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ORIGINAL CONTRIBUTIONS

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Studies on the molecular interaction of safranin-T with surfactants

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Abstract The spectrophotometric studies of safranin-T (Saf-T) dye in an aqueous solution containing three different types of surfactants such as CTAB (cationic), SLS (anionic) and Triton X-100 (TX-100), Tween-20, 40, 60 and 80 (nonionic) show that Saf-T forms a 1:1 molecular complex with TX-100, Tweens and SLS. Such a type of interaction is absent in Saf-T and CTAB. The thermodynamic and spectrophotometric properties of these complexes suggest that Saf-T forms a strong charge transfer (CT) complex with TX-100 and Tweens, whereas the interaction of Saf-T with SLS is coulombic in nature. Photogalvanic and photoconductometric studies also support the above interactions. In addition to this, the electron-donating ability among the nonionic surfactants i.e. TX-100 and Tweens towards dye, role of surface in CT interaction, the site of CT interaction and the intensity and stability of CT interaction between Saf-T and nonionic surfactants have been pointed out.

Keywords Safranin-T · Tweens · CT Complex · Photogalvanic effect · Oscillator strength (f)

Introduction

Surfactants are long-chain molecules which can form organized structures [1] like micelles and reverse micelles due to the presence of both hydrophobic and hydrophilic groups within the same molecule. The most outstanding properties of surfactants are their ability to solubilize a variety of molecules insoluble in aqueous solution and their substantial catalytic effect on many chemical reactions [2, 3]. On the other hand, studies of photoinduced electron transfer reactions in surfactant solutions have added a new dimension for efficient energy conversion and storage through dispersion of photoproducts in surfactants and reducing the back recombination of oxidized species readily [4–8].

Corrin et al. [9] and others [10–12] observed the change in the colour of ionic dyes in the presence of oppositely charged ionic surfactants in solutions and also proposed dimer and multimer formation of dye molecules in the surfactant micelle. Hayashi [13] studied the interaction of congo red with cetyltrimethylammonium bromide (CTAB) and Triton X-100 (*p*-tert-octylphenoxypolyoxyethanol), and interpreted the spectrophotometric data in terms of 1:2 dye-surfactant complex formation. Matibinkov et al. [14] studied the effect of sodium lauryl sulfate (SLS) on xanthane dyes and observed shifts in their λ_{max} at lower surfactant concentrations. Bhowmik et al. [15–17] reported photovoltage generation in an aqueous solution of nonionic surfactants containing phenosafranin and thiazine dyes. These photoinduced effects have been explained in terms of the generation of electroactive species by charge transfer (CT) or electron-donor-acceptor (EDA) interaction between the dye as an electron acceptor and the surfactant as an electron donor.

To obtain a better understanding of the nature of the dye-surfactant interaction, studies of spectral characteristics as well as thermodynamic properties of dyes in the presence of surfactants are essential. For this purpose, spectrophotometric and thermodynamic properties of safranin-T, a cationic phenazine dye have been studied in aqueous solutions of different surfactants of diverse nature such as cationic, anionic, and nonionic. These studies have been substantiated by photogalvanic and photoconductivity effects of dye-surfactant systems and the results are presented in this paper.

Experimental details

Safranin-T (3,6-diamino-2,7-dimethyl-5-phenylphenazinium chloride), supplied by Sigma Chemicals was recrystallized from ethanol water. The surfactants (a) nonionic: TritonX-100, Tween-20 (polyoxyethylene sorbitan monolaurate), Tween-40 (polyoxyethylene sorbitan monopalmitate), Tween-60 (polyoxyethylene sorbitan monostearate), and Tween-80 (polyoxyethylene sorbitan monooleate), (b) cationic: CTAB and (c) anionic: SLS were obtained either from BDH (England) or Sigma Chemicals (USA); they were of AR grade and used as received.

Absorption spectra were recorded on a Shimadzu UV-Vis spectrophotometer (model UV-160) with a matched pair of stoppered glass cells of 1-cm optical path length.

The photogalvanic effect of Saf-T in the presence of surfactant solution was studied in an H-shaped photoelectrochemical cell with standard joint stoppers (Fig. 1). The light source was a projector lamp (220 V, 300 W). Both chambers of the H-shaped cell, separated by 2 cm, were of the same dimension (diameter 2 cm, length 8 cm), one was kept in the dark while the other was illuminated. An approximately 1-cm^2 platinum plate electrode was located at the centre of each chamber. An aqueous solution containing surfactant ($\sim\times10^{-2}$ mol dm^{-3}) and Saf-T ($\sim\times10^{-5}$ mol dm^{-3}) was taken in the illuminated chamber and a saturated solution of I_2 in iodide was taken in the dark chamber. The solutions were deoxygenated by bubbling N_2 gas into the cell through side tubes for at least 30 min. The photovoltage was measured by connecting the electrodes to a digital electrometer (model 4022) and conductance was measured with a conductivity bridge (model 201).

Results and discussion

The visible absorption spectra of mixed solutions with a fixed concentration of Saf-T and varying concentrations of Tween-40 above the CMC in aqueous media at 298 K are given in Fig. 2. The dye, Saf-T absorbs maximally at 520 nm. The spectrum shifts to 533 nm in the presence of Tween-40 with an isosbestic point at 518 nm. Saf-T with other nonionic surfactants, TX-100, Tween-20, Tween-60, and Tween-80 above their CMC in aqueous media show visible absorption spectras similar to Saf-T–Tween-40 system but the shift of spectrums are 534.2, 532, 534, and 535 nm, respectively. According to the literature available [18], CMC of the nonionic surfactants e.g. TX-100, Tween-20, Tween-40, Tween-60, and Tween-80 in aqueous media are 2.5, 0.5, 0.23, 0.21, and 0.10 ($\times10^{-4}$) mol dm^{-3}, respectively.

In the presence of anionic surfactant, SLS (CMC, 8.0×10^{-3} mol dm^{-3}) absorption maxima of Saf-T shifts to 530 nm with an isosbestic point at 508 nm which is shown in Fig. 3. But the spectrum of Saf-T is not perturbed at all in the presence of the cationic surfactant, CTAB (CMC, 1.0×10^{-3} mol dm^{-3}) which indicates that CTAB and Saf-T do not interact. The sharp isosbestic points indicate 1:1 complex formation between Saf-T and surfactants (nonionic and anionic).

The spectrophotometric data were employed to calculate the thermodynamic as well as spectrophotometric properties of dye–surfactant interaction. For a 1:1 complex, the equilibrium constant (K_c) and molar extinction coefficient (ε_c)can be determined by using Scott's equation [19] in the following modified form:

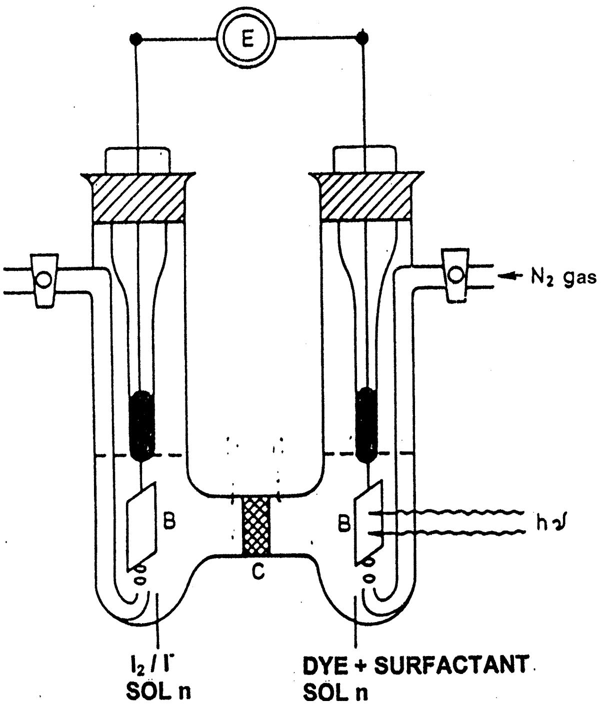

Fig. 1 Schematic diagram of experimental H- shaped photoelectrochemical cell: (E) electrometer; (B) Pt foil electrode; (C) sinterglass membrane

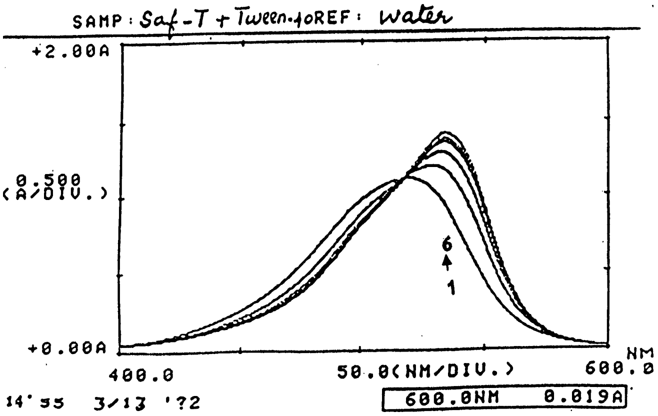

Fig. 2 The visible absorption spectra of Saf-T and Tween-40 in water at 298 K. Concentration of Saf-T: 3.948×10^{-5} mol dm^{-3} and concentrations of Tween-40 (10^{-2} mol dm^{-3}): *1* 0.0, *2* 0.199, *3* 0.498, *4* 0.995, *5* 1.493, and *6* 1.991

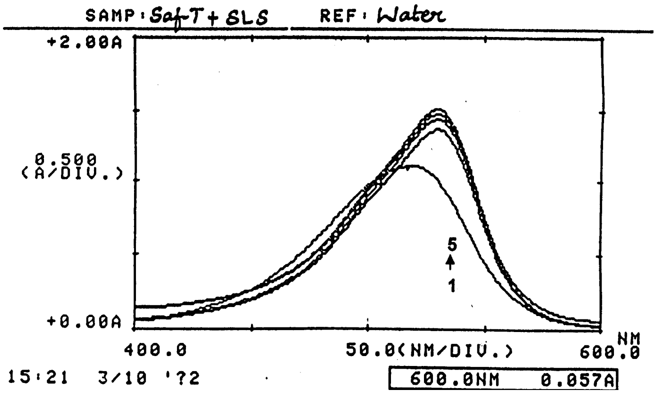

Fig. 3 The visible absorption spectra of Saf-T and SLS in water at 298 K. Concentration of Saf-T: 3.948×10^{-5} mol dm^{-3} and concentrations of SLS (10^{-2} mol dm^{-3}): *1* 0.0, *2* 1.086, *3* 3.259, *4* 6.518, and *5* 8.691

$$\frac{[D][S]\ell}{d-d_o} = \frac{[S]}{\varepsilon_c-\varepsilon_o} + \frac{1}{K_c(\varepsilon_c-\varepsilon_o)} \tag{1}$$

where [D] and [S] are the initial concentrations of dye and surfactant, respectively, ℓ is the optical path length of the solution; d and d_o are the absorbances of the dye at the absorption maximum of the complex with and without surfactant, respectively, and ε_c and ε_o are the respective molar extinction coefficient of the complex and dye at the absorption maximum of the complex. However, it is a prerequisite for the equation in the present form that the condition [S] > > [D] should hold and that the complex absorbs at a wavelength where the surfactant is completely transparent. $[D][S]\ell/d-d_o$versus [S] were plotted for Saf-T with anionic and nonionic surfactants in aqueous media at 298 K which were found to be linear in all cases confirming the 1:1 complex formation (Fig. 4). From the slope and intercept of each plot and with the value of ε_o, 2,368 m^2 mol^{-1} of Saf-T at λ_{max} of the complex, K_c and ε_c of the dye–surfactant interaction were calculated. The thermodynamic quantity ($-\Delta G^o$) of these complexes were obtained from the equilibrium constants at room temperature by the usual

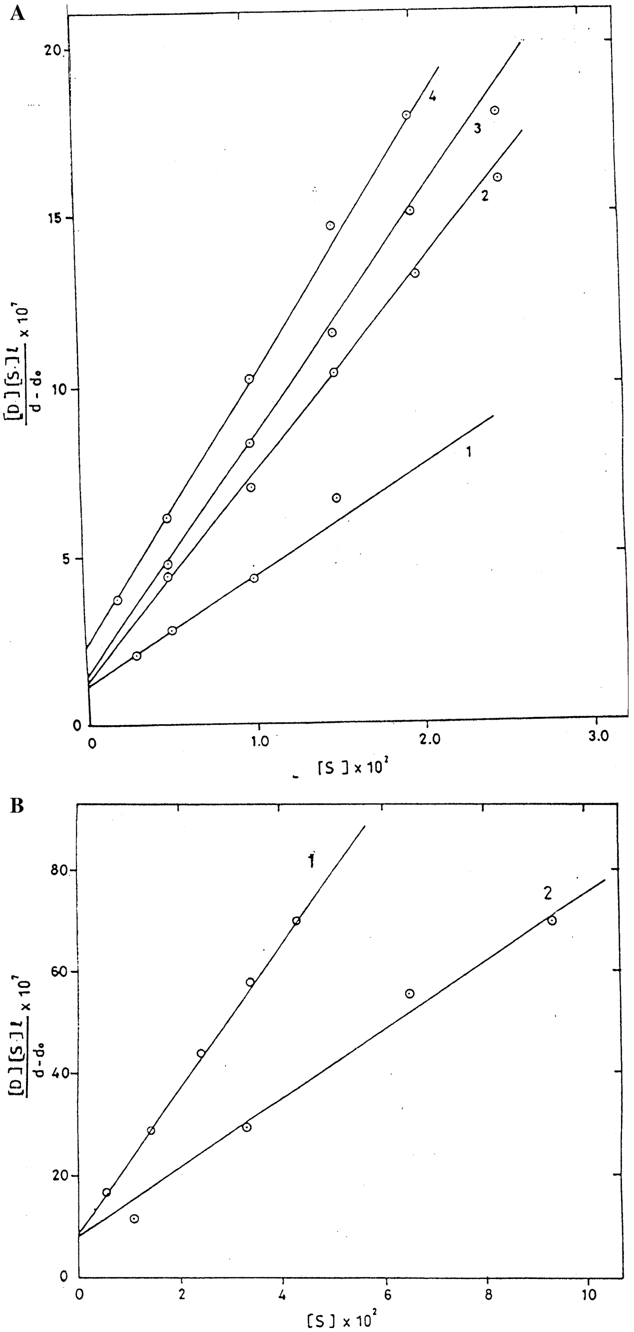

Fig. 4 Plots of $[D][S]\ell/d-d_o$vs. [S] for Saf-T complexes with different nonionic and anionic surfactants (A): *1* Tween-20, *2* Tween-60, *3* Tween-80, and *4* Tween-40 and (B): *1* Triton X-100 and *2* SLS in aqueous media at 298 K

method. The absorption maximum of the dye when completely complexed with the surfactant in aqueous media has been calculated with the help of equilibrium constant values. From these calculated spectra of the complexes, the absorption maximum and molar extinction coefficient are obtained. The experimental oscillator strength (*f*) and transition dipole moment (*D*) were calculated from the spectra of complexes using Eqs. 2 and 3, respectively [20]:

$$f = 4.319 \times 10^{-9} \varepsilon_{\max} \Delta \bar{v}_{1/2} n^{-2} \qquad (2)$$

$$D = 0.09582 \left[\frac{\varepsilon_{\max} \Delta \bar{v}_{1/2}}{\bar{v}_{\max} n} \right]^{1/2} \qquad (3)$$

where n is the refractive index of the medium, $\varepsilon_{\max}$ is the maximum molar extinction coefficient, $\Delta \bar{v}_{1/2}$ is the width in cm^{-1} of the band at half intensity, and $\bar{v}_{\max}$ is the wave number of the maximum absorption in cm^{-1}. All the thermodynamic and spectrophotometric parameters of the complexes in aqueous media are presented in Table 1.

The photogalvanic effect of dye-different surfactant systems were studied in deoxygenated aqueous solution. Only, Saf-T–nonionic surfactant systems generated photovoltages, which were almost reversible and reproducible. Saf-T–SLS and Saf-T–CTAB systems did not respond to irradiation and no photovoltage developed under the same conditions. The growth and decay of photovoltage with the time of irradiation for Saf-T–nonionic surfactant systems at 298 K are shown in Fig. 5. The photovoltage gradually builds up after the start of illumination and attains a maximum value within a few minutes. When the illumination is stopped, the photovoltage decreases gradually and returns nearly to the original dark value. The photovoltage was observed to be generated only in deoxygenated solutions and the solutions did not bleach on illumination. The open-circuit photovoltage (V_{oc}) of the dye-surfactant systems are listed in Table 2.

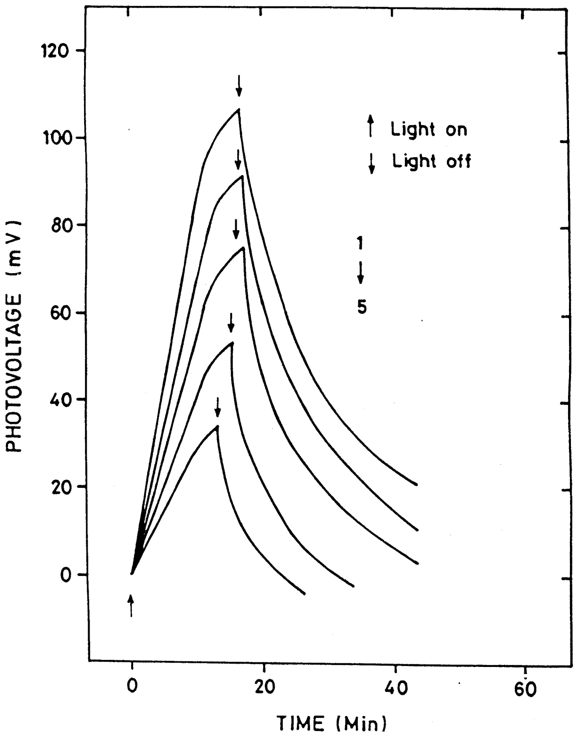

Fig. 5 Growth and decay photovoltage of Saf-T-nonionic surfactant systems at 298 K. The surfactants are: *1* Tween-80, *2* Tween-60, *3* Tween-40, *4* Tween-20, and *5* Triton X-100

The measured dark conductivities of Saf-T in the presence of nonionic surfactants changed on illumination and these changes were almost reversible and reproducible. The growth and decay of photoconductivities induced by illumination at 298 K are shown in Fig. 6. The dark and photoconductivity of Saf-T–nonionic surfactant systems are presented in Table 2. In the case of SLS or CTAB, the dark conductivity was 8.126×10^{-4} mho cm^{-1} which is very high compared to the value in the presence of nonionic surfactants. This is apparently due to the presence of excess ions of CTAB

Table 1 Thermodynamic and Spectrophotometric properties of Saf-T-Surfactants complexes in aqueous media at 298 K

Surfactant[a]	$K_c \times 10^{-2}$ ($\mathrm{dm}^3\ \mathrm{mol}^{-1}$)[b]	$-\Delta G^0$ (kJ mol^{-1})	Complexed band				
			$\lambda_{\max}$ (nm)	Band shift $\Delta\bar{v}$ (cm^{-1})	ε_c ($\mathrm{m}^2\ \mathrm{mol}^{-1}$)	f (m mol^{-1})	D (10^{-20}C)
SLS	0.833	10.957	530	363	3,860	2.068	1.702
Triton X-100	1.634	12.626	534.2	511	3,779	2.070	1.762
Tween-20	2.954	14.131	532	434	4,132	2.072	1.769
Teween-40	3.261	14.379	533	469	3,701	2.083	1.791
Tween-60	5.606	15.681	534	505	3,989	2.151	1.805
Tween-80	5.937	15.823	535	540	3,771	2.252	1.849

[a] Concentration range of surfactants is $0.2–8.7 \times 10^{-2}$ mol dm^{-3} with a fixed concentration of Saf-T, 3.948×10^{-5} mol dm^{-3}
[b] K_c values are the average of four to five measurements with an average deviation of 5%

Table 2 Open-circuit photovoltage (V_{oc}) and conductivities of Saf-T–Surfactant systems in aqueous media at 298 K

Surfactant[a]	Photovoltage (V_{oc}) (mv)	Dark conductivity (mho cm^{-1})	Photoconductivity (mho cm^{-1})
CTAB	–	–	–
SLS	–	–	–
Triton X-100	34	11.124×10^{-5}	12.251×10^{-5}
Tween-20	52	15.398×10^{-5}	18.107×10^{-5}
Tween-40	76	17.172×10^{-5}	21.133×10^{-5}
Tween-60	92	18.427×10^{-5}	21.491×10^{-5}
Tween-80	106	20.779×10^{-5}	22.973×10^{-5}

[a] Concentrations of Saf-T and surfactants are 3.364×10^{-5} and 2.501×10^{-3} mol dm^{-3}, respectively

or SLS in the solution. The conductivity of Saf-T with SLS or CTAB did not change on illumination.

The experimental data presented above are direct spectrophotometric evidence of molecular interaction between Saf-T and surfactants. Since Saf-T is a cationic dye, it is expected that the dye should form a strong complex with the anionic surfactant, SLS, favoured by oppositely charged species. But the results presented in Tables 1 and 2 show that Saf-T forms strong complexes with all nonionic surfactants, whereas a weak complex is formed with SLS.

From these observations, it can be concluded that the nature of interaction of Saf-T with nonionic surfactants is different from that with SLS. This is further confirmed from the thermodynamic and spectrophotometric parameters. Both the equilibrium constant (K_c) and band shift ($\Delta\bar{\nu}$) are high in the case of Saf-T–nonionic surfactant systems. In the neutral surfactant micelle, the cationic dye can penetrate the micelle to form a strong CT complex at a polar site on the oxygen of the hydroxyl group for having comparatively high electron density. This was also verified from the absorption spectra of Saf-T in solvents of diverse nature. The molecular interaction between Saf-T and nonionic surfactants in aqueous medium is considered to be a CT interaction. On the other hand, with negatively charged micelles of SLS, the cationic dye will be held in the stern region due to coulombic interaction and with positively charged micelles of CTAB, the dye will be repelled.

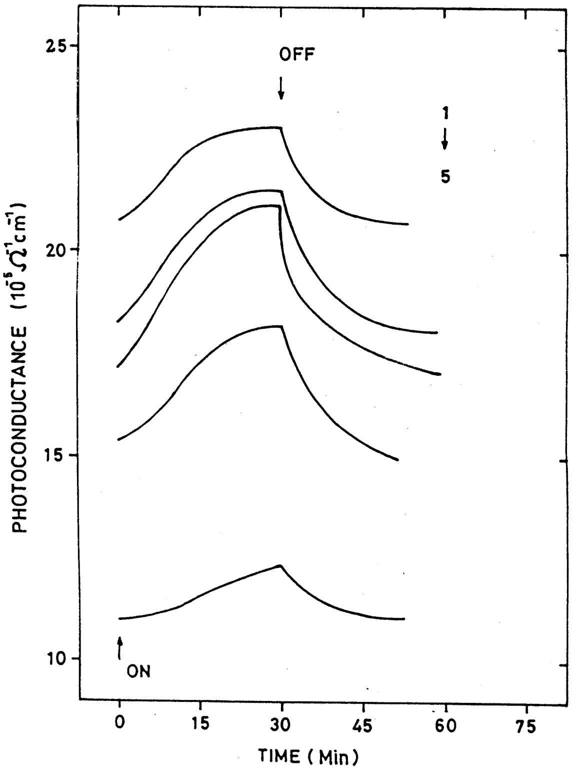

Fig. 6 Growth and decay photoconductivity of Saf-T-nonionic surfactant systems at 298 K. The surfactants are: *1* Tween-80, *2* Tween-60, *3* Tween-40, *4* Tween-20, and *5* Triton X-100

The generation of photovoltages with Saf-T and surfactants can be explained if we assume that the interaction of Saf-T with nonionic surfactants is of CT or electron-donor-acceptor type where surfactants act as electron donor and the dye acts as electron acceptor. During the photovoltage generation, the colour of solutions does not change appreciably. In the presence of oxygen, photovoltage is not generated, which supports the participation of triplet dye in photovoltage generation according to the following scheme:

$$\mathrm{D} + h\nu \rightarrow {}^1\mathrm{D}^* \rightarrow {}^3\mathrm{D}$$

$${}^3\mathrm{D} \rightarrow \mathrm{D}$$

$${}^3\mathrm{D} + \mathrm{S} \rightleftharpoons ({}^3\mathrm{D}\ \text{- - -}\ \mathrm{S}) \rightleftharpoons (\mathrm{D}^-\ \ldots\ \mathrm{S}^+)$$

$$\rightarrow \mathrm{D} + \mathrm{S}^+ + \mathrm{e}^- \quad \text{(Anode reaction)}$$

$$\frac{1}{2}\mathrm{I}_2 + \mathrm{e}^- \rightarrow \mathrm{I}^- \quad \text{(Cathode reaction)}$$

where D and S represent the dye and surfactant, respectively. Photovoltage is not produced in the absence of nonionic surfactants, which indicates that the interaction of triplet dye and nonionic surfactant is mainly responsible for generation of photovoltage through the formation of CT complex. According to Mulliken's CT theory [21], the CT complex is mostly nonionic in nature in the ground state, but is predominantly ionic in the excited state. In the case of Saf-T–SLS system, the interaction is ionic in nature, so no new ionic species are generated when the system is illuminated. Due to this, in conductometric measurement, conductivity remains the same for both dark and illuminated conditions. On the other hand, the interaction of Saf-T with nonionic surfactants is of the CT type, so a slight increase in conductivity during illumination can be explained; this change is reversible, i.e. new ionic species are generated only in the excited state of the complex.

From the experimental results presented in Tables 1 and 2, it is revealed that the strength of nonionic surfactants as electron donor towards Saf-T in an aqueous media follow the order: Tween-80 > Tween-60 > Tween −40 > Tween-20 > TX-100 and this is in accordance with the increasing alkyl hydrocarbon chain length, which in turn, increases the electron density at the electron donating centre of the molecule, due to inductive effect. The presence of an aryl group in TX-100 results in opposite effect.

It is an implication of the CT model that a relation between the intensity of the CT absorption band and the stability of the complex should exist if CT resonance is the dominant factor in stabilizing the complex [22]. As the extent of CT increases, the intensity of the transition which is measured by *f* or *D*, should increase. At the same time, the strength of the interaction as measured by $-\Delta G^0$ or K_c is expected to increase. So, a good correlation is expected between the intensity of the CT absorption band and the stability of the complex. The correlation between the intensity and stability of CT interaction of Saf-T with nonionic surfactants is shown in Fig. 7. Thus, the experimental results from the spectrophotometric and thermodynamic parameters of the CT complexes agree well with the theoretical point of view.

From the present study, it has been found that prominent interaction takes place only when the concentration of the surfactant is above the CMC value. Thus, the surface formation in the form of a micelle is a necessary criterion for complex formation. The interfaces (micelle/water) favour the complex formation due to adsorption of Saf-T from solution and thus increase the concentration of the complex, a phenomenon related to surface catalysis.

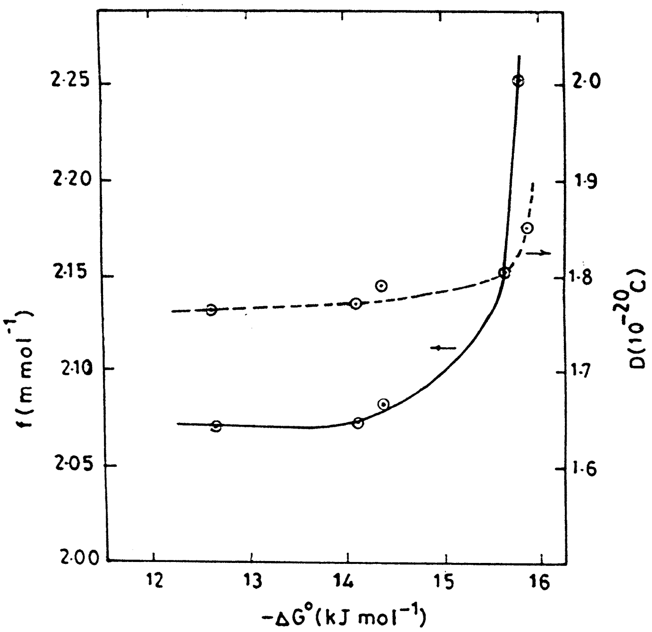

Fig. 7 Correlation between the intensity of the CT absorption band (oscillator strength, *f* and transition dipole moment, *D*) and the stability of the complex (free energy change, $-\Delta G^0$) for the CT complexes of Saf-T with Triton X-100 and Tweens in aqueous media. The dotted and solid curves represent the variation of *D* and *f* from Triton X-100, Tween-20, to Tween-80 (with increase in number of Tweens)

Finally, it can be concluded that the nature of interaction of Saf-T, a cationic phenazine dye with three types of surfactant, varies: CT interaction with nonionic surfactants by the donation of a lone pair of electrons of the oxygen atom of the –OH group of Triton X-100 and Tweens to the lowest vacant molecular orbital of Saf-T, ionic interaction with negatively charged SLS and no interaction with positively charged CTAB.

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