Fluorescence spectra of thiazine dyes in micellar solution of different surfactants[†]

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The fluorescence spectra of thiazine dyes such as thionine, azure A, azure B, azure C and methylene blue have been studied in aqueous solution of different surfactants. The results, which show the enhancement and red-shift of fluorescence bands of these dyes in surfactant solution, account for the interaction of excited dyes with surfactants. An attempt has been made to determine the stability constant of the excited state interaction between thionine and surfactants as well as between Triton X-100 and thiazine dyes from the enhancement of fluorescence intensities and this determination is qualitative. The electron-donating capacities of surfactants interacting with thionine are in the order : Tween 80 > Tween 60 > Tween 40 > Tween 20 > Triton X-100 > SLS. On the other hand, the electron-accepting capacities of thiazine dyes interacting with Triton X-100 are in the order : azure C > thionine > azure A > azure B > methylene blue.

The studies of photoinduced electron transfer reactions in surfactant solution are very interesting and relevant to the understanding of photobiology, specially the model systems mimicking biomembranes[1]. They are also potentially important for efficient photochemical conversion and storage of solar energy, since surfactant solutions help to achieve the separation of photoproducts of the photoinduced electron transfer reactions by means of hydrophilic-hydrophobic interaction between the photoproducts and the interfaces[2-6]. From the spectral and photoelectrochemical studies of phenazine and thiazine dyes in aqueous solution of surfactants[7-11], it has been concluded that all the dyes act as electron-acceptors and form 1 : 1 charge transfer (CT) or electron-donor-acceptor (EDA) complexes with nonionic surfactants, which act as electrondonors. There is no interaction of these dyes with CTAB whereas the interaction with SLS is coulombic in nature. Since the CT complex is represented by a resonance hybrid of a nonionic ground state structure and an ionic excited state structure[12], the study of fluorescence spectra of these dyes in surfactant solutions may provide further information regarding the interaction of excited dye molecule with surfactants. For this purpose, the fluorescence spectra of thiazine dyes, such as thionine, azure A, azure B, azure C and methylene blue have been studied in different surfactant solutions and the results are reported here.

Results and discussion

The fluorescence spectra of mixed solutions with a fixed concentration of the thiazine dye in water as well as in aqueous solution of surfactants, such as Tween 20, Tween 40, Tween 60, Tween 80, Triton X-100, CTAB and SLS

above their critical micelle concentration (cmc) have been studied. The fluorescence intensities of these thiazine dyes have been found to be enhanced with a red-shift in presence of all surfactants except CTAB. The fluorescence spectra of mixed solutions with a fixed concentration of thionine dye in aqueous solution of Tween 40, a nonionic surfactant of varying concentrations at 298 K are shown in Fig. 1. The fluorescence spectra of thionine dye in presence of other surfactants (nonionic and anionic) except CTAB and the
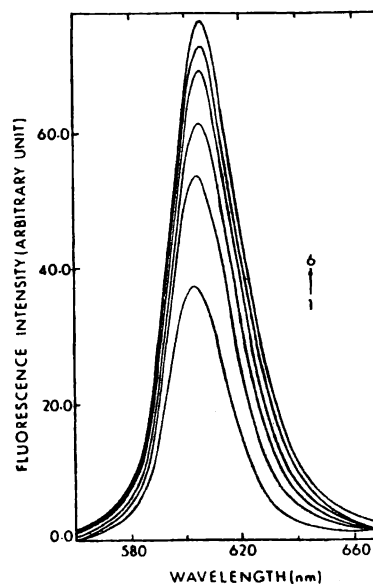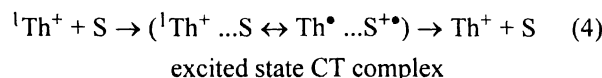

Fig. 1. Fluorescence spectra of thionine (concn. 5×10^{-6} mol dm^{-3}) in aqueous solution of nonionic surfactant Tween 40 at 298 K. Concentrations of Tween 40 : (1) 0.00, (2) 3.00×10^{-3}, (3) 1.00×10^{-2}, (4) 2.00×10^{-2}, (5) 3.00×10^{-2}, (6) 4.00×10^{-2} mol dm^{-3}.

[†]Dedicated to Professor R. P. Rastogi.

fluorescence spectra of other thiazine dyes in presence of Triton X-100 above their cmc behave similarly except the intensity and band position. In many cases, exciplex formation takes place by enhancement of fluorescence and in some cases, a spectral shift along with enhancement has been observed[13]. In our case, it should be the excited state CT interaction since the dyes interact with the surfactant in the ground state[8,9]. It is also interesting to mention that the fluorescence intensity of thionine dye is enhanced on going from aqueous medium to nonaqueous nonpolar media, which indicates that the hydrophobic interaction between the excited dye and the solvents plays an important role for enhancing fluorescence intensity with a red-shift[14]. A possible mechanism of fluorescence enhancement of thionine (Th^+) and also thiazine dyes by surfactant (S) in micellar medium may be represented as follows :

$$Th^+ + h\nu_a \rightarrow {}^1Th^+ \qquad (1)$$

$${}^1Th^+ \rightarrow Th^+ + h\nu_f \qquad (2)$$

$${}^1Th^+ \rightarrow Th^+ + heat \qquad (3)$$

$${}^1Th^+ + S \rightarrow ({}^1Th^+ ...S \leftrightarrow Th^\bullet ...S^{+\bullet}) \rightarrow Th^+ + S \qquad (4)$$

excited state CT complex

Eqn. (4) shows the excited state CT interaction of surfactant with singlet excited dye (${}^1Th^+$) and this interaction, hydrophobic in nature, enhances the fluorescence intensity of the dye in micellar medium with increasing concentration of surfactant. The stability constant (K^*) of this excited state CT interaction can be calculated by assuming the relative increase of fluorescence intensity of dye in presence of surfactant is due to the excited state CT complex, then we can write from eqn. (4),

$$K^* = \frac{[{}^1Th^+ ...S]}{\{[{}^1Th^+] - [{}^1Th^+ ...S]\}[S]} \qquad (5)$$

and

$$\frac{F - F^0}{F^0} = \varepsilon_F [{}^1Th^+ ...S] \qquad (6)$$

where F^0 and F are the fluorescence intensities of dye in absence and in presence of surfactant and ε_F is the proportionality constant and it is equivalent to the fluorescence coefficient of the complex in the excited state. Putting the values of $(F - F^0)/F^0$ for [${}^1Th^+ ...S$] in eqn. (5), we have

$$\left(\frac{F^0}{F - F^0}\right) [{}^1Th^+][S] = \frac{[S]}{\varepsilon_F} + \frac{1}{K^* \varepsilon_F} \qquad (7)$$

The concentration of ${}^1Th^+$ is related to the initial concentration of Th^+ by [${}^1Th^+$] = β [Th^+], where $\beta = e^{-\Delta E/RT}$, ΔE is the energy difference between the first excited (singlet) state and ground state of thionine dye, R the molar gas constant and T the temperature in (K). Using the value of [${}^1Th^+$] in terms of [Th^+] in eqn. (7), the final equation is

$$\left(\frac{F^0}{F - F^0}\right) [Th^+][S] = \frac{[S]}{\beta\varepsilon_F} + \frac{1}{\beta K^* \varepsilon_F} \qquad (8)$$

This is an empirical relation which can be used to determine the stability constant of the interaction between the singlet excited dye and surfactant to form excited state CT complex before coming to the ground state with fluorescence emission. The plots of [Th^+][S]$\{F^0/(F-F^0)\}$ against [S], the initial concentration of surfactant, should yield a straightline for excited state complex formation between singlet excited dye and surfactant. From the slope and intercept of this plot, K^*, the stability constant of the dye-surfactant excited state CT complex can be estimated. These plots are shown in Fig. 2 at 298 K and the results are presented in Table 1 along with the fluorescence characteristics of the dyes in surfactant solution. The results show that the donor strengths
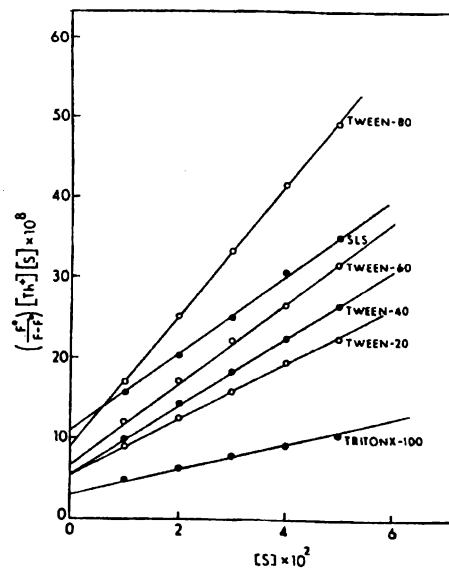

Fig. 2. Plots of $\{F^0/(F-F^0)\}$[Th^+][S] against [S] of thionine-surfactant systems at 298 K for determination of K^* using eqn. (8).

of surfactants forming excited state CT complexes with Th^+ are in the order : Tween 80 > Tween 60 > Tween 40 > Tween 20 > Triton X-100 > SLS. This is also confirmed from the magnitude of red-shift of fluorescence band of Th^+ dye in presence of surfactants. The cationic dyes are expected to interact strongly with anionic surfactant, SLS, but the

Table 1. Excited state stability constant (K^*) and fluorescence characteristics of thiaizine dyes in surfactant solution
Concn. of dye = 5×10^{-6} mol dm^{-3}, concn. of surfactants = $1 \times 10^{-2} - 5 \times 10^{-2}$ mol dm^{-3}, temp. = 298 K

(a) Thionine dye – surfactants

Surfactants	–	SLS	Triton X-100	Tween 20	Tween 40	Tween 60	Tween 80
K^*		43.29	58.80	66.20	75.76	80.13	94.70
λ_{max} (fluo), nm	614	616	616.5	617	618	619	620
$\Delta\bar{\nu}$ shift, cm^{-1}	0	53	66	80	106	132	158

(b) Thiazine dyes – Triton X-100

Dyes	Methylene blue	Azure B	Azure A	Thionine	Azure C
λ_{max} (fluo) in water, nm	632	635	633	614	623
λ_{max} (fluo) in Triton X-100, nm	633	636	635	616.5	631
$\Delta\bar{\nu}$ shift, cm^{-1}	25	25	50	66	203

experimental results show that thionine dye forms stronger complexes with all the nonionic surfactants compared to SLS. The nature of interaction of thionine with the nonionic surfactants is therefore different from its interaction with SLS. On the other hand, the acceptor strengths of thiazine dyes forming excited state CT complex with Triton X-100 as evident from the magnitude of red-shift of fluorescence bands of thiazine dyes in aqueous solution of Triton X-100 are in the order : azure C > thionine > azure A > azure B > methylene blue. The same relation has been observed when thiazine dyes interact with these surfactants in the ground state[8,9].

The study of fluorescence spectra of dyes in nonpolar solvent is restricted due to sparingly solubility of dyes and the evidence of dye excimer can be shown only in nonpolar solvent as it is to be expected from the inherently less polar nature of excimer since the electron transfer is not so pronounced for excimers as for complex formation. The red-shift of the fluorescence band of thiazine dyes in presence of surfactant is due to the transition from the excited polar CT state to nonpolar CT state, which in turn, is very stable as studied by absorption spectra[8,9]. Thus we can conclude that the enhancement of fluorescence intensity as well as the red-shift of fluorescence band are due to the excited state CT interaction of singlet excited dye with surfactant. This indicates that the energy difference between the excited CT state and the ground CT state of dye-surfactant is smaller than the difference between excited state and ground state of dye. According to Mulliken's CT theory[12], the CT complex is represented by a resonance hybrid of a nonionic ground state structure and an ionic excited state structure. The excited state or CT state, is formed by the transfer of electron from the surfactant, an electrondonor to dye, an electronacceptor on light absorption of suitable energy. So the fluorescence study of the dye-surfactant complexes involves the transition

from the more polar nature of the complex to the less polar nature in the ground state.

Experimental

The thiazine dyes, namely, thionine, methylene blue, azure A, azure B and azure C (all Sigma), were crystallized twice from ethanol-water and their purity was checked by absorption and fluorescence spectra. The cetyltrimethyl-ammonium bromide (CTAB), sodium lauryl sulfate (SLS), Triton X-100, Tween 20, Tween 40, Tween 60 and Tween 80 were (all A.R.; B.D.H./Sigma) used as received.

Fluorescence spectra were recorded on a Shimadzu RF 540 spectrophotometer using silica cell of 1 cm optical pathlength. The photomultiplier tube (R 212-09) was sensitive to both red and blue regions of the visible spectrum.

Acknowledgement

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