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Spectroscopic studies of the interaction of the dye safranine T with Brij micelles in aqueous medium

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Abstract

The visible spectra of safranine T (ST) in micellar solutions of Brij 52, Brij 56 and Brij 58 indicate 1 : 1 charge transfer complex formation of ST with non-ionic Brij micelles. The complexing strength follows the order Brij 52 > Brij 56 > Brij 58. The fluorescence spectra of ST in micellar solutions of Brij also support 1 : 1 ST–micelle complex formation as in the ground state. The equilibrium constant of the dye–micelle complex is directly proportional to the micellar aggregation number and inversely proportional to the surfactant critical micellar concentration (CMC). The solvent parameters, i.e. the Kosower Z value, intramolecular charge transfer energy E_T^{30} and dielectric constant of the micellar medium, were evaluated. The binding constant, micellar aggregation number and solvent parameters remain constant over a certain range of Brij concentration, but vary beyond this range. © 1997 Elsevier Science S.A.

Keywords: Absorbance; Brij micelles; Fluorescence; Solvent parameters; Safranine T

1. Introduction

Dyes interact with surfactants in solution forming micellar complexes having characteristic physicochemical features [1,2]. The dye safranine T (ST) forms 1 : 1 charge transfer complexes with non-ionic and ionic micelles [3]. The non-ionic surfactants studied have included Triton X-100 and Tweens (Tween 20, 40, 60 and 80; esters of long-chain fatty acids containing sorbitan-linked, fixed polyethylene oxide (POE) groups (20) as the polar head). The complexing strengths of the Tween micelles follow the order Tween 80 > Tween 60 > Tween 40 > Tween 20, i.e. increasing length of non-polar tail has an increasing effect on the interaction. To understand the role of the POE group on the charge transfer interaction between ST and Tweens, a detailed study [4] of the interaction of ST with polyethylene glycols (PEGs) with varying degrees of polymerization has been performed, and the efficiency has been found to depend on the number of ethylene oxide (EO) residues [5–8]. The bound POE groups in Tweens show lower activities than the free POE groups in PEGs [1]. Since, in Tweens, the number of POE groups is fixed and the polymethylene non-polar tail varies in length, the ST–micelle interaction with Brij, in which the non-polar tail is fixed and the POE head group varies, would be physicochemically interesting to obtain a better understanding of the involvement of the POE moiety under different chemical conditions.

In this investigation, the ground and excited state spectral properties of the photosensitive dye ST have been studied in the micellar media Brij 52, Brij 56 and Brij 58 in order to obtain an understanding of the nature and extent of interaction (complex formation) in solution. The observed spectral shifts have been analysed as in previous studies [1–12] and used for the evaluation of the solvent parameters, i.e. Kosower Z value, intramolecular charge transfer energy E_T^{30} and medium dielectric constant D. The results obtained in aqueous Tween micelles, PEG and Brij micelles have been compared.

2. Experimental details

ST (E. Merck, Germany) was crystallized twice from an ethanol–water mixture. Brij 52, Brij 56 and Brij 58 were Aldrich (USA) products. Doubly distilled conductivity water was used for solution preparation.

Absorption spectra were recorded using a Shimadzu (160 A) UV–visible spectrophotometer with a matched pair of silica cuvettes (path length, 1 cm). Fluorescence spectra were measured using a Fluorolog F 111 A spectrofluorometer (Spex. Inc, NJ, USA) with a slit width of 2.5 nm. The excitation and emission wavelengths were 520 and 586 nm

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respectively. All spectral measurements were duplicated in a constant-temperature water bath at 300 K (accurate within ±0.5 °C), and the mean values were processed for data analysis.

The viscosity of aqueous solutions of Brij (10^{-3} mol dm^{-3}) was measured in a calibrated Ostwald viscometer (flow time of 125 s for 15 ml of water at 300 K).

3. Results and discussion

3.1. Critical micellar concentration (CMC) of Brij

The absorbance of ST increases with [Brij]. The ratio of the absorbance in the presence of Brij (A) to that in the absence of Brij (A_0) at the absorbance maximum (520 nm), when plotted against log [Brij] (Fig. 1), shows a break in the linear plot. This break is considered to be the CMC of Brij. The values are given in Table 1; they correspond nicely with the literature values obtained by other methods.

3.2. Absorption behaviour of the ST–Brij system

In the presence of non-ionic Brij, there is an enhancement in the absorption with a bathochromic spectral shift at a surfactant concentration above the CMC. Fig. 2 shows the spectral features of ST in aqueous Brij solution. The spectrum of the ST–Brij system exhibits two isosbestic crossings at 437 and 500 nm, supporting the formation of a 1 : 1 dye–micelle complex similar to that reported for ST–Tween micellar systems [3].

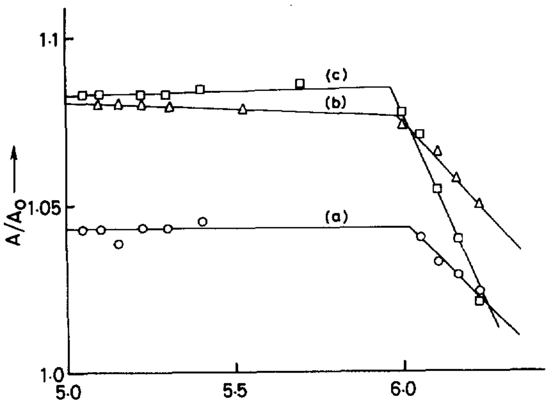

Fig. 1. Plot of A/A_0 vs. log [Brij] at 300 K: (a) Brij 52; (b) Brij 56; (c) Brij 58.

For the quantification of the complexation process, the surfactant (D) micelle has been considered to be in the pseudophase, i.e. the monomer concentration is constant and equal to the CMC. The concentration of the micelle is then equal to $([D]-\text{CMC})/n$, where n is the micellar aggregation number. In actual practice, $[D] \gg \text{CMC}$; the micellar concentration [M] then equals $[D]/n$. For the interaction of the dye with the micelle, the following complexation equilibrium is considered

$$A+M\ (\text{or } D/n) \overset{K_c}{\rightleftarrows} DM \qquad (1)$$

where A, M and DM represent the dye, micelle and dye–micelle complex respectively and K_c is the complexation constant. For the determination of K_c, the modified equation of Lang [13] has been used

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

where the new terms D, l, A, ϵ_0, ϵ and ϵ_c represent the surfactant, path length, dye and extinction coefficients of the dye in water, the dye in the presence of micelle and the complex respectively.

Comparable K_c values are obtained using the Benesi–Hildebrand equation [14]. In processing the results, the n values derived from the fluorescence measurements and reported in the next section were used. The results presented in Fig. 3 show that two sets of straight lines are obtained for all the Brij micelles in the concentration ranges 1–5 mmol dm^{-3} and 5.5–9 mmol dm^{-3}. The K_c values derived from the slope and intercept of the straight lines are presented in Table 1. At higher [Brij], ST binds strongly with Brij micelles.

The dye–micelle complexes have different degrees of affinity following the order: Brij 52 > Brij 56 > Brij 58. The cationic ST is located in the polar aqueous mantle of the Brij micelles and can undergo charge transfer interaction with the POE groups. The order of the binding constant (K_c) repre-

Table 1
CMC, n, K_c and K'_c for Brij and ST–Brij micelles at 300 K

Surfactant	Absorption		Emission		$K_c^{\text{ave}} \times 10^{-4}$ (dm^3 mol^{-1})
	CMC × 10^6 (mol dm^{-3})	$K_c \times 10^{-4}$ (dm^3 mol^{-1})	$K'_c \times 10^{-4}$ (dm^3 mol^{-1})	n	
Brij 52	0.955	2.0^a	1.61^a	54	1.81^a
		11.11^b	10.18^b	182	10.65^b
Brij 56	1.05	1.48^a	1.46^a	32	1.47^a
		9.30^b	9.09^b	141	9.20^b
Brij 58	1.07	0.69^a	0.70^a	12	0.70^a
		7.50^b	7.32^b	92	7.41^b

^{a}[Brij] = 1–5 mmol dm^{-3}.
^{b}[Brij] = 5.5–9 mmol dm^{-3}.

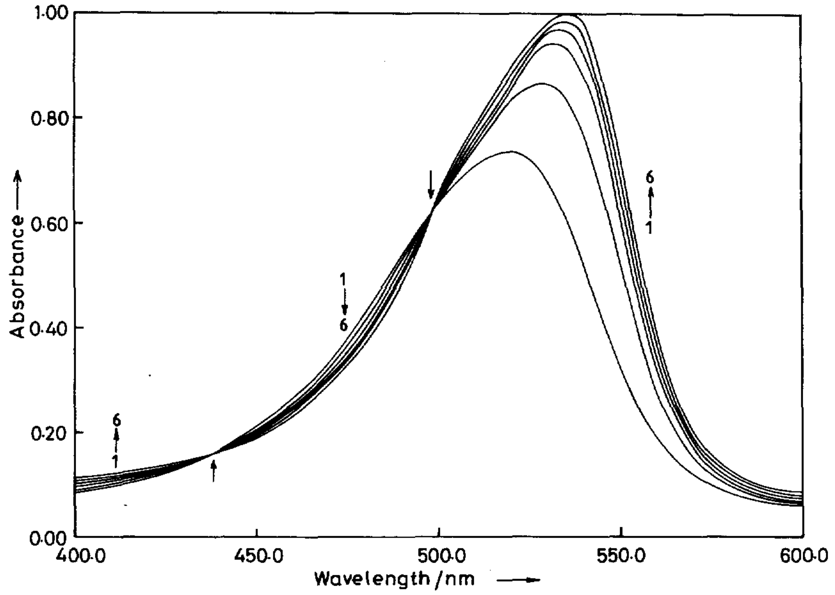

Fig. 2. Visible absorption spectra of ST in aqueous Brij 58 solution at 300 K. [ST] = 10 μmol dm^{-3}. Curves 1–6 represent [Brij] = 0–5.0 mmol dm^{-3}.

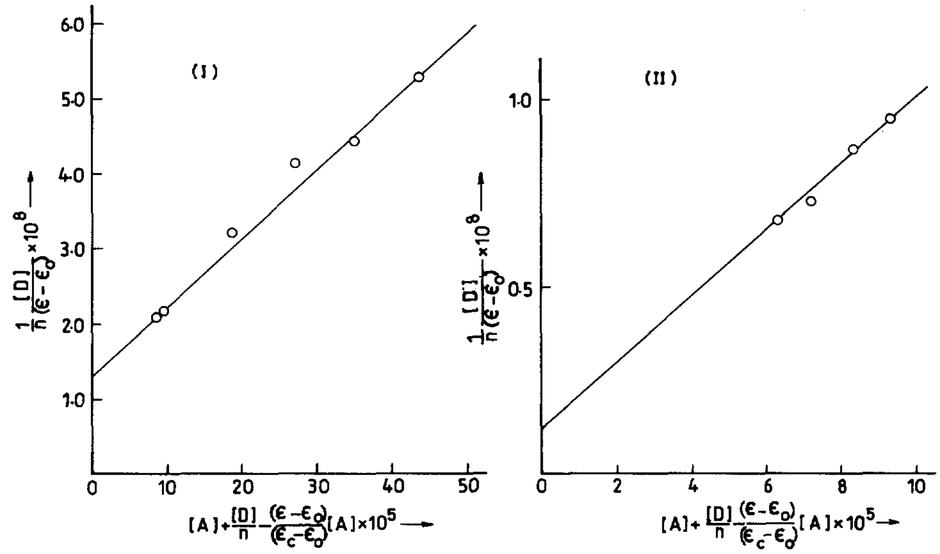

Fig. 3. Plot of $[D]/n(\epsilon-\epsilon_0)$ vs. $[A]+([D]/n)-[\{(\epsilon-\epsilon_0)[A]\}/(\epsilon_c-\epsilon_0)]$ for Brij 58: I, [Brij] = 1–5 mmol dm^{-3}; II, [Brij] = 5.5–9 mmol dm^{-3}.

sents the effectiveness of the surfactant micelle. Since the Brij micelles possess identical tail groups, the difference in the K_c values may be attributed essentially to the activities of the hydrophilic head groups and their association in the micelle. Brij 52, Brij 56 and Brij 58 possess 2, 10 and 20 EO residues respectively; their micellar aggregation numbers are 54, 32 and 12 respectively. The total numbers of EO residues in the respective micelles are thus 108, 320 and 240. The K_c values do not proportionately follow the trend; other factors, e.g. the interfacial viscosity, polarity, orientation, etc., must be considered for a quantitative elucidation of the experimental observations. The log K_c values vary linearly with n_{EO}; two courses for the two concentration ranges are obtained. This point will be discussed further in the next section.

The CMCs of the studied Brij micelles are only slightly different from one another; they are virtually constant. Therefore the differences in K_c cannot be correlated with the CMC as previously attempted [3,12] on Tween and other micelles.

The two sets of K_c values in the two concentration ranges of Brij (1–5 mmol dm^{-3} and 5.5–9.0 mmol dm^{-3}) indicate either transformation of the micelles from one form (geometry) to another or a perceptible increase in the aggregation number at the higher concentration. A larger inductive effect on the ST molecule may produce a stronger charge transfer interaction. This point requires further examination.

3.3. Fluorescence behaviour of the dye–detergent system

The fluorescence of ST is enhanced in aqueous solutions of Brij (Fig. 4), which is significant at concentrations greater

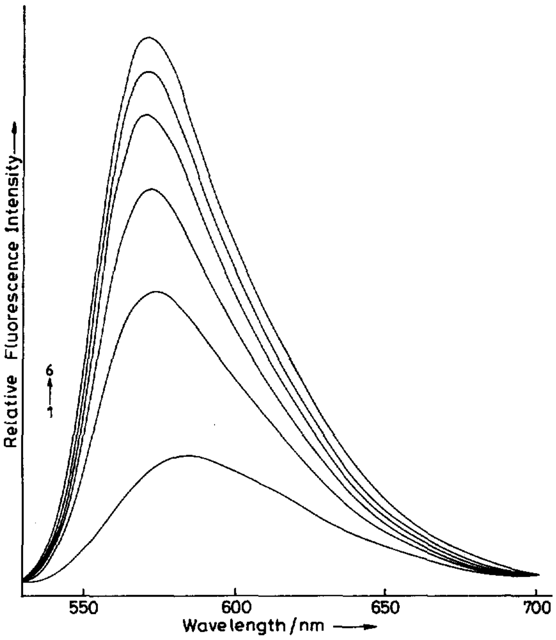

Fig. 4. Fluorescence emission spectra of ST in aqueous Brij 58 at 300 K. Curves 1–6 represent [Brij] = 0–5 mmol dm^{-3}.

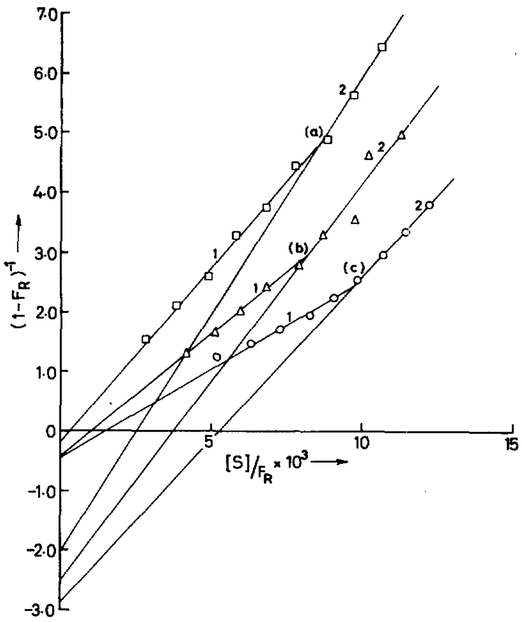

Fig. 5. Plot of $1/(1-F_R)$ vs. $[S]/F_R$: (a) Brij 58; (b) Brij 56; (c) Brij 58; 1, [Brij] = 0–5 mmol dm^{-3}; 2, [Brij] = 5.5–9 mmol dm^{-3}.

than the CMC: for [ST] = 10 μmol dm^{-3}, a nearly fourfold increase in fluorescence intensity is observed on changing [Brij] from 0.1 to 10 mmol dm^{-3}. With increasing [Brij], the fluorescence intensity F forms a plateau. Considering that ST forms a 1 : 1 complex with Brij micelles, the $F_{max}-F_0$ values can be taken as being proportional to [complex]. The F value at any stage other than F_{max} can be related similarly to the complexed dye. The ratio of the enhanced fluorescence intensity at any stage to its maximum value is therefore a measure of the fraction of the dye in the complexed form (F_R). In accordance with the complexation equilibrium (Eq. (1)), the fluorescence intensity can be used to evaluate the binding constant K'_c from Eq. (3) as reported previously [3]

$$\frac{1}{(1-F_R)}=K'_c/n\frac{[S]}{F_R}-K'_c[D_T] \qquad (3)$$

A plot of $1/(1-F_R)$ vs. $[S]/F_R$ shows two different straight lines (Fig. 5) with different slopes in the concentration ranges 1–5 and 5.5–9 mmol dm^{-3}. Two sets of K'_c and n values are obtained which are presented in Table 1. The log K'_c values, like log K_c, show a linear dependence on n_{EO}. The two sets of K_c^{ave} (average of K_c and K'_c) values follow the linear relations

$$\log K_c^{ave}=4.38-0.025n_{EO} \qquad (4a)$$

and

$$\log K_c^{ave}=5.04-0.008n_{EO} \qquad (4b)$$

as exemplified in Fig. 6.

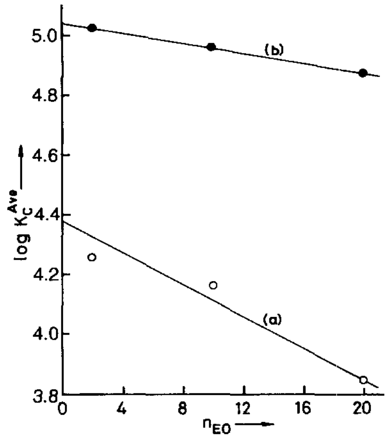

Fig. 6. Dependence of log K_c^{ave} on the number of EO residues (n_{EO}) of Brij: (a) [Brij] = 1–5 mmol dm^{-3}; (b) [Brij] = 5.5–9 mmol dm^{-3}.

In Fig. 7, the dependence of the aggregation number n on n_{EO} for the two concentration regions is presented. The following correlative relations are valid

$$n=59-2.25n_{EO} \qquad (5a)$$

$$n=192-5.00n_{EO} \qquad (5b)$$

The intercepts of Eqs. (4a) and (4b) and Eqs. (5a) and (5b) refer to the binding constants and aggregation numbers independent of EO interactions in Brij micelles. K_c^{ave} finds a direct correlation with n; similar features have also been exhibited by the ST–Tween system [3]. In the inset of Fig. 7, the binding constant/n profile is illustrated; a surfactant-dependent degree of interaction is observed. The Tween micelles are more reactive. Brij (I) corresponds to the lower concentration range of Brij and Brij (II) corresponds to the higher concentration range.

3.4. *Solvent parameters of Brij micellar media*

The absorption and emission spectra of ST in Brij (presented in Figs. 2 and 4) show a shift in the 0–0 transition,

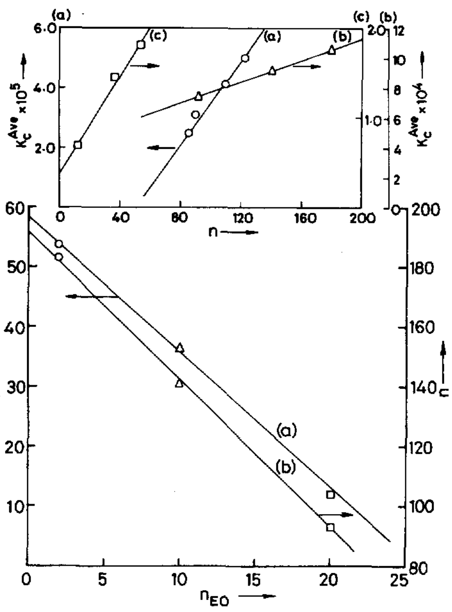

Fig. 7. Dependence of the aggregation number (n) on the number of EO residues (n_{EO}) for Brij micelles: (a) [Brij] = 1–5 mmol dm^{-3}; (b) [Brij] = 5.5–9 mmol dm^{-3}; ○, Brij 52; △, Brij 56; □, Brij 58. Inset: dependence of K_c^{ave} on the aggregation number (n) for Tween micelles (a), Brij micelles of concentration 5.5–9 mmol dm^{-3} (b) and Brij micelles of concentration 1–5 mmol dm^{-3} (c).

due to solvent interaction in the ground and excited states of the molecule, with a change in the intensity. The absorption and emission maxima in the micellar media occur in the ranges 520–537 nm and 571–586 nm respectively. The spectral shifts $\Delta\bar{\nu}=\bar{\nu}_a-\bar{\nu}_f$ observed can be used as a guide to the interaction of the dye with the surfactant micelles. The Stokes spectral shift shows a hyperbolic curve vs. the concentration of the surfactant in the medium (Fig. 8). For a fixed concentration of surfactant, the Stokes shift shows a linear relationship with the aggregation number and the number of EO moieties in Brij (Fig. 9). The spectral shifts $\Delta\bar{\nu}$ for Brij micelles at different concentrations are presented in Table 2. The solvent polarity parameters, i.e. dielectric constant (D), can be correlated with the Stokes spectral shift. For ST, the shifts in the solvent system have been correlated with the Kosower Z value and the transition energy for intramolecular charge transfer (E_T^{30}). The correlations of $\Delta\bar{\nu}$ with both Z and E_T^{30} are fairly linear, an observation observed previously [4,12].

Assuming that similar correlations of $\Delta\bar{\nu}$ with both Z and E_T^{30} also hold in aqueous Brij, the Z and E_T^{30} values for the Brij micelles were estimated using the measured $\Delta\bar{\nu}$ values shown in Fig. 10. The values are also given in Table 2. The $\Delta\bar{\nu}$ values of the solvents do not show a direct correlation with the dielectric constant D. An indirect procedure, as performed previously [12], has been adopted here for the evaluation of D in Brij micelles. In this estimation, Z and E_T^{30} derived from the spectral shifts ($\Delta\bar{\nu}$) were used to obtain D, since the latter can be linearly correlated with both Z and E_T^{30}.

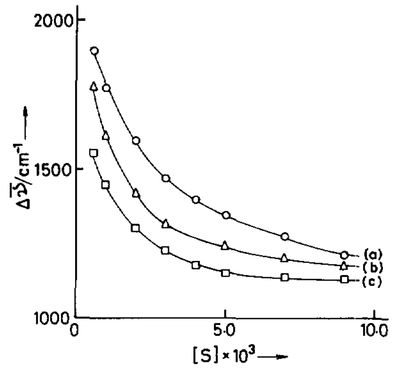

Fig. 8. Dependence of the Stokes spectral shift ($\Delta\bar{\nu}$) on the concentration of the surfactant micelles [S]: (a) Brij 52; (b) Brij 56; (c) Brij 58.

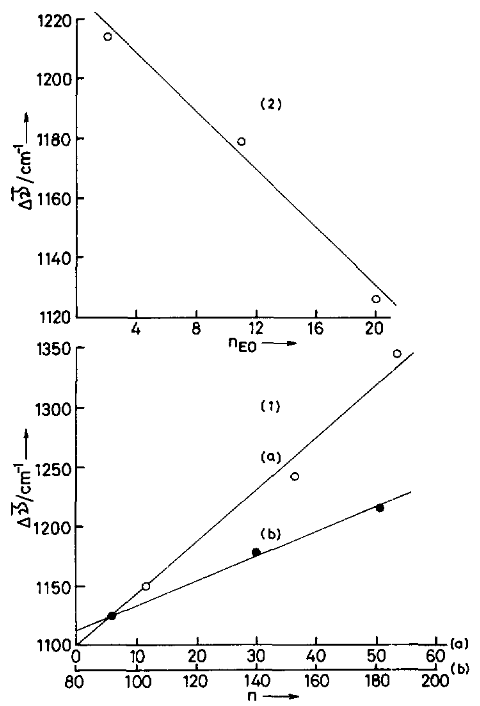

Fig. 9. Dependence of the Stokes spectral shift ($\Delta\bar{\nu}$) on the aggregation number of Brij (1) ((a) [Brij] = 1–5 mmol dm^{-3}; (b) [Brij] = 5.5–9 mmol dm^{-3}) and the number of EO moieties of Brij (2).

The Z, E_T^{30} and D values (Table 2) decrease with increasing molar mass of Brij with a consequent decrease in $\Delta\bar{\nu}$. The linear correlation of $\Delta\bar{\nu}$ with the aggregation number n follows the best fit relation (6a) for the concentration range 1–5 mmol dm^{-3} and (6b) for the concentration range 5.5–9 mmol dm^{-3}. Thus

$$\Delta\bar{\nu}=1.1\times10^3-4.25n \qquad (6a)$$

$$\Delta\bar{\nu}=1.113\times10^3-n \qquad (6b)$$

The $\Delta\bar{\nu}$ values and solvent parameters Z, E_T^{30} and D show perceptible decrease with increasing [Brij]. The viscosity coefficients of the Brij micelles are similar. The effect of the solvent fluidity on the photophysicochemical process has not been elucidated. However, it has been found to be responsible for this observation in Tweens [15].

Table 2
Viscosity and solvent parameters of Brij at different concentrations at 300 K

Solvent	Viscosity (cP)	[Brij] × 10^3 (mol dm^{-3})	$\bar{\nu}_a$ (cm^{-1})	$\bar{\nu}_f$ (cm^{-1})	$\Delta\bar{\nu}$ (cm^{-1})	Z (kcal mol^{-1})	E_T^{30} (kcal mol^{-1})	D
Brij 52	0.8862	0.6	19142	17241	1901	90.0	57.5	80
		1.0	19102	17331	1771	86.0	55.0	72
		5.0	18797	17452	1345	70.5	44.5	32
		9.0	18727	17513	1214	65.5	41.0	20
Brij 56	0.8909	0.6	19106	17331	1775	85.5	54.5	70
		1.0	19040	17422	1618	80.0	51.0	57
		5.0	18755	17513	1242	66.5	42.0	22
		9.0	18692	17513	1179	64.5	40.5	17
Brij 58	0.8937	0.6	18975	17422	1553	77.5	49.5	50
		1.0	18896	17452	1444	73.5	46.5	40
		5.0	18664	17513	1151	63.5	40.0	15
		9.0	18639	17513	1126	62.5	39.0	12

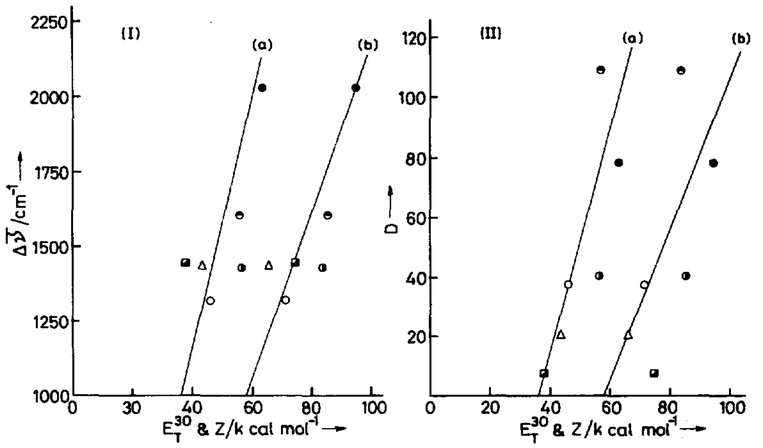

Fig. 10. Plot of the Stokes shift ($\Delta\bar{\nu}$) vs. (a) the transition energy for the charge transfer complex (E_T^{30}) and (b) the Kosower Z value (I). Plot of the dielectric constant (D) vs. (a) E_T^{30} and (b) Z (II).

4. Conclusions

1. Brij micelles undergo charge transfer interaction with ST in aqueous medium, the efficiency of which depends on the number of EO residues in the head group.
2. The aggregation number and CMC of the Brij micelles, derived from the results, correlate well with the derived solvent parameters.
3. The equilibrium constants of the complexes are linearly related to the aggregation number and CMCs of the Brij micelles.
4. The Stokes spectral shift $\Delta\bar{\nu}$ shows a direct correlation with Z, E_T^{30} and D. The local polarity of the micelle decreases systematically with increasing number of EO residues in the Brij molecule.

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