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The surfactant concentration-dependent behaviour of safranine T in Tween (20, 40, 60, 80) and Triton X-100 micellar media

Kamala Rani Acharya, Subhash C. Bhattacharya *, Satya P. Moulik
Physical Chemistry Laboratory, Jadavpur University, Calcutta 700 032, India

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Abstract

The visible and fluorescence spectra of the dye safranine T were studied in micellar solutions of non-ionic surfactants in different concentration ranges. The complexing strengths (1 : 1 dye : micelle charge transfer complex formed between the dye and micelle) of the non-ionic micelles increase with increasing concentration of the surfactant in the micellar solution. The aggregation number and several solvent parameters, i.e. the Kosower z value, intramolecular charge transfer energy E_T^{30}, dielectric constant of the micellar medium and viscosity of the micellar solution, were evaluated. These values remain constant over certain concentration ranges, but vary in different concentration regions of a surfactant. © 1997 Elsevier Science S.A.

Keywords: Absorbance; Aggregation number; Fluorescence; Safranine T; Solvent parameters; Tweens

1. Introduction

Self-organizing systems can influence equilibrium and kinetic processes, and are thus physicochemically important [1–11]. The ground and excited state behaviour of photoactive compounds (such as dyes) is often influenced by micelles, microemulsions, liposomes, etc. Recently, we have studied the interaction of the dye safranine T (ST) with the ionic and non-ionic micelles sodium dodecyl sulphate (SDS), cetyltrimethylammonium bromide (CTAB), polyoxyethylene sorbitan-monolaurate, -monopalmitate, -monostearate and -monooleate (Tweens), *p*-tert-octylphenoxypolyoxyethylene ether (TX-100) and polyoxyethylene-laurate (Brij-35) [12–15]. The binding constant of ST with the micelles and the critical micelle concentration (CMC) and aggregation number of the micelles were estimated, together with the solvent characteristics (polarity, dielectric constant, intramolecular charge transfer formation (E_T^{30}) and Kosower z value), exploiting the ground and excited state spectral measurements. For an understanding of the individual role of the non-polar tail and polar head of the non-ionic amphiphiles, studies were also conducted [16,17] in polyethyleneglycol medium, whose repeating polyoxyethylene units constitute the head groups of the non-ionic amphiphiles investigated (TX-100, Tweens and Brij-35).

In all the previous studies [12–17], the surfactant concentrations were kept just above their CMCs. The extent of amphiphile aggregation is dependent on the stoichiometric concentration [18]; primary micelles may form secondary micelles by aggregation or may increase in size by the continuous accommodation of amphiphile molecules at concentrations greater than the CMC.

This area can thus be explored by extending the physicochemical studies of amphiphiles to concentrations much greater than the CMC. In this investigation, such attempts have been made with ST and the Tweens (Tween 20, 40, 60 and 80) in the concentration range 10^{-4}–10^{-2} mol dm^{-3} by taking visible and fluorescence spectral measurements. It has been observed that the characteristics of the Tween micelles strongly depend on the amphiphile concentration.

2. Experimental details

The surfactants *p*-tert-alkylphenoxypolyoxyethylene ether (Triton X-100 or TX-100), polyoxyethylene sorbitan-monolaurate (Tween 20), -monopalmitate (Tween 40), -monostearate (Tween 60) and -monooleate (Tween 80) were either BDH (UK) or Sigma (USA) products. The dye safranine T (ST) (E. Merck) was crystallized twice from an ethanol–water mixture. Doubly distilled conductivity water was used for solution preparation.

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* Corresponding author.

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Absorption spectra were recorded using a Shimadzu 160A UV–visible spectrophotometer with matched pairs of silica cuvettes (path length, 1 cm). Fluorescence spectra were measured using a Fluorolog F 111A spectrofluorometer (Spex. Inc., NJ, USA) with a slit width of 2.5 nm. The excitation and emission wavelengths were 520 and 587 nm respectively. All spectral measurements were taken four times in a constant-temperature water bath (accurate within ±0.1 K) and the mean values were processed for data analysis. The absorption and fluorescence spectra were measured for dilute solutions (10^{-5} M) of ST with gradual addition of the surfactants to an overall concentration in the range 0.1–10 mmol dm^{-3}. The viscosities of the surfactant solutions were measured in a calibrated Ostwald viscometer. All measurements were taken at 300±0.1 K.

3. Results

3.1. Fluorescence behaviour of the dye–detergent systems

The fluorescence intensity of ST in micellar medium is enhanced; the micellar environment is obviously different from an aqueous environment. Three- and five-fold increases in the fluorescence intensity (F) are observed at $[\mathrm{S}]=0.1$ and 1 mmol dm^{-3} respectively. At a constant [ST], increasing [S] causes an increase in F, ultimately leading to the formation of a plateau with maximum F (F_{max}).

For quantification of the results, the following 1 : 1 ST–micelle equilibrium has been considered

$$\mathrm{D}+\mathrm{M}(\text{or }[\mathrm{S}]/n) \overset{K_c}{\rightleftharpoons} \mathrm{DM} \qquad (1)$$

where D, M, S, n, DM and K_c represent the dye, micelle, surfactant, aggregation number, complex and equilibrium constant respectively. From the fluorescence behaviour, considering Eq. (1), the following equation has been formulated

$$\frac{1}{1-F_R}=\left(\frac{K'_c}{n}\right)\frac{[\mathrm{S}]}{F_R}-K'_c[\mathrm{D_T}] \qquad (2)$$

where F_R and K'_c are the fraction of the dye in the complexed form and the equilibrium constant determined in the excited state respectively. The F_R value was estimated by comparing F at any [S] with F_{max} of the plateau formation region mentioned above and demonstrated previously [1]. A plot of $(1-F_R)^{-1}$ vs. $[\mathrm{S}]/F_R$ (Fig. 1) shows three linear regions in the concentration range 0.1–10 mmol dm^{-3}. The slopes and intercepts of the lines provide three sets of n and K'_c values. The results are presented in Table 1. Both n and K'_c depend on the range of surfactant concentration.

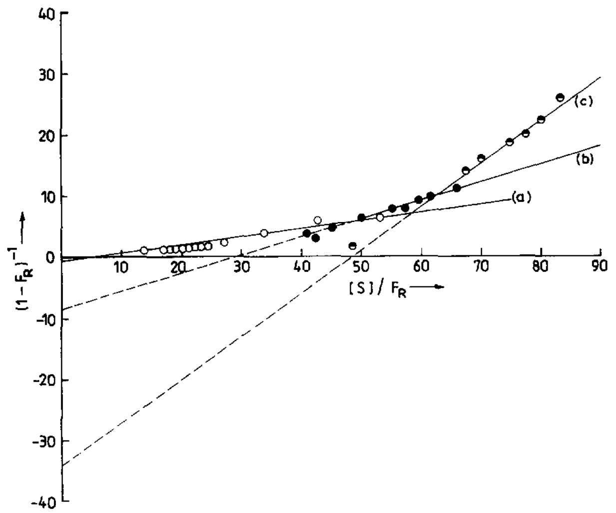

Fig. 1. Plot of $(1-F_R)^{-1}$ vs. $[\mathrm{S}]/F_R$ for Tween 20 in different concentration ranges: (a) 0.1–0.9 mmol dm^{-3}; (b) 1.0–6.0 mmol dm^{-3}; (c) 6.5–9.5 mmol dm^{-3}.

3.2. Absorption behaviour of the dye–detergent systems

In general, surfactants above their CMC enhance the absorbance of ST with bathochromic shifts. The ST–Tween and ST–TX-100 combinations studied behave in the same way. The 1 : 1 ST–micelle interaction model (given in Eq. (1)) and the modified equation of Lang [19] (Eq. (3)) used previously [1,15,16] have been employed for data analysis

$$\frac{[\mathrm{S}]l}{n(\epsilon-\epsilon_0)}=\frac{1}{(\epsilon_c-\epsilon_0)}\left\{[\mathrm{D}]+[\mathrm{S}]-\frac{(\epsilon-\epsilon_0)[\mathrm{D}]}{(\epsilon_c-\epsilon_0)}\right\}+\frac{1}{K_c(\epsilon_c-\epsilon_0)} \qquad (3)$$

where D and S represent the dye and surfactant respectively, ϵ_0, ϵ and ϵ_c are the molar extinction coefficients of the dye, solution and complex respectively and n and K_c are the aggregation number and binding constant respectively. The $[\mathrm{S}]/\{n(\epsilon-\epsilon_0)\}$ vs. $[[\mathrm{D}]+[\mathrm{S}]-\{(\epsilon-\epsilon_0)[\mathrm{D}]\}/(\epsilon_c-\epsilon_0)]$ profiles for the surfactants are presented in Fig. 2. In computing $[\mathrm{S}]/\{n(\epsilon-\epsilon_0)\}$, the fluorescence-derived n values (Table 1) were used.

As in fluorescence, three sets of n and K_c values in three concentration ranges were obtained for the Tweens and TX-100.

The K_c values increase with increasing number of the Tweens, i.e. with increasing length of the surfactant non-polar tail. This corroborates the findings of previous studies [1,20,21]. K_c also increases with increasing aggregation number. In Fig. 3, the average equilibrium constant values (average of K_c and K'_c) are plotted against the aggregation number. The Tweens tend to follow one course, whereas TX-100 follows another. The non-linear course followed by the Tweens suggests the influence of factors other than the micellar size. Larger micelles bind ST with greater strength. According to a previous report [17], the strength of the binding of the cationic dye ST increases with increasing number of ethyleneoxide (EO) residues in polyethyleneglycols. The number of EO residues in the Tween micelles increases with increasing aggregation number. Larger micelles thus bind ST with greater strength yielding higher K_c values.

Table 1
Binding constants and aggregation numbers of ST with surfactants at different surfactant concentrations

Surfactant	Concentration range (mol dm^{-3})	Aggregation number	$K_c^{ab} \times 10^{-5}$	$K_c^{cm} \times 10^{-5}$	$K_c^{ave} \times 10^{-5}$
Tween 20	0.1–0.9	22	0.08	0.05	0.07
	1.0–6.0	82	1.9	1.8	1.85
	6.5–9.5	150	8.3	8.4	8.4
Tween 40	0.1–0.9	23	0.08	0.06	0.07
	1.0–6.0	90	2.6	2.2	2.4
	6.5–9.5	157	12.0	10.0	11.0
Tween 60	0.1–0.9	24	0.09	0.09	0.09
	1.0–6.0	103	2.9	2.3	2.6
	6.5–9.5	164	14.0	12.0	13.0
Tween 80	0.1–0.9	27	0.12	0.10	0.11
	1.0–6.0	120	3.9	3.2	3.6
	6.5–9.5	178	20.0	18.0	19.0
TX-100	1.0–6.0	135	0.9	0.8	0.85
	6.5–20.0	181	2.1	2.0	2.0
	21.0–50.0	250	2.8	2.6	2.7

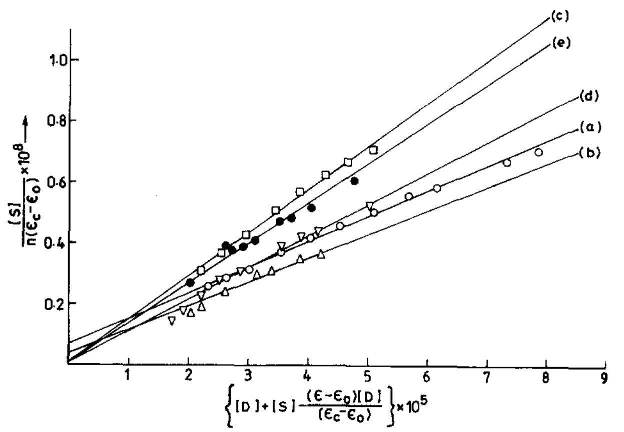

Fig. 2. Plot of $[S]/\{n(\epsilon-\epsilon_0)\}$ vs. $[[D]+[S]-\{(\epsilon-\epsilon_0)[D]\}/(\epsilon_c-\epsilon_0)]$ for different surfactants: (a) Tween 20; (b) Tween 40; (c) Tween 60; (d) Tween 80; (e) TX-100.

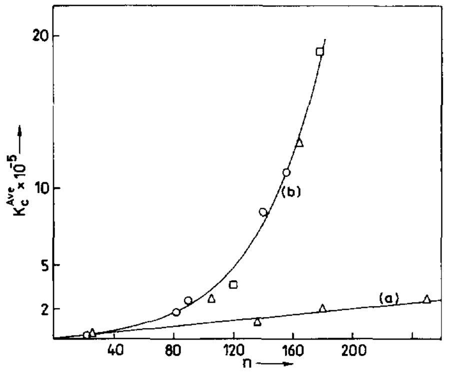

Fig. 3. Plot of K_c^{ave} vs. aggregation number of surfactant: (a) TX-100; (b) Tweens.

3.3. Solvent properties of the micellar environment

The solvent parameters (dielectric constant and refractive index) can be correlated with the Stokes spectral shift. The spectral shifts of ST in the different solvent systems studied previously [12] have been correlated with the Kosower z value and the transition energy for intramolecular charge transfer (E_T^{30}). The Stokes shifts in micellar solution have also been correlated with the above solvent parameters. Since ST exhibits poor solubility in hydrocarbons, it is anticipated that the aqueous interface of the micelle will be the preferred location of the dye which is expected to possess weak polarity and low dielectric constant. Following the line of treatment of our previous work [12,17], the z and E_T^{30} values for the present micellar media (Tweens and TX-100) were obtained from the measured Stokes shifts ($\Delta \bar{\nu}$). The values are presented in Table 2. Two sets of dielectric constants (D) were obtained from the correlation with z and E_T^{30}.

The dependence of the Stokes shifts ($\Delta \bar{\nu}$) on [S] is shown in Fig. 4. The E_T^{30} and D values also follow the same trend. The results indicate that the local environment of ST becomes less polar with greater micellar size. Partial penetration of the dye within the micellar interface is anticipated. The palisade layer and the interfacial region of the micelles guide the spectral manifestations of ST. In Fig. 5, the K_c^{ave} vs. $\Delta \bar{\nu} - n$ correlative profiles are presented. The pattern of TX-100 is different from those of the Tweens. The former is an erect, four-sided, convex-top, fence-like structure, whereas the latter are erect, four-sided structures whose tops are significantly concave (the concave feature increases with increasing Tween number). The mid-regions of the latter are also tapered. The differences between the diagrams indicate that TX-100 has an entirely different kind of tail compared with the Tweens.

4. Discussion

Above the CMC, the surfactants aggregate, and it is normally considered that the micellar concentration increases with increasing concentration of the surfactant. The increasing number of micelles may cause intermicellar interaction, affecting the aggregation number, in addition to other phys-

Table 2
Spectral characteristics of ST in different concentration ranges of surfactant and solvent parameters z, E_T^{30} and D_{ave} [a]

Surfactant	Concentration range (mmol dm^{-3})	$\bar{\nu}_a$ (cm^{-1})	$\bar{\nu}_f$ (cm^{-1})	$\Delta\bar{\nu}$ (cm^{-1})	z	E_T^{30}	D_{ave}	η (cP)
Tween 20	0.1–0.9	19083	17271	1812	88	56	48	0.85
	1.0–6.0	18796	17482	1314	71	43	38	0.86
	6.5–9.5	18726	17544	1182	66	39	14	0.92
Tween 40	0.1–0.9	19065	17331	1734	85	54	38	0.88
	1.0–6.0	18761	17482	1279	69	42	33	0.89
	6.5–9.5	18726	17543	1183	66	39	14	0.95
Tween 60	0.1–0.9	19048	17422	1626	81	51	24	0.90
	1.0–6.0	18726	17513	1213	67	40	18	0.93
	6.5–9.5	18691	17543	1148	65	38	9	1.01
Tween 80	0.1–0.9	19048	17422	1626	81	51	24	0.91
	1.0–6.0	18709	17513	1196	67	39	26	0.94
	6.5–9.5	18657	17543	1114	64	36	9	1.02
TX-100	1.0–9.0	18726	17513	1213	67	40	18	0.89
	9.5–20.0	18622	17544	1078	63	36	8	0.90
	21.0–50.0	18587	17574	1013	61	34	5	0.92

[a] Average of D obtained from the correlation of $\Delta\bar{\nu}$ with z and E_T^{30}.

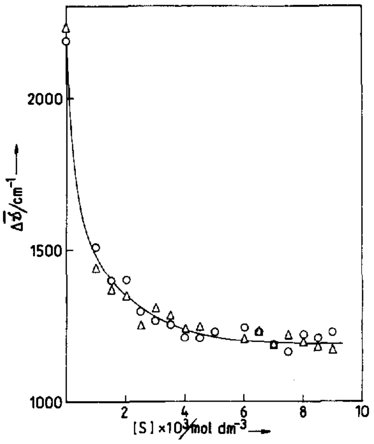

Fig. 4. Plot of Stokes shift vs. [S].

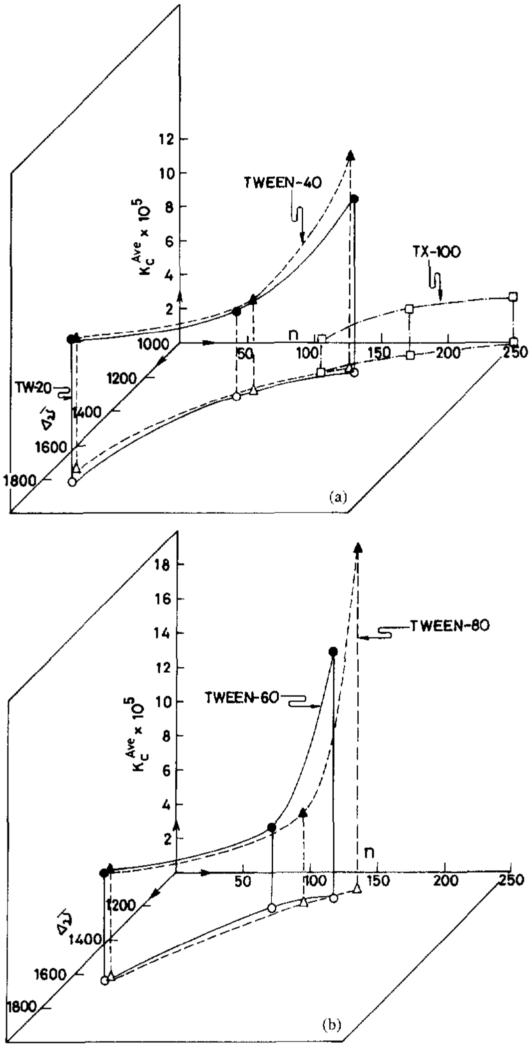

Fig. 5. Three-dimensional plot of K_c^{ave} vs. $\Delta\bar{\nu} - n$: (a) Tween 20, Tween 40, TX-100; (b) Tween 60, Tween 80.

icochemical manifestations, such as the activity, solubilization capacity, hydration (or solvation), counterion binding (in the case of ionic surfactants) and complexing interactions with additives, i.e. dyes, drugs, etc. These complex and multiple manifestations have not been explored in detail. The present fluorescence study has shown an increase in the aggregation number in different concentration ranges. The number can increase via the continuous transfer of monomers from solution to the micelles with increased accommodation as well as by intermicellar fusion or association. Geetha and Mandal [22] have recently reported a concentration-dependent increase in the micellar size (or aggregation number) for methoxypolyethyleneglycol-based macromonomers from fluorescence measurements. These results corroborate earlier reports [18] of an increasing aggregation number with increasing surfactant concentration. In this study, the increase is non-linear and significant at higher [Tween]; histogram representations are illustrated in Fig. 6. Of the three ranges, the middle range is wider and the area-wise order is

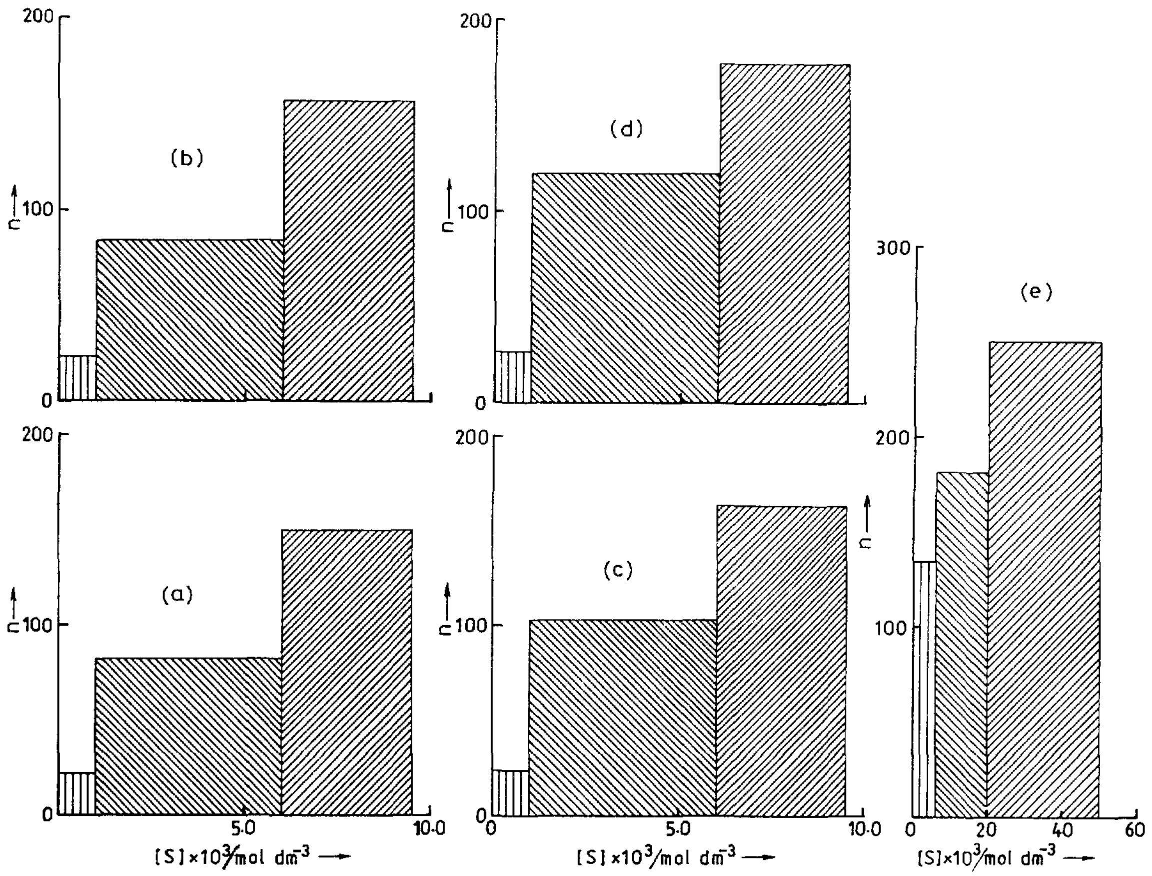

Fig. 6. Histogram representing the variation of the aggregation number with the concentration of the surfactant: (a) Tween 20; (b) Tween 40; (c) Tween 60; (d) Tween 80; (e) TX-100.

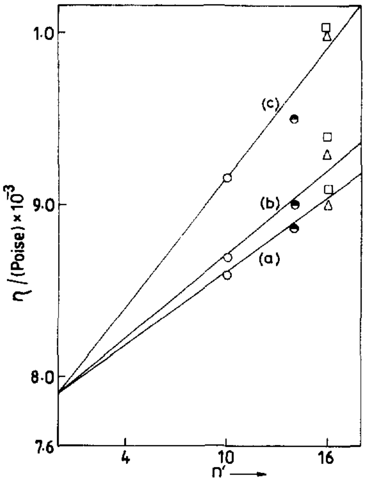

Fig. 7. Plot of the viscosity (η) vs. the number of EO groups (n') in the Tween head group for different concentration ranges: (a) 0.1–0.9 mmol dm^{-3}; (b) 1.0–6.0 mmol dm^{-3}; (c) 6.5–9.5 mmol dm^{-3}; ○, ■, △, □ indicate Tween 20, Tween 40, Tween 60 and Tween 80 respectively.

middle > higher > lower for the Tweens. It is higher > middle > lower for TX-100. The results on the Tweens (Table 2) apparently support the association of four primary micelles to form a secondary micelle and seven primary micelles to form a tertiary micelle. The association of two secondary micelles to form a tertiary micelle overestimates the number. The ratio of the aggregation number in the higher concentration range to that of the primary micelles of TX-100 is not an integer but a fraction which indicates that it is not the aggregation of the primary micelles, but their fusion, which is the underlying principle of concentration-dependent micellar growth.

In addition to the changing aggregation number, the polarity of the micellar local environment and the ST–micelle interaction alter with increasing micellar size. The observations reported here are therefore part of the varied manifestations of micellar characteristics at concentrations appreciably higher than the CMC. The micellar local polarity decreases, whereas the ST–micelle binding constant increases, with increasing n. The increased association leads to desolvation of the interfacial region, resulting in a decrease in polarity and increase in the electrostatic and hydrophobic (i.e. non-polar) interactions between ST and micelle, yielding higher K_c and K'_c values. Similar, related investigations are necessary to obtain a fundamental understanding of self-organizing systems.

The K_c^{ave}–n profiles for ST–Tween and ST–TX-100 combinations are not the same (Fig. 3). For the Tweens, the dependence is non-linear. This apparent difference mainly stems from the environmental specificities (polarity, viscosity, etc.) of the micelles. The dielectric constant of the interfacial region of the Tween micelles varies non-linearly with n. The polyethyleneoxide residues in the palisade regions of the micelles form networks via dipolar interaction into which water molecules are organized by hydrogen bonding; therefore the ST environmental viscosity increases significantly with increasing *n*. This is supported by the increasing order of the slopes of the plots (Fig. 7) between the relative viscosity η and the number of polyethyleneoxide residues in the surfactant head groups n' at equal surfactant concentration obeying the relation $\eta = 7.9 \times 10^{-3} + mn'$. The slopes ($m$) are 0.75×10^{-4}, 0.83×10^{-4} and 1.3×10^{-4} for surfactant concentrations of 0.5, 1.0 and 9.0 mmol dm^{-3} respectively. The concerted effects of a lower dielectric constant and a higher viscosity lead to a non-linear dependence of K_c^{ave} on n. TX-100, containing 50% less EO residues than the Tweens, forms a less complex environment giving a linear K_c^{ave}–n profile.

5. Conclusions

1. The aggregation numbers of Tween and TX-100 micelles increase with increasing surfactant concentration.
2. The strength of ST–micelle binding increases with increasing micellar size.
3. The Stokes spectral shift and the solvent parameters (D, E_T^{30}, z and viscosity) are also functions of the micellar size.

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