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Photophysics of xanthene dyes in surfactant solution

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Abstract

The spectral (both absorption and fluorescence) and photoelectrochemical studies of some anionic xanthene dyes namely erythrosin B, rose bengal and eosin have been carried out in micellar solution of cationic cetyl trimethyl ammonium bromide (CTAB), anionic sodium dodecyl sulphate (SDS) and neutral triton X-100 (TX-100). The results show that all these dyes form 1:1 electron-donor-acceptor (EDA) or charge-transfer (CT) complexes with TX-100, which acts as an electron donor. There is no interaction of these dyes with SDS, whereas the interaction with CTAB is mainly electrostatic in nature. In presence of TX-100, these dyes show enhancement of fluorescence intensity with a red shift and develop photovoltage in a photoelectrochemical cell. A good correlation has been found among the photovoltage generation in the systems consisting of these dyes and TX-100, spectral shift due to complex formation and thermodynamic properties of these complexes.
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Keywords: Dye–surfactant interaction; Xanthene dyes; Charge-transfer interaction; Photogalvanic effect; Surfactant

1. Introduction

The studies of photoinduced electron transfer or redox reactions in surfactant solution are very interesting and relevant to the understanding of photobiology, specially the model systems mimicking biomembranes. They are also important for efficient photochemical conversion and storage of solar energy, since surfactant solutions help to achieve the separation of photoproducts by means of hydrophilic–hydrophobic interaction between the photoproducts and the interfaces [1–5]. On the other hand, the electron-donor-acceptor (EDA) or charge transfer (CT) interaction of nonionic surfactants with different cationic phenazine and thiazine dyes have been reported [6–11] and the interaction leads to the photovoltage generation when the system consisting of aqueous solution of dye and surfactant is studied in a photoelectrochemical cell. The spectral and photophysical studies of some new rhodamine derivatives and ketocyanine dyes in micellar medium of cationic, anionic and neutral surfactants indicating interaction of dye with surfactant have been reported [12,13]. Recently, the interaction of safranin-O, a cationic dye, with various surfactants viz., anionic, neutral, cationic and zwitterionic have been studied spectrophotometrically [14]. For their outstanding photophysical properties, the anionic xanthene dyes are very efficient laser dyes [15–17] and fluorescent probes [18,19]. While we are interested to study the spectral and photoelectrochemical characteristics of some anionic dyes in the presence of surfactant, the automatic choice lies in the selection of anionic xanthene dyes. For this purpose, the spectra of some anionic xanthene dyes namely erythrosin B, rose bengal and eosin have been studied in micellar solution of TX-100 (neutral), SDS (anionic) and CTAB (cationic) and the spectral studies have been complimented with the photoelectrochemical studies of these dyes in aqueous solution of these surfactants and the results are reported here.

2. Experimental

All the xanthene dyes namely erythrosin B, rose Bengal and eosin were supplied by Sigma Chemicals. These were re-

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crystallized twice from ethanol–water and the purity of these dyes was checked by absorption and fluorescence spectra. The cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl sulphate (SDS) and *p*-tert-octyl-phenoxy-poly-oxy ethanol (Triton TX-100 or TX-100) were supplied by BDH and Sigma Chemicals and these were used without further purification. Aqueous solutions were prepared in doubly distilled water.

The absorption and fluorescence spectra of the solutions were recorded on a Shimadzu 160 A UV–vis spectrophotometer and Shimadzu RF-540 spectrofluorophotometer, Japan respectively using silica cells of 1 cm optical pathlength placed in a thermostated cell holder at different temperatures. The photogalvanic effect of these dyes in surfactant solution was studied in a photoelectrochemical (PEC) cell, which consisted of an H-shaped cell with a 300 W tungsten lamp of 30 mW cm^{-2} intensity; the experimental details of photovoltage measurements have been described earlier [20]. All the measurements were done with freshly prepared solutions.

3. Results and discussion

The visible absorption spectra of solutions with a fixed concentration erythrosin B (1×10^{-5} mol dm^{-3}) in water as well as in aqueous solution of cationic surfactant CTAB, anionic surfactant SDS and neutral surfactant TX-100 at 298 K are shown in Fig. 1. This figure also includes the difference spectra of mixed solution with a fixed concentration of erythrosin B (1×10^{-5} mol dm^{-3}) and surfactant in water balanced against erythrosin B in water at 298 K. The absorption spectra of erythrosin B are perturbed in presence of different surfactants, indicating molecular interaction of erythrosin B with the surfactants in aqueous medium. The visible absorption band of erythrosin B in water appears at 527 nm. In presence of CTAB and TX-100, the difference spectra show the shifted absorption bands at 542 and 546 nm, respectively. In presence of SDS, the spectra are not perturbed at all, indicating no interaction between erythrosin B and SDS. In Fig. 2, the visible absorption spectra of erythrosin B along with the different spectra of mixed solutions with a fixed concentration of erythrosin B (1×10^{-5} mol dm^{-3}) and varying concentration of TX-100ranging from 0.5×10^{-3} to 5×10^{-3} mol dm^{-3} in aqueous medium at 298 K are shown. A sharp isosbestic point at 533 nm indicates 1:1 molecular complex formation. The absorption spectra of other anionic xanthene dyes namely rose bengal and eosin are also perturbed in the presence of TX-100and CTAB with concentration above the cmc of the surfactants. The absorption bands of rose bengal and eosin appearing at 549 and 521 nm in water are shifted to 571 and 542 nm, respectively, in presence of TX-100and 566 and 537 nm, respectively, in presence of CTAB. The spectral data with a fixed concentration of the xanthene dye and varying concentration of surfactant (CTAB and TX-100) have been utilized to calculate the equilibrium constant (K_C) and molar extinction coefficient (ε_c) of the dye complexes with

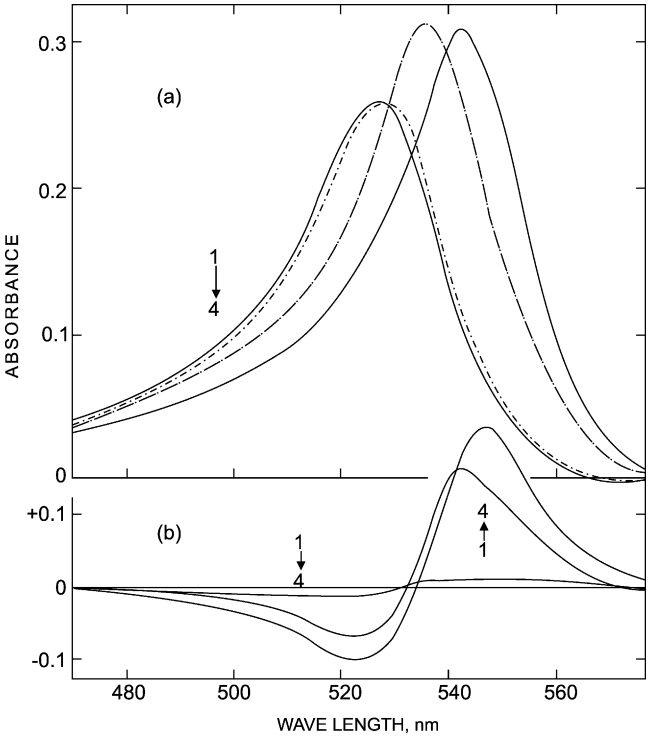


Fig. 1. (a) The visible absorption spectra of erythrosin B in water (1), in aqueous solution of anionic surfactant SDS (2), cationic surfactant CTAB (3) and neutral surfactant TX-100 (4) at 298 K. (b) The difference spectra of erythrosin B in water (1), in aqueous solution of SDS (2), CTAB (3) and TX-100 (4) balanced against the same concentraton of erythrosin B in water at 298 K. Concentration of erythrosin B: 1×10^{-5} mol dm^{-3}; SDS: 5×10^{-2} mol dm^{-3}, CTAB: 1×10^{-2} mol dm^{-3} and TX-100: 1×10^{-2} mol dm^{-3}.

all these surfactants using Rose and Drago's absolute method [21]. In this method various values of $(\varepsilon_c - \varepsilon_o)$ are selected at random for a given set of experimental data and the corresponding values of K_C^{-1} are calculated using the following equation:

$$K_C^{-1} = \frac{(\varepsilon_c - \varepsilon_o)[D][S]\ell}{(d - d_o) - [S]} \quad (1)$$

where d_o and d are the absorbances of the solution containing dye at the absorption maximum of the complex without and with surfactant; ε_c and ε_o are the respective molar extinction coefficients of the complex and dye at the absorption maximum of the complex, ℓ is the optical pathlength of the solution, [D] and [S] are the initial concentration of the dye and surfactant respectively. The values of K_C^{-1} are plotted against $(\varepsilon_c - \varepsilon_o)$ and a straight line is constructed. Now, from several sets of experimental data all the straight lines almost intersect at a point (actually in relatively small area). From the point of intersection K_C and ε_c are determined. Such plots are shown in Fig. 3. at three different temperatures (288, 298 and 310 K) for erythrosin B-TX-100 system only. The other xanthene dyes namely rose bengal and eosin with TX-100 and all the three dyes with CTAB follow Rose and Drago's absolute methods similarly. All the thermody-

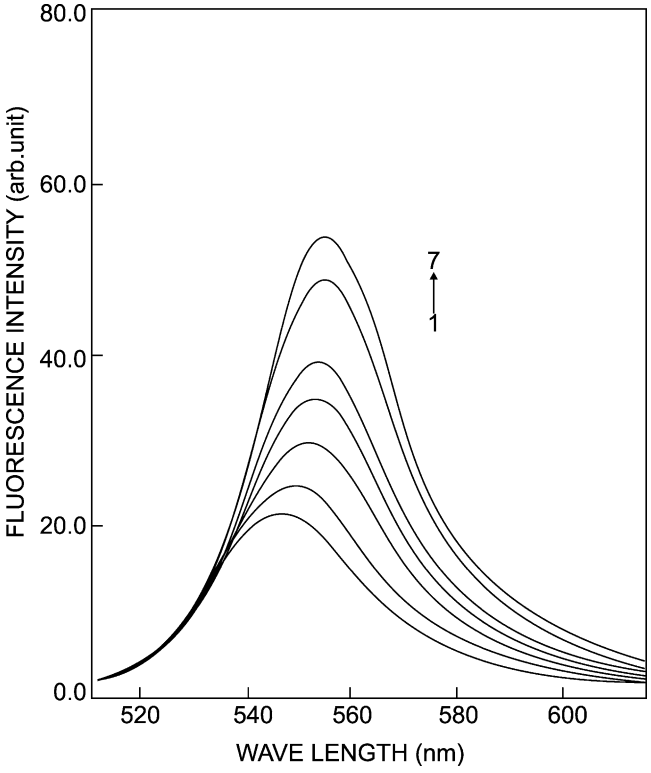


Fig. 2. (a) The visible absorption spectra of erythrosin B in aqueous solution of TX-100 of different concentrations at 298 K. (b) The difference spectra of erythrosin B and TX-100 balanced against the same concentration of erythrosin B in water 298 K. Concentration of erythrosin B: 1×10^{-5} mol dm^{-3}; and concentration of TX-100 (10^{-3} mol dm^{-3}), (1) 0.0; (2) 0.5; (3) 1.0; (4) 1.5; (5) 2.0; (6) 3.0; (7) 4.0 and (8) 5.0.

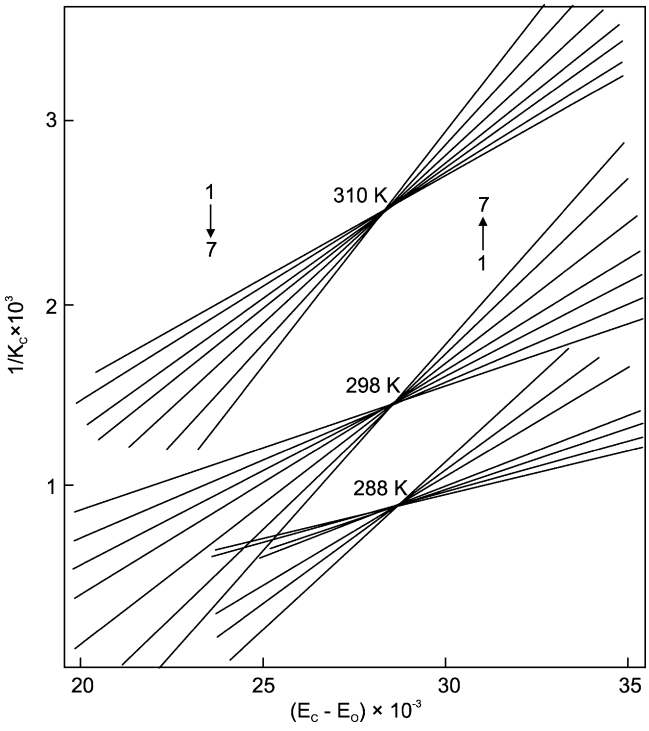


Fig. 3. Spectral determination of equilibrium constant and molar extinction coefficient of erythrosin B-TX-100 complex at 288, 298 and 310 K respectively by Rose–Drago's method. The numbers 1–7 indicate sets of experimental data used.

namic and spectrophotometric properties calculated from this method are summarized in Table 1.

The fluorescence spectra of the anionic xanthene dyes, namely erythrosin B, rose bengal and eosin are also perturbed in presence of neutral surfactant TX-100 and cationic surfactant CTAB. There is no change of fluorescence spectra of xanthene dyes in presence of anionic surfactant SDS. In presence of TX-100 and CTAB, the fluorescence intensities of these xanthene dyes has been found to be enhanced with a red shift indicating molecular interaction of the dyes with these surfactants in the excited state. The fluorescence spectra of mixed solutions with a fixed concentration of erythrosin B (1×10^{-5} mol dm^{-3}) in aqueous solution of TX-100 of varying concentrations at 298 K are shown in Fig. 4. The fluorescence spectra of rose bengal and eosin in aqueous solution of TX-100 and the fluorescence spectra of all the three xanthene dyes in aqueous solution of CTAB behave in a similar manner. In many cases, exciplex formation takes place by enhancement of fluorescence and in some cases, a spectral shift along with enhancement has been observed [22]. In these cases, it should be the excited state charge transfer (CT) or excited state elec-

Table 1
Thermodynamics and spectral characteristics of dye–surfactant interaction at 298 K from absorption spectra

Dye	Thermodynamic characteristics				Spectral characteristics				Shift $\Delta\bar{\nu}$ (cm^{-1})
					In water		In surfactant		
	K_c (dm^3 mol^{-1})	$-\Delta G^\circ$ (kj mol^{-1})	$-\Delta H^\circ$ (kj mol^{-1})	$-\Delta S^\circ$ (J mol^{-1} deg^{-1})	λ_{max} (nm)	ε_{max} (m^2 mol^{-1})	λ_{max} (nm)	ε_{max} (m^2 mol^{-1})	
(a) Xanthene dyes–Triton X-100									
Erythrosin B	714×10^2	16.26	36.03	66.34	527	2.36×10^3	546	2.56×10^3	660
Rose bengal	9.59×10^2	17.01	49.00	107.35	549	9.30×10^3	571	9.50×10^3	701
Eosin	12.72×10^2	17.71	65.00	158.69	521	5.93×10^3	542	5.77×10^3	743
(b) Xanthene dyes–CTAB									
Erythrosin B	5.70×10^2	15.72	29.00	44.56	527	2.36×10^3	542	2.68×10^3	525
Rose Bengal	6.49×10^2	16.04	32.50	55.23	549	9.30×10^3	566	10.92×10^3	547
Eosin	9.20×10^2	16.91	46.50	99.29	521	5.93×10^3	537	7.08×10^3	572

Concentration of dye used in each case is 1×10^5 mol dm^3 and concentrations of surfactants used are in the range 0.5×10^3 to 5×10^3 mol dm^{-3} in all cases.

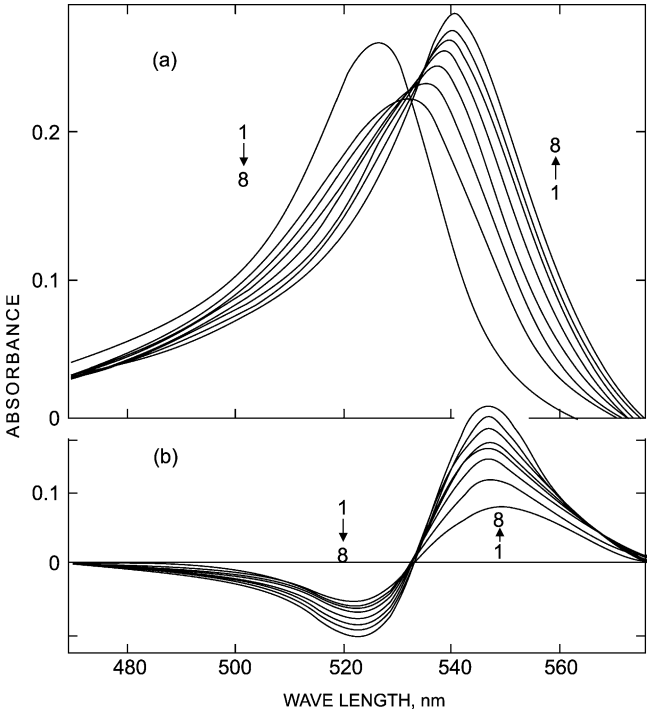


Fig. 4. The fluorescence spectra of erythrosin B in aqueous solution of TX-100 at 298 K. Concentration erythrosin B:1 × 10^{-5} mol dm^{-3}; and concentration of TX-100 (10^{-3} mol dm^{-3}), (1) 0.0; (2) 0.3; (3) 0.4; (4) 0.5; (5) 0.6; (6) 0.80 and (7) 1.0.

trostatic interaction since the dyes interact with TX-100 and CTAB in the ground state and the nature of interaction is different. A possible mechanism of fluorescence enhancement of these anionic xanthene (xanthene$^-$) dyes by surfactant [S] in miceller solution may be represented as follows:

$$\text{xanthene}^- + h\nu \rightarrow {}^1\text{xanthene}^- \quad (2)$$

$${}^1\text{xanthene}^- \rightarrow \text{xanthene}^- + h\nu_f \quad (3)$$

$${}^1\text{xanthene}^- \rightarrow \text{xanthene} + \text{heat} \quad (4)$$

$${}^1\text{xanthene}^- + \text{S} \rightarrow \underset{\text{excited state CT interaction}}{({}^1\text{xanthene}^- \cdot\cdot \text{S} \leftrightarrow \text{xanthene}^{-2\bullet}\text{—S}^{+\bullet})} \rightarrow \text{xanthene}^{-1} + \text{S} \quad (5)$$

$${}^1\text{xanthene}^- + \text{S}^+ \rightarrow \underset{\text{excited state electrostatic interaction}}{({}^1\text{xanthene}^-\text{—S}^+)} \rightarrow \text{xanthene}^- + \text{S}^+ \quad (6)$$

The Eq. (5) shows the excited state CT interaction of TX-100 (S), as electron donor with single excited xanthene$^-$ dye, as electron acceptor and this interaction enhances the fluorescence intensity of the dye in micellar medium with increasing concentration of TX-100. The Eq. (6) shows the excited state electrostatic interaction of cationic CTAB (S^+) with singlet excited xanthene$^-$ dye. The stability constant (K_c^*) of this excited state interaction can be calculated by assuming that the relative increase of fluorescence intensity of xanthene dye in presence of surfactant is due to the excited state complex formation, then we can write from Eq. (5),

$$K_c^* = \frac{\text{xanthene}^- \cdot\cdot\cdot\cdot \text{S}}{[\text{xanthene}^- \cdot\cdot\cdot\cdot \text{S}]^-[\text{xanthene}^- \cdot\cdot\cdot \text{S}]\,\text{S}} \quad (7)$$

and

$$\frac{F - F_0}{F_0} = \varepsilon_F[\text{xanthene}^- \ldots \text{S}] \quad (8)$$

where F_0 and F are the fluorescence intensities of xanthene dye in absence and presence of surfactant and ε_F is the proportional constant and is equivalent to the fluorescent coefficient of the complex in the excited state. Putting the values of

$$\frac{F - F_0}{F_0} = \text{for}\,[{}^1\text{xanthene}^- \cdot\cdot \text{S}]$$

in Eq. (7), we have

$$\frac{F - F_0}{F_0}\,[{}^1\text{xanthene}^-\text{S}] = [\text{S}] \frac{\varepsilon_F}{} + \frac{1}{K_c^* \varepsilon_F} \quad (9)$$

The concentration of ^{1}xanthene$^-$ is related to the initial concentration of xanthene$^-$ by [^{1}xanthene$^-$] = β [xanthene$^-$] where β = $e^{-\Delta E/RT}$, ΔE is the energy difference between the first excited (singlet) state and ground state of xanthene dye, R is the gas constant and T is the temperature in Kelvin. Using the value of [^{1}xanthene$^-$] in terms of [xanthene$^-$] in Eq. (9), the final equation is

$$\frac{F_0}{F - F_0}\,[\text{xanthene}^-][\text{S}] = [\text{S}] \frac{\beta\varepsilon_F}{} + \frac{1}{\beta K_c^* \varepsilon_F} \quad (10)$$

By using Eq. (6), we can deduce the same Eq. (10) where [S] should be replaced by [S^+], the concentration of cationic surfactant.

This empirical relation [11,23] can be used to determine the statbility constant (K_c^*) of the interaction between the singlet excited dye and surfactant to form excited state complex (CT or electrostatic) before coming to the ground state with fluorescence emission. The plots of [xanthene$^-$] [S] $F_0/F-F_0$ against [S], the initial concentration of surfactant should yield a straight line for excited state complex formation between singlet excited dye and surfactant. From the slope and intercept of this plot, K_c^*, the stability constant of the dye–surfactant excited state interaction can be estimated. The plots are shown in Fig. 5 at 298 K for the interaction of excited state xanthene dyes with TX-100. Similar plots are also obtained in the case of excited state interaction between xanthene dyes and CTAB. These results are presented in Table 2 along with the fluorescence characteristics of xanthene dyes in water as well as in micellar solution of TX-100 and CTAB. According to Mulliken's CT theory [24], the CT interaction in the excited state is prominent compared to the interaction in the ground state. The stability constants, both K_c and K_c^* of xanthene dye interaction with TX-100 support this (Tables 1 and 2). On the other hand, the stability con-

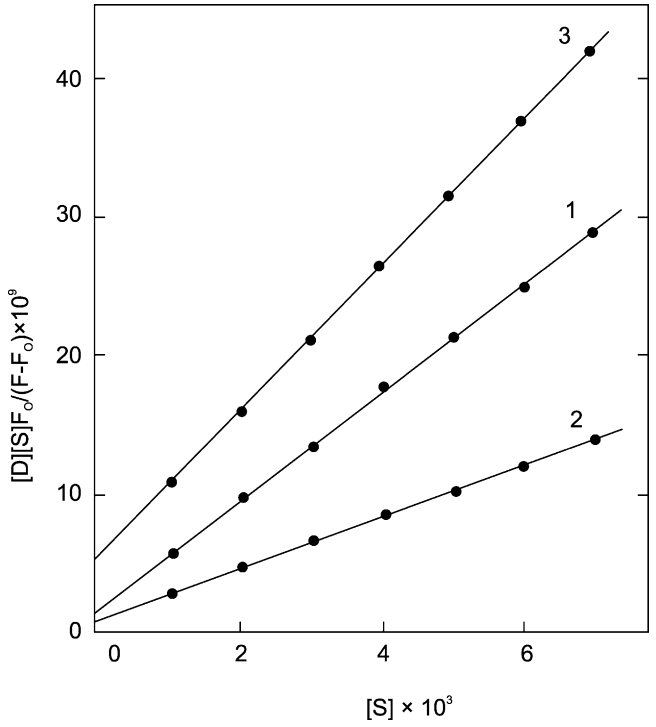


Fig. 5. Plots of [D] [S] $F_0/(F-F_0)$ against the concentration of TX-100 at 298 K. Here, D and S represent xathene dye and TX-100 and the numbers 1, 2, 3 refer to erythrosin B, rose bengal and eosin respectively. Concentration of xanthene dye: 1×10^{-5} mol dm^{-3} in all cases and concentration of TX-100 (mol dm^{-3}): 1×10^{-3} to 7.0×10^{-3}.

stants of xanthene dyes with CTAB are almost same in both excited and ground state.

A photovoltage generation has been observed on illumination of one compartment of the cell consisting of surfactant, TX-100 (1×10^{-2} mol dm^{-3}) and anionic xanthene dye (1×10^{-5} mol dm^{-3}) using platinum electrode in the illuminated compartment and counter saturated calomel electrode in the dark compartment. The illuminated electrode acts as an anode. The photovoltage attains a maximum value within a few minutes. The systems consisting of the anionic xanthene dyes in aqueous solution of the cationic surfactant CTAB and anionic surfactant SDS do not generate significant photovoltage. The growth and decay of photovoltage can be reproduced at least 5–6 cycles establishing the reversibility of the photoinduced effect. The photovoltage attained by the anionic xanthene dyes erythrosin B, rose bengal and eosin are 53, 43 and 33 mV, respectively. In these systems, the deoxygenation is not essential. It indicates that the excited state interaction between singlet xanthene dye and TX-100 is mainly responsible for the generation of photovoltage. The possible mechanism of photoinduced electron transfer from TX-100 (S) to singlet excited anionic xanthene dye (xanthene$^-$) leading to the generation of photovoltage in a photoelectrochemical cell is as follows,

$$\text{xanthene}^- + h\nu \rightarrow {}^1\text{xanthene}^- \tag{11}$$

$$\begin{aligned} {}^1\text{xanthene}^- + \text{S} &\rightarrow ({}^1\text{xanthene}^- \cdots \text{S} \leftrightarrow \text{xanthene}^{-2\bullet}\text{—}\text{S}^{+\bullet}) \\ &\rightarrow \text{xanthene}^{-2\bullet} + \text{S}^{+\bullet} \end{aligned} \tag{12}$$

$$\text{xanthene}^{-2\bullet} \rightarrow \text{xanthene}^- + \text{e}^- (\text{anode reaction}) \tag{13}$$

At the cathode compartment:

$$1/2\text{Hg}_2\text{Cl}_2 + \text{e}^{-\bullet} \rightarrow \text{Hg} + \text{Cl}^- \tag{14}$$

At the junction, i.e., platinum foil separator between anode and cathode compartments:

$$\text{S}^{+\bullet} + \text{Cl}^- \rightarrow \text{S} + 1/2\text{Cl}_2 \tag{15}$$

The platinum foil separator plays an important role since it prevents recombination of dye radical and $S^{+\bullet}$ by behaving as a double electrode [25,26], with oxidation in the dark compartment and reduction in the illuminated compartment. The overall forward (light) and backward (dark) reaction in the cell under continuous illumination in represented by

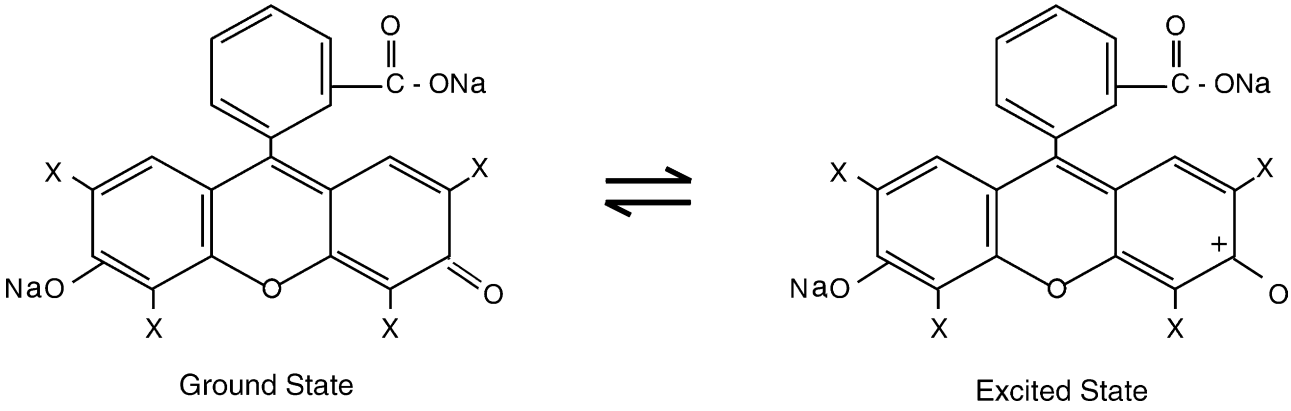
$$\text{xanthene}^- + \text{S} \underset{\text{dark}}{\overset{\text{light}}{\rightleftarrows}} \text{xanthene}^{-2\bullet} + \text{S}^{+\bullet} \tag{16}$$

Thus, the photoelectrochemical cell containing xanthene dye and TX-100 absorbs photon energy and this energy is partly converted into electrical energy by the electrode reactions through the formation of an excited state CT complex, (^{1}xanthene$^-\cdots$S $\leftrightarrow$ xanthene$^{-2\bullet}\cdots$ S$^{+\bullet}$) where S (TX-100)

Table 2
Excited state stability constant (K_c^*), fluorescence characteristics and open-circuit photovoltage of the systems consisting of xanthene dyes and surfactant in aqueous solution at 298 K

Dye	Excited state stability constant K_c^* (dm^3 mol^{-1})	Fluorescence characteristics		Shift $\Delta\bar{\nu}$ (cm^{-1})	Photovoltage (mV)
		In water λ_{max} (nm)	In surfactant λ_{max} (nm)		
(a) Xanthene dyes–Triton X-100					
Erythrosin B	2.54×10^3	545	558	428	53
Rosebengal	1.80×10^3	569	582	393	43
Eosin	0.87×10^3	540	551	370	33
(b) Xanthene dyes–CTAB					
Erythrosin B	7.35×10^2	545	556	363	
Rosebengal	6.55×10^2	569	580	334	
Eosin	5.73×10^2	540	549	304	

Concentration of dye used in each case is 1×10^5 mol dm^{-3} and concentrations of surfactants used are in the range 0.3×10^3 to 1×10^{-3} mol dm^3 in all cases.



Scheme 1.

acts as an electron donor and xanthene dye as an electron acceptor. The formation of an anion radical of xanthene dye (xanthene$^{-2\bullet}$) has been confirmed by flash photolysis spectra of erythrosin$^{-2\bullet}$, which shows the absorption around 400–420 nm region and this absorption increases with deoxygenation of the dye solution. In the case of CTAB with xanthene dyes the interaction is ionic in nature i.e., no electron transfer occurs when the system consisting of CTAB and xanthene dye is illuminated and there is no photovoltage generation.

From the thermodynamic and spectrophotometric results in the ground state, it can be concluded that the electron accepting abilities of xanthene dyes towards neutral surfactant TX-100 are in the order: eosin > rose bengal > erythrosin B. However, photoelectrochemical and fluorescence results in the excited state show the electron accepting abilities of the xanthene dyes are in the reverse order: erythrosin B > rose bengal > eosin. The resonating structures of erythrosin B and eosin may be represented as follows in the ground and excited states (Scheme 1):

Where *X* is I for erythrosin B and Br for eosin. The acceptor strength of the dye in the excited state will depend on the creation of the positive centre, where the surfactant molecule will attach itself. In the case of eosin, which is bromo-substituted, the positive centre will be less stable compared to that of erythrosin B, which is iodo-substituted, due to the fact that bromine is more electronegative than iodine. Thus, erythrosin B will be a better acceptor than eosin in the excited state.

In the ground state, however, the surfactant molecule attaches itself to the oxygen atom of the dye molecule. When *X* is bromine, the electron density on the oxygen atom will decrease as bromine will pull the electron pair towards the benzene ring. This will be more pronounced for bromine than for iodine, as the former is more eletronegative than the latter. Thus, eosin is a better acceptor than erythrosin B in the ground state. The nature of interaction of the xanthene dyes with different surfactants is different; they undergo CT interaction with neutral surfactant TX-100, ionic or electrostatic interaction with cationic surfactant CTAB and no interaction with anionic surfactant SDS. Surfactants in water form ordered aggregate structure (micelles) above a given concentration. Results indicate that the surface formation in micelle of surfactant is a necessary criterion for complex formation between dye and surfactant. The interface (micelle/water) catalyses the complex formation due to adsorption of dye from solution. From the results we can conclude that a good correlation has been found among the photovoltage generation of the systems, spectral shifts (both absorption and fluorescence) due to complex formation and thermodynamic properties of these complexes.

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