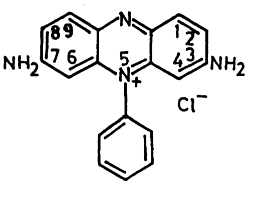
April, 1992] *Bull. Chem. Soc. Jpn., 65, 1089—1095 (1992)*

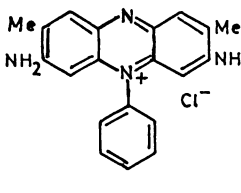
Dye-Surfactant Interaction in Submicellar Concentration Range

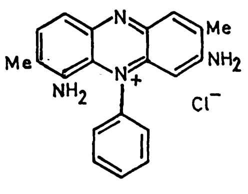
Robin Kumar DUTTA and Subray Narayan BHAT*
Department of Chemistry, North-Eastern Hill University, Shillong 793003, India
(Received August 3, 1991)

Interactions of cationic dyes, viz., phenosafranine (PSF), safranine O (SFO) and safranine T (SFT) with anionic surfactants, viz., sodium dodecyl sulfate (SDS) and sodium octyl sulfate (SOS) in submicellar concentration ranges have been investigated spectroscopically. The interaction has been shown to be an induced protonation of the dye in the dye–surfactant ion pair. Even though the opposite charges on the dye and the surfactant are the primary requirements for the ion pair formation, it is the hydrophobicity of the surfactant as well as of the dye which induces the protonation. The spectroscopic and thermodynamic parameters show that the orders of effectiveness of the dyes and the surfactants for the interaction are, SFO>SFT>PSF and SDS≫SOS.

There has been an increasing interest in the study of interaction of dyes with surfactants as the knowledge of dye–surfactant interaction is of great value in understanding the chemical equilibrium, mechanism and kinetics of surfactant sensitized color and fluorescence reactions.[1)] Many researchers had noticed the change in color of the ionic dyes when they were dissolved in oppositely charged ionic micelles.[1—12)] Most of the previous studies on dye-surfactant interactions are carried out with the concentration of the surfactants above the critical micellar concentration, cmc, and the color changes have been explained on the basis of the interaction between the surfactant micelles and the dyes and the equilibrium between conjugate acid and base forms of the dye. However, there is not much information available regarding the nature and mechanism of the interaction between dyes and surfactants when the concentrations of the surfactants are much below the cmc. Therefore, it was thought worthwhile to carry out systematic spectroscopic and thermodynamic investigations in order to understand the nature of this interaction between ionic dyes and oppositely charged surfactants of very low concentrations, i.e., far below their cmc. The dyes chosen for such studies were phenosafranine (PSF), safranine O (SFO), and safranine T (SFT) (all phenazinium dyes), and the surfactants were sodium dodecyl sulfate (SDS) and sodium octyl sulfate (SOS), both are anionic surfactants.


PSF


SFO


SFT

Experimental

Phenosafranine, (3,7-diamino-5-phenylphenazinium chloride), and safranine O (3,7-diamino-2,8-dimethyl-5-phenylphenazinium chloride) were Sigma products and safranine T (3,6-diamino-2,7-dimethyl-5-phenylphenazinium chloride) was a Fluka product. They were recrystallized twice from water–ethanol mixture before use. Sodium dodecyl sulfate and sodium octyl sulfate were obtained from Aldrich and Eastman Kodak Company, respectively. The surfactants were stirred overnight in ether and recrystallized from ethanol. Triply distilled water was used as solvent. The electronic absorption spectra were recorded with a Hitachi-330 spectrophotometer using a matched pair of 1 cm path length cells in a thermostated cell holder. The temperatures were maintained within ±0.1 K.

Results and Discussion

PSF-SDS. The electronic absorption spectra of phenosafranine alone and in the presence of varying concentrations of SDS (much below the cmc) in aqueous solutions are shown in Figs. 1a and 1b. In visible region, PSF has an absorption band with $\lambda_{max}=520$ nm. We did not observe any change either in the λ_{max} or in molar absorptivity with the variation in concentration of PSF in the range of 1×10^{-6} M to 1×10^{-4} M (1 M=1 mol dm^{-3}). In addition, the absence of any significant variation in the spectral character with the variation in temperature (between 283.15 to 318.15 K) indicates that the dye is (probably) in the monomeric form in the experimental range of the concentration. As the concentration of SDS is slowly increased from ca. 1.6×10^{-4} M (the lowest concentration at which there was detectable decrease/increase in absorbance of PSF bands) to ca. 3×10^{-3} M, the λ_{max} of PSF band gradually shifted from 520 to 528 nm with a gradual decrease in intensity of the λ_{max} band, accompanied by an increase in absorbance in the longer wavelength region of ca. 550 to ca. 700 nm. The red shift of the PSF band from 520 to 528 nm can be attributed partly to a change in the environment of the chromophore of PSF and partly to the

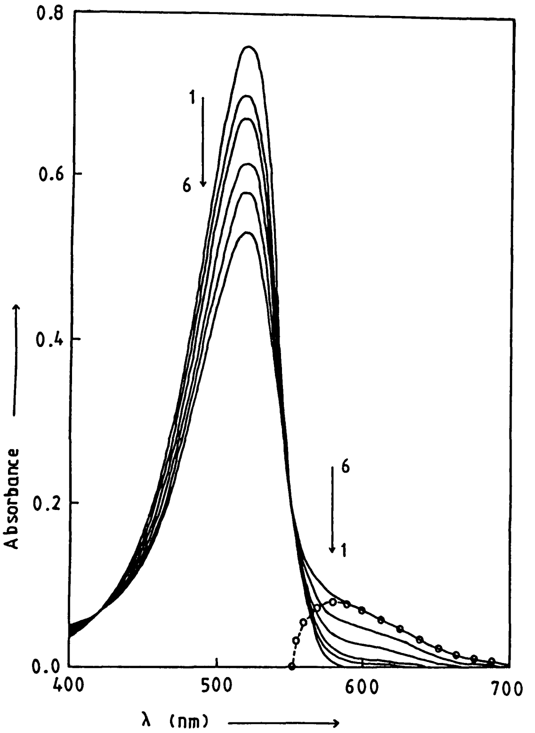


Fig. 1a. Effect of variation in concentration of SDS on the spectra of PSF: [PSF]=2.13×10^{-5} M; [SDS]×10^4 M=(1) 0.00, (2) 1.66, (3) 1.94, (4) 2.77, (5) 3.18, (6) 4.43; O--O--O, difference spectra of (6) and (1).

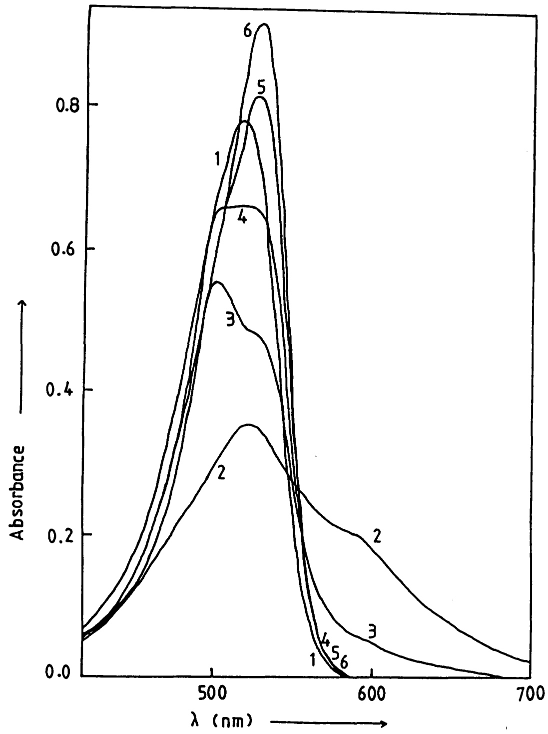


Fig. 1b. Effect of variation in concentration of SDS on the spectra of PSF: [PSF]=2.20×10^{-5} M; [SDS]×10^3 M=(1) 0.00, (2) 2.21, (3) 4.37, (4) 5.83, (5) 9.30, (6) 13.90.

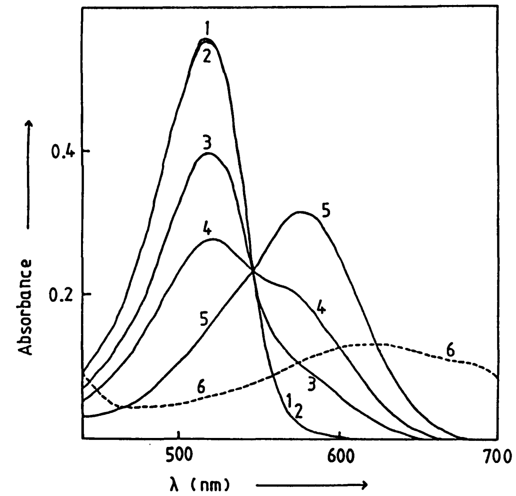


Fig. 2. Effect of H_2SO_4 on the spectra of PSF: [PSF]=1.60×10^{-5} M; (1) without acid, (2) to (6) with increasing [H_2SO_4], (2) pH 1.2, (6) 96% H_2SO_4.

overlapping of the 520 nm band with the new band in the longer wavelength region. The enhancement in the absorbance on the higher wavelength side of the PSF band is quite pronounced and increases with the increase in the concentration of SDS. No maximum was observed in the absorption curves for the mixtures, but inspection of the differences in absorbances of the PSF bands in the presence and absence of SDS reveals that the difference passes through a maximum at 582 nm. It can be seen from Fig. 1a, that increasing the concentration of SDS upto ca. 4×10^{-4} M, for a fixed concentration of PSF of 2.13×10^{-5} M, gives a series of spectra that go through a sharp isosbestic point at 550 nm (Table 1). It is quite interesting to note that the spectra of PSF in low concentration of SDS are similar to those of PSF in strong acidic media of varying concentrations of acid (Fig. 2). Gopidas and Kamat[13)]

Table 1. Spectral Properties of Phenazinium Dyes and Their Protonated Ion Pairs (Complexes) with SDS and SOS in Submicellar Concentration Ranges at 298.15 K

Dye	Surfactant	λ_{max} of dye	ε_{max} of dye	λ_{iso}	ε_{iso}	λ_{max} of complex	ε_{max} of complex
		(±1) nm	(±50) $m^2 M^{-1}$	(±1) nm	(±100) $m^2 M^{-1}$	(±2) nm	(±100) $m^2 M^{-1}$
PSF	SDS	520	3600	550	1250	582	2250
PSF	SOS	520	3600	540	1970	565	2280
SFO	SOS	520	3700	545	1310	576	2380
SFT	SOS	520	2900	548	1230	580	2150

had reported that PSF^+ in 2 M HCl has absorption band at 580 nm which can be attributed to $HPSF^{2+}$. We have noticed that with the increase in concentration of strong acids, e.g., H_2SO_4, $HClO_4$ etc., PSF gave rise to three bands viz., at 580, 625, and 690 nm. Similarly, with the increase of BF_3 in ether the absorption maxima of PSF were at 578, 622, and 688 nm successively. The appearance of a new band at ca. 582 nm, which increases with the increase in concentration of SDS (upto ca. 3×10^{-3} M) and decreases with increase in temperature, and the presence of an isosbestic point are indicatives of the presence of an equilibrium between the free PSF, SDS and "complexed PSF" (an interaction product of PSF and submicellar SDS).

When the concentration of SDS was increased above ca. 1.2×10^{-3} M, the nature of the spectra had changed. The spectra were no longer passing through the isosbestic point. It is quite interesting to note that when the concentration of SDS were increased from ca. 3×10^{-3} to ca. 5.8×10^{-3} M the absorbance around 582 nm had started decreasing (Fig. 3) and at the same time new bands started appearing at 520 and 505 nm. The band at 582 nm had completely disappeared at ca. 5×10^{-3} M of SDS, whereas, the intensities of 520 and 505 nm bands continued to increase till the concentration of SDS had reached ca. 5.8×10^{-3} M and at this concentration of SDS both the bands merged with one another resulting in a λ_{max} at 510 nm. The decrease in intensity of 582 nm band and the increase in intensities of 520 and 505 nm bands can be attributed to the formation of higher order aggregates of the cationic dye (facilitated by the surfactant) at the cost of the monomeric dye–submicellar surfactant complex. With the increase in concentration of SDS above cmc (which is found to be ca. 6×10^{-3} M in presence of 2.2×10^{-5} M PSF), the 520 nm band shifts to higher wavelength, 531 nm (ε=4550 $m^2\,M^{-1}$), which is attributed to the association of the dye with the surfactant micelles. There was hardly any change in the position and intensity of this band with further addition of SDS.

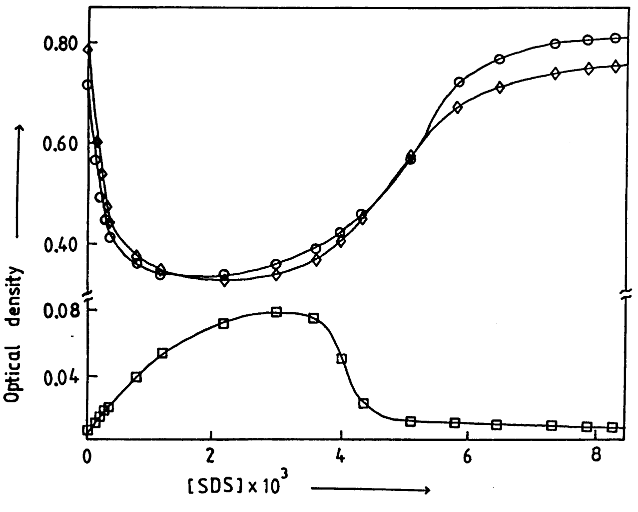


Fig. 3. Variation of optical density of PSF–SDS system with concentration of SDS at various wavelengths: [PSF]=2.20×10^{-5} M; ◇, λ=520 nm; ○, λ=531 nm; □, λ=582 nm.

The color change observed in many dyes on the addition of very small amount of oppositely charged surfactant has been attributed to ion pair formation,[4] dye–surfactant salt formation,[9] the formation of dye dimer or higher aggregates,[14] micelle and mixed micelle formation,[6,11] etc. However, Lewis[15] had pointed out that the ion pair formation, a phenomenon in itself (like PSF^+SDS^-), does not alter the spectral absorption of the associated ions. Moreover, in the case of cationic dyes, like phenazinium and thiazinium dyes, the dimerizations are known to cause hypsochromic shifts in the spectra.[16,17] Therefore, the band at ca. 582 nm, which is at longer wavelength, is not due to dimeric "species" of the dye. The formation of mixed micelle or dye-rich induced micelle, which is expected to provide a relatively less polar environment to the chromophore, should lead to a hypsochromic shift; whereas in the present case a bathochromic shift by ca. 60 nm has been observed. Diaz-Garcia et al.,[1] citing various researchers, have pointed out how the studies and basic knowledge (available so far) on micellar interactions may be contradictory and insufficient to permit a clear choice between different possible interpretations of dye–surfactant interactions.

We did not observe any interaction of the phenazinium dyes with *N*-hexadecylpyridinium chloride (a cationic surfactant) and Triton X 100, $(CH_3)_3CCH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_{10}OH$ (a nonionic surfactant) in the submicellar concentration range. This indicates that the opposite charge on the dye and the surfactant is the primary requirement for this interaction. Therefore, it can be suggested that as the oppositely charged ions, viz., PSF^+ and SDS^-, come closer to each other due to electrostatic attraction, the hydrophobic nature of the large organic ions and hydrogen-bonded water structure enforce them to form closely associated ion pairs, PSF^+SDS^-.[4,18,19] The role of hydrophobic force is clear from the fact that the addition of Na_2SO_4 does not change the electronic spectra of PSF. This water-structure enforced ion pair poorly soluble (compared to the free ions) in water due to hydrophobicity[9] and that is what has been observed in the present case. The slight scattering of light from the solutions and slight sticking of solid mass to the surface of the cell are indications of the lower solubility of the ion pairs.

Thus, it is clear that some more change, in addition to the ion-pair formation, has to occur to the chromophore to effect the large shift of the absorption band. Gopidas and Kamat[13] reported that PSF gets protonated and gives a band at 583 nm when it is bound to H^+-Nafion, a polymer which exhibits a strong acidic environment to the dye in aqueous solution.[20] We have seen that the PSF absorption band remained unperturbed even on lowering of the pH of the aqueous

PSF solution till 1.2. Only below pH 1.2, the 580 nm band of PSF appears. On the other hand, in the entire experimental submicellar concentration range of SDS, the pH's of the aqueous SDS solutions were found to be ca. 6.5. Therefore, it can be said that the 582 nm band of PSF in submicellar SDS may also be due to the protonated PSF, viz., $HPSF^{2+}$, caused by a strong acidic environment exhibited by monomeric SDS^- bound to PSF^+ in the hydrophobic ion pair of PSF^+SDS^-. If protonation is a part of the interaction, the interaction should be favored by lower pH. Unfortunately, we could not study the effect of pH as SDS is hydrolyzed in acidic medium (which is quite appreciable at the low experimental concentrations of SDS) and is precipitated out in basic medium. Moreover, use of buffer may affect the dye–surfactant interaction as a result of the interaction of the buffer constituents with the dye or surfactant.21)

The protonation can be explained in terms of the Hamaker constant.18) The Hamaker constant H_{123} for the dispersion/hydrophobic interaction between the species, viz., PSF^+, 1, and SDS^-, 2, in water, 3, can be represented as

$$H_{123}=H_{12}-(H_{13}+H_{23}-H_{33}). \qquad (1)$$

Water tries to retain its ordered structure and due to the hydrophobic repulsion between PSF^+ and water, and SDS^- and water, the terms H_{13} and H_{23} are very low compared to H_{33} and this makes the Hamaker constant very high. The value of H_{123} becomes so high that it is enough to induce protonation of the dye. The protonation stabilizes the ion paired system as the ionic hydrogen bonds are stronger than hydrogen bonds between neutral molecules by about an order.22) After protonation, due to the stronger interaction of the ammonium ion of the protonated dye, $HPSF^{2+}$, with water, the ion pair is more stabilized. The addition of Na_2SO_4 to PSF in water does not affect the spectra of PSF as there is no hydrophobic ion pairing and hence no hydrophobic force induced protonation taking place.

Determination of Equilibrium Constant. The interaction of PSF^+ with SDS^- in aqueous medium can be represented by:

$$PSF^+ + SDS^- + H^+ \overset{K_e}{\rightleftarrows} HPSF^{2+}SDS^- \qquad (2)$$

or

$$K_e=\frac{[HPSF^{2+}SDS^-]}{[PSF^+][SDS^-][H^+]} \qquad (3)$$

The pH of the mixed solution (i.e., of PSF and SDS) remained 6.5 (within the submicellar experimental concentration range of SDS). Therefore, assuming that $[H^+]$ virtually remains constant, the above equation can be written as:

$$K_c=K_e[H^+]=\frac{[HPSF^{2+}SDS^-]}{[PSF^+][SDS^-]} \qquad (4)$$

Using the Ketelaar's23) equation

$$\frac{[D]_0}{d-d_0}=\frac{1}{\varepsilon_c-\varepsilon_0}+\frac{1}{K_c(\varepsilon_c-\varepsilon_0)[S]_0} \qquad (5)$$

one can obtain the equilibrium constant, K_c. Here d and d_0 are the observed optical densities of the dye in the presence and in the absence of the surfactant, ε_0 and ε_c are the molar extinction coefficients of the dye in the free and the associated (viz., $HPSF^{2+}SDS^-$) forms, and $[D]_0$ and $[S]_0$ are the initial concentration of the dye and the surfactant, respectively.

The plots of $[PSF]_0/(d-d_0)$ vs. $(1/[SDS]_0)$ for various temperatures yielded straight lines in a wide range of the concentration of SDS. Deviations from the straight lines were observed towards higher concentrations of

Table 2. Equilibrium Constants and the Other Thermodynamic Parameters of the Submicellar Interaction Product of Phenazinium Dyes and Anionic Surfactants

Dye	Surfactant	Temp	K_c a)	K_e b)	$-\Delta G$	$-\Delta H$	ΔS
		K	M^{-1}	M^{-2}	kJ M^{-1}	kJ M^{-1}	J M^{-1} K^{-1}
PSF	SDS	288.15	670	2.1×10^9	51.5	38.0	46.4
		298.15	380	1.2×10^9	51.8		
		308.15	210	6.6×10^8	52.0		
PSF	SOS	288.15	13.3	2.1×10^7	40.4	20.7	72.5
		298.15	10.2	1.6×10^7	41.2		
		308.15	7.8	1.2×10^7	41.8		
SFO	SOS	288.15	28.8	4.6×10^7	42.2	21.2	73.5
		298.15	23.8	3.8×10^7	43.2		
		308.15	16.2	2.6×10^7	43.7		
SFT	SOS	288.15	19.4	3.1×10^7	41.3	21.7	73.0
		298.15	15.3	2.4×10^7	42.1		
		308.15	10.1	1.6×10^7	42.5		

a) Error limit=±20 M^{-1} for SDS and ±0.6 M^{-1} for SOS. b) Error limit=$\pm1.5\times10^7$ M^{-2} for SDS and $\pm2\times10^6$ M^{-2} for SOS.

SDS which was due to the disappearance of the protonated ion pairs as a result of solubilization of the dye by mixed micelle or micelle formation.[6]

It is quite interesting that the molar extinction coefficient of $HPSF^{2+}SDS^-$, (at $\lambda_{max}=582$ nm) is found to be 2250 $m^2 M^{-1}$, which is very close to the molar extinction coefficient of 2260 $m^2 M^{-1}$ of $HPSF^{2+}$ at 580 nm (in aqueous acids). The apparent equilibrium constant, K_c, obtained from the plot of $[PSF]_0/(d-d_0)$ vs. $1/[SDS]_0$, were found to be 670, 380, and 210 $dm^3 M^{-1}$ at 288.15, 298.15, and 308.15 K, respectively. These high values of the apparent equilibrium constants are comparable to those reported for the interaction of cationic dyes with large organic anions.[24]

The true equilibrium constant, K_e (where $K_e=K_c/[H^+]$), along with the thermodynamic parameters are given in Table 2. The high values of the ΔH and ΔS can be attributed to the formation of ionic hydrogen bonds involving the resulting ammonium ions.[22] The positive entropy suggests that the free dye and surfactant ions are more ordered than the protonated ion pair in water due to the tendency of water to retain its ordered structure. Here it can be mentioned that similar observations, i.e., positive entropy changes in case of hydrophobic interactions, have been reported[25,26] earlier.

PSF-SOS. SOS has a shorter hydrocarbon chain than SDS and therefore it is expected to show weaker interaction with PSF (due to lesser hydrophobicity)[27] than that of SDS. The electronic absorption spectra of PSF in aqueous media—with (from 2.21×10^{-3} to 2.21×10^{-2} M) and without SOS are given in Fig. 4. The spectral behaviors of PSF in SOS are similar to those of PSF in SDS. The λ_{iso} and the λ_{max} (from the difference in the spectral absorbance) were found to be at 540 and 565 nm, respectively. For a fixed concentration of PSF (2.20×10^{-5} M), the absorbance at 565 nm increases with the increase in concentration of SOS and the absorbance reaches a maximum value at ca. 2.5×10^{-2} M of SOS, and then started decreasing. At the same time the intensity of the 520 nm band started increasing with a slight shift of 520 nm band to longer wavelength. At and above 1.4×10^{-1} M of SOS, the absorbances of 565, 520, and 531 nm bands remained almost constant. The breaks in the plots of absorbance vs. concentration of SOS are at ca. 1.4×10^{-1} M indicate that the cmc of SOS, in the presence of ca. 9×10^{-6} M PSF, is ca. 1.4×10^{-1} M. The lower λ_{max} of PSF-SOS interaction product compared to the λ_{max} of the singly protonated PSF indicates that in this case the transfer of the proton to the dye may not be as complete as in the case of PSF-SDS, i.e., in the former the situation may be intermediate between complete proton transfer from solvent to the dye and hydrogen bonding between the solvent water and the dye.

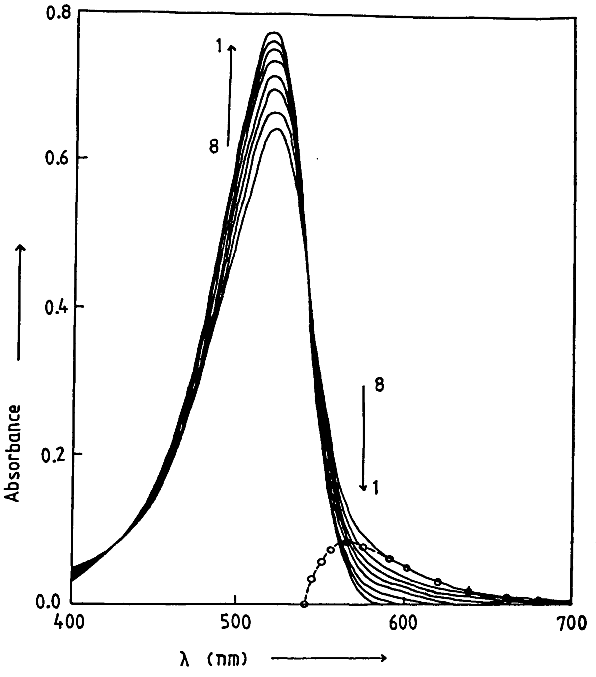


Fig. 4. Effect of variation in concentration of SOS on the spectra of PSF: $[PSF]=2.20\times10^{-5}$ M; $[SOS]\times10^3$ M=(1) 0.00, (2) 2.21, (3) 4.42, (4) 6.63, (5) 8.84, (6) 11.10, (7) 17.70, (8) 22.10; O---O---O, difference spectra of (8) and (1).

The equilibrium constants and the thermodynamic parameters were determined at pH 6.2 (the pH of the SOS solutions in the experimental concentration range of SOS below cmc) using Eqs. 4 and 5, and the results are summarized in Table 2. From the equilibrium constants and the other thermodynamic parameters it is evident that the interaction of PSF with SOS is much weaker compared to that with SDS. The slightly lower value of ΔS for PSF-SDS may be due to more ordering of the protonated ion pair in water, as SOS is relatively less hydrophobic compared to SDS.

Degree of Interaction. As a complementary to the equilibrium constants, we have examined the degree of interaction of PSF with SDS and SOS about the interaction in the entire submicellar concentration range. The degree of interaction was determined using Klotz equation,[28]

$$\alpha=(\varepsilon_{app}-\varepsilon_c)/(\varepsilon_0-\varepsilon_c), \tag{6}$$

where α is the fraction of the free dye, and ε_{app} is the apparent molar extinction coefficient. The values of ε_c for the interaction products were obtained from the Ketelaar's plots.

The degree of bound PSF vs. concentration of surfactants is shown in Fig. 5. It can be seen from the figure that the fraction of PSF bound to SDS is much larger compared to that bound to SOS, which implies that the interaction of PSF with SDS is much stronger compared to that with SOS. The fraction of hydrophobic-force-induced-protonated ion pairs increases upto a certain concentration of the surfactant (ca. 3×10^{-3} M for SDS and ca. 2.5×10^{-2} M for SOS), then starts decreasing with the increase in concentration of the surfactant

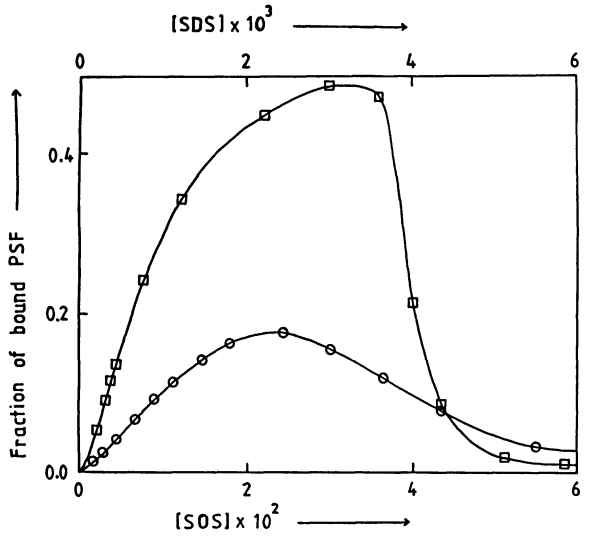


Fig. 5. Fraction of bound PSF vs. concentration of surfactant: [PSF]=2.20×10^{-5} M; □, SDS; ○, SOS.

till it becomes nearly zero at ca. 6×10^{-3} and ca. 1.4×10^{-1} M of SDS and SOS respectively.

SFO-SOS and SFT-SOS. SFO is a 2,8-dimethyl derivative of phenosafranine and SFT is a positional isomer of SFO. Both of these dyes have absorption maxima at 520 nm in the visible range. The spectral changes in the aqueous solutions of SFO and SFT on addition of SOS were similar to those of PSF–SDS and PSF–SOS. The spectra of SFO and SFT alone and in presence of SOS in the submicellar concentration range of SOS passed through isosbestic points at 545 and 548 nm, respectively. The $\lambda_{\max}$'s of the protonated ion pairs, viz., $HSFO^{2+}SOS^-$ and $HSFT^{2+}SOS^-$ have been found (from difference spectra) to be 576 and 580 nm, respectively.

The K_e and K_c of SFO–SOS and SFT–SOS systems were determined using Eq. 5, and the results along with the thermodynamic parameters are summarized in Table 2. From the table it can be seen that the submicellar interactions of SOS with SFO and SFT are stronger than that with PSF. This can be understood from the presence of two additional methyl groups in SFO and SFT over PSF, which makes the former two slightly more hydrophobic than the latter. The amino and methyl groups which are at 7- and 8-positions in SFO are at 6- and 7-positions in SFT. The difference in the strength of the interaction of SFO and SFT with SOS may be due to difference in basicities, and the unequal steric hindrance experienced by the amino groups at 7-position in SFO and at 6-position in SFT.

PSF, SFO and SFT, being cationic dyes,did not show any interaction with *N*-hexadecylpyridinium chloride, a cationic surfactant, even above the cmc, as expected. On the other hand, the visible absorption spectra of PSF, SFO and SFT in Triton X 100, a nonionic surfactant, show that there is interaction between these dyes and Triton X 100. From the spectral behavior, it is clear that there is no indication of induced protonation. This again supports the fact that hydrophobic ion pair formation and hence the opposite charges on the dye and the surfactant are the primary requisites for the hydrophobic force induced protonation. The appearance of new absorption bands at ca. 537 nm with clear isosbestic points for all the three dyes, on addition of the surfactant, clearly indicates the presence of an equilibrium, and the equilibrium constants were determined using Eq. 5. The equilibrium constants for SFO, SFT, and PSF with the surfactant were 400, 380, and 155 $dm^3 M^{-1}$, respectively, at 298.15 K. The strength of the interaction of the dyes with Triton X 100 varies in the order, SFO>SFT>PSF. This trend goes in parallel to that of the dyes with SOS. The values of K_e for the formation of protonated ion pairs of the phenazinium dyes with the two anionic surfactants are of the order of 10^7 to 10^9. These high values can be compared with the equilibrium constant of the order of 10^6 for the deprotonation of Methyl Orange by octadecyltrimethylammonium bromide.[29)]

Conclusion

Our experimental results indicate that the cationic dyes, viz., PSF, SFO, and SFT interact strongly with anionic surfactants even when the concentrations of the surfactants are very low (far below the cmc). Opposite charges on the dye and the surfactant are the primary requirements for the ion pair formation, and this process is facilitated by the hydrophobic forces. The interaction product is a protonated ion pair induced by hydrophobic force. From the present study, it can be concluded that the hydrophobicity of the surfactant plays an important role in the ion pair formation as well as in induced protonation of the dye in the ion pair.

References

1) M. E. Diaz-Garcia and A. Sanz-Medel, *Talanta,* **33**, 255 (1986).

2) R. C. Kapoor, *J. Indian Chem. Soc.*, **63**, 541 (1986).

3) W. L. Hinze, "Solution Chemistry of Surfactants," ed by K. L. Mittal, Plenum Press, New York (1979), p. 79.

4) J. H. Callahan and K. D. Cook, *Anal. Chem.*, **56**, 1632 (1984).

3) K. K. Rohatgi-Mukherjee, P. Choudhuri, and B. B. Bhowmik, *J. Colloid Interface Sci.*, **106**, 45 (1985).

6) R. L. Reeves and S. A. Harkaway, in "Solution Chemistry of Surfactants," ed by K. L. Mittal, Plenum Press, New York (1979), p. 819.

7) B. K. Kim, A. Kagayama, Y. Saito, K. Machida, and T. Uno, *Bull. Chem. Soc. Jpn.*, **48**, 1394 (1975).

8) V. C. Reinsborough and J. F. Holzwarth, *Can. J. Chem.*, **64**, 955 (1986).

9) P. Mukerjee and K. J. Mysels, *J. Am. Chem. Soc.*, **77**, 2937 (1955).

10) G. S. Bertolotti, J. J. Cosa, H. E. Gsponer, M. Hamity, and C. M. Previtali, *Can. J. Chem.*, **64**, 846 (1986).

11) H. Sato, M. Kawasaki, K. Kasatani, Y. Kusumoto, N.

Nakasima, and K. Yoshihara, *Chem. Lett.*, **1980**, 1529.

12) C. J. Drummond, F. Grieser, and T. W. Healy, *J. Chem. Soc., Faraday Trans. 1,* **85**, 521, 537, 551, 561 (1989).

13) K. R. Gopidas and P. V. Kamat, *J. Phys. Chem.*, **94**, 813 (1990).

14) E. L. Colichmann, *J. Am. Chem. Soc.*, **73**, 1795 (1951).

15) G. N. Lewis, T. T. Magel, and D. Lipkin, *J. Am. Chem. Soc.*, **64**, 1774 (1942).

16) R. D. Stichler, T. Chen, and W. M. Clark, *J. Am. Chem. Soc.*, **55**, 891 (1933).

17) P. Mukerjee and A. K. Ghosh, *J. Am. Chem. Soc.*, **92**, 6403 (1970).

18) A. W. Adamson, "Physical Chemistry of Surfaces," John Wiley & Sons, New York (1982), p. 244.

19) R. N. Diamond, *J. Phys. Chem.*, **67**, 2513 (1963).

20) D. Weir and J. C. Scaiano, *Tetrahedron,* **43**, 1617 (1987).

21) C. A. Bunton and M. J. Minch, *J. Phys. Chem.*, **78**, 1490 (1974).

22) M. Meot-Ner, "Molecular Structure and Energetics," ed by J. F. Liebman and A. Greenberg, VCH Publishers, Inc., New York (1987), Vol. 4, p. 71.

23) J. A. A. Ketelaar, C. Van de Stolpe, and H. R. Gersmann, *Rec. Trav. Chim.*, **70**, 499 (1952).

24) S. Hamai, *Bull. Chem. Soc. Jpn.*, **58**, 2099 (1985).

25) A. Wishnia, *J. Phys. Chem.*, **67**, 2079 (1963).

26) E. Tomlinson, S. S. Davis, and G. I. Mukhayer, "Solution Chemistry of Surfactants," ed by K. L. Mittal, Plenum Press, New York (1979), p. 889.

27) M. Tanigushi, A. Yamagichi, and T. Iwamoto, *J. Phys. Chem.*, **94**, 2534 (1990).

28) I. M. Klotz, *J. Am. Chem. Soc.*, **68**, 2299 (1946).

29) C. F. Hiskey and T. A. Downey, *J. Phys. Chem.*, **58**, 835 (1954).