

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

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Abstract. Effect of added NaCl on the spectral and kinetic properties of cationically charged dye (cresyl violet) and anionically charged surfactant (sodium dodecyl sulphate) were studied in the pre-micellar and micellar regions. Addition of 0.2 M NaCl to dye-surfactant solution decreased the critical micellar concentration for the micellization of the dye in sodium dodecyl sulphate to 1.2×10^{-3} M. Time-resolved studies using a stopped-flow spectrometer showed that NaCl influences the dynamics of micellisation. Addition of NaCl during the dye-surfactant complex formation converted the complex into micellized form at NaCl concentration of 0.01 to 0.05 M. In contrast, much higher concentration of NaCl (2 M) is required for the salting-out effect of the dye-surfactant complex for conversion to the micellized form.

Keywords. Cresyl violet; surfactant; salt effect; absorption; stopped-flow.

1. Introduction

Cresyl violet, a cationic dye (CV^+ , scheme 1) belonging to the phenoxazine class, finds application in diverse areas wherein its redox chemistry plays an important role.^{1,2} It is used as a sensitizer in photo-electrochemical devices for harnessing solar energy. In homogeneous aqueous system, the photochemical devices show very poor power-conversion efficiency due to slow discharge of photo-produced intermediates at the cell electrode as compared to radical-radical recombination reactions in the bulk of the solution.³ Therefore, it is important to know the conditions under which such radical reaction are slowed down. Attempts have been made in the past to slow down the bulk reactions in a suitable micellar media.⁴ Cresyl violet, a phenoxazine dye is of current interest particularly for harnessing solar energy and various other applications.⁵⁻⁷ 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 the biomembranes and can act as model redox systems.⁸⁻¹⁰ In view of the profound influence micellar media can have on the reaction rates, we have undertaken detailed studies on dye-surfactant interactions. Among the various surfactants employed for such studies, the anionic surfactant (sodium dodecyl sulphate, SDS) showed a marked effect, although there are some reports where cationic (cetyl trimethyl ammonium bromide, CTAB) and neutral (Triton X-100) surfactants have also shown changes in the

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spectroscopic properties of the dye. The interaction between cationic dye and charged surface is also of interest in numerous applications ranging from the design of electronic devices to the characterization of drug-delivery systems. In view of this interest, we have initiated this study to understand the kinetic and spectroscopic properties of cresyl violet and SDS interactions. Earlier we reported the association constant for the formation of the dye–surfactant complex and the binding constant for the micellization of the dye, both in the absence and presence of electrolyte.¹¹ From these studies, the dielectric constant experienced by cresyl violet within the SDS micelles has been found to decrease due to micellization of the dye. 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 micelle. In the present study, we have followed the kinetic and spectral changes in dye–surfactant complex by the addition of NaCl.

2. Experimental

2.1 Chemicals

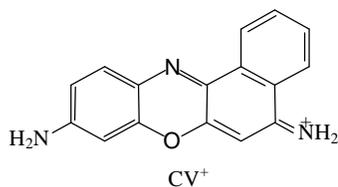
Cresyl violet (Aldrich, suitable as laser grade, CV⁺, scheme 1) was used as such without any further purification. Sodium dodecyl sulphate (SDS) (Fluka) was further purified by repeated washing with petroleum ether and finally drying the sample under vacuum. All other chemicals and reagents, were of ‘Analar’ grade and used as such.

2.2 Steady state studies

Solutions were prepared in ‘nanopure’ water with conductivity of 0.1 mS cm⁻¹, obtained from a Barnstead nanopure water purification system, and freshly prepared solutions were used for each experiment. Absorption experiments were recorded on a Hitachi spectrophotometer, model 330.

2.3 Time-resolved studies

Kinetics of dye (cresyl violet)–surfactant (SDS) interactions were studied using stopped-flow reaction analyzer Model SX 18 MV (Applied Photo Physics, UK). It was used in a single mixing mode with averaging facility and the reaction was followed by absorption detection in the wavelength region 400–700 nm. The dead time of the instrument is 1.3 ms and mixing volume is 100 μl. The solutions were mixed in 1 : 1 ratio and the concentration of each reactant becomes half its original value on mixing inside the reaction chamber. The studies were carried out at 25°C and the optical path length was



Scheme 1.

1 cm. The concentrations of the reactants are selected in such a way that even after mixing, the chemical state (micellar or complex) remains the same. The rate of the reaction at any given wavelength is determined by fitting either the decay or formation trace to a single exponential function. The concentrations of the reagents mentioned in the results correspond to the concentration inside the stopped-flow cell.

3. Results and discussion

3.1 Steady state studies

The optical absorption spectrum of cresyl violet in aqueous solution exhibits an absorption band at 580 nm. At a concentration of the dye where the aggregation is negligible, the nature of the spectrum is affected in the presence of SDS. The absorbance remains nearly constant when [SDS] is increased from 10^{-6} to 6×10^{-6} M. When [SDS] is increased from 6×10^{-6} to 6×10^{-5} M, the absorbance starts decreasing and the dye absorption band at 580 nm disappears with the appearance of two new absorption bands with I_{\max} at 490 and 640 nm. In the concentration range of SDS from 1×10^{-4} to 2×10^{-3} M, the nature of the spectrum remains the same. Further, a sharp increase in the absorbance is observed when SDS concentration is greater 2×10^{-3} M. In this condition, the absorption bands at 490 and 640 nm disappear and the dye band shows I_{\max} at 600 nm ($\epsilon_{600} = 59,800 \pm 500 \text{ M}^{-1} \text{ cm}^{-1}$). The nature of the spectrum remains the same when [SDS] is greater than 2×10^{-2} M.

In the high concentration region of SDS, increase in the absorbance with a red shift of 20 nm is related to the formation of surfactant micelles in which the dye is incorporated $(CV^+)_m$ as,



CV^+ and SDS^- represent the dye and surfactant respectively. From the absorbance changes in the concentration region of SDS from 2×10^{-3} to 1×10^{-2} M, the critical micelle concentration (CMC) is 2.6×10^{-3} M. In the low surfactant concentration region, (6×10^{-5} – 2×10^{-3} M), changes in the dye absorbance are attributed due to electrostatic interactions between oppositely charged molecules forming molecular complexes.^{12,13} The evidence that these interactions are due to oppositely charged molecules also comes from the fact that similarly charged dye–surfactant systems have shown the absence of such spectral changes.¹³ Therefore, these spectral changes should not be due to microcrystals of dye–surfactant complex or adsorption at the walls of the cell. In some dye–surfactant interactions a single broad band is observed.¹⁴ Although the exact nature of the transition involved for the formation of two bands at 490 and 640 nm is not known, the formation of dye–surfactant complex, $(CVS)_c$ is represented by



In order to establish that the two bands at 490 and 640 nm, formed in the pre-micellar region, are due to the same species, $(CVS)_c$, the absorbance (OD) at 490 and 640 nm was monitored at various concentrations of CV (0.5 – 3) $\times 10^{-5}$ M containing SDS = 6×10^{-4} M. The Benesi–Hildebrand relationship (see (3) below), assuming a 1:1

complex, is applied to determine the equilibrium constant (K) and extinction coefficient (ϵ) of the complex (CVS)_c, where l is the optical path length (1 cm). The analysis of data at 490 and 640 nm shows good linearity (figure 1), suggesting the formation of a 1:1 complex, and that both the bands are due to the same species. The equilibrium constants 490 and 640 nm are 1.9×10^4 and $2.2 \times 10^4 \text{ M}^{-1}$ respectively. The extinction coefficient at 490 and 640 nm is estimated to be 2.16×10^4 and $1.72 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ respectively.

$$\frac{[SDS^-]}{OD} = \frac{1}{K\epsilon l} \times \frac{1}{[CV^+]} + \frac{1}{\epsilon l} \quad (3)$$

Addition of NaCl (0.2 M) to the dye–surfactant solutions (in the pre-micellar region), results in the disappearance of the absorption bands at 490 and 640 nm with the formation of micellised dye band at 600 nm. The variation of absorbance at 600 nm as a function of SDS concentration reveals that the CMC, in presence of 0.2 M NaCl, has decreased to $1.2 \times 10^{-3} \text{ M}$. Lowering of CMC in presence of electrolyte is due to the electrostatic screening effect rendered by Na^+ ions on the negatively charged surfactant because of which the dye gets micellized even at much lower concentrations.^{15,16} Except for this lowering of the CMC in the presence of NaCl, the nature of the spectrum in the micellar and pre-micellar regions remains the same. Similar red-shift of 20 nm in the absorption spectrum and increase in the extinction coefficient of dye band by a factor of 1.3 have also been observed in the presence of NaCl.

3.2 Time resolved studies

To determine the various possible kinetic steps involved in the dye–surfactant interactions, time-resolved studies in time-scales ranging from 0.1 to 200 s were carried

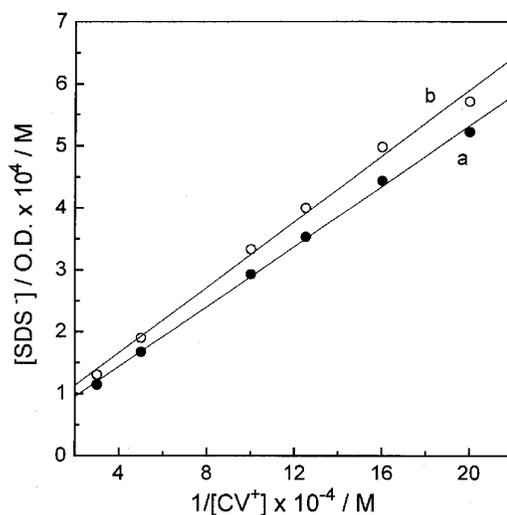


Figure 1. Linear plot showing variation of $[SDS]/OD$ with $1/[CV]$ at (a) 490 and (b) 640 nm.

out using a stopped-flow spectrometer. These studies were carried out both in the pre-micellar and micellar regions. In the micellar region ($\text{SDS} \sim 1 \times 10^{-2} \text{ M}$), micellization of the dye is over in 100 ms (reaction (1)).

In the pre-micellar region, two distinct steps are observed. These steps take place in less than 100 ms and 5 s respectively. In the first step, the dye absorption at 580 nm decreases with simultaneous formation of two bands at 515 and 640 nm. In the second step, the 515 nm absorption decreases with the formation of two bands at 490 and 640 nm, corresponding to dye-surfactant complex. Based on these results, it is concluded that the formation of dye-surfactant complex proceeds through one intermediate step in which a contact pair of oppositely charged dye and surfactant are formed.

Time-resolved studies on the reaction of dye and SDS in the presence of NaCl were also carried out using a stopped-flow spectrometer. The effect of NaCl has been investigated in three different ways: (1) Pre-mixing NaCl with dye and then mixing this solution with SDS in the stopped-flow cell; (2) pre-mixing NaCl with SDS and then mixing this solution with dye in the stopped-flow cell; (3) pre-mixing dye and SDS and then mixing this solution with NaCl. All these experiments under different conditions were carried out at constant dye and surfactant concentrations and variable concentrations of NaCl. Under the first matrix conditions, dye containing different concentrations of NaCl (5 to 30 mM) was mixed in the stopped-flow cell with SDS ($1 \times 10^{-3} \text{ M}$) and the growth of a band at 600 nm was observed. The rate of the formation of the 600 nm band was studied at various NaCl concentrations and the formation rate was seen to increase linearly with NaCl concentration (figure 2). The inset of figure 2 shows the absorption-time plot at 600 nm. The parent absorption initially decayed within mixing time followed by an increase in the absorption at 600 nm within 40 ms. This suggests that NaCl interrupts formation of dye surfactant in the intermediate stage only and converts the

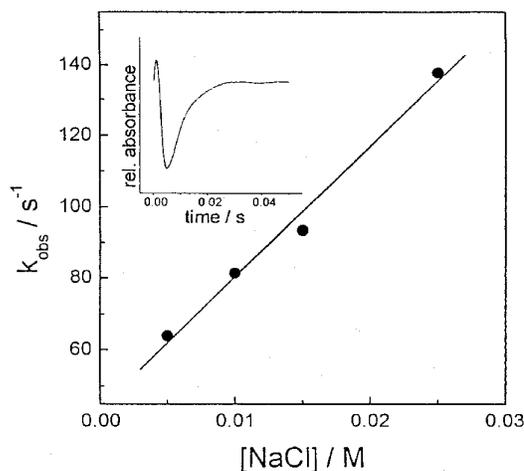


Figure 2. Linear plot showing variation of formation rate constant (600 nm) with NaCl concentration obtained on mixing CV ($4 \times 10^{-6} \text{ M}$) containing different concentrations of NaCl with a solution of SDS ($5 \times 10^{-4} \text{ M}$). Inset shows absorption-time plot at 600 nm under the same conditions in presence of $10 \times 10^{-3} \text{ M}$ NaCl.

complex to the micellized form and these changes are observed at NaCl concentrations of 10 to 20 mM.

Under the second matrix conditions, SDS (1×10^{-3} M) containing different concentrations of NaCl (2 to 30 mM) was mixed in the stopped flow cell with dye solution (4×10^{-6} M). At very low concentration of NaCl (2×10^{-3} M), the dye-surfactant absorption bands at 490 and 640 nm remained unaffected. At higher concentrations of NaCl (10 to 30 mM), the absorbance of dye-surfactant complex bands started decreasing with increased absorbance at 600 nm, which is due to the formation of dye-surfactant micelles. Time-resolved studies presented in figure 3 show that the absorption spectra in presence of NaCl differ significantly from that of the complex and that the system under these conditions approaches micellization as observed in the previous case. The inset of figure 3 shows spectral changes at different NaCl concentrations. It can be seen that the absorbance at 600 nm increases with increasing NaCl concentrations.

Under the third matrix conditions, the dye-surfactant complex was prepared by pre-mixing dye solution with SDS and the complex was mixed with different concentrations of NaCl (0.1 to 2 M). The dye is present as a complex with absorption bands at 490 and 640 nm. At low concentration of NaCl (up to 0.1 M), no distinct change in the absorption can be seen. At higher concentrations of NaCl, absorption due to dye-surfactant complex bands at 490 and 640 nm started decreasing, with the formation of a band at 600 nm. Time-resolved changes in the presence of 2 mol dm^{-3} NaCl are shown in figure 4 and two isosbestic points are observed at 525 and 625 nm. The formation of the 600 nm band matched the depletion of the band at 640 nm (inset of figure 4). The formation of the band at 600 nm is due to micellization of the dye. The rate of formation of the 600 nm band was observed to increase linearly with increasing NaCl concentration (inset c of figure 4). Under these conditions, much higher concentrations of NaCl (almost 10 times

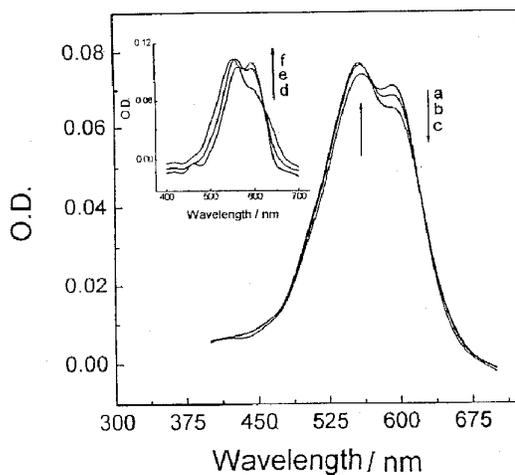


Figure 3. Time-resolved spectra obtained on mixing CV with a solution of SDS containing NaCl (0.02 M) after (a) 0.25, (b) 2.5 and (c) 10 seconds. Inset shows steady state spectral changes in presence of (d) 0.01, (e) 0.02 and (f) 0.03 M concentrations of NaCl.

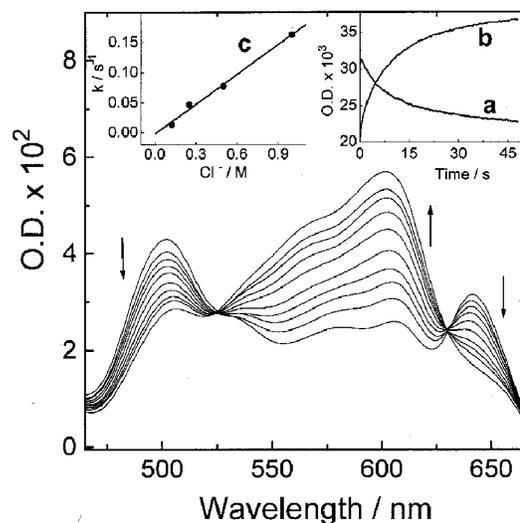


Figure 4. Time-resolved transient absorption spectra obtained on mixing the solution of CV (4×10^{-6} M) containing SDS (5×10^{-4} M) with a solution of NaCl (2 M) after 0.25, 0.75, 1.25, 1.75, 2.5, 3.75, 5.45, 6.25, 7.5 and 10 s. Inset shows absorption-time profiles at (a) 640, (b) 600 nm and (c) variation of first-order rate constant, as a function of Cl^- concentration.

more than that required in the first two cases) are required to convert the complex into the micellized form and the reaction proceeds on a much slower time scale. This confirms that the salting-out process of the dye-surfactant complex is much less effective than the electrostatic screening effect.

4 Conclusions

Effect of added NaCl on the spectral and kinetic properties of the complex formed between cationically charged dye cresyl violet and anionically charged surfactant sodium dodecyl sulphate were studied in the pre-micellar and micellar regions. In the presence of NaCl, the critical micellar concentration is lowered to 1.2×10^{-3} M. Time-resolved studies indicated that dye-surfactant complex formation proceeds with the intermediacy of one step. NaCl intercepts the dye-surfactant complex in different ways. NaCl, when added before complex formation, interferes in the intermediate stage and converts the complex into the micellized dye at NaCl concentration of 10–20 mM. This process takes place in less than 50 ms. Due to the electrostatic screening effect, the lowering of critical micellar concentration is responsible for the conversion of dye-surfactant complex to micellized dye. However, when NaCl is added after complex formation, conversion of dye-surfactant complex into the micellized form of dye requires higher concentration of NaCl, and micellization of dye takes place over the much longer time-scale of 50 s.

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