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Spectroscopic studies of interaction of Safranine T with nonionic micelles and mixed micelles

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Abstract

The visible spectra of Safranine T (ST) in micellar solution of Brij 58, Tween 20 and Tween 40 and mixed micellar solution of Brij 58/Tween 20 and Brij 58/Tween 40 indicate formation of 1:1 charge transfer (CT) complex between acceptor ST and donor nonionic micelles and mixed micelles. The experimental CT transition energies are well correlated (through Mulliken's equation) with the vertical ionization potential of the donors. The solvent parameters, i.e. the intramolecular charge transfer energy $E_T(30)$ have been determined from the Stokes spectral shift. Variations of ionization potential and micropolarity in the mixed micellar region have been investigated as a function of surfactant composition and the obtained results in mixed micellar medium has been compared to the normal micelles. The critical micelle concentration (CMC) values determined at various surfactant compositions are lower than the ideal values indicating a synergistic interaction. The interaction parameter (β) and micellar stability has been calculated using regular solution theory.

Keywords: Charge transfer; Vertical ionization potential; Micropolarity; Micellar stability

1. Introduction

The dye Safranine T forms 1:1 charge transfer complex with ionic and nonionic micelles. We have studied the interaction of the dye with ionic micelles SDS, CTAB and nonionic micelles Triton X100, Tweens, Brijs and Igepals [1–5]. The complexing strength of 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 and for Brij micelles, the efficiency of charge transfer interaction increases with increasing number of ethylene oxide residues in the head groups. The local polarity of the micelle decreases systematically with increasing number of ethylene oxide residues in the Brij molecule and for Tween micelles the micropolarity are also functions of micellar size. To understand the role of poly(oxyethylene) group on charge transfer interaction between ST and Tween and ST and Brij, a detail study of the interaction of ST with polyethylene glycols [6] with varying degree of polymerization has been performed and the efficiency is found to depend on the number of ethylene oxide residues.

In continuation to the work, charge transfer interaction has been observed between ST and mixed micelles of nonionic surfactants (Tween 20/Brij 58 and Tween 40/Brij 58) and a comparison between the charge transfer interaction of normal micelles and mixed micelles have also been included in our present study. Pyrene [7,8] is a widely used fluorescent probe to determine CMC, aggregation number, micropolarity, etc. of mixed micellar systems. Besides pyrene, polarities sensitive probe prodan [9], intramolecular charge transfers probe ketocyanine [10] have been studied in mixed micellar medium. With the intension of finding the location of the probe in different micellar and mixed micellar systems, polarity parameters surrounding the dye have been studied [1–5,10–12] in addition to the iodide ion induced fluorescence quenching. A systematic study of micro-environmental properties of binary mixed surfactant system as a function of surfactant composition has also been done.

Surfactants are very often used in mixed systems to obtain some desired performance. In such cases, many kinds of blending effects occur, and these effects correspond to the

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so-called synergism. The synergistic effect can be obtained, as expected, when some interaction is present between the surfactant components and it leads to non-ideal behavior of the mixed micelles [13–17]. The interaction parameter β [18] has been calculated using regular solution theory to identify surfactant–surfactant interaction and stability of the mixed micelles over the normal micelles. This theoretical model has been used to explain the experimental observation. As the probe, ST, is adsorbed on the interface of the nonionic micelles and nonionic/nonionic mixed micelles, so this is the first attempt to observe the associated change in spectral properties on mixed micellar interface.

2. Experimental details

Polydisperse polyoxyethylene sorbitan monolaurate (Tween 20), polyoxyethylene sorbitan monopalmitate (Tween 40) and polyoxyethylene cetyl ether (Brij 58) were of Aldrich products and used without any further purification [3,4]. Prior to the use, these surfactants were checked and found no absorption or fluorescence in the spectral region where the studies were made. Triple distilled water was used for solution preparation. Safranine T (ST) (E. Merck) was recrystallised twice from ethanol–water mixture [1–5]. The concentration of ST in the solution was of the order of 0.01 mmol dm^{-3}. All the measurements were taken under thermostated conditions at 300 ± 0.1 K.

Absorption spectra of the aqueous dye solution in absence and presence of surfactants were recorded using a Shimadzu UV–vis spectrophotometer (UV-1700) with a matched pair of silica cuvettes. Fluorescence was measured using a Fluorolog F-IIA spectrofluorimeter (Spex Inc., NJ, USA) with a slit width 1.25 nm. All spectral measurements were taken four times to get reproducible results.

3. Results and discussion

3.1. Absorption behavior of the ST-nonionic micelles and ST-nonionic/nonionic mixed micelles

In presence of non-ionic surfactant Brij 58, absorbance enhances with increasing surfactant concentration and above CMC absorbance increases with bathochromic shift in spectral maxima. The spectrum of the ST-Brij 58 system exhibits two isosbestic crossing at 437 and 500 nm. In presence of nonionic surfactants Tween 20 and Tween 40, absorbance enhances with increasing surfactant concentration and above CMC absorbance increases with bathochromic shift in spectral maxima. The spectra of ST-Tween 20 and ST-Tween 40 system exhibit two isosbestic crossing at 382 and 528 nm. From the absorption spectra of ST in nonionic micelle Brij 58, Tween 20 and Tween 40, it has been observed that the absorption maxima has been shifted from 520 nm, in aqueous dye solution, to 544, 540 and 540.5 nm, respectively. The higher wavelength band is identified as charge transfer band and charge transfer occurs from organized aqueous mantle of the nonionic micelle to the acceptor ST [3,4].

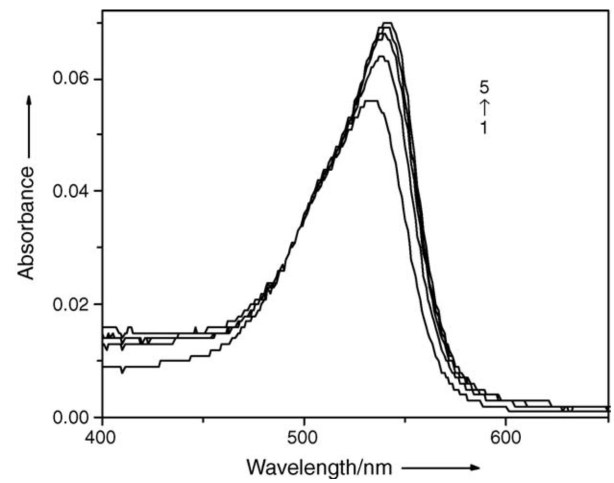

Fig. 1. Absorption spectra of Safranine T in Brij 58/Tween 20 system (Brij 58:Tween 20 = 1:1) where [SURFACTANT]: (1) 0.22 mmol dm^{-3}; (2) 0.38 mmol dm^{-3}; (3) 0.52 mmol dm^{-3}; (4) 0.63 mmol dm^{-3} and (5) 0.8 mmol dm^{-3}, respectively.

In the absorption spectra of ST in the mixed micellar medium of Tween 20/Brij 58 and Tween 40/Brij 58 at their different compositions, absorbance remains unchanged with increasing concentration of mixture before CMC and above CMC absorbance increases with increasing concentration of mixture having bathochromic shift in spectral maxima (Fig. 1) and the values of λ_{max}^{abs} are given in Table 1. The bathochromic spectral shift of ST in mixed micellar medium is lower than the micellar medium and from Table 1 it is evident that the bathochromic shift in λ_{max}^{abs} is lower for Brij 58/Tween 40 systems compared to Brij 58/Tween 20 systems. Absorbance of the binary mixture increases with increasing mole fraction of Brij 58 in mixed micelle. The isosbestic point at 500 nm (Fig. 1) may indicate formation of 1:1 complexa-

Table 1
Absorption wavelength, fluorescence wavelength, vertical ionization potential and degree of charge transfer of Safranine T in Brij 58/Tween 20 and Brij 58/Tween 40 mixed micellar systems at different compositions

System	$\alpha_{Brij\ 58}$	λ_{max}^{abs} (nm)	λ_{max}^{fl} (nm)	I_D^V (eV)	α
Tween 20–Brij 58	0.00	540	571	0.85862	0.03863
	0.25	531	576	0.85789	0.03864
	0.33	533	575	0.85798	0.03864
	0.50	533	575	0.85798	0.03864
	0.67	532	575	0.85792	0.03864
	0.75	532	575	0.85871	0.03863
	1.00	544	570	0.85915	0.03862
Tween 40–Brij 58	0.00	540.5	571	0.85862	0.03864
	0.25	527	579	0.85764	0.03864
	0.33	529	577	0.85772	0.03864
	0.50	529	577	0.85772	0.03864
	0.67	529	577	0.85772	0.03864
	0.75	528	578	0.85766	0.03863
	1.00	544	570	0.85915	0.03862