[PS^+]_T l - \varepsilon_c\}^{-1} = (\varepsilon_m - \varepsilon_c)^{-1} + \{(\varepsilon_m - \varepsilon_c) \times K_B([M]_T - f_m[PS^+]_T)\}^{-1} \qquad (16)$$

where l is the optical path length, and a plot of $\{A/[PS^+]_T l - \varepsilon_c\}^{-1}$ vs. $\{([M]_T - f_m[PS^+]_T)\}^{-1}$ should be linear with binding constant K_B(K_B = intercept/slope). As f_m is not known, an initial plot was drawn with $f_m = 0$ (Fig. 7a). The approximate value of K_B obtained was used to get the value of f_m from Eq. (17), which is quadratic in f_m.

$$K_B[PS^+]_T f_m^2 + \{-(K_B[M]_T + K_B[PS^+]_T + 1)\} f_m + K_B[M]_T = 0 \qquad (17)$$

From the above quadratic equation the root with a value <1 is taken, as f_m is a fraction. A more accurate plot is

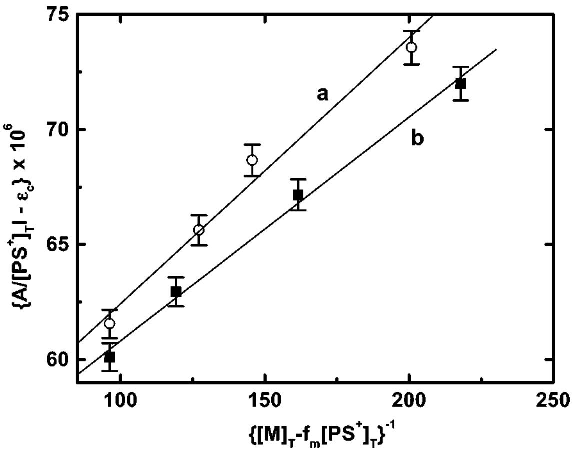


FIGURE 7 Plot of $\{A/[PS^+]_T l - \varepsilon_c\}^{-1}$ vs $\{([M]_T - f_m[PS^+]_T)\}^{-1}$ with (a) $f_m = 0$ and (b) $f_m = 0.545$.

now constructed using these f_m values and the successive approximation procedure is repeated until K_B and f_m become invariant. The binding constant K_B so evaluated (Fig. 7b) was found to be 261 ± 20 $dm^3\ mol^{-1}$. The dye band at 520 nm was found to be red shifted by $\sim$11 nm with increase in the extinction coefficient of the dye in micellar medium. It may be noted that our value of K_B is lower than that reported by Bhat et al. at room temperature [17a]. In their method for evaluating K_B, the authors have considered the equilibrium [18] involving free dye rather than dye–surfactant complex in the premicellar region, although they have suggested [17a] formation of such a complex. In the iteration method adopted by us for computation of K_B, we have considered this aspect in the equilibrium (Eq. 14). We feel that a lower value of K_B in fact is in agreement with our observation that the CMC curve (Fig. 4) is not sharp but is spread over a wide concentration range of SDS to reach the plateau.

Medium Polarity Effect. As mentioned earlier, there is an appreciable red shift of the dye band in the anionic micellar media followed by the increase in extinction coefficient, for example, in 0.04 mol dm^{-3} SDS the λ_{max} of the dye band is red shifted by $\sim$11nm and the extinction coefficient in this micellar medium is about 9% higher as compared to the homogeneous aqueous medium. The red shift and increase in extinction coefficient both indicate a decrease in the polarity or the dielectric constant of the medium surrounding the probe molecule. Thus, for example, in water–alcohol mixtures of different dielectric constants or in the presence of solvents of different polarity, similar changes in absorption properties were also observed [24]. It is seen that as the dielectric constant of the solution in water–alcohol mixture decreases or the medium is changed from high to low polar solvents the dye band intensity increases with progressive red shift of the band. The change in extinction coefficient of PS^+ with the medium polarity and also the dielectric constant gave a linear plot (Fig. 8A and 8B). From the change in extinction coefficient in SDS micelle, and using the above plot, the dielectric constant experienced by PS^+ was read off and the value was estimated to be 55. Similarly, the polarities of the environment of PS^+ in this micelle was inferred form the above plot to correspond to E_T (solvent polarity parameter) value [26] lying between that of water and glycerol [Fig. 8A]. Similarly, the red shift of the PS^+ absorption maximum also shows a correlation with dielectric constant or the solvent polarity parameter, but since the shifts are rather small, accurate evaluation would be difficult and hence no attempt has been made to estimate using this property.

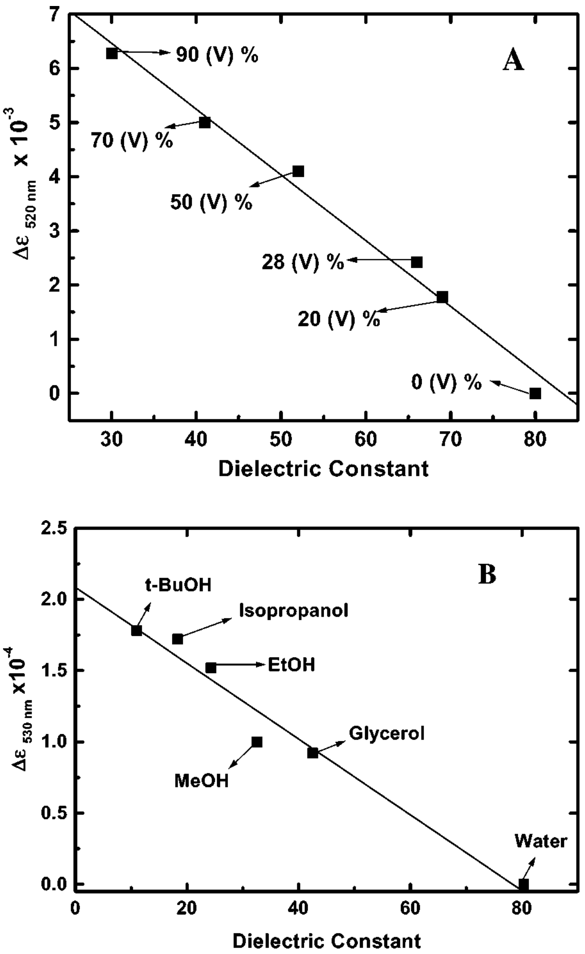


FIGURE 8 Relative increase in the extinction coefficient ($\Delta\varepsilon$) of PS^+ (8×10^{-5} mol dm^{-3}) in ethanol–water mixtures of different compositions expressed in V% of ethanol.(A) and the dielectric constant of different solvents.

One-Electron Reduction by e_{aq}^{-} in Micellar Medium. The transient absorption spectrum of the semireduced PS^{+} recorded in SDS micellar medium is shown in Fig. 9b. For a ready comparison absorption spectrum of the transient semireduced species recorded in neat aqueous solution is also shown in the Fig. 9a. It is seen that the transient band is red shifted by ~30 nm indicating incorporation of the transient into the micelle. The rate constant for the reaction of e_{aq}^{-} with PS^{+}, which was 2.1×10^{10} dm^3 mol^{-1} s^{-1} in homogeneous aqueous medium decreased to a value of $\sim 9.4 \times 10^{9}$ dm^3 mol^{-1} s^{-1}, assuming the presence of entire dye in the micelle. In the case of SDS, the negatively charged micelle surface hinders like charged e_{aq}^{-} to approach because of electrostatic repulsion and therefore reaction of e_{aq}^{-} with the micellised PS^{+} is expected to be slow. The rate constant for the reaction of e_{aq}^{-} with solute like pyrene, in similar micellar systems, has been found to be lower by several orders of magnitude (from 10^{10} to less than 10^{7} dm^3 mol^{-1} s^{-1}). But in this system surprisingly we found that the rate constant is only nominally lower and cannot be explicable on the basis of the extent of micellisation of the dye into the SDS micelles [27]. In the case of a phenothiazine dye Safranine T similar behavior was observed [28], which was explained assuming a finite concentration of the solute in the bulk aqueous phase. Under the conditions of our present work, SDS undergoes micelle formation above about 2.6×10^{-3} mol dm^{-3} concentration. In the micellar medium at surfactant concentration ~0.04 mol dm^{-3}, where most of the dye is incorporated into the micelle, a small but finite dye concentration would exist in the bulk aqueous phase as the complex (Eq. (13)). Because of the existence of an equilibrium (Eq. (13)), it is expected that both free and complexed dye species would be present in the bulk aqueous phase and would undergo fast reaction with e_{aq}^{-}. However, reaction of e_{aq}^{-} with the micellized dye is to be considered to account for the slowness of the reaction. The observed rate constant therefore would reflect on the reactions of e_{aq}^{-} with the bulk as well as micellised dye species. As regard to the decay of the semireduced PS^{+}, the $2k/\varepsilon\ l$ value observed in the homogeneous aqueous medium was as high as 8.5×10^{4} s^{-1}, but the decay in SDS micellar system was found to be almost arrested at least in the millisecond time scale (inset of Fig. 9). Because of the low absorption cross section of the transients, it is difficult to carry out the experiments at still low doses because of poor signal-to-noise ratio. The absorption–time profile of the transient in the

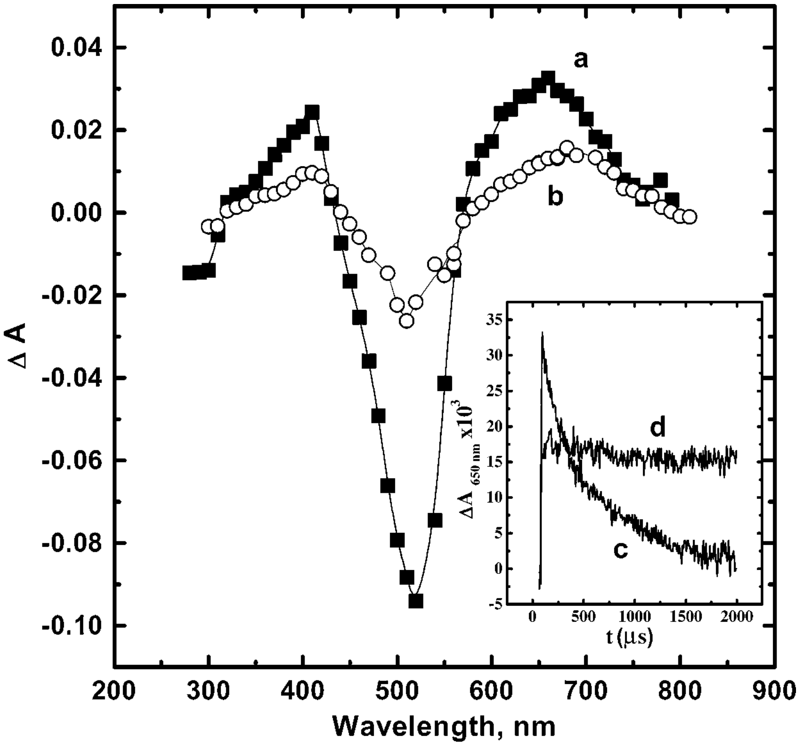


FIGURE 9 Transient absorption spectra obtained on pulse radiolysis of N_2-saturated aqueous (pH = 7) solution of PS^{+} (8×10^{-5} mol dm^{-3}) containing *tert*-butyl alcohol (0.3 mol dm^{-3}) in absence of SDS (a) (9 μs after the pulse) and in presence of SDS (0.03 mol dm^{-3}) (b) (21 μs after the pulse). Inset show absorption time profiles of radical decay in absence (c) and presence of SDS (d) at 650 nm.

presence and absence of SDS are shown in the inset of Fig. 9.

CONCLUSION

The reactivity of phenosafranine PS^+ dye towards pulse radiolytically generated reducing radicals is very high and the rate constant is close to the diffusion controlled value. of $H^\cdot$ atoms react with PS^+ by both electron transfer and addition.

The present study clearly demonstrates that the spectral properties of PS^+, a cationic dye are affected in anionic micellar media. From the data of solvent effect on PS^+, it is evident that environment around PS^+ in the anionic micelles of SDS is highly polar. Electrostatic attraction between the PS^+ dye (cationic dye) and SDS (anionic micelle) would favour location of PS^+ close to the head groups. The results of the pulse radiolysis experiments on one-electron reduction in micellar system clearly indicate that the decay kinetics of the semireduced PS^+ can be profoundly altered, leading to the stabilization of transient in the micelles.

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