

Effect of NaCl on the spectral of cresyl violet (CV)-sodium dodecyl sulphate (SDS) complex.

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Abstract:

In this research we study the effect of added NaCl with concentration of (0.2, 0.02) M on the spectral of cationically charged dye (cresyl violet) and anionically charged surfactant (sodium dodecyl sulphate) with different concentrations, the result show two peaks appearance the first attributed to micelle and the other formation of the dye - surfactant complex, in addition to the increase in the quantum efficiency of emission spectrum and shifted toward long wavelength ($\lambda_{\text{max}} = 692.5\text{nm} - 626\text{nm}$).

Keywords: Cresyl viole; surfactant; salt effect.

Introduction:

Dye – surfactant interactions in dilute aqueous solution have been extensively studied by spectral techniques [1]. Aggregation is reflected by changes in absorption or fluorescence spectra of the dyes. Cresyl violet a phenoxazine dye is of current interest particularly for harnessing solar energy and various other application [2]. The dye – surfactant interactions have also been the subject of many studies in view of the fact that they mimic many biological processes taking place between the large organic molecules and biomembranes and can act as model redox systems [3,4]. Cresyl violet a cationic dye (CV^+) belonging to the phenoxazine class, finds application in diverse areas wherein its redox chemistry plays an important role [5, 6]. Among the various surfactants employed for such studies, the anionic surfactant sodium dodecyl sulphate (SDS) showed marked effect shown changes in the spectroscopic properties of the dye.

We have study the effect of surfactant on absorption, emission characteristic and quantum yield of the dye. The luminescence of quantum yields are almost always determined relative to some standard [7]. The environment around CV^+ in the anionic micelles of SDS is highly polar and electrostatic attraction between CV^+ and anionic micelles would favour location of dye close to the head groups of the micelles. We followed the spectral changes in dye – surfactant complex by the addition of NaCl.

Experimental:

The dye cresyl violet (CV^+) was supplied from Lambda physiks used without any further purification. The surfactant sodium dodecyl sulfate (SDS) (Fluka) was used without purification. All solution were prepared in nanopure water with conductivity of $0.1 \mu S cm^{-1}$, obtained from water treatment laboratory in AL- dora electricity generating plant and the solutions prepared freshly were used for each experiment. The concentration of CV was $1 \times 10^{-5} M$ with different concentrations of SDS rang $1 \times 10^{-6} - 1 \times 10^{-1} M$. All solution was mixed in 1:1 ratio. The chemical structure of dye [8] and surfactant [9] are shown in figure 1.

The absorption spectra were recorded by using UV- Visible spectrophotometer (UV-160 Shimadzu), with 1cm path length cells fitted in cell holder. The fluorescence measurements were carried out using SL-174 Spectrofluorometer.

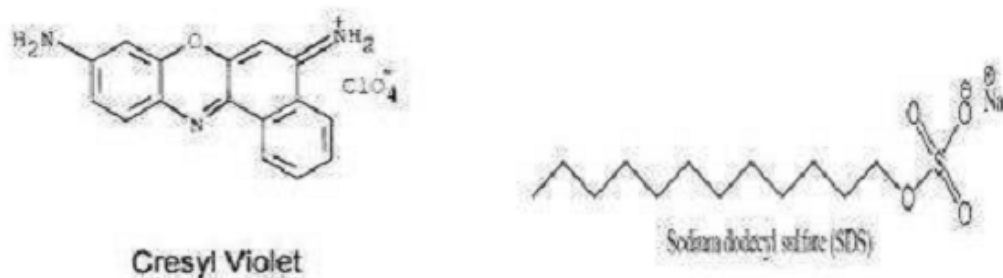


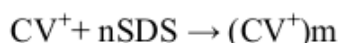
Figure (1): Molecular structure of dye CV and surfactant SDS

Results and Discussion:

Absorption spectra of cresyl violet solution in the absence and in the presence of different sodium dodecyl sulfate concentrations are presented in figure 2. It can be observed that in the absence of surfactant, the absorption spectrum of cresyl violet at concentration $10^{-5} M$ in aqueous solution shows a broad band at 513.5 nm ($\epsilon = 2486 M^{-1} cm^{-1}$). In the presence of SDS, the intensity of the band gradually decreasing, when SDS concentration is increased from 1×10^{-4} to $1 \times 10^{-1} M$, the position of absorption maximum shifts towards a shorter wavelength initially followed by a shift to higher wavelength at high SDS concentration. When SDS concentration is greater $3 \times 10^{-3} M$, two new absorption bands with increasing absorbance appeared at 320 and 606 nm.

When SDS solution at very low concentration is added to the CV solution, changes in the absorbance are attributed due to electrostatic interaction between oppositely charged molecules (ion-ion interaction) in the system. Cresyl violet is a cationic dye, while SDS is anionic surfactant. Hence, an interaction between

cresyl violet and surfactant are attributed to electrostatic interactions forming molecular complexes [10, 11]. In high concentration of SDS, increase in the absorbance with shift the spectrum toward long wavelength of 92.5 nm is assigned to formation of surfactant micelles in which the dye is incorporated $(CV^+)_m$ as



CV^+ and SDS represent the dye and surfactant respectively. This result is agreement with K I Priyadarsini [12].

The formation of dye – surfactant complex, $(CVS)_c$ is represented by

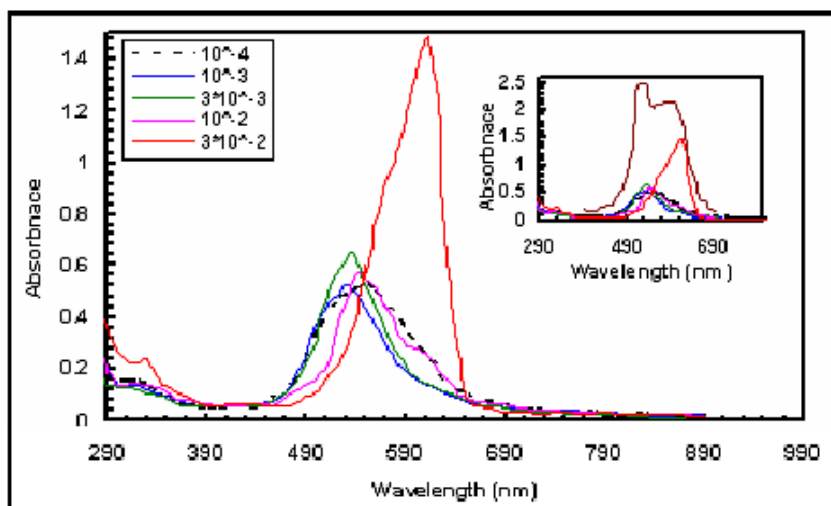
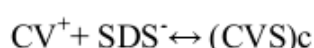


Figure 2: Absorption spectra of CV dye in presence of different SDS Concentrations

At room-temperature fluorescence spectrum of an aqueous solution of CV dye shows broad band with maxima at 692.5 nm. Addition of SDS leads to quenching of the dye fluorescence with shift in the wavelength of the spectrum [13], therefore the figure 3 shows the fluorescence spectra of CV dye as a function of surfactant concentrations. With an increase in the concentration of SDS in an aqueous solution of the CV, the fluorescence intensity shows gradually decreasing and then suddenly it shows a very high

incensement with shift the spectrum toward red shift (66.5nm). Our observations with the dye - surfactant system qualitatively agree with the earlier reports from Pal et al. and Duemie and Baraka while investigating the photophysical properties of rhodamine derivatives in SDS micelles [14, 15]. The fluorescence intensity of the dye shows an initial decrease at lower surfactant concentrations. A similar decrease in the fluorescence quantum yield at the lower surfactant concentrations and is ascribed to the formation of pre-micellar aggregates [16]. The effect in fluorescence quantum yield with increase of surfactant concentrations listed in table 1.

That leads the cationic band intensity decreases before micelle formation and after micelle formation a huge enhancement in the emission of CV dye in the SDS micellar environments, indicates that the cationic dye stabilized in SDS environment and the effect can be assigned to an electrostatic interaction between the anionic surface charge of the SDS micellar and the cationic of CV [15].

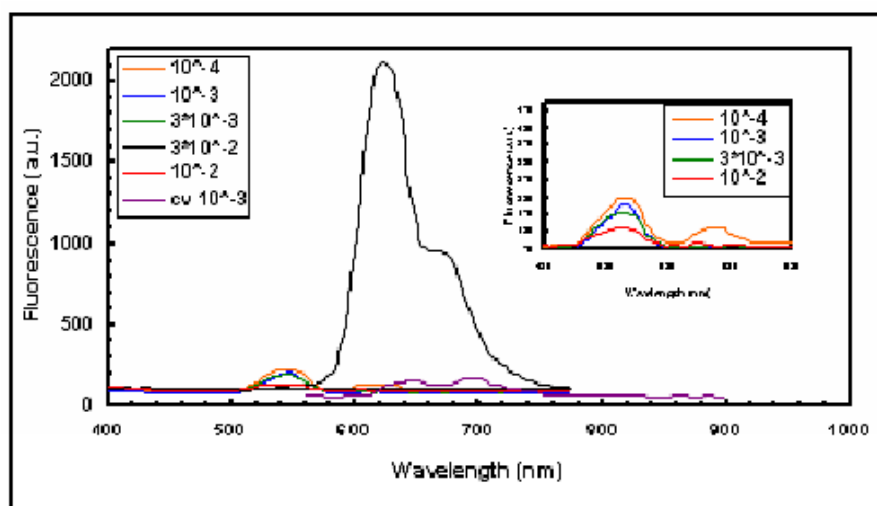


Figure 3: Fluorescence spectra of CV dye in the presence of different SDS Concentrations

Fluorescence quantum yield for CV in absence of SDS is 0.019

CV 1×10^{-3} [M]	
SDS Concentration [M]	Quantum Yield Φ_{FM}
1×10^{-4}	0.049
1×10^{-3}	0.044
3×10^{-3}	0.039
1×10^{-2}	0.039
3×10^{-2}	0.21

Table 1: Fluorescence quantum yield for CV in presence of different SDS concentrations

Later we have studied the effect concentrations of an added electrolyte NaCl (0.2, 0.02) M on the absorption and emission spectrum on the dye-surfactant complex as shown in Figure (4, 5, 6, 7).

At NaCl (0.2, 0.02M) no distinct change in the absorption spectrum can be seen (Figures 4, 5). But we observed in presence NaCl (0.2M) increase in absorbance at high concentration of SDS (10^{-2} M) and the absorption band at 320 nm disappear with the formation of micellised dye band due to the electrostatic screening effect by Na^+ ions on the negatively charged surfactant [17].

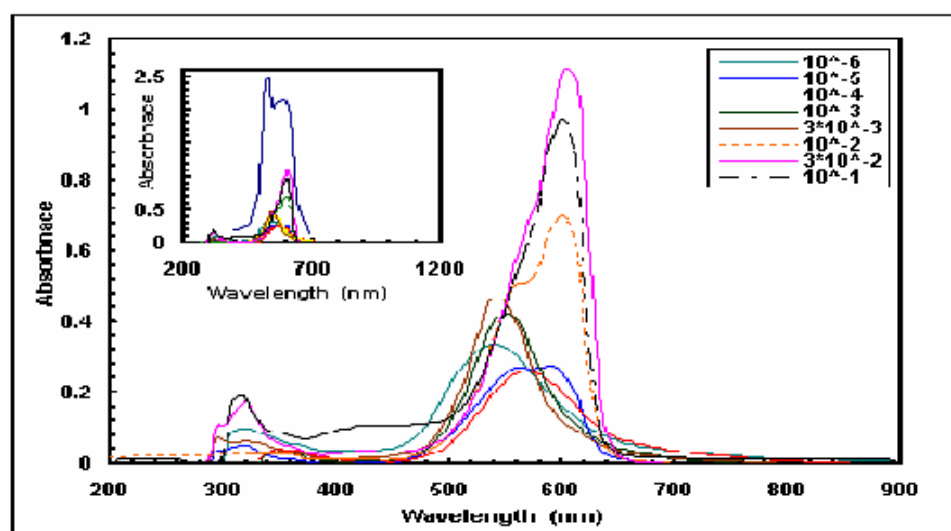


Figure 4: Absorption spectra of CV dye in presence of different SDS concentrations containing NaCl (0.2 M)

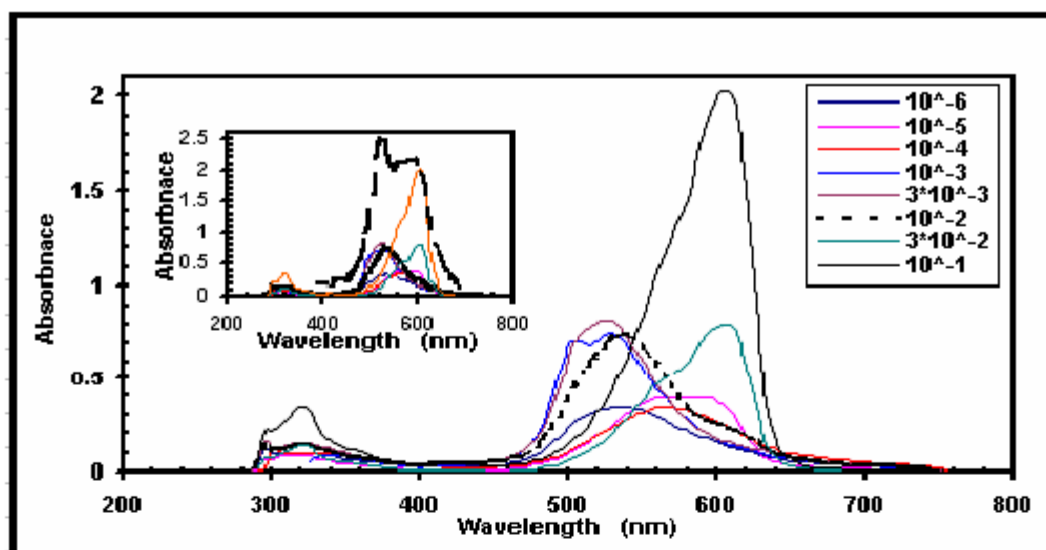


Figure 5: Absorption spectra of Cvdye in presence of different SDS concentrations containing NaCl (0.02 M)

Figure 6 and Table 2 shows the effect concentration of an added electrolyte NaCl (0.2) M, the fluorescence intensity and quantum yield decreasing to the zero and followed by high incensement in the fluorescence intensity in the high concentration of SDS. Fluorescence intensity decrease to the zero that leads to self-absorption quenching and it changes the quantum yield. The effect of NaCl on the dye - surfactant complex leads to weakening of electrostatic attraction between the positively charged CV molecule and negative charged SDS [13, 18]. In low concentration the monomeric surfactant species moves freely and hence they are able to interact with cresyl violet .When NaCl is added, clusters may be formed, which may electrostatically form larger clusters with dye – surfactant complex. In high concentration of SDS (formation of surfactant micelles) added NaCl also due to decrease the repulsion between the similarly charged and increasing the aggregation [10]. And that's the same happen when NaCl (0.02) M. Figure7 and Table 3 shows that, but the addition of NaCl in higher concentration (0.2) M has much higher effect on the fluorescence intensity compared to (0.02) M.

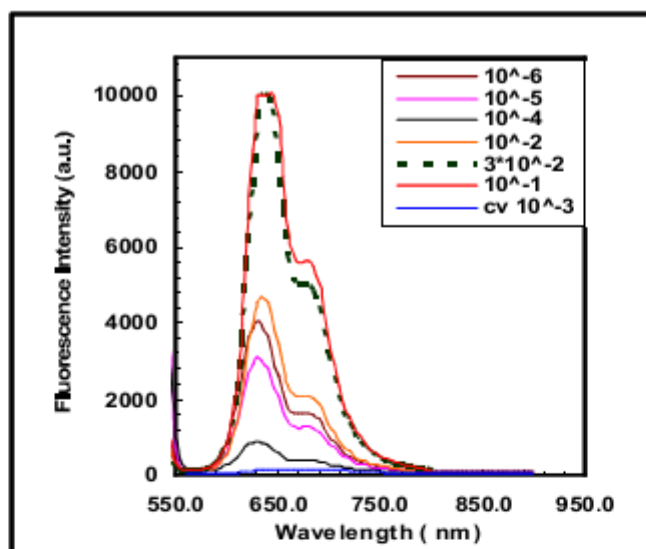


Figure 6: Fluorescence spectra in the presence of different SDS concentrations containing NaCl (0.2 M)

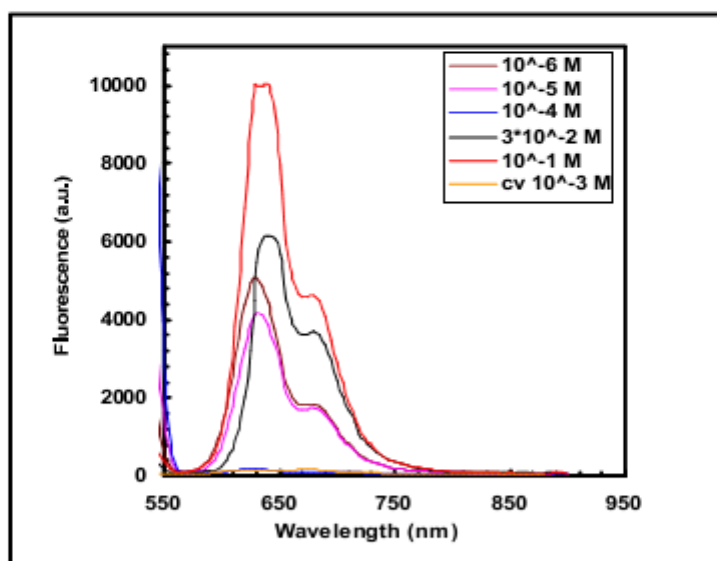


Figure 7: Fluorescence spectra of CV dye in the presence of different SDS concentrations containing NaCl (0.02 M)

CV 1×10^{-3} [M]	
SDS Concentration [M]	Quantum Yield Φ_{FM}
1×10^{-6}	0.68
1×10^{-5}	0.65
1×10^{-4}	0.23
1×10^{-3}	0.00
3×10^{-3}	0.00
1×10^{-2}	0.36
3×10^{-2}	0.49
1×10^{-1}	0.62

Table 2: Fluorescence quantum yield for CV in presence of different SDS concentrations containing NaCl (0.2 M)

CV 1×10^{-3} [M]	
SDS Concentration [M]	Quantum Yield Φ_{FM}
1×10^{-6}	0.79
1×10^{-5}	0.67
1×10^{-4}	0.042
1×10^{-3}	0.00
3×10^{-3}	0.00
1×10^{-2}	0.00
3×10^{-2}	0.45
1×10^{-1}	0.61

Table 3: Fluorescence quantum yield for CV in presence of different SDS concentrations containing NaCl (0.02 M)

Conclusions:

Effect of added NaCl on the spectral of the complex formed between cationically charged dye cresyl violet and anionically charged surfactant sodium dodecyl sulphate were studied, the result show the intensity of the band, gradually decreasing, when SDS concentration is increased from 1×10^{-4} to 1×10^{-1} M and the position of absorption maximum shifts towards a longer wavelength and appear two peaks, the first is attributed to micelle and the other formation of the dye - surfactant complex. Also the result show increases the quantum yield of emission spectrum and shifted toward long wavelength.

Addition of NaCl during the dye- surfactant complex formation at NaCl concentration of (0.2) M appear the formation of surfactant micelles at lower concentration due to the electrostatic screening effect. Also added NaCl caused increasing the fluorescence intensity.

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