

Dye surfactant interaction: Surfactant assisted slippage in stacking of styryl pyridinium dyes

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Stacking, assisted by hydrophobic interaction, has been investigated in a series of cyanine dyes with varied alkyl chain length. Both plane-to-plane and end-to-end stacking have been observed simultaneously in the presence of surfactants. Slippage in stacking due to functional group of surfactants has been proposed.

Some ketocyanine dyes, which are insoluble both in water and hexane, go into solution in micellar media¹. With the help of their solvent sensitive absorption and emission spectra^{2,3}, the localization site of the dyes are reported to be the micelle-water interface¹. The ketocyanines have weak hydrophilic group capable of forming hydrogen bond with water⁴ and have strong hydrophobic characteristics. However, compounds with strong hydrophilicity and weak hydrophobicity are found to form turbidity within a certain concentration range of surfactant in solution^{5,6}. The turbidity is reported to be due to interaction of surfactant with dyes forming some kinds of non-micellar aggregates.

In this study we have investigated the behaviour of a series of cyanine dyes (**I**) having a charged hydrophilic group (assumed to be a strong hydrophilic group due to the charge) and varying hydrophobicity (alkyl chain of varied length) in various surfactant systems, viz., anionic sodium dodecyl sulphate (SDS),

alkyl olefinic sulphonate (AOS) and linear alkyl benzene sulphonate (LABS), cationic (cetyl trimethyl ammonium bromide (CTAB) and nonionic (Triton X-100) surfactants.

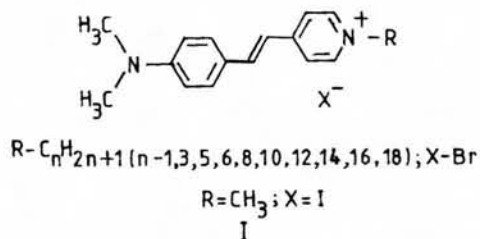
Cyanine dyes have been used extensively as sensitizers in photographic systems^{7,8}. Due to their solvent sensitivity these dyes have been used as probes to study various microenvironments. Further, in aqueous solutions or on solid surfaces, aggregation of self-association of these dyes has been reported^{9,10}. The aggregation may be of H- or J-type, which is composed of parallel dye molecules stacked in a plane-to-plane or end-to-end manner leading to hypsochromism or bathochromism respectively in the absorption spectra¹¹. From the theoretical calculations using point dipole¹², extended dipole¹³, and transition energy¹⁴ it has been shown that the bathochromism and hypsochromism depend upon the angle of slippage, α , between successive molecular planes (where α defines the angle between the line-of-centers of a column of dye molecules and the long axis of any one of the parallel molecules). Large molecular slippage (e.g. $\alpha < 32^\circ$) results in a bathochromic shift while small slippage ($\alpha > 32^\circ$) results in a hypsochromic shift¹⁴. Experimental evidence in favour of this hypothesis is given in the present work.

Experimental

N-Alkylstyrylpyridinium dyes (**I**) were synthesized as reported earlier¹⁵. The surfactants, SDS (SISCO, Mumbai) and CTAB (SLR, Mumbai), were purified by standard method¹⁶. AOS (SMZS, Pune), LABS (SMZS, Pune) and TX-100 (SISCO, Mumbai) were used without further purification. Stock solution of the dyes were made in methanol, and the solution was added to varying concentrations of surfactant solutions. The methanol was kept at 2% v/v in the surfactant-dye solution as well as in aqueous-dye solution. All the absorption spectra were recorded on a Hitachi-200 UV-Vis spectrophotometer with thermostatic cell holder.

Results and discussions

The C₁ to C₁₄ dyes show absorption maxima at 450-456 nm whereas C₁₆ and C₁₈ dyes have the λ_{max} values at 416 nm with shoulders at 398 and 478 nm in 2% methanol-water (v/v) solution. While analyzing



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Table 1—Concentration ranges of surfactants for turbidity in the dye solutions (The absorption maxima in nm in the turbidity zone are given in parentheses)

Dye	[SDS]×10 ³ M	[AOS]×10 ³ M	[LABS]×10 ³ M	[CTAB]×10 ³ M
C ₁	NT	NT	0.110-0.80 (459-465)	NT
C ₃	0.06-2.00 (453-466)	NT	0.230-0.46 (459-465)	NT
C ₅	0.05-2.00 (461-485)	NT	0.035-0.46 (462-468) ^a	NT
C ₆	0.05-2.00 (458-460)	0.035-0.340 (454-459)	0.011-0.46 (455-477) ^b	NT
C ₈	0.01-0.10 (452-452)	0.035-0.340 (448-418)	0.011-0.46 (453-449) ^c	NT
C ₁₀	0.02-0.05 (455-455)	0.011-0.230 (463-421)	0.011-0.34 (457-446) ^d	NT
C ₁₂	NT	0.011-0.230 (455-445) ^e	NT	1.00-3.50 (454-459)
C ₁₄	NT	NT	NT	0.10-3.50 (444-398)
C ₁₆	NT	NT	NT	NT
C ₁₈	NT	NT	NT	NT

NT: No turbidity

^aShoulder at 550 nm, ^bShoulder at 550 nm, ^cShoulder at 510 nm, ^dShoulder at 500 nm and ^eShoulder at 391 nm.

Table 2—Absorption maxima (in nm) of the dyes without surfactant and at [surfactant] > cmc

Dye	No Surfactant	[SDS] 20 mM	[AOS] 5.8 mM	[LABS] 5.8 mM	[CTAB] 10 mM	[TX-100] 11.79 mM
C ₁	450	477	473	482	451	457
C ₃	453	484	480	486	453	462
C ₅	453	486	483	488	455	474
C ₆	454	485	483	488	459	478
C ₈	453	485	483	488	471	484
C ₁₀	455	484	483	488	476	487
C ₁₂	455	459	484	490	478	489
C ₁₄	457	456	484 ^a	489	478	489
C ₁₆	416 ^c	442	485 ^b	487	478	489
C ₁₈	416 ^c	442	475 ^b	487	479	489

^a[surfactant]=28 mM; ^b[surfactant]=52 mM; ^c478 (sh) 398 (sh)

the spectral behaviour of C₁₆ in CTAB solution, Mishra *et al.*¹⁷ have reported the presence of two species, namely, (i) the monomeric form absorbing at 475 nm and (ii) the dimeric form absorbing at 395 nm. They have attributed the formation of the dimeric form to the hydrophobic effect due to C₁₆ alkyl chain in the dye. Thus in 2% methanol-water medium the

dyes up to C₁₄ remain as monomer only, while C₁₆ and C₁₈ dyes remain as monomer (478 nm) ⇌ dimer (398 nm) ⇌ some higher ordered species (416 nm).

On addition of surfactants like SDS, AOS, LABS and CTAB to the dye solutions, turbidity was observed within certain surfactant concentration range (Table 1). Beyond this concentration range the dye

solutions remained clear. No turbidity was observed on addition of TX-100 to the dye solutions. In almost all the cases the turbidity appeared below the critical micelle concentration (CMC) of the surfactants. The disappearance of the turbidity beyond CMC is attributed to the solubilization of the dyes in the micelles. Bathochromic shift of the absorption maxima of the dyes in the micellar medium is an indication of its interaction in the micellar medium (Table 2). No appreciable change was observed in the absorption maxima in CTAB micellar medium with dyes of relatively short alkyl chain. This is attributed to the localization of the dyes in bulk aqueous medium due to electrostatic repulsion of cationic micellar surface and the cationic dyes. In the case of dyes with higher alkyl chain the solubility in CTAB is due to hydrophobic interaction¹⁸. Similarly, the anomalies in absorption spectra for dyes with long alkyl chain (C_{16} and C_{18}) have been ascribed to the compatibility factor of the alkyl chain in the micellar media.

The change in alkyl chain length has a substantial effect on the dye-micellar interaction. Dyes with short alkyl chain length behave as solubilizes only, while

dyes with longer alkyl chain behave as substrates as well as cosurfactants/surfactants. Alkyl chains with 5-6 carbon atoms are in the transition zone of this demarcation. This is substantiated by the spectral data of the dyes in CTAB solutions. When the dyes behave as substrates (solubilizes), the dyes remain in the bulk aqueous medium due to electrostatic repulsion. With increasing alkyl chain length the dyes penetrate into the micelles due to hydrophobic interaction and a large bathochromic shift is observed.

The spectra of the samples in the turbidity zone are found to be interesting. In the case of SDS surfactant solution, except for C_5 , the change in $\lambda_{\max}$ in the turbidity zone is similar to the trend with change in SDS concentration. In the case of C_5 , a bathochromic shift is observed in $\lambda_{\max}$ up to 486 nm, which is the $\lambda_{\max}$ in micellar medium. Therefore a micellar environment for the C_5 dyes is assumed in the turbid medium.

In the case of AOS, turbidity occurs for C_6 , C_8 , C_{10} and C_{12} dyes and except for C_6 , there is a hypsochromic shift in the other dye solutions. The hypsochromism may be ascribed to an alkyl group-assisted dye-dye interaction where there is a large head-on interaction of p -orbitals of the chromophoric group due to plane-to-plane stacking. The disappearance of turbidity at high temperature is also indicative of weak interaction of the dyes. For C_6 dye,

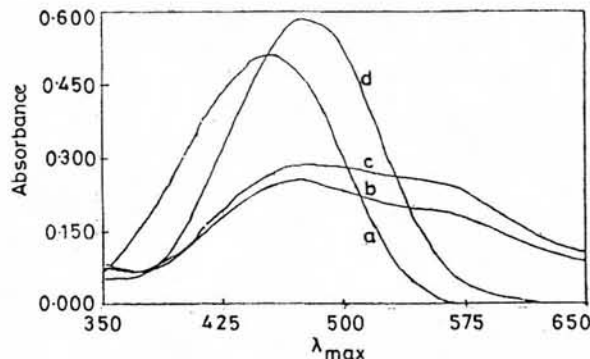


Fig. 1—Absorption spectra of C_6 dye in varying concentration of LABS: [a, 0.00; b, 0.046; c, 0.056; d, 0.68 mM]

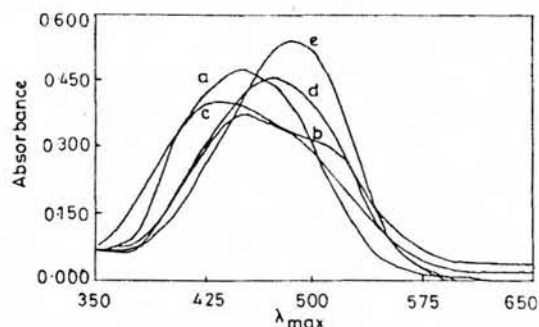


Fig. 3—Absorption spectra of C_8 dye in varying concentration of LABS [a, 0.00; b, 0.035; c, 0.23; d, 0.80; e, 2.31]

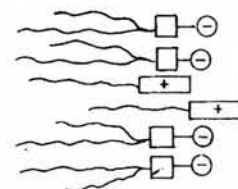


Fig. 2—Schematic representation of LABS assisted slippage of C_6 dyes: $\ominus$ — $\square$ — $\sim$ refers to one unit of LABS and $\square$ — $\sim$ refers to cationic dye.

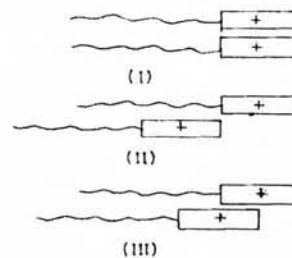


Fig. 4—Schematic representation of stacking of dyes: (I), Plane-to-plane stacking ($\lambda \sim 410$ nm, H-aggregate); (II), end-to-end stacking ($\lambda \sim 550$ nm, J-aggregate) and (III), Slip in J/H aggregate ($\lambda \sim 500$ nm)

the absorption maxima increase with the increase in concentration of AOS indicating the presence of monomeric form of the dye in the turbid medium.

In the case of LABS, turbidity appears for C_1 dye and the $\lambda_{\max}$ is found to be in the same trend as that for in increasing LABS concentration. However, in the case of C_3 , C_5 and C_6 dyes, along with the normal spectra as in the case of C_1 , a shoulder appears at 550 nm (Fig. 1). Absorption spectra of the dyes were recorded in various solvents and no $\lambda_{\max}$ was obtained in this region with any solvent¹⁹. The bathochromic shift to such an extent can be rationalized by proposing a J-aggregation (end-to-end stacking) of dyes in the turbid medium assisted by the surfactant, LABS (Fig. 2). For C_8 and C_{10} dyes, turbidity appears with a hypsochromic shift in the $\lambda_{\max}$ and a shoulder at 510 and 500 nm respectively (Fig. 3). With increasing chain length, the dyes behave as cosurfactants and probably the end-to-end stacking as proposed by Emerson *et al.*¹¹ experiences a greater slippage towards plane-to-plane stacking. The stacking phenomena of the dyes can be represented schematically as shown in Fig. 4.

The turbidity of the dyes C_{12} and C_{14} in CTAB medium may be attributed to the non-compatibility of the alkyl chain length. These dyes can be precipitated out by the addition of surfactant monomers and can be solubilized again in CTAB micelles, whereas, dyes with longer alkyl chain, having chain length compatible with CTAB can remain either as dimer (CTAB assisted) or be solubilized in CTAB micelles. The dyes with smaller alkyl chain behave as good solubilizates and remain soluble throughout the CTAB concentration studied.

Thus, surfactants having specific functional group can tune the absorption maxima of the tailor made cyanine dyes within a range of 130 nm (550 nm for

end-to-end stacking and 420 nm for plane-to-plane stacking). Further investigation is in progress to characterize the dyes in turbid medium.

Acknowledgement

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