Salt effects on surfactant aggregation and dye-micelle complexation

Kamala R Acharya, Subhash C Bhattacharya* & Satya P Moulik

Physcial Chemistry Section, Chemistry Department, Jadavpur University, Calcutta 700 032, India

Physical parameters for characterizing the structure of micelles are necessary for their surface chemical understanding. The effects of salts on physical characteristics (viz. critical micelle concentration, aggregation behaviour, counter ion binding, dye binding, etc.) of micelles have been investigated. The critical micelle concentration of ionic surfactant (sodium dodecylsulphate) has been found to decrease with addition of salt while for nonionic surfactants (Tweens) the change is insignificant. The aggregation number as well as safranine T and phenosafranine micelle binding constants show increase for ionic micelles in salt environment. The effects of salt in the above regards on nonionic micelles are negligible.

Micelles and microemulsions exhibit interesting properties that have generated interest for their detailed physicochemical exploration employing a great variety of techniques[1]. Studies of their structural behaviours in solution find important place in literature[2-5]. Salt addition into ionic micellar solution modifies the coulombic repulsions between polar head groups and alters the micellar structure. Micellar shape may undergo a salt induced sphere to rod transition at and above a threshold concentration and sizeable micellar growth under such a condition may occur[6].

Ionic surfactants have comparatively high CMC values (with monovalent counter ions). Multivalent counter ions fairly decrease the CMC[6] as a result of lower volume requirement for the bound counter ions. Nonionic surfactants have much lower CMC values, a much wider range of CMC is offered to them by different polar group structures. It is desirable to research on factors that influence CMC in order to design kinetic experiments of micellar catalysis and inhibition, as well as hydrophobic interaction. Like CMC, aggregation numbers are dependent on the surfactant type, solvent medium, the presence of inorganic and organic additives and on temperature[6]. Since the effectiveness of micellar solution depend on micellar size and geometry, informations on these properties along with CMC are required for meaningful interpretation of kinetic and equilibrium data.

Among different methods employed in micellar studies, fluoresence technique is advantageous in elucidating CMC, aggregation number and micellar microenvironment[7-14]. Alghough salt effect on micellar aggregation number has been studied the dependence at various concentration levels remain less explored. The aggregation behaviour can be conveniently followed from fluorescence measurements. The salts normally cause a decrease in CMC and increase in aggregation number of ionic micelles; the counter ion binding (condensation) is also altered. Nonionic surfactants are least affected by moderate addition of salt, the minor property variation may arise due to altered activities of surfactant monomers by the salt, it may be termed as a salting out phenomenon. The objective of the present investigation is an extension of our previous photophysical studies in terms of quantification of surfactant aggregation and dye-micelle interaction with reference to the process energetics.

Materials and Methods

Safranine T (E. Merck) and phenosafranine (E. Merck) were recrystallised twice from ethanol water before use. The surfactants sodium dodecylsulphate (SDS), octyl phenyl polyoxyethylene ether (Triton X-100) presented as TX-100), polyoxyethylene sorbitan monolaurate (Tween 20), monopalmitate (Tween 40), monostearate (Tween 60) and monooleate (Tween 80) were either BDH or Sigma products. Their characteristics and purity standards were the same as reported previously[15,16]. Doubly distilled conductivity water was used for solution preparation. Sodium chloride and bromide used were E. Merck products.

Absorption spectra were recorded using a Shimadzu (Japan) UV-vis spectrophotometer (160A) with a matched pair of silica cuvettes (path length 1 cm). Fluorescence spectral measurements were recorded on a spectrofluorometer (Fluorolog

F IIIA spectrofluorometer, Spex Inc., NJ, USA)
with a slit width of 2.5 nm. The excitation and
emission wavelengths were 520 nm and 587 nm
respectively.

All spectral measurements were duplicated in a
constant temperature water bath, 25°C, accurate
to within ±0.1°C and the mean values were
processed for data analysis.

The concentrations of safranine T (ST) and
phenosafranine (PSF) used in the micellar solu-
tions were of the order of 10^{-5} mol dm^{-3}. The
concentrations of Tweens were 10^{-3} mol dm^{-3} in
solution while that of SDS was 10^{-2} mol dm^{-3}.
The concentration of NaCl was in the range of
1-7×10^{-1} mol dm^{-3}.

Fig. 1—OD/OD$_0$ versus log[C] a, b, c, d represent the salt
concentration 0.1 M, 0.3 M, 0.5 M and 0.7 M respectively for
Tween 20.

Results

Critical micelle concentration

The absorbance and emission intensities of ST
and PSF are enhanced in micellar solution in the
presence of the added salt. From the measurement
of absorbance of dye at different concentrations of
surfactants in the presence of salt, the CMC va-
lues are obtained from the A/A_0 versus
log [surfactant] plots (Fig. 1). The values are given
in Table 1. The results indicate that the CMC
value decreases with increase in salt concentration.
The phenomenon is prominent for ionic surfact-
ants, it is minor for nonionic surfactants. A linear
variation of log CMC with log{[salt]+CMC} has
been observed in all cases, a graphical illustration
is shown in Fig. 2. From the slope of the plot, the
fraction of counter ions (m/n) bounded to micelle
has been obtained according to the relation,
log CMC = constant $- m/n$ log[C$_i$], where n is the
aggregation number and m is the number of coun-
ter ions [C$_i$] bound per micelle.

The m/n values are given in the last row of
Table 1. It is 0.65 for SDS. For nonionic surfact-
ants, counter-ion binding is not meaningful but mi-
nor slopes in the range of 0.12-0.15 are observed
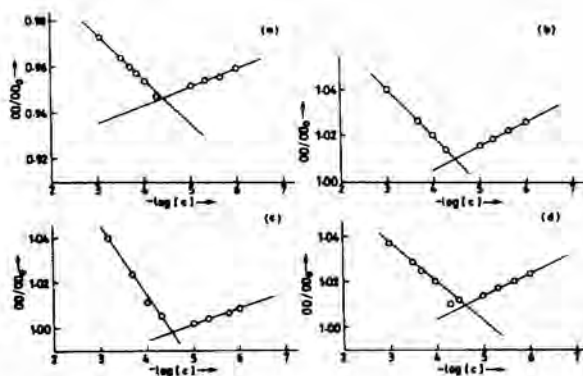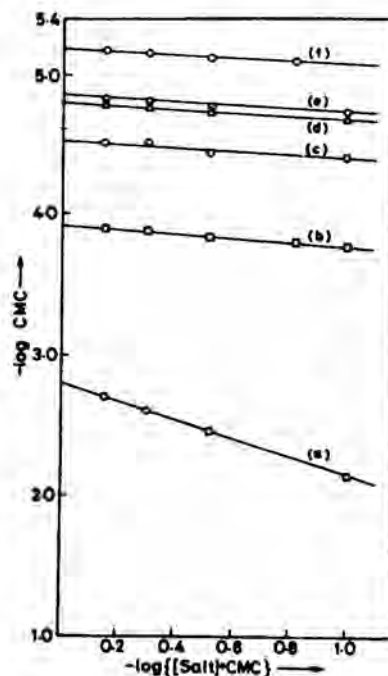for which we have no explanation. The results

Fig. 2—log CMC versus log{[salt]+CMC}, a, b, c, d, e, f, rep-
resent SDS, Triton X-100, Tween 20, Tween 40, Tween 60
and Tween 80 respectively.

Table 1—Salt effect on CMC of the surfactants at 300 K

[NaCl] mol dm^{-3}	CMC × 10^4/ mol dm^{-3}					
	Tween 20	Tween 40	Tween 60	Tween 80	Triton X-100	SDS
0.1	0.40	0.21	0.18	0.091	1.8	65
0.3	0.36	0.20	0.17	0.089	1.4	54
0.5	0.30	0.14	0.16	0.085	1.3	42
0.7	0.25	0.10	0.15	0.080	1.2	31
m/n	0.13	0.14	0.14	0.125	0.15	0.65

suggest that 65% of the counter ions are bound to the micelles of SDS. This is lower than the reported m/n on SDS[21]. The addition of salt to ionic micellar solutions modifies the coulombic repulsions between polar head groups and alters the micellar structure. The results of course contain an element of uncertainity because the aggregation number of micelles has been assumed to be independent of salt concentration in the derivation of Eq. (3) which is not correct in the true sense because micelles of variable sizes should possess variable capacity of holding counter ions. This is subsequently elaborated.

Binding constants

The complex formation was also quantified from absorbance measurements. On the pseudophase model, [micelle] = ([S]-CMC)/n. For [S] ≫ CMC, the micellar concentration [M] = [S]/n, and dye interacts with M according to the equilibrium

$$Dye + M \overset{K_c}{\rightleftharpoons} DM \qquad \dots (1)$$

where K_c is the binding constant. K_c was determined by the modified equation of Lang as reported earlier[17].

$$\frac{[S]}{n(\varepsilon - \varepsilon_o)} = \frac{1}{(\varepsilon_c - \varepsilon_o)} \left\{ [D] + \frac{[S]}{n} - \frac{(\varepsilon - \varepsilon_o)[D]}{(\varepsilon_c - \varepsilon_o)} \right\}$$
$$+ \frac{1}{K_c(\varepsilon_c - \varepsilon_o)} \qquad \dots (2)$$

where [D] stands for dye, [S] for surfactant and ε, ε_c and ε_o are the molar absorptivities of the solution, complex and the dye solution respectively, n is the aggregation number of the micelles. Representative plots of

$$\frac{[S]}{n(\varepsilon - \varepsilon_o)} \text{ versus } \left\{ [D] + \frac{[S]}{n} - \frac{(\varepsilon - \varepsilon_o)[D]}{\varepsilon_c - \varepsilon_o} \right\}$$

for Tweens and Triton X-100 are illustrated in Fig. 3. The 1:1 dye-micelle complex formation takes place with different degrees of affinity following the order, Tween 80 > Tween 60 > TX-100 > Tween 40 > Tween 20 > SDS[17]. In this study, the effect of salt on K_c has been determined. The K_c values are calculated using Eq. (2), and the results are given in Table 2. With increase in concentration of salt, both K_c and K_c' values have increased. With nonionic micelles the increment is minor. The plot of $\log K_c$ ($\log K_c'$) versus

[salt] is given in Fig. 4.

Aggregation number

The fluorescence of the dyes (at a constant concentration) is enhanced in aqueous surfactant environment[17] which is perceptible above CMC. For SDS the dye ST has been found to yield inconsistant results which is consistent for nonionics, TX-100 and the Tweens. The results with PSF for SDS are consistent and are therefore herein reported. The fluorescence and absorption of the dye in the aqueous solution of surfactants in the presence of different concentrations of NaCl have been measured with increasing surfactant concentration. At constant [dye] and [salt], the fluorescence intensity (F_0) has increased with [surfactant] forming a plateau (F_{max}). Considering a 1:1 complexation of dye with the micelle, the $F_{max} - F_0$ can be taken to be proportional to $[D_{comp}]$, i.e.

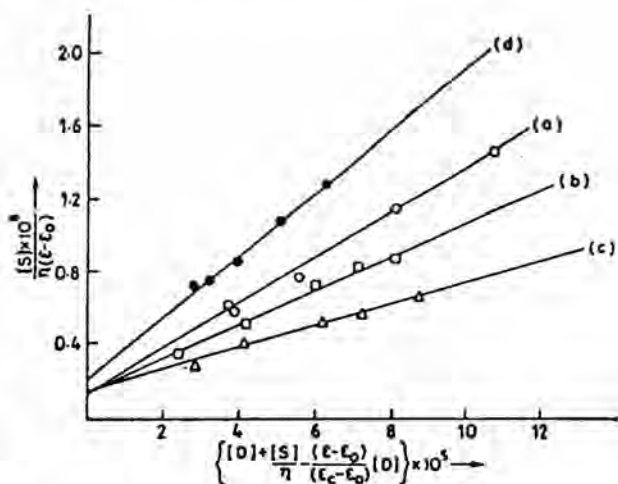Fig. 3—$[S]/n(\varepsilon - \varepsilon_o)$ versus $\{[D] + [S]/n - (\varepsilon - \varepsilon_o)/(\varepsilon_c - \varepsilon_o)[D]\}$ for Tween 20 where a, b, c, d represent 0.1 M, 0.3 M, 0.5 M and 0.7 M salt concentration respectively.

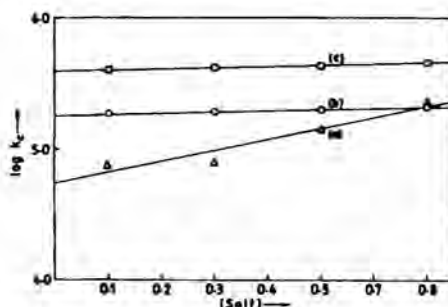Fig. 4—$\log K_c$ versus [salt] where a, b, c represents SDS, Tween 20 and Tween 80 respectively.

$$(F_{max} - F_0) = K[D_{comp}] \qquad \ldots (3)$$

where $[D_{comp}]$ is the maximum concentration of dye micelle combine.

At any other state of enhanced fluorescence, F

$$(F - F_0) = K[D'_{comp}] \qquad \ldots (4)$$

where $[D'_{comp}]$ is the [complex] corresponding to F.
Combining Eqs 1, 3, and 4 we get,

$$\frac{1}{(1 - F_R)} = \left(\frac{K'_c}{n}\right) \frac{[S]}{F_R} K'_c [D_T] \qquad \ldots (5)$$

A plot of $1/(1 - F_R)$ versus $[S]/F_R$ should be linear to yield K'_c and n from the intercept and the slope respectively (Fig. 5). The K'_c and n values are presented in Table 2. The derived n and K'_c values are aggregation number and binding constants in the presence of salt. For SDS, sharp increase in n values were observed in the presence of NaCl. For nonionic surfactants n remains independent of salt concentration as expected.

The aggregation number has been found to depend on the concentration of the surfactant used, it has increased with increasing concentration of SDS. This has been also observed earlier[18], elaborate studies are on the other hand lacking.

Discussion

The results indicate that salt has appreciable effects on micellisation characteristics of ionic surfactant SDS. The charged head groups of micel-lised monomers and a part of the relatively small counter ions are located in the microscopic Stern layer of the micellar solution interface which guides the net charge on the micelle. Majority of the counter ions are, on the other hand, located in the Gouy-Chapman electrical double layer where they are completely dissociated from the charged aggregate and are able to exchange with ions in the bulk of the solution. Addition of counter NaCl in solution of SDS increases the fraction of ions in the double layer. The thickness of the electrical double layer is reduced and chances of counter ion condensation on micelle increase. Reduced surface charge by the process lowers the repulsion between surfactant ions, resulting in the formation of micelles with increased aggregation number. The shapes of the micelles may change from spherical to ellipsoidal to cylindrical structures with increased aggregation number[1,6]. The increase in the aggregation number is paralleled by the decrease in CMC of ionic surfactants. The CMC of
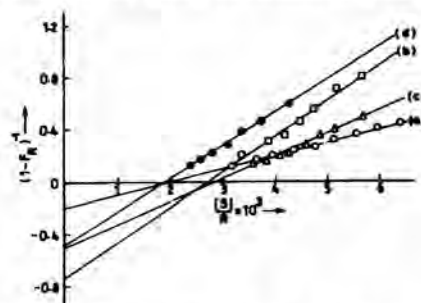

Fig. 5—$(1 - F_R)^{-1}$ versus $[S]/F_R$ for Tween 20 where a, b, c, d represent salt concentration 0.1 M, 0.3 M, 0.5 M and 0.7 M.

Table 2—Variation of binding constants and aggregation number with concentration of salt (K_c is obtained from absorption measurements and K'_c from emission measurement)

[NaCl] mol dm^{-3}	$K_c \times 10^{-5}$ $K'_c \times 10^{-5}$ n	Surfactants					
		SDS	Triton X-100	Tween 20	Tween 40	Tween 60	Tween 80
0.05	K_c	0.7					
	K'_c	0.75					
	n	90					
0.1	K_c	0.76	2.4	1.9	2.0	3.0	4.0
	K'_c	0.82	2.6	1.8	2.8	3.9	4.4
	n	118	136	80	95	110	120
0.3	K_c	0.8	2.4	1.9	2.0	3.2	4.2
	K'_c	0.98	2.8	1.8	3.0	3.9	4.5
	n	135	136	80	95	110	120
0.5	K_c	1.4	2.5	2.0	2.2	3.4	4.4
	K'_c	1.32	3.0	2.0	3.4	4.1	4.7
	n	186	136	82	95	110	120
0.7	K_c	2.3	2.6	2.1	2.4	3.6	4.5
	K'_c	2.8	3.2	2.0	3.5	4.1	4.7
	n	403	136	82	95	110	120

SDS decreases[5] with [NaCl]. A sharp decrease in the lower range of concentration has been reported[5,6]. The present results are higher and the decrease in CMC is not significantly sharp at the initial stage. The spectral (visible and fluorescence) methods have shown higher CMC. The CMC decrease with salt measured by the surface tension method is comparable to the value obtained using light scattering technique.

The CMC and aggregation number of nonionic amphiphiles are not appreciably affected by the addition of strong electrolytes. Minor variation at high salt concentration by the alteration of the amphiphile activity may be only envisaged.

Light scattering measurements of Ikeda et al.[19] on sodium dodecylsulphate, have envisaged preferential micelle-solvent interaction, the aggregation numbers remaining moderately dependent on the addition of NaCl. Similar reporting has been made by Doughty[20] and Turro and Yekta[22] from isopiestic distillation measurements on SDS. According to Mazer et al.[3] transition to cylindrical micelles from spherical increases the aggregation number to 1000 at 0.6 mol dm^{-3} NaCl at 25°C. The results herein presented are in line with the observations of Hayashi and Ikeda[5]. The reported n by Mazer et al.[3] at 0.6 mol dm^{-3} NaCl is nearly three fold higher. It is interesting to note that by the same light scattering method Hayashi and Ikeda have reported lower n values than Mazer et al.[3] In Fig. 6 the reported salt dependent n values of SDS are presented. It is seen that disagreement occurs at higher salt concentration.

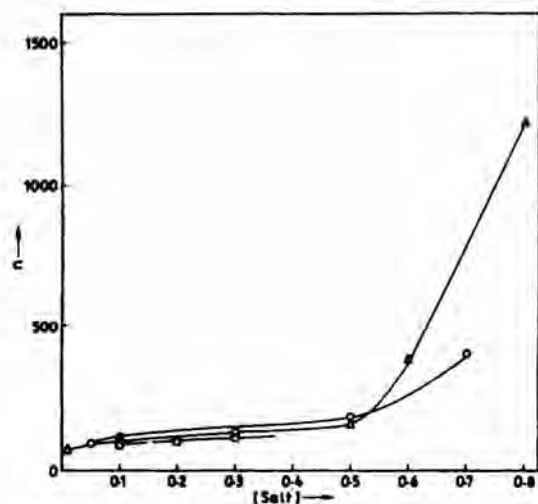A striking difference between the nonionic surfactants and the ionic surfactants is the much wider range of CMC provided by different polar group structures. In general, it is observed that the CMC is reduced by adding electrolyte containing the same counter ion as in the micelle for ionic surfactants. For nonionic surfactants, electrolytes that are known to be capable of salting out' i.e. NaCl etc. reduce the CMC slightly. For SDS about 65% Na$^+$ ions have been estimated to associate with the micelles. This is lower than literature reports[21] based on other kinds of measurements.

In our estimation, the counter ion condensation has been considered to remain unchanged in the range of varied [NaCl] which is also the essential condition of electrochemical methods used for such determinations.

The increased K_c or K'_c with increasing micellar size (as a consequence of increasing aggregation number due to salt effect) presented in Fig. 7 suggests enhanced formation of the 1:1 dye-micelle complex. The agreement between K_c and K'_c is fair. They are mildly dependent on [NaCl]. The effective micellar charge for SDS is not appreciably affected by the presence of NaCl which is in accordance with the unchanged degree of counter ion binding in the studied range of concentration. Non-specific hydrophobic interaction seems to be more important then electrostatic interaction. Higher K_c and K'_c values with nonionic micelles end support to this rationale.

The presence of electrolytes in micellar solutions may affect the physical state of the aqueous medium in different ways. The presence of salt in aqueous solution modifies the hydrogen bonded structure of water and the interfacial polarity of micelles at the microscopic level. These factors have their contributions on the dye-micelle formation process.
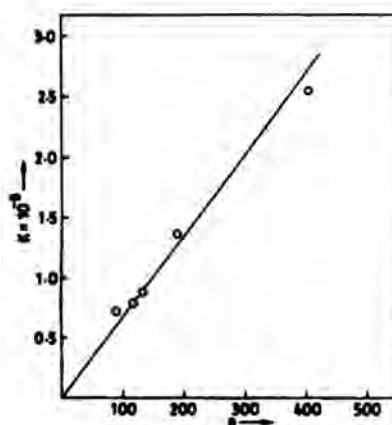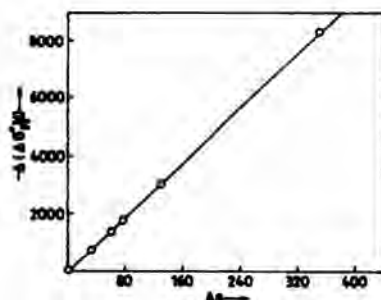

Fig. 6—n versus [salt] where O represents PSF probe in SDS-NaCl system and Δ represents results from reference 19. □ represents results from reference 22.

Fig. 7—K versus n where O represents SDS-NaCl where K is average of K_c and K'_c.

Table 3—Variation of n, ΔG_m^0, $\Delta(\Delta G_M^0)$, at various salt concentrations

Surfactant	[NaCl]/[NaBr] (mol dm^{-3})	n	ΔG_m^0 (kJ mol^{-1})	ΔG_M^0 (kJ mol^{-1})	$-\Delta(\Delta G_M^0)$ (kJ mol^{-1})	Δn
	0	58	−19.6	−1136.8	0	0
	0.05	90	−20.3	−1827	690.2	32
	0.10	118	−20.6	−2430.8	1294	60
SDS	0.30	135	−21.3	−2875.5	1738.7	77
	0.50	186	−22.4	−4166.4	3029.6	128
	0.70	403	−23.6	−9510.8	8374	350
	0	80	−28.0	−2241	—	—
	0.1					
	0.3					
T-20	0.5					
	0.7					
	0	95	−30.0	−2885	—	—
	0.1					
	0.3					
T-40	0.5					
	0.7					
	0	110	−30.6	−3366	—	—
	0.1					
T-60	0.3					
	0.5					
	0.7					
	0	120	−32.3	−3877	—	—
	0.1					
T-80	0.3					
	0.5					
	0.7					
	0	136	−24.0	−3270	—	—
	0.1					
TX-100	0.3					
	0.5					
	0.7					

Fig. 8—$\Delta(\Delta G_M^0)$ versus Δn, O represents SDS-NaCl.

Free energy of micellisation

The standard free energy change of micellisation per mole of surfactant (ΔG_m^0) on mass action model is given by the relation

$$\Delta G_m^0 \left(= \frac{\Delta G_M^0}{n} \right) = (1 + m/n)RT \ln \text{CMC} \quad \ldots (6)$$

where m/n is the fraction of counter ion bound to a micelle and ΔG_m^0 is the standard free energy of micellisation expressed per mole of micelle.

For nonionic micelle $\Delta G_m^0 = RT \ln \text{CMC} \ldots (7)$

The ΔG_M^0 is obtained by multiplying ΔG_m^0 with the micellar aggregation number n. The results are given in Table 3 with other related parameters. The variation of ΔG_m^0 with [NaCl] for SDS is appreciable compared to ΔG_M^0. The increase in the aggregation number with salt addition in a way demonstrates salting out of monomers from the aqueous to micellar environment. The $[(\Delta G_M^0)_{salt} - (\Delta G_M^0)_{no\ salt}] = \Delta(\Delta G_M^0)$ may thus account for the free energy contribution to this phenomenon.

Its variation with Δn $(n_{salt}\text{-}n_{no\ salt})$ is given in Fig. 8. The linear plot obeyed the equation $-\Delta(\Delta G_M^0) = 23\ \Delta n$ for SDS with excellent correlation. The slope of the line stands for the salting out free energy contribution per mole change in the aggregation number of the micelle.

Based on the above observations it can be concluded that (i) the CMC value of SDS decreases with [NaCl] whereas the CMCs of nonionic surfactants are only minorly affected by salt; (ii) the aggregation number of ionic surfactant SDS increases with increasing [NaCl] which remains practically unaffected for nonionic surfactants; (iii) the mild salt effect on the binding of the dye with SDS micelle as well as comparable K_c and K_c' values for the ionic SDS and nonionic Tween micelles support hydrophobic rather than electrostatic interaction guiding the complexing process and (iv) the free energy of transfer of SDS monomer in micelle from aqueous to salt environment has an excellent linear correlation.

References

1 Desgranges G R, Bordere S & Roux A H, *J Colloid interface Sci*, 162 (1994) 284.

2 Reiss-Husson F & Luzzati V, *J phys Chem*, 68 (1964) 3504.

3 Mazer N A, Benedek G B & Carey M C, *J phys Chem*, 80 (1976) 1075.

4 Ekwall P, Mandel L & Solyom P, *J Colloid interface Sci*, 35 (1971) 519.

5 Hayashi S & Ikeda S, *J phys Chem*, 84 (1980) 744.

6 Fendler J H & Fendler E J, *Catalysis in micellar and macromolecular systems* (Academic Press, New York) (1975).

7 Lianos P & Zana R, *J Colloid interface Sci*, 84 (1981) 100.

8 Lianos P & Zana R, *J phys Chem*, 84 (1980) 3339.

9 Almgreen M & Swarup S, *J Colloid interface Sci*, 91 (1983) 256.

10 Almgreen M & Swarup S, *J phys Chem*, 87 (1983) 876.

11 Almgreen M & Swarup S, *J phys Chem*, 86 (1982) 4212.

12 Lofroth J E & Almgreen M, *J phys Chem*, 86 (1982) 1636.

13 Bhattacharya S C, Das H & Moulik S P, *J photochem photobiol A : Chem*, 79 (1994) 109.

14 Bhattacharya S C, Das H & Moulik S P, *J photochem photobiol A : Chem*, 79 (1994) 109.

15 Moulik S P, Gupta S & Das A R, *Can J Chem*, 67 (1984) 356.

16 Moulik S P, Roy S & Das A R, *J phys Chem*, 81 (1977) 1766.

17 Bhattacharya S C, Das H & Moulik S P, *J photochem photobiol A : Chem*, 74 (1993) 293.

18 Malliaris A, Binana-Limbele W & Zana R, *J Colloid interface Sci*, 110 (1986) 114.

19 Ikeda S, Hayashi S & Imae T, *J phys Chem*, 85 (1981) 106.

20 Doughty D A, *J phys Chem*, 83 (1979) 2621.

21 Zana R, *J Colloid interface Sci*, 78 (1980) 330.

22 Turro N J & Yekta A, *J Am chem Soc*, 100 (1975) 5951.