

Study of the Tautomeric Behaviour of Fluorescein Dye due to Surfactant Interaction

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The tautomeric behaviour of fluorescein dye has been studied in different micellar solutions employing fluorescence and absorption spectroscopy. The fluorescence intensity decreases on the addition of non-ionic surfactants while it increases on the addition of anionic surfactants. In the case of cationic surfactants, the fluorescence intensity decreases initially but increases on further addition of the surfactants and $\lambda_{\max}$ increases towards longer wavelengths. The effect of ethanol is similar to that of nonionic surfactants. The changes observed are attributed to the interaction of surfactant micelle with dye molecules resulting in the change of coloured quinonoid form to colourless lactone form.

Many workers have studied the effect of various surfactants on the spectral behaviour of a number of dyes¹⁻⁹. The effect of organic solvents and some nonionic surfactants on the absorption spectra of fluorescein has been studied by Nash¹⁰. The influence of ethanol on the spectrum of fluorescein has been studied by Oster¹¹ while Pant and coworkers¹² have studied the effect of concentration and temperature on fluorescein solution. In the present note we report the results of fluorescence and absorption spectral studies on the tautomeric change occurring in the fluorescein dye in the presence of various surfactants and ethanol.

The fluorescence studies were carried out using an Amnico-Bowman spectrofluorophotometer with a cell of 1 cm path length. The absorption studies were carried out on a Carl Zeiss spectrophotometer model SPEKOL. All the reagents were of AR grade. The following surfactants were used:

Cationic: Cetyl trimethylammonium bromide (CTAB) and cetyl pyridinium bromide (CPB).

Anionic: Dioctyl sodium sulphosuccinate (DSSS) and dodecyl benzene sodium sulphonate (DBSS).

Nonionic: Polyoxyethylene teroctyl phenol (TX-100) and polyoxyethylene sorbitain monoleate (Tween-80).

The purities of surfactants were checked by measuring their cmc values by drop weight method; the values compared well with the reported values. All the surfactants were Sigma (U.S.A.) products and were used as such.

Solution of fluorescein ($10^{-3}M$) was prepared in

ethanol which was further diluted to ($10^{-5}M$) keeping ethanol concentration at 1%.

The 1% ethanolic solution of fluorescein dye ($10^{-5}M$) showed absorption $\lambda_{\max}$ at 482 nm and a shoulder at 455 nm. The fluorescence spectrum of the dye in 1% ethanolic solution showed maximum excitation wave length at 480 nm and maximum emission wave length at 512 nm. A shoulder at 468 nm was also observed in the excitation spectrum whereas emission spectrum showed no shoulder.

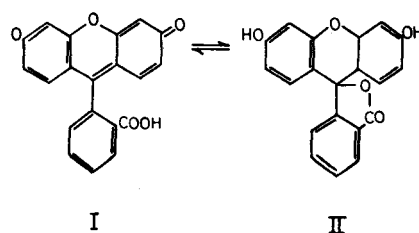
Nonionic surfactants

On addition of a nonionic surfactant, a slight shift in the position of absorption of $\lambda_{\max}$ was observed due to change in the polarity of solvent. The absorption peak height of the fluorescein dye decreased on the addition of nonionic surfactants. The colour of the solution also disappeared with decrease in the peak height in the presence of surfactant. Fig. 1(a) shows the changes in absorption spectrum of fluorescein on changing the concentration of Tween-80.

Fluorescence intensity of the dye decreased on the addition of nonionic surfactants with decolourization of the dye solution. Shape of spectrum remained unchanged in presence of nonionic surfactants. Changes in fluorescence spectra of fluorescein dye on changing the concentration of Tween-80 are shown in Fig. 2(a).

The interaction between dye molecules and surfactant micelle causes change in the geometry of dye molecules. The changes observed indicate tautomeric transformation of the fluorescein dye.

In the case of nonionic surfactants the experimental observations can be explained on the basis of the hypothesis that change takes place in the structure of fluorescein molecule from quinoid(I) to non-quinonoid lactone(II) form which is non fluorescent. These changes can occur due to the presence of polyoxyethylene group present in nonionic surfactants. It is well established that fluorescein dye retains its lactone form in presence of solvents having oxygen containing groups e.g., ether, ketone, esters



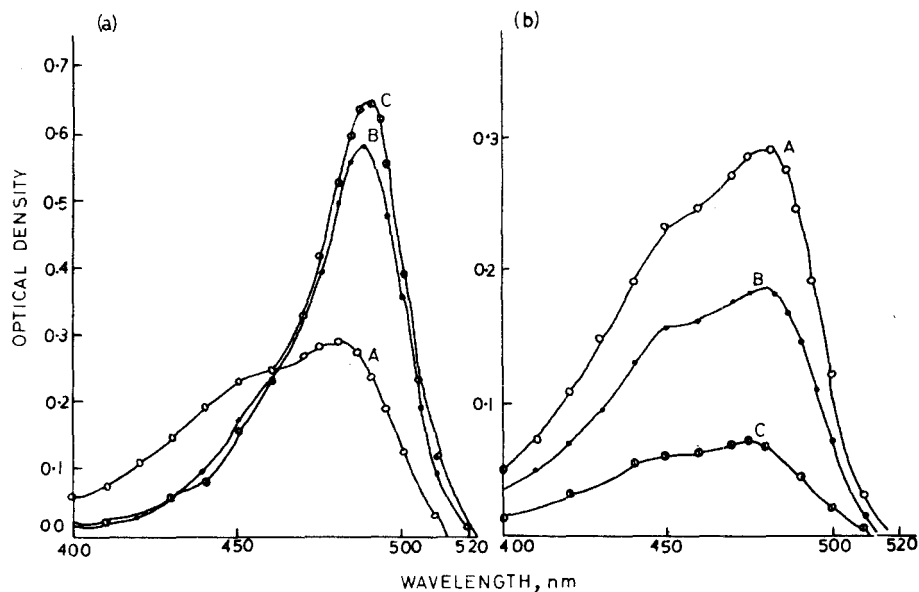


Fig. 1(a) — Changes in absorption spectrum of fluorescein ($10^{-5} M$) on changing the concentration of Tween-80 (A, fluorescein; B, fluorescein + 0.10% Tween-80; C, fluorescein + 0.20% Tween-80).

Fig. 1(b) — Changes in absorption spectrum of fluorescein ($10^{-5} M$) on changing the concentration of DBSS (A, fluorescein; B, fluorescein + 0.02% DBSS; C, fluorescein + 0.50% DBSS).

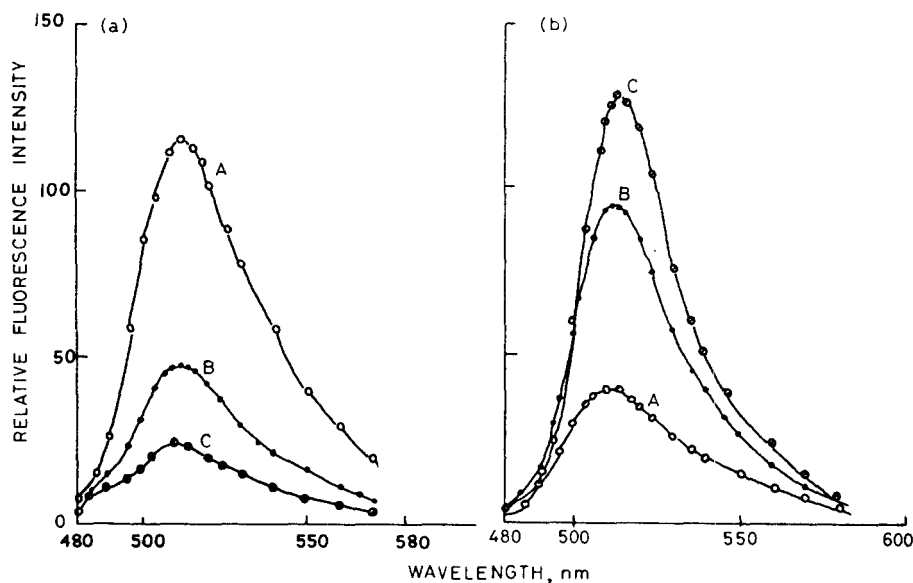


Fig. 2(a) — Changes in fluorescence spectrum of fluorescein ($10^{-5} M$) on changing the concentration of Tween-80 (A, fluorescein; B, fluorescein + 0.15% Tween-80; C, fluorescein + 0.45% Tween-80).

Fig. 2(b) — Changes in fluorescence spectrum of fluorescein ($10^{-5} M$) on changing the concentration of DBSS (A, fluorescein; B, fluorescein + 0.05% DBSS; C, fluorescein + 0.90% DBSS).

etc. The effect of nonionic surfactants on fluorescein has been studied by Nash¹⁰ who has also observed the change of dye into its colourless lactone form. The results obtained with ethanol (*vide infra*) support the above explanation since fluorescence intensity decreases on the addition of ethanol also as a result of the presence of hydroxyl group.

Anionic surfactants

A shift of 6-8 nm towards longer wavelength was observed initially in the absorption $\lambda_{\max}$ on adding the anionic surfactant. Further addition caused enhancement in absorbance (Fig. 1b).

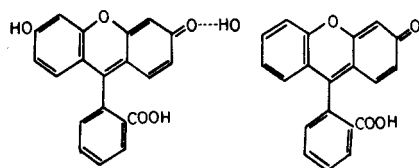
Initial addition of surfactant results in the shift in $\lambda_{\max}$ due to the interaction between fluorescein dye

molecule and anionic part of surfactant molecule. Large enhancement in the fluorescence intensity was observed on further increase in the surfactant concentration at the shifted wavelength. A limiting value was obtained in the presence of 2% DBSS when the fluorescence intensity became three times of its original value.

Fig. 2b, shows the changes observed in fluorescence spectrum of fluorescein on changing the concentration of DBSS.

On the addition of anionic surfactants the quinonoid form of the dye, which is fluorescent, undergoes disaggregation due to its interaction with the anionic part of the surfactant. At the initial stage in the absence of surfactant the quinonoid form of fluorescein exists which remains in dimeric or multimeric form due to the hydrogen bonding as shown below(III).

In the presence of surfactant, the dimer or multimer of the dye undergoes disaggregation into monomeric forms. The increase in fluorescence intensity occurs due to the increase in the monomeric form of molecules



III

only since the shape of the spectrum remains unchanged. The lactone form of dye can exist as a monomer hence a shift in $\lambda_{\max}$ is due to the transformation of quinonoid form to lactone form.

Cationic surfactants

A decrease in absorbance was observed during initial addition of the cationic surfactants. On further addition a shift in $\lambda_{\max}$ towards longer wavelength (by 17 nm) was observed which was followed by a large enhancement in the absorbance of dye solution (Fig. 3a).

During initial addition of the surfactants the fluorescence intensity decreased and reached zero value at 0.01% CTAB. The fluorescence intensity remained low up to a certain concentration level of surfactant. Further increase in the (surfactant) shifted the $\lambda_{\max}$ with a large enhancement in the fluorescence intensity at the shifted $\lambda_{\max}$. The spectral changes occurring in the fluorescence spectrum of fluorescein on changing the concentration of CTAB are shown in Fig. 3b.

During initial addition of cationic surfactants the fluorescence intensity is reduced while its colour becomes orange. Similar changes occur in its absorption spectrum which indicate a change in the geometry of the dye molecule. The decrease in fluorescence intensity and appearance of orange colour can be explained on the basis of interaction

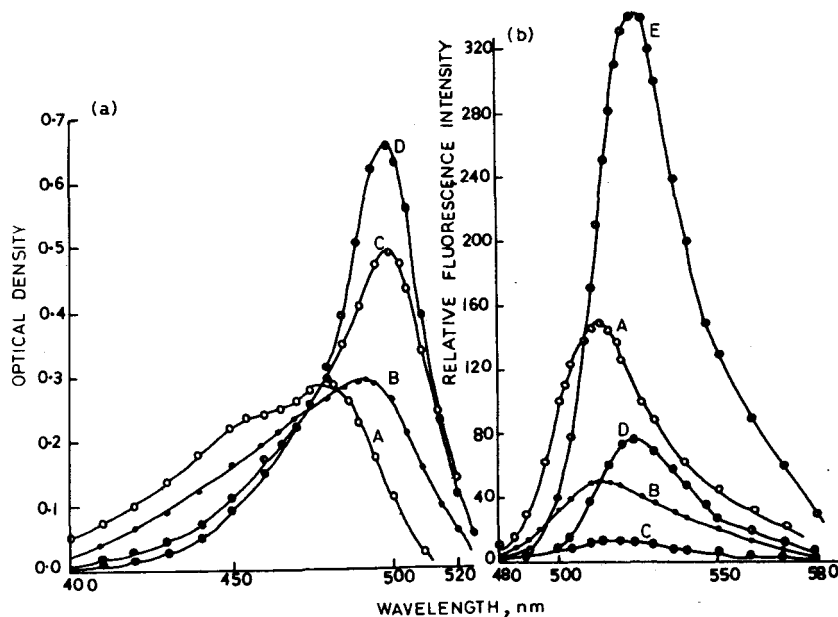


Fig. 3(a) – Changes in absorption spectrum of fluorescein ($10^{-5} M$) on changing the concentration of CTAB (A, fluorescein; B, fluorescein + 0.004% CTAB; C, fluorescein + 0.010% CTAB; D, fluorescein + 0.080% CTAB).

Fig. 3(b) – Changes in fluorescence spectrum of fluorescein ($10^{-5} M$) on changing the concentration of CTAB (A, fluorescein; B, fluorescein + 0.005% CTAB; C, fluorescein + 0.010% CTAB; D, fluorescein + 0.030% CTAB; E, fluorescein + 0.090% CTAB).

between the dye and the cationic part of the surfactant. The cationic part of surfactant[†] interacts with the fluorescing group in the fluorescein molecule. Thus the geometry of the dye molecule changes due to the dye-surfactant interaction or trapping which results in a shift in λ_{max} . Further addition of surfactant enhances the fluorescence intensity due to the disaggregation of dye molecules and due to the formation of monomeric form.

Effect of ethanol

The fluorescence intensity of fluorescein dye solutions decreased on the addition of ethanol. At lower concentrations of ethanol (up to 20%) very little effect was observed on the fluorescence intensity of the dye solution. The influence became prominent at higher concentrations of ethanol. The effect of the addition of ethanol appeared to be similar to that of nonionic surfactants.

Thus, absorption and fluorescence spectral studies confirm the view that tautomeric changes occur in the

fluorescein dye solution due to its interaction with surfactant micelles.

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