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Spectral and fluorimetric studies on the effect of surfactants on thionine

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Abstract. The effect of surfactants on the absorption and emission properties of thionine (TH^+) have been studied in detail. Among the various surfactants investigated sodium lauryl sulphate (SLS) has marked effect on these properties. Changes in the absorption spectrum and the decrease in fluorescence intensity at [SLS] below the critical micelle concentration (CMC) are attributed to the formation of a dye-surfactant complex. At [SLS] above CMC, the restoration of dye spectrum with increased extinction coefficient at the λ_{max} and a small but definite red shift of the λ_{max} are interpreted as due to the incorporation of the dye into the SLS micelle. The absorbance and spectral shift data suggest the thionine cation to be localized near the micelle Stern layer in the case of SLS micelles but completely outside the micelle in the aqueous environment in the case of CTABr. From the absorbance and fluorescence data, the association constant for the formation of the TH^+–SLS complex in the premicellar region, and the binding constant for the incorporation of the dye into the micelle in the micellar region have been computed. The values of both these constants were found to increase markedly in the presence of electrolytes.

Keywords. Thionine ; dyes ; surfactants ; micelles ; critical micelle concentration ; fluorescence.

1. Introduction

The behaviour of dyes in the presence of surfactant molecules is important for understanding the thermal and light-induced reactions in biomembranes (Singhal *et al* 1970; Hevesi *et al* 1970). Such reactions occur through the mediation of excited and free radical species whose behaviour in a micellar medium can be significantly different from that in a homogeneous aqueous medium. Our main interest was the study of the photoredox reactions of the cationic dye thionine, TH^+. Our work on this dye in homogeneous aqueous solutions has been reported earlier (Guha *et al* 1979). Before studying the photoredox chemistry in micellar systems we considered it worthwhile to study its location and interactions in such systems. We have therefore investigated the absorption and emission characteristics of this dye in the presence of various surfactants. The thionine-SLS system was studied in detail and the results are reported here.

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2. Experimental

Thionine (Fluka, puriss) was purified by repeated extraction with chloroform till the red colour due to impurities disappeared in the organic phase. This was followed by twice crystallization from an aqueous HCl solution. SLS (Fluka, pract. grade) and sodium dodecyl benzene sulfonate, SDDBS (Fluka, Tech. grade) were purified by repeated washing with diethyl ether followed by drying over fused calcium chloride in a vacuum desiccator. Triton X-100 (Koch-Light, scintillation grade), Brij-35 (Pierce Chem. Co., specially purified grade) and Cetyl pyridinium chloride, CPC (E. Merck) were used as such. Cetyl trimethyl ammonium bromide, CTABr (Hopkin and Williams) was purified by dissolving the substance in the minimum quantity of methanol, precipitating with diethyl ether and drying in a vacuum desiccator over fused $CaCl_2$. All other chemicals were the purest commercially available. Solutions were prepared in triply distilled water. Requisite volumes of stock solutions of thionine (10^{-3} mol dm^{-3}) and the surfactant (10^{-1} mol dm^{-3}) were diluted together to give solutions containing the two at the required concentrations. Absorption spectra were recorded on a Hitachi Perkin Elmer UV-visible spectrophotometer employing appropriate blanks, and fluorescence measurements were carried out using an Aminco-Bowman spectrophotofluorometer.

3. Results

3.1. *Sodium lauryl sulphate*

The results of both spectral and fluorescence measurements for 10^{-5} mol dm^{-3} thionine at different SLS concentrations are summarized in figure 1. Similar behaviour was observed at other dye concentrations. It is seen that with increasing SLS concentration the absorbance at 597 nm (λ_{max} of thionine) as well as fluorescence at 622 nm (for $\lambda_{excitation}$ = 597 nm) both first decrease, reach a minimum at 10^{-3} mol dm^{-3} SLS, steeply rise between 1-3 × 10^{-3} mol dm^{-3} SLS and level off thereafter. In the low surfactant concentration region where the absorbance of the 597 nm dye band and fluorescence intensity decrease, two new bands at 515 nm and 635 nm appear (figure 2) whose absorbances increase to a maximum at 1 × 10^{-3} mol dm^{-3} SLS and sharply decrease to zero in the 1-3 × 10^{-3} mol dm^{-3} SLS region. Similar changes in absorption spectra and fluorescence of dyes in presence of surfactant molecules of opposite charge have been reported in the past (Corrin and Harkins 1947; Mukherjee and Mysels 1955; Malik and Chand 1972; Hevesi and Rozsa 1971). In the case of the cationic dye pinacyrol and anionic surfactant SLS, a new absorption band has been observed (Mukherjee and Mysels 1955), which is not present in the pure aqueous solution. For 3,3-diethylthiacarbocyanine iodide, a cationic dye, significant change in the absorption spectrum in presence of SLS has been reported (Sato *et al* 1980). The disappearance of the dye absorption band and formation of new bands known as metachromism generally observed when the dye and surfactant bear mutually opposite charges. In the thionine-SLS (Hevesi and Rozsa 1971) and thionine-Rh6G-SLS systems (Lohoczki and Hevesi 1972) additional band at 465 nm has been assigned to a dye-surfactant complex. However, this band was observed by us only when

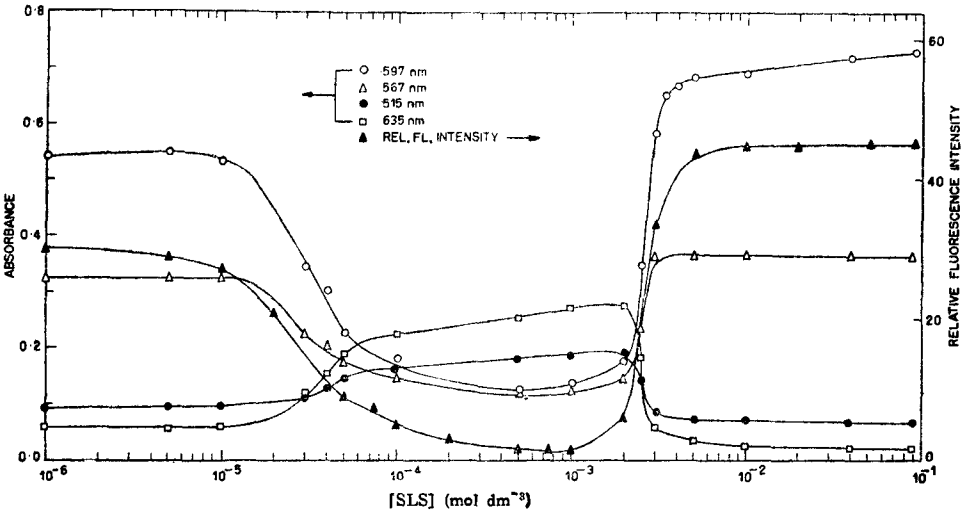

Figure 1. Effect of SLS on the absorbance and fluorescence of thionine solutions.

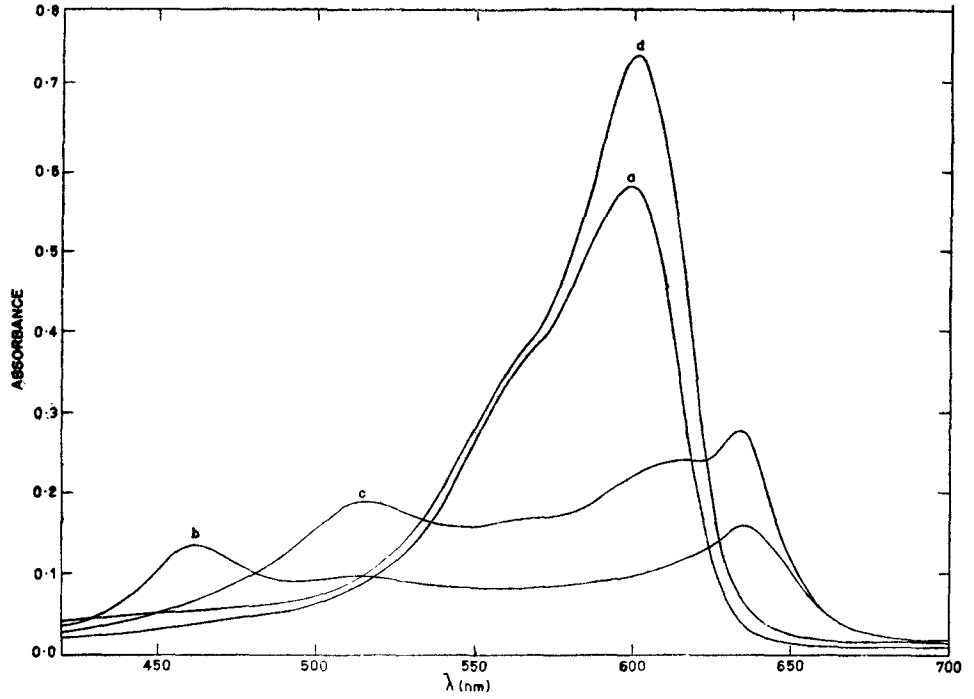

Figure 2. Absorption spectra of thionine (10^{-5} mol dm^{-3}) : (a) in absence of SLS ; and in the presence of (b) unpurified SLS, 10^{-3} mol dm^{-3}, (c) purified SLS, 10^{-3} mol dm^{-3}, (d) purified SLS 0·09 mol dm^{-3}.

unpurified SLS was used (Curve 1, figure 2). By mass spectral analysis the impurity recovered by evaporation of the ether extract obtained during the purification of SLS was found to be dodecanol. Since the solubility of this impurity in water

was low, thionine prepared in its saturated solution did not exhibit the 465 nm band but on addition of an aliquot of this saturated solution to thionine-pure SLS system (with [SLS] $\sim 10^{-3}$ mol dm^{-3}) the 465 nm band was observed alongwith bands at 515 and 635 nm. Decanol similarly added was found to show the same effect.

The colour changes observed at low surfactant concentration have been variously attributed in the past to formation of ion pairs (Colichman 1950), complexes (Malik and Chand 1972), insoluble complex salts (Klevens 1947) and dye aggregates (Corrin and Harkins 1947). The fact that such a behaviour is characteristic of oppositely charged dye and surfactant molecules agrees with the first three possibilities. Mukherjee and Mysels (1955) have in fact characterised and isolated a 1 : 1 dye-detergent complex salt in the case of methylene blue. In the pinacyanol–SLS system, a highly insoluble salt was found to form a stable suspension in the presence of somewhat more than stoichiometric amounts of the detergent (Mukherjee and Mysels 1955). In the present thionine–SLS system, a precipitate was observed only at 3×10^{-5} mol dm^{-3} TH^+ and 10^{-4} mol dm^{-3} SLS. At other compositions the solutions were optically clear and precipitation could not be induced by any means. In the transition region 10^{-5}–10^{-4} mol dm^{-3} SLS where the dye band intensity diminishes abruptly and new bands at 515 and 635 nm appear, thionine spectra were found to exhibit isobestic points at 530 and 620 nm (figure 3). Such a spectral behaviour and also the change in fluorescence intensity can be interpreted as due to an equilibrium involving association of the dye cation (D^+) and the lauryl sulfate anions (S^-) :

$$D^+ + S^- \rightleftharpoons DS. \qquad (1)$$

At [TH^+] $= 5 \times 10^{-5}$ mol dm^{-3}, [SLS] $= 3{\cdot}5 \times 10^{-3}$ mol dm^{-3}, Balint *et al* (1977) observed bands at 465, 515 and 635 nm in addition to the monomer band at 597 and the dimer band at 656 nm. They assigned the 465 nm band to the dye-surfactant complex and the 635 nm band to higher dye aggregates. The 515 nm band was not discussed. As mentioned before, the 465 nm band is due to interaction with the dodecanol impurity in SLS. Formation of dye aggregates in other dye-detergent systems have also been reported (Mataga and Koizumi 1954; Sato *et al* 1980). To explain the behaviour of anthraquinoid acid dyes in the presence of surfactant molecules Datyner (1961) assumed that the dye surfactant complex may aggregate to form larger particles. Except at one composition as noted above there was no precipitate formation in the thionine–SLS system and hence such aggregation of the complex to larger particles does not seem to be favoured in this system.

From figure 1 it may be seen that the disappearance of the thionine band at 597 nm and formation of the new bands at 515 and 635 nm are accompanied by decrease in thionine fluorescence. In fact at 10^{-3} mol dm^{-3} SLS when the thionine band has virtually disappeared and the absorbance at 515 and 635 nm are maximum no fluorescence is observed with λ_{ex} 515, 597 and 635 nm. Hence, it is to be concluded that the TH^+–SLS complex is non-fluorescent. This must be due to rapid degradation of excitation energy *via* internal conversion facilitated by the long hydrocarbon chain in the SLS moity in the complex.

Both absorbance and fluorescence data can be used to compute the association constant (K_a) between the dye cation and surfactant anion involved in equilibrium 1.

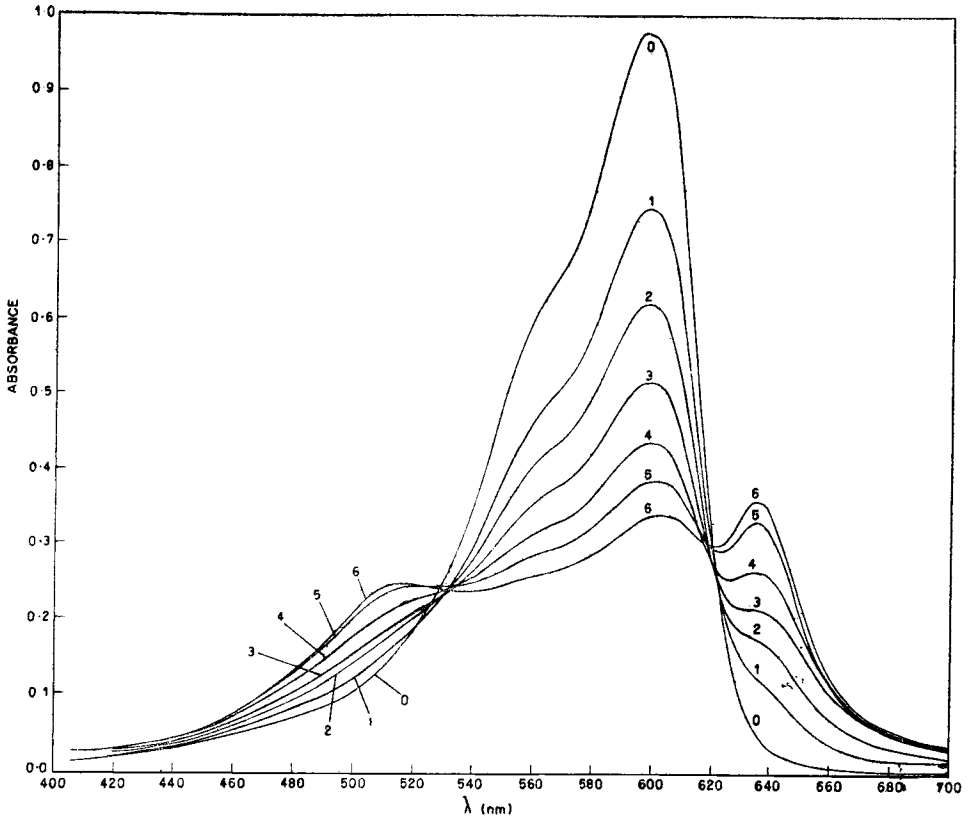

Figure 3. Absorption spectra of thionine (3×10^{-5} mol dm^{-3}) at different concentrations of purified SLS (0) 0, (1) 2×10^{-5}, (2) 3×10^{-5}, (3) 4×10^{-5}, (4) 5×10^{-5}, (5) 6×10^{-5} and (6) 7×10^{-5} mol dm^{-3}.

Thus if the extinction coefficients of the free (or aqueous) and associated (or complexed) thionine species at a given wavelength are respectively ϵ_a and ϵ_c, the measured absorbance is given by:

$$A = \epsilon_{aq}(1 - f_c)\,[D]_t\, l + \epsilon_c\, f_c\, [D]_t\, l, \tag{2}$$

where f_c, the fraction of the dye present as complex is given by

$$f_c = 1 \Big/ \left\{ + \frac{1}{K_a([S]_t - f_c\,[D]_t)} \right\}, \tag{3}$$

l is the cell pathlength and $[D]_t$ and $[S]_t$ are the total thionine and surfactant concentrations. Substituting the value of f_c in (2), the measured absorbance can be shown to be related to the surfactant concentration according to:

$$\left\{ \epsilon_{aq} - \frac{A}{[D]_t\, l} \right\}^{-1} = (\epsilon_{aq} - \epsilon_c)^{-1} + \{(\epsilon_{aq} - \epsilon_c)\, K_a\, ([S]_t - f_c\,[D]_t)\}^{-1}. \tag{4}$$

Similarly the variation in the observed fluorescence intensity I_{obs} should follow the equation:

$$10^{-A}\,\mathrm{em}/I_{obs} = K + KK_a\,([S]_t - f_c\,[D]_t), \tag{5}$$

where K is a constant involving the instrumental efficiency of the fluorimeter and the excited state life times, and A_{ex} and A_{em} the absorbances of the solution at the excitation and emission wavelengths. From (4) and (5) it follows that a plot of

$$\left\{\epsilon_{aq} - \frac{A}{[D]_t\, l}\right\}^{-1} \text{ vs } \{[S]_t - f_c\,[D]_t\}^{-1} \text{ or } 10^{-A}\,\text{em}/I_{obs} \text{ vs } ([S]_t - f_c[D]_t)$$

should be linear and K_a can be calculated from the intercept and slope of such plots. As f_c is not known, first an approximate plot can be constructed using $[S]_t$ instead of $[S]_t - f_c\,[D]_t$ and the approximate K_a so evaluated then used to compute f_c at each surfactant concentration from (3). A more accurate plot is now constructed using these f_c values and this successive approximation procedure is repeated until the K_a and f_c values become invariant. From the intercept of the plot corresponding to (4), ϵ_c can be calculated as ϵ_{aq} is known. The K_a values so obtained from the measured absorbances at 597 nm and the fluorescence intensities at 622 nm agree with each other within ± 10%, the average value being $2{\cdot}11 \times 10^4$ dm^3 mol^{-1}. K_a values were similarly computed from the absorbances at 515 nm ($2{\cdot}33 \times 10^4$ dm^3 mol^{-1}) and 635 nm ($1{\cdot}8 \times 10^4$ dm^3 mol^{-1}).

The extinction coefficient of the complex computed from the intercept is $0{\cdot}41 \times 10^4$ dm^3 mol^{-1}cm^{-1} which is about a factor of three smaller than that corresponding to the measured absorbance at 10^{-3} mol dm^{-3} SLS wherein the absorbance in the 597 nm band is at a minimum. The discrepancy is attributable to an appreciable contribution from the micelle bound thionine which, as will be seen later has an extinction coefficient at 597 nm even higher than the aqueous thionine (monomeric) species.

The sharp changes in the absorbance and fluorescence occurring in the region of SLS concentration $1\text{–}3 \times 10^{-3}$ mol dm^{-3} are related to the formation of surfactant micelles in which the dye is incorporated. Such sharp changes have in the past been made use of for the determination of the CMC of surfactants (Corrin and Harkins 1947; Mukherjee and Mysels 1955). The CMC of SLS evaluated from the inflexion points of curves in figure 4 are summarized in table 1. As observed by Mukherjee and Mysels (1955) the CMC values so obtained are lower than the ones obtained by light scattering, conductivity and viscosity measurements. Also they increase and approach the latter with increasing thionine concentration.

As mentioned before, thionine is present almost exclusively as the complex at 10^{-3} mol dm^{-3} SLS and hence at this surfactant concentration the absorbance at 597 nm and fluorescence are at a minimum and the absorbances at 515 nm and 635 nm are at a maximum. Addition of electrolytes such as Na_2SO_4, H_2SO_4 and NaCl was found to restore fluorescence and absorbance at 597 nm and bleach the 515 and 635 nm bands. Measurements made at a xed concentration of Na_2SO_4 and varying concentrations of SLS revealed that the CMC of the latter is lowered in presence of the electrolyte (figure 4). As a result 10^{-3} mol dm^{-3} of SLS is well above the CMC in presence of 0·02 mol dm^{-3} Na_2SO_4 and hence the changes observed on addition of electrolytes to a thionine solution in 10^{-3} mol dm^{-3} SLS can be attributed to micellization and incorporation of the dye in the micelle (figure 5). This lowering of CMC on addition of electrolyte is in agreement with previous reports in the literature (Corrin and Harkins 1947;

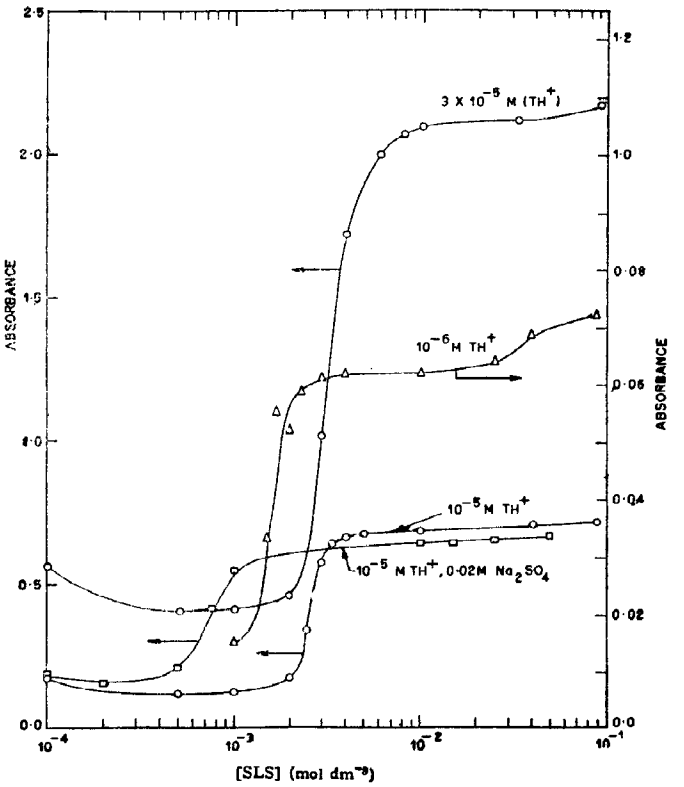

Figure 4. Dependence of absorbance (at λ_{max} = 597 nm) on SLS concentration at different thionine concentrations and the effect of added Na_2SO_4.

Table 1. Effect of thionine concentration on the CMC of SLS micelles.

$[TH^+] \times 10^6$ (mol dm^{-3})	CMC of SLS $\times 10^3$ (mol dm^{-3})
1·0	1·7
5·0	2·3
10·0	2·6
30·0	3·3

Muto *et al* 1973). The log-log relationship between CMC and electrolyte concentration generally observed in the case of ionic surfactants (Corrin and Harkins 1947; Schick 1964; Birdi *et al* 1980) holds good.

The restoration of the 597 nm band and the characteristic thionine fluorescence at SLS concentrations well above the CMC would indicate that the dye surfactant complex is unstable in the micellar environment. At high surfactant concentrations ($\sim$ 0·1 mol dm^{-3}) the absorbance at the λ_{max} (597 nm band) as well as the fluorescence intensity are appreciably higher than in the absence of the surfactant

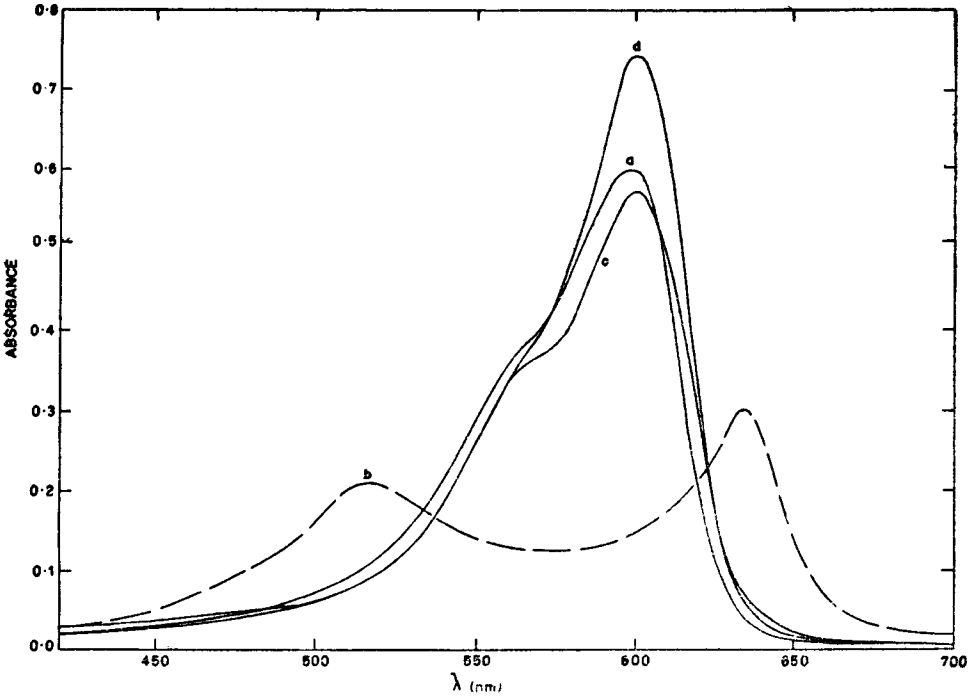

Figure 5. Effect of Na_2SO_4 on the absorption spectrum of thionine (10^{-5} mol dm^{-3}) in presence of SLS (a) neat aqueous solution, (b) 10^{-3} mol dm^{-3} SLS, (c) 10^{-3} mol dm^{-3} SLS and 0·02 mol dm^{-3} Na_2SO_4 and (d) 0·09 mol dm^{-3} SLS.

(figure 2). Similar behaviour in other dye-detergent systems had been attributed (Kapoor and Mishra 1976) to the disaggregation of dye aggregates in the surfactant micelles to give the fluorescent monomeric species. In the thionine–SLS system, however, comparison of the absorption spectrum in the absence of surfactant and at high [SLS] revealed the presence of the dimer band in both cases although somewhat reduced in intensity in the latter (figure 2). If dye disaggregation was solely responsible for these changes then fluorescence yield after correction for reabsorption in the system should be constant, but was found to increase with increasing [SLS] above the CMC. The λ_{max} of thionine monomer band also exhibited a small but definite red shift. A more plausible explanation of the change in absorption and fluorescence in the micellar system would be that the dye in the micellar environment has a different extinction coefficient and radiative life time as compared to the pure aqueous environment. Since the dye is present as the complex in the premicellar region, the equilibrium

$$DS^+ + M \overset{K_b}{\rightleftharpoons} D^+M \tag{6}$$

would be established in the micellar region, and the following equations can be derived:

$$\{(A/[D]_t\, l) - \epsilon_o\}^{-1} = (\epsilon_m - \epsilon_o)^{-1} + \{(\epsilon_m - \epsilon_o)\, K_b\, ([M]_t - f_m\, [D]_t)\}^{-1}, \tag{7}$$

$$10^{-A}\, \mathrm{em}/I_{obs} = K + K\{K_b\, ([M]_t - f_m\, [D]_t)\}^{-1}, \tag{8}$$

where f_m is the fraction of the dye in the micellar form D^+M, and $[M]_t$ is the total micelle concentration given by

$$[M]_t = ([S]_t - \text{CMC})/\text{aggregation no.} \quad (9)$$

From the above equation it is possible, as before, to compute the dye-micelle binding constant K_b by successive approximation. The values computed from absorbance and fluorescence data agree with each other. The average value was found to be $1{\cdot}37 \times 10^6$ dm^3 mol^{-1}. From the intercept of the plot corresponding to (7) the extinction coefficient for the micelle-bound thionine at 597 nm was found to be $6{\cdot}9 \times 10^4$ dm^3 mol^{-1} cm^{-1} which closely agrees with the value corresponding to the measured absorbance at the highest SLS concentration.

3.2. *Effect of electrolyte addition*

Both the dye-surfactant association constant K_a and the dye-micelle binding constant K_b were found to appreciably increase on addition of electrolytes such as Na_2SO_4. The values of these constants for a few typical concentrations of Na_2SO_4 are summarized in table 2. In the region of electrolyte concentration employed, the micelle structure is not altered. In SLS, for example, the transition to rod like micelle occurs at electrolyte concentration above 0·45 mol dm^{-3} (Ikeda *et al* 1981). However, at lower electrolyte concentrations there is a small and gradual increase in micelle molecular weight and hence aggregation number. In the computation of K_b we have ignored this. The effect of this would be to give a value of K_b lower than the true value. Therefore the observed increase in binding constant with increasing concentration of electrolyte is inferred to be genuine and not an artefact of neglecting the increase in aggregation number in presence of electrolytes.

3.3. *Medium polarity effects*

It has been mentioned earlier that the absorbance of thionine solutions at 597 nm which reaches a minimum at $\sim 10^{-3}$ mol dm^{-3} steeply rises near the CMC and levels off to a plateau of small positive slope beyond 3×10^{-3} mol dm^{-3} SLS. There is also an appreciable red shift of the λ_m, *e.g.*, in 0·09 mol dm^{-3} SLS the maximum is shifted to 602·5 nm. At the respective maxima the extinction coefficient in 0·09 mol dm^{-3} SLS micellar medium is about 20% higher as compared to the homogeneous aqueous medium. The red shift and increase in extinction coefficient both reflect a decrease in the polarity or the dielectric constant of

Table 2. Effect of electrolyte addition on K_a and K_b values

NaCl (mol dm^{-3})	K_a (dm^3 mol^{-1})	K_b (dm^3 mol^{-1})
NCl	$2{\cdot}11 \times 10^4$	$1{\cdot}37 \times 10^6$
Na_2SO_4 (0·02)	$4{\cdot}8 \times 10^4$	$7{\cdot}5 \times 10^6$
NaCl (0·10)	$1{\cdot}5 \times 10^8$	$1{\cdot}5 \times 10^8$

the medium around the probe molecule. Thus, for example, in water-alcohol mixtures, the extinction coefficient increases linearly with decreasing dielectric constant (figure 6). From this plot the dielectric constant experienced by thionine in the SLS micellar system can be read off as $\sim$ 56 against the observed $\triangle\epsilon_m$ of $1{\cdot}1 \times 10^4$ dm^3 mol^{-1}cm^{-1}. Similarly, as shown in figure 6 the $\triangle\epsilon_m$ values also follow linear variations with the solvent polarity parameter, E_T (see Reichard 1965 for E_T values). Deviations from the linear correlation may be noted in the case of DMSO and dioxane. Ignoring this deviation, the polarity of the environment of thionine in the 0·09 mol dm^{-3} SLS micellar system can be inferred to correspond to an E_T value of 57·5, i.e., the polarity is between that of water and methanol. The red shift of the thionine absorption maximum also shows a correlation with the solvent polarity parameter, but as the shifts are rather small their accurate measurement is rather difficult and hence no attempt has been made to evaluate the solvent polarity parameter from this correlation.

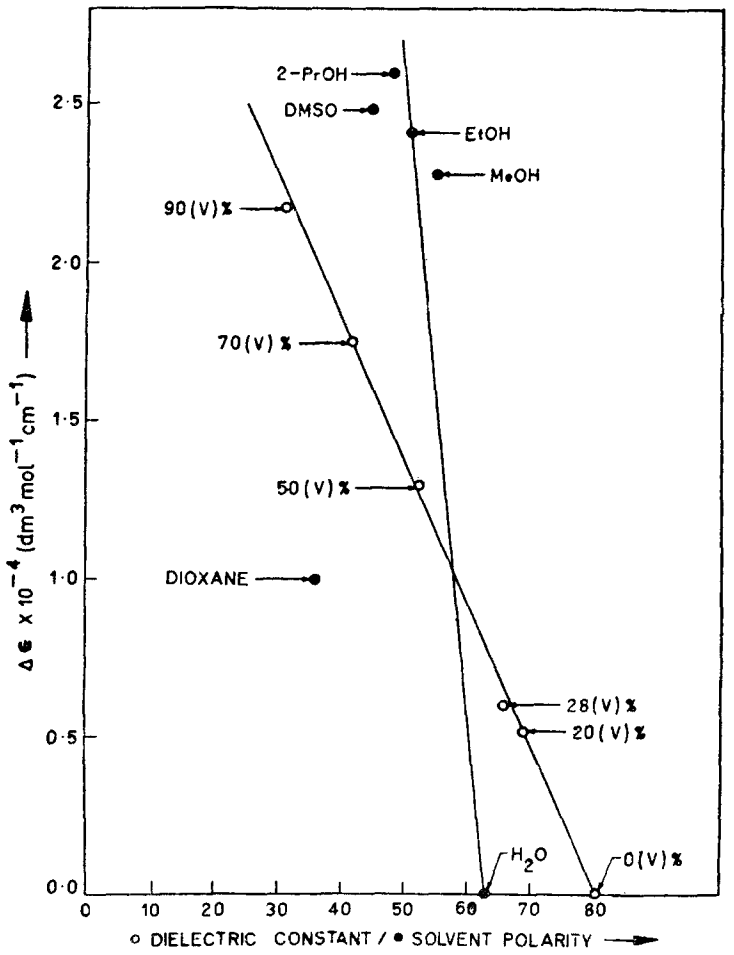

Figure 6. Dependence of thionine extinction coefficient on the dielectric constant of the medium (○) and the solvent polarity parameter, E_T (●) [numbers inside the figure refer to the composition of water-ethanol mixture in % ethanol by volume].

3.4. *Other surfactants*

Among the other surfactants investigated, the behaviour of thionine in the anionic surfactant SDDBS closely paralleled the behaviour in SLS: a decrease in the absorbance at 597 nm and the fluorescence intensity with increasing [SDDBS] up to $\sim 5 \times 10^{-4}$ mol dm^{-3} followed by a sharp increase in the region $1 - 2_{\theta} \times 10^{-3}$ mol dm^{-3} culminating in a plateau beyond $\sim 3 \times 10^{-3}$ mol dm^{-3}. It may be noted that the CMC of SDDBS is $1{\cdot}2 \times 10^{-3}$ mol dm^{-3}. The initial decrease was accompanied by the appearance of new bands at 550 and 635 nm. As in the case of SLS the new bands disappeared at [SDDBS] > CMC. These observations are subject to the same interpretation as in the case of SLS. Association and binding constants were not calculated.

In sharp contrast to the case of SLS and SDDBS the behaviour in presence of the neutral surfactants Triton X-100 and Brij-35 and the cationic surfactants CTABr and CPC was very different. There was no decrease in the absorbance at 597 nm nor did new bands appear at surfactant concentrations below the CMC. The ion-pair type of complex is obviously not possible in the case of the cationic surfactants as thionine and surfactant head groups bear like charges. Although the neutral surfactant Triton X-100 is known to form charge transfer complex with strong electron acceptors such as TCNQ (Muto *et al* 1970) thionine seems to be too poor an electron acceptor to form such a complex with the rather poor electron donors, *viz.*, Triton X-100 and Brij-35. Beyond the CMC there was a small but definite red shift of the thionine absorption maximum and also an increase in ϵ_m. These data together with the inferred values for the dielectric constants and solvent polarity parameters as deduced from the linear plots of figure 6 are given in table 3.

4. Discussion

Several publications have appeared on the study of micelles ever since Mc. Bain suggested aggregation of surfactant molecules above a critical concentration and Hartley's (1935) model of micelle as a tiny oil droplet in an ionic coat of hydrated ions. However many aspects of micelles pertaining to micelle shape,

Table 3. Solvent polarity and dielectric constant of different surfactant micelles as probed by TH.

Surfactant (well above CMC)	$\Delta\epsilon$	SP	DC
SLS (+0·8 M NaCl)	$1{\cdot}5 \times 10^4$	56·0	47·0
SLS	$1{\cdot}1 \times 10^4$	57·5	56·0
SDDBS	$1{\cdot}5 \times 10^4$	58·0	56·0
Triton X-100	$1{\cdot}0 \times 10^4$	58·5	57·0
Brij-35	$0{\cdot}6 \times 10^4$	60·5	67·0
CPC	$0{\cdot}4 \times 10^4$	61·5	71·5
CTABr	$0{\cdot}2 \times 10^4$	62·5	76·0

$\Delta\epsilon$: Extinction coefficient increment, SP : Solvent polarity parameter, DC : Dielectric constant.

water penetration, surface roughness, adsorption sites, interior viscosity and chain conformation are not yet fully understood (Menger 1979). The main point of controversy in the recent past, with which of course the other questions above are to some extent tied up, is water penetration into micelles (See Wennerström and Lindman 1979 and Menger and Bonicamp 1981 for two divergent viewpoints). Whereas one extreme, the "reef" model views the micelle interior as completely dry with all the surfactant methylene groups lying entirely within the ionic coat, the opposite extreme, the "Fjord" model allows water percolation nearly to the micelle centre. Experimental results on micelles are often interpreted as evidence to support either of these extreme view points or some median viewpoint. Such evidences are invariably deduced on the basis of certain preconceived notions, notable among them being (i) the micelle is a closed entity (Franses *et al* 1981) with an impervious (but imaginary) boundary separating the lipopoic moieties in the interior from the hydrophilic head groups on the exterior and (ii) a solubilizate used as a probe molecule is localized in the lipopoic interior and does not perturb the micelle structure. As pointed out by both Menger (1979) and Lindman and Wennerström (1981) such questionable conclusions are due to the methodology employed in experiments designed to probe the micelle interior. In this one compares the spectroscopic properties of probe molecules in the micelle and different solvents or solvent mixtures and presupposes a correlation between such properties and the polarity of the environment indicated in terms of the dielectric constant or some empirical solvent polarity parameter. Although such correlations do exist (figure 6) what is in doubt is whether any solvent or solvent mixture can be assumed to simulate a micellar environment. Also, as is evident from figure 6, beyond a certain polarity, the measured spectroscopic parameter may exhibit an opposite trend.

In connection with this controversy regarding water penetration into micelles may be mentioned a recent neutron scattering study (Hayter and Penfold 1981), the results of which reconcile the two extreme viewpoints by supporting the idea of 'a little water penetration' into the paraffin core due to entrainment of water by the bound counterions.

Although the question regarding the nature of micelle interior is still unresolved, there is some agreement on the location of solubilizates (Menger 1979; Lindman and Wennerström 1981). The majority of solubilizates, including the water insoluble compounds such as benzophenone, bromobenzene, pyrine, etc., prefer the highly aqueous micelle surface to the lipopoic interior. Such being the case, the location of an ionic highly water soluble compound such as thionine used in the present study should unquestionably be the highly aqueous micellar surface. In experiments employing such probe molecules, the question one has to ask is not how much water-like the micelle interior is, but how much water-unlike the surface region is. From the data summarized in table 3 it is evident that in all cases the environment around thionine is highly polar, the polarity being somewhere between that of water and methanol. The highest polarity is observed in CTABr micelles and the least in SLS micelles. Due to electrostatic repulsion of likecharged ions of TH^+ and the headgroup in CTABr, the location of TH^+ in this micellar system is expected to be farther out in the region of counter ions than in the case of the anionic SLS micelle where electrostatic attraction would favour location of TH^+ closer to the headgroup. The somewhat less polar nature of

the surface region in these micelles as compared to water is accountable on the basis of the surface roughness of micelles arising from their dynamic nature, i.e., monomeric units constantly enter into and exit from micelles. On an average, there is considerable protrusion of the methylene groups into the headgroup region (Aniasson 1978). This at once rules out the picture of a micelle as a closed impervious compartment and would obviously allow for penetration of water into the micelle. The water so penetrated cannot be expected to behave entirely like bulk water, but somewhat like a less extensively hydrogen bonded structure filling the crevices between the paraffin chains.

It is known (Ikeda et al 1981) that in the presence of high concentration of electrolytes larger rodlike aggregates of surfactants are formed. In such larger aggregates one can expect more methylene protrusion per micelle. This is reflected in the lower value for the polarity around thionine in SLS micellar solutions containing 0·8 mol dm^{-3} NaCl (table 3). The gradual increase in the absorbance of thionine solutions beyond the CMC (figure 1) is also attributable to the same, as it is known that larger aggregates are favoured with increasing surfactant concentration.

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