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Journal of Photochemistry and Photobiology A: Chemistry 97 (1996) 57–63

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A:CHEMISTRY

Visible and fluorescence spectral studies on the interaction of Safranine T with reverse micelles of Triton X-100 and Tweens in chloroform

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Received 19 September 1995; accepted 9 January 1996

Abstract

The visible spectra of Safranine T in reverse micelles indicate 1:1 (dye:reverse micelle) charge transfer complex formation with the non-ionic surfactants Triton X-100, Tween 20, Tween 40, Tween 60 and Tween 80. The complexing strength follows the order Tween 80 > Tween 60 > Triton X-100 > Tween 40 > Tween 20. The fluorescence spectrum of the dye is also enhanced by the reverse micellar solution confirming the formation of 1:1 complex having comparable complexing strength as revealed from the ground state spectra. The equilibrium constants of the dye–reverse micelle complex are directly proportional to the carbon number of the non-polar tail of Tweens and their aggregation number. The latter has been determined together with the critical micelle concentrations of the reverse micelles as well as their core polarities.

Keywords: Safranine T; Reverse micelle; Fluorescence; Absorbance; Critical micelle concentration; Aggregation number

1. Introduction

Photophysical processes may exhibit special characteristics at the interfaces. The micelles produce non-polar–polar interfaces where absorption and emission properties of dyes etc. become enhanced or quenched. Such phenomena may in most occasions be conveniently exploited to account for the nature and strength of the interaction as well as establishing physicochemical characteristics of the surfactants, i.e. critical micelle concentration (CMC), aggregation number, micellar polarity etc. In the literature, studies on dye–surfactant interaction in aqueous (polar) media are found in abundance [1–10]; quantification of results on the basis of appropriate equations has also been reported [3,9,10]. Very recently, we have worked on the interaction of the dye Safranine T (ST) with the surfactant micelles of cetyl trimethyl ammonium bromide, sodium dodecylsulphate, *tert*-butyl phenyl polyoxyethylene ether (Triton X-100) and polyoxy ethylene sorbitan monolaurate, mono palmitate, mono stearate and monooleate (Tweens 20, 40, 60 and 80 respectively); the characteristics of the normal micelles and their interactions with ST have been reported [9,10]. In a separate study [11], we have examined the photophysical behaviours of ST in polyethylene glycols (PEGs) of varying molar masses which constitute the polar head groups of Triton X-100 and Tweens and many other non-ionic surfactants. The interaction characteristics of the ST–PEG systems have been quantitatively estimated.

It is known that the polar–non-polar interface of reverse micelles differs from that of the normal micelles; the interior water core may exhibit properties different from those of bulk water [12,13]. The acid–base equilibria (manifested in p*K*) may be significantly influenced by the reverse micelles [12,13]; the kinetics of hydrolytic, oxidation and reduction reactions may also be significantly influenced by reverse micelles [14,15]. There are reports on studies of the photophysical properties in reverse micellar media [16–19].

In continuation of our interest in the photophysical studies using ST as the probing component, we herein report the absorption and emission characteristics of the dye in reverse micellar systems of the Tweens (20, 40, 60 and 80) and Triton X-100 in chloroform medium. The ST has very low solubility in $CHCl_3$ and high solubility in water. The aqueous dye solution added in the $CHCl_3$–Tween mixture formed the aqueous core of the reverse micelles and the photophysical changes observed can, therefore, be recognized as consequences of the influence of the $CHCl_3$–H_2O interface and the water pool of the reverse micelles.

2. Experimental details

ST (E. Merck) was crystallized twice from ethanol–water before use. The surfactants octylphenylpolyoxyethylene

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PII 1010-6030(96)04308-0

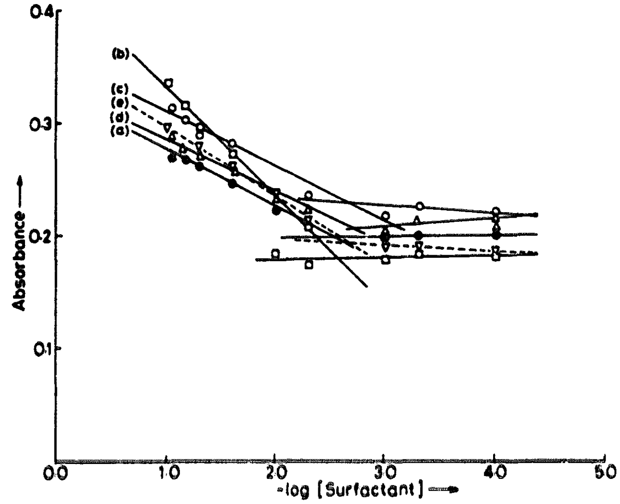

Fig. 1. Plot of absorbance vs. log [S] at 520 nm at 298 K: curve a, Tween 20; curve b, Tween 40; curve c, Tween 60; curve d, Tween 80; curve e, Triton X-100.

ether (Triton X-100), polyoxyethylene sorbitan monolaurate (Tween 20), polyoxyethylene sorbitan monopalmitate (Tween 40), polyoxyethylene sorbitan monostearate (Tween 60) and polyoxyethylene sorbitan monooleate (Tween 80) were either BDH or Sigma products. Their characteristics and purity standards were the same as reported previously [20,21]. Doubly distilled conductivity water was used for solution preparation. Spectroscopic grade chloroform from E. Merck was used. Chloroform was dried according to standard procedures and purified by fractional distillation. The presence of impurities was checked by emission and they were found to be absent.

Absorption spectra were recorded using a Shimadzu (Japan) 160A UV–visible spectrophotometer with a matched pair of silica cuvettes. Fluorescence spectra were measured using a Fluorolog F111 A spectrofluorimeter (Spex Inc., NJ, USA) with a slit width of 2.5 nm. All spectral measurements were duplicated in a constant temperature water bath accurate to within ±0.1°C, and the mean values were processed for data analysis.

3. Results

3.1. The critical micelle concentration

The CMC of reverse micelles of the non-ionic surfactants in $CHCl_3$ was determined from spectral measurements. The absorbances of ST at different concentrations of the surfactant were measured and the absorbance vs. log [S] plot yielded two straight lines; the point of their intersection corresponded to the CMC. Such graphical representations are shown in Fig. 1. They indicate decreased CMC with increased hydrophobic tail in the Tweens. The CMC values are presented in Table 1.

3.2. Absorption behaviour of the dye in reverse micelles

The absorption spectra of ST in reverse micelles of Triton X-100 and Tweens are presented in Fig. 2(a). The dye ST exhibits a maximum absorption at 518 nm with an extinction coefficient ϵ of 16 000 $dm^3\ mol^{-1}\ cm^{-1}$ at 295 K in chloroform. In the reverse micelle, there is an enhancement in the absorbance with a bathochromic spectral shift of 20 nm. Fig. 3 represents the absorption spectra of the dye in Tween 60 surfactant in chloroform. The change in the spectrum of the dye itself to that of the complex (formed by its interaction with the reverse micelle) passes through an isosbestic point. This supports the formation of a 1:1 dye–reverse micelle complex.

The analysis of the complexing equilibrium was performed according to the following rationale. The reverse micelle is considered to be in "pseudophase" (i.e. the monomer concentration is constant and equal to the CMC); its concentration is then equal to $([S]-[M]_C)/n$, where [S] is the concentration of the surfactant, $[M]_C$ is the CMC and n is the aggregation number. Since [S] was kept much larger than the CMC, the micellar concentration in chloroform was virtually equal to $[S]/n$. The following dye–micelle equilibrium was considered.

$$D+M\ (\text{or } S/n) \overset{K_c}{\rightleftharpoons} DM \tag{1}$$

where D, M and DM represent the dye, micelle and 1:1 dye–micelle complex respectively, and K_c is the complexation constant. For the determination of K_c, the modified equation of Lang [22] was used.

$$\frac{[D]\ell}{n(\epsilon-\epsilon_0)}=\frac{1}{\epsilon_c-\epsilon_0}\left([A]+[D]-\frac{\epsilon-\epsilon_0}{\epsilon_c-\epsilon_0}[A]\right)+\frac{1}{K_c(\epsilon_c-\epsilon_0)} \tag{2}$$

where ϵ_c, ϵ and ϵ_0 are the extinction coefficients of the complex, the dye–surfactant mixture and the non-aqueous dye solution respectively at the absorption maximum of the complex. [A] and [D] are the initial molar concentrations of ST and the surfactant respectively and ℓ is the path length (1 cm in the present experiment).

Since [S] was 10^3 times or more greater than [ST], Eq. (2) reduces to the form

$$\frac{[D]}{\epsilon-\epsilon_0}=\frac{[D]}{\epsilon_c-\epsilon_0}+\frac{1}{(\epsilon_c-\epsilon_0)K_c} \tag{3}$$

which is the same as that deduced by Ketelaar et al. [23]. The plots of $[D]/(\epsilon-\epsilon_0)$ against [D] were found to be linear (Fig. 4) suggesting a 1:1 D–RM complex. ϵ_c and K_c were evaluated from the slopes and intercepts of the linear plots based on a least-squares procedure according to Eq. (3). The results are presented in Table 1. A relation similar to Eq. (3) derived on the basis of a 2:1 D–RM complex could not fit the experimental data further, supporting the formation of a 1:1 complex. It is shown in Section 3.3 that the fluorescence data also supported a 1:1 complex.

The 1:1 D–RM complexes formed with different degrees of affinity; the K_c values follow the order Tween 80 > Tween 60 > Triton X-100 > Tween 40 > Tween 20. Since the Tweens possess identical head groups, the differences in their reactivity may be ascribed to the hydrocarbon chain lengths. With increase in the hydrocarbon chain length the sizes of the reverse micelles increase and so also do their aggregation numbers. K_c varies linearly with the carbon number n_C of the non-polar tails of the Tweens. The profile is shown in Fig. 5(a). It fits in the equation

$$\log K_c = 3.18 + 0.108 n_C \tag{4a}$$

for absorption or

$$\log K_c = 3.52 + 0.111 n_C \tag{4b}$$

for emission.

The value of the intercept refers to log K_c at zero carbon number of the hydrophobic end of the reverse micelles. This may indicate the complexing interaction of ST with the hydrophilic polyoxyethylene head groups of the Tweens.

3.3. Fluorescence behaviour of the dye–reverse micelle systems

The emission spectra of ST in reverse micelle of Triton X-100 and Tweens are presented in Fig. 2(b). The enhancement of the fluorescence intensity of the dye in reverse micellar media is illustrated in Fig. 6. The dye resides in the inner core of the reverse micelles (solubility of ST is poor in $CHCl_3$) and undergoes a changed state of emission on excitation at 518 nm. The fluorescence intensity F of ST at a constant concentration is enhanced in the reverse micelles of Tweens and Triton X-100. With increase in RM concentration, F increases forming a plateau. Assuming that the dye forms a 1:1 D–RM complex, $F_{max} - F_0$ (where F_0 is the fluorescence intensity of D in the absence of micelles and F_{max} corresponds to the maximum intensity at large concentration of micelles) can be considered to be proportional to [complex]. Thus

$$F_{max} - F_0 = K[D_{comp}] \tag{5}$$

where K is the proportionality constant and $[D_{comp}]$ is the concentration of the dye in the complexed form (i.e. the total dye in the present context).

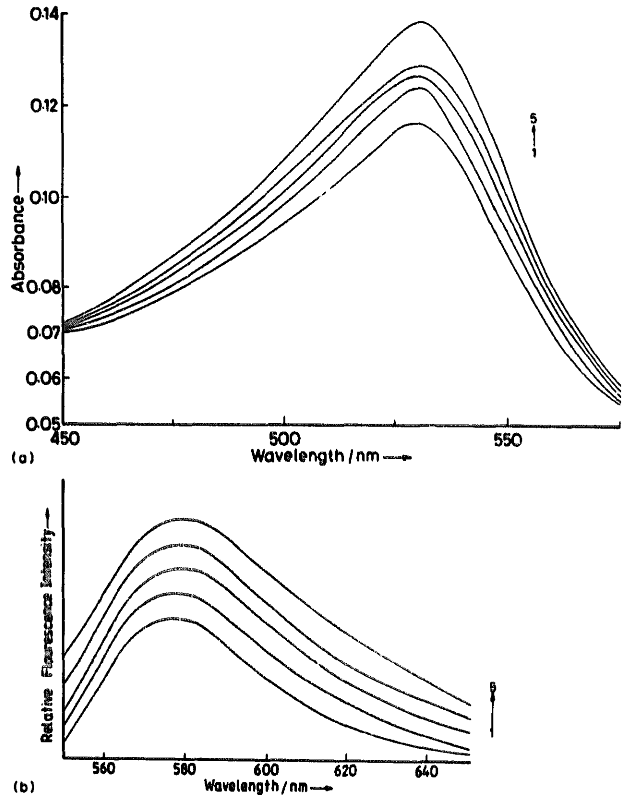

Fig. 2. (a) Absorption spectra of the dye in different reverse micelles at 298 K at $[ST] = 6.082 \times 10^{-6}$ mol dm^{-3}: spectrum 1, Tween 20; spectrum 2, Tween 40; spectrum 3, Tween 60; spectrum 4, Tween 80; spectrum 5, Triton X-100. (b) Emission spectra of the dye in different reverse micelles at 298 K at $[ST] = 6.082 \times 10^{-6}$ mol dm^{-3}: spectrum 1, Tween 20; spectrum 2, Tween 40; spectrum 3, Tween 60; spectrum 4, Tween 80; spectrum 5, Triton X-100.

The F value at any stage other than F_{max} can be related similarly to the complexed dye $[D'_{comp}]$ as

$$F - F_0 = K[D'_{comp}] \tag{6}$$

Combining Eqs. (5) and (6), we have

$$\frac{[D'_{comp}]}{[D_{comp}]} = \frac{F - F_0}{F_{max} - F_0} = F_R \tag{7}$$

Therefore, the ratio of the enhanced fluorescence intensity at any stage to its maximum value is a measure of the fraction of the dye in the complexed form. Using the complexation

Table 1
Binding constants, aggregation number and critical micelle concentration values of the reverse micelles at 298 K

Surfactant	$K_c \times 10^{-5}$ (dm^3 mol^{-1}) for absorption	$K'_c \times 10^{-5}$ (dm^3 mol^{-1}) for emission	n	CMC × 10^3 (mol dm^{-3})
Triton X-100	1.45 (3.5)	1.3 (2.2)	145 (135)	2.18 (0.25)
Tween 20	0.21 (2.0)	0.8 (3.0)	117 (86)	2.66 (0.05)
Tween 40	0.35 (2.6)	1.0 (3.6)	163 (91)	2.63 (0.023)
Tween 60	1.15 (4.0)	2.0 (4.2)	182 (111)	1.99 (0.021)
Tween 80	2.07 (5.2)	3.0 (4.8)	204 (123)	1.90 (0.01)

Values in parentheses refer to results obtained for ST interaction with normal micelles [10].

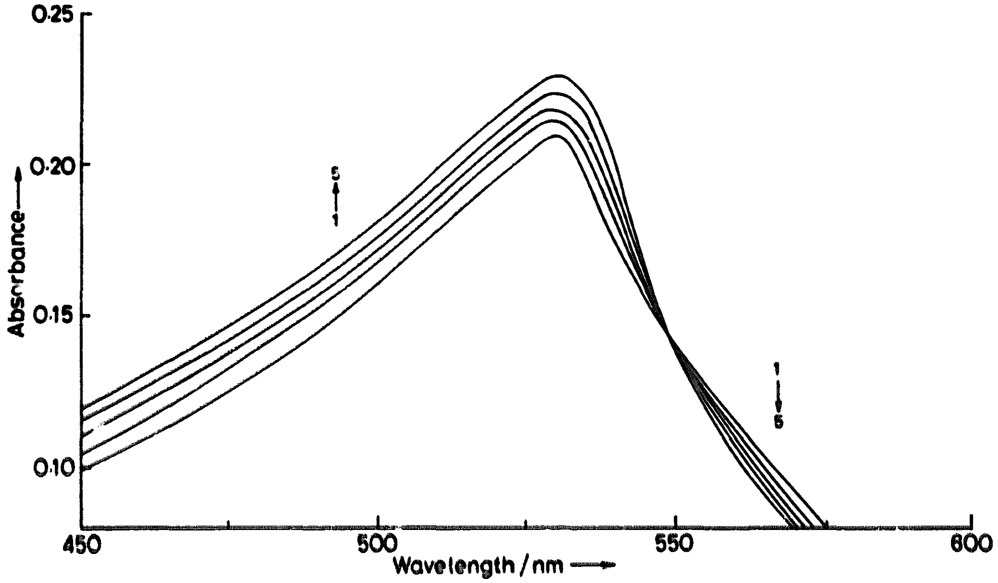

Fig. 3. Absorption spectra of the dye in Tween 60 surfactant in chloroform at 298 K ([ST] = 6.685×10^{-6} mol dm^{-3} for the following values of [Tween 60] ($\times 10^{-3}$ mol dm^{-3})): spectrum 1, 0.0; spectrum 2, 1.0; spectrum 3, 3.0; spectrum 4, 5.0; spectrum 5, 6.0.

equilibrium (1) and the same model as reported earlier, [10], we obtain

$$\frac{1}{1-F_R} = \frac{K'_c}{n}\frac{[S]}{F_R} - K'_c[D_T] \tag{8}$$

A plot of $1/(1-F_R)$ vs. $[S]/F_R$ should be linear to yield K_c and n from the intercept and the slope respectively. The fluorescence results treated in this manner (Fig. 7) have yielded K_c values that fairly compare with those K_c found using visible spectral measurements (Table 1). The K_c and n values are also reported in Table 1. The log K_c (also log K'_c) vs. aggregation number plots for the Tweens are exemplified in Fig. 5(b). The correlation is fairly linear and the results fit the equations,

$$\log K_c = 3.04 + 0.011 n_{agg} \tag{4}$$

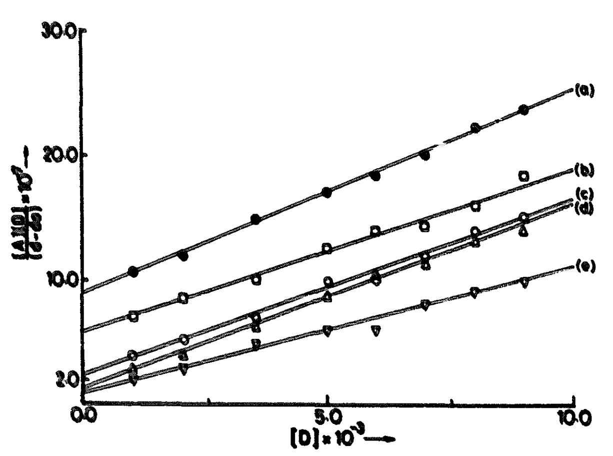

Fig. 4. Plot of $[A][D]/(d-d_0)$ vs. [D] from absorption curve: curve a, Tween 20; curve b, Tween 40; curve c, Tween 60; curve d, Tween 80; curve e, Triton X-100.

for absorption and

$$\log K'_c = 3.56 + 0.009 n_{agg} \tag{9}$$

for emission.

3.4. Solvent parameters

In the pure solvents acetonitrile, ethanol, dioxane, formamide, tetrahydrofuran, ethyleneglycol and acetone, the visible spectral transitions of ST occur in the range 524–535 nm [24] which is 526–530 nm in reverse micelles. The emission maxima in the two types of media occur in the ranges 565–587 nm and 577–580 nm respectively.

The spectral shifts $\Delta\bar{\nu}$ of ST in various solvent systems, studied earlier [15], are correlated with the Kosower Z values and the transition energies $E_T(30)$ for intramolecular charge transfer in Fig. 8; this is a reproduction of an earlier presentation. Except for dioxan the correlations of $\Delta\bar{\nu}$ with both Z and $E_T(30)$ are fairly linear. However, the $\Delta\bar{\nu}$ values of the solvents do not exhibit a direct correlation with the dielectric constant D. Assuming that similar correlations of $\Delta\bar{\nu}$ with both Z and $E_T(30)$ values also hold in reverse micelles, the Z and $E_T(30)$ values for the micellar media have been found using the measured $\Delta\bar{\nu}$ values from the appropriate lines in Fig. 8. The values are presented in Table 2. Since $\Delta\bar{\nu}$ does not bear a direct correlation with the dielectric constant D, an indirect method has been adopted for its evaluation in reverse micellar solution. It has been observed [24] that D bears a linear correlation with both Z and $E_T(30)$ (illustrations not shown). For the reverse micellar systems the above-derived Z and $E_T(30)$ values have been used to estimate the corresponding D values from the linear plot (not shown) between either D and Z or D and $E_T(30)$ as has been done earlier [24] for normal micellar systems. The D values realized are presented in Table 2.

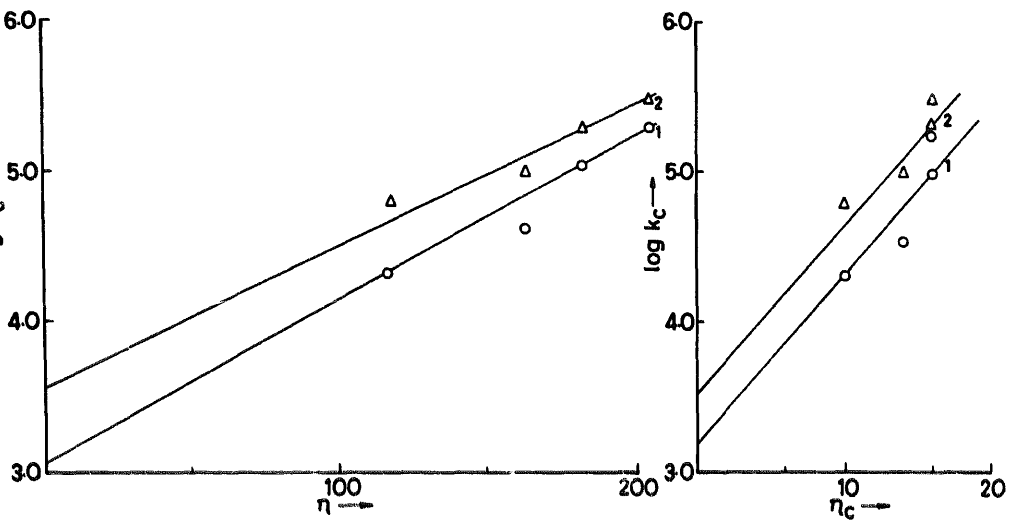

Fig. 5. (a) Plots of log K_c vs. number of carbon atoms in the nonpolar tails: curve 1, absorption; curve 2, emission. (b) Plots of log K_c vs. aggregation number: curve 1, absorption; curve 2, emission.

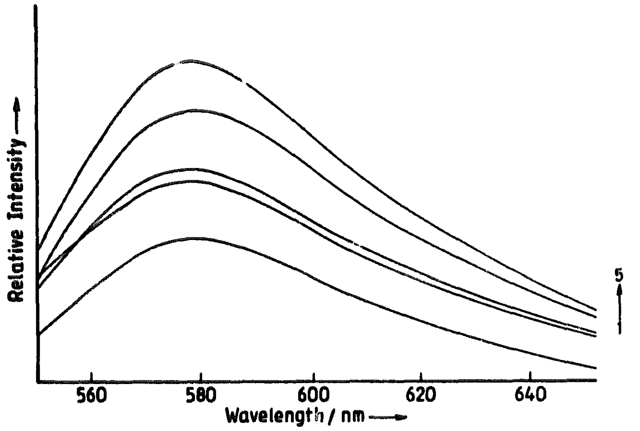

Fig. 6. Emission spectra of the dye in Tween 60 surfactant in chloroform at 298 K ([ST] = 6.685×10^{-6} mol dm^{-3}) for the following values of [Tween 60] ($\times 10^{-3}$ mol dm^{-3}): spectrum 1, 0.0; spectrum 2, 1.0; spectrum 3, 3.0; spectrum 4, 5.0; spectrum 5, 6.0.

4. Discussion

D–RM complex (1:1) formation is established from both ground and excited state properties. The association constant values are also of the same magnitude in the two states. Earlier publications [25–28] on molecular complexes of dyes and other electron acceptors with surfactants in micellar and reverse micellar media have not considered the micelles or reverse micelles to be the reacting entities; the surfactant molecules have been taken as the interacting species. Spectral shifts and equilibrium constants of low magnitude have been obtained and the interactions have been considered to be of charge transfer type. In line with the earlier work and our observations, the bathochromic spectral shift of ST in RM supports charge transfer interaction; the appearance of this shift above the CMC has indicated that the micelles are active species in this interaction. The location of the interaction is the micellar core where the dye resides to generate the photophysical phenomenon. This is supported by the high solubility of ST in water and very low solubility in chloroform. Since the interacting entities are RMs, the equation

$$D + \frac{S}{n} \rightleftharpoons \text{Complex}$$

is appropriate for the evaluation of K_c and K'_c from ground and excited state measurements according to Eqs. (3) and (8) respectively. As in normal micelles [10], log K_c and log K'_c bear linear relations with the aggregation number n.

Since the Stokes shift of ST occurs as a result of association of the surfactant molecules in the form of reverse micelles in non-aqueous solvent, it is also expected to be a function of n. In Fig. 9, $\Delta\bar{\nu}$ is plotted against n. An inverse relation

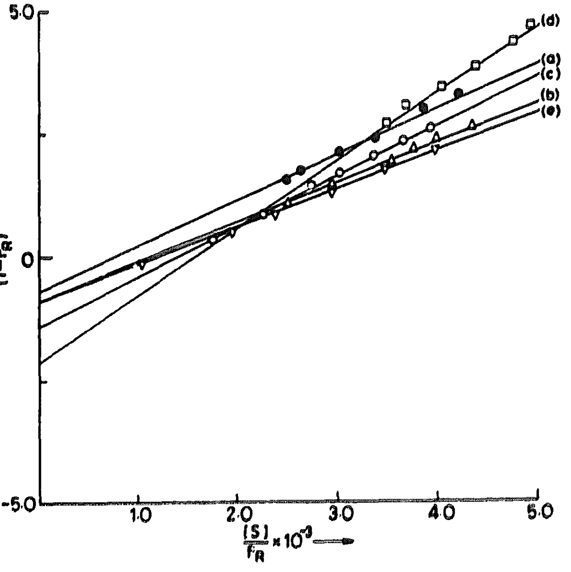

Fig. 7. Plot of $(1-F_R)^{-1}$ vs. $[S]/F_R$ from emission results: curve a, Tween 20; curve b, Tween 40; curve c, Tween 60; curve d, Tween 80; curve e, Triton X-100.

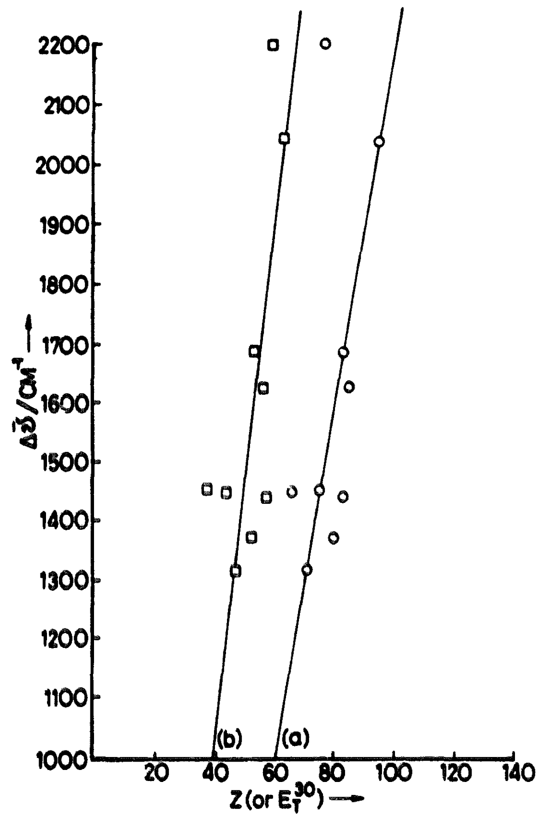

Fig. 8. Plot of $\Delta\bar{\nu}$ vs. (a) Kosower Z value and (b) $E_T(30)$ for various solvents.

between $\Delta\bar{\nu}$ and n is observed in which the Tweens correlate well with the line from which Triton X-100 deviates. The results suggest that increased population of the head group has a reverse effect on the Stokes shift. Triton X-100 deviates from this relationship because of the different molecular structure of the amphiphile (the average number of polyoxyethylene residues in the head group of Triton X-100 is 9.5, whereas in the Tweens it is 20).

In Table 1, the K_c, K'_c, n and CMC values obtained for D–RM interaction in reverse micelles of Triton X-100 and Tweens are compared with those obtained for normal micelles. The K_c values in reverse micelles are distinctly lower. The aggregation numbers are significantly higher and so the CMCs. Interactions with lower K_c (and K'_c) and higher n and CMC are envisaged. It has been reported [11] that the number of polyoxyethylene groups ($-CH_2-CH_2-O-$) is a deciding factor for ST interaction with PEG in aqueous medium. This has also been found to be the rationale for the trends in both K_c and K'_c in the RM environment. The dye ST resides in the interior (core) of the RM and undergoes charge transfer interaction with the polar polyoxyethylene ($-CH_2-O-CH_2-$) head groups; increased concentration (because of increased n where n is the aggregation number) may result in increased K_c and K'_c. The interior of the RM has a higher polarity than that of normal micelles (as manifested in the derived D values). This has included weaker charge transfer interaction in RMs compared with normal micelles (NMs) (Table 3). The lower fluidity of the core region of RMs may have a reducing effect on photooxidation and photoreduction processes compared with aqueous media. However, a comparison between the efficacies of the process in normal and reverse micellar solution may not be out of place. The Tweens have identical head groups composed of twenty polyoxyethylene (POE) moities which essentially undergo interaction with ST; their non-polar tails (although different) are not directly involved in the process. Whether it is normal or reverse micelles, the number of POE groups in a micelle should primarily contribute to the efficiency of the process. The total number of POEs in a Tween micelle is equal to 20. Division of the average of K_c and K'_c by 20 offers the contribution per POE group to the binding extent. Such results on normal and reverse micelles are compared in the fifth column of Table 3. The results reveal significant lowering of the binding constants in a reverse micellar medium. The compartmentalized aqueous medium has adversely

Table 2
Spectral characteristics of Safranine T in various media and solvent parameters

Medium	$\bar{\nu}_a$ (cm^{-1})	$\bar{\nu}_f$ (cm^{-1})	$\bar{\nu}_a - \bar{\nu}_f$ (cm^{-1})	Z (kcal mol^{-1})	D	$E_T(30)$
ACN	19048	17730	1318	71.3	37.4	46.0
AC	19084	17637	1447	65.7	20.7	43.2
EL	18762	17391	1371	79.6	24.6	51.9
EG	18762	17152	1610	85.1	40.7	56.3
DX	19231	17036	2195	76.7	2.2	49.0
Water	19157	17123	2034	94.6	78.5	63.1
FA	18797	17361	1436	83.3	109.5	56.6
THF	18692	17241	1451	75.0	76.0	37.4
Triton X-100	18957	17331	1626	81.0	27.0	43.5
Tween 20	19011	17361	1650	82.0	31.0	44.0
Tween 40	18957	17331	1626	81.0	27.0	43.5
Tween 60	18921	17331	1590	80.0	24.0	43.0
Tween 80	18857	17331	1526	81.0	27.0	43.5

ACN, acetonitrile; AC, acetone; EL, ethanol; EG, ethylene glycol; DX, dioxane; FA, formamide; THF, tetrahydrofuran.

Table 3
Comparison of behaviours of normal and reverse micelles for the charge transfer interaction with Safranine T at 298 K

Surfactant	n		D		$\bar{K}_c \times 10^{-5}$ (dm^3 mol^{-1})		$(\bar{K}_c/n) \times 10^{-2}$ (dm^3 mol^{-1})	
	RM	NM	RM	NM	RM	NM	RM	NM
Triton X-100	145	135	27	5	1.38	2.8	9.52	19.31
Tween 20	117	86	31	12	0.05	2.5	0.43	21.36
Tween 40	163	91	27	12	0.68	3.1	4.17	19.01
Tween 60	182	111	24	5	1.58	4.1	8.68	22.52
Tween 80	204	123	27	5	2.53	5.0	12.40	40.65

NM, normal micelle; RM, reverse micelle; $\bar{K}_c$, average binding constant (average of K_c and K_c').

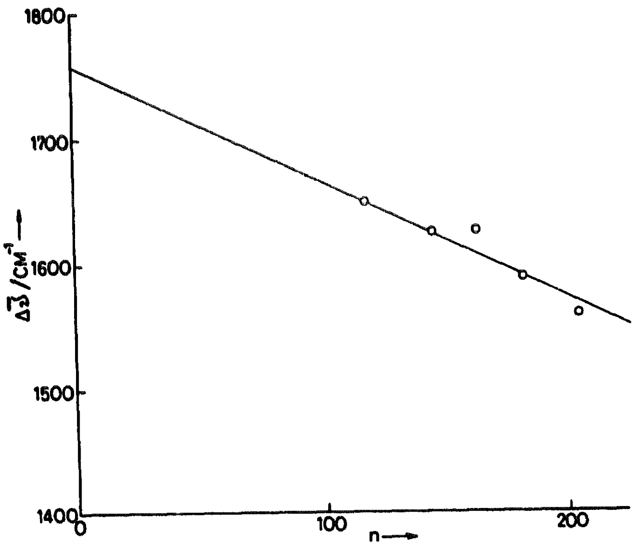

Fig. 9. Plot of $\Delta\bar{\nu}$ vs. average aggregation number $\bar{n}$ of various surfactants.

affected the D–RM interaction process. The physical chemical state of the core water in RM is distinctly different from the aqueous environment in the interfacial region of normal micelles in terms of influencing the transfer of charge between ST and the POE centres. The polarity of the aqueous core of RMs has been found to be greater than that of the interfacial region of the normal micelle (results shown in Table 3). This may be an important reason for the comparatively retarded charge transfer process in the former.

Acknowledgement

One of the authors (S. Nandi) thanks the Physical Chemistry Section of the Department of Chemistry of Jadavpur University for laboratory facilities.

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