

Interaction of Victoria Blue Dye in Anionic and Cationic Micellar Media: Spectroscopic Study

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Summary: This manuscript has reported the micellar interaction of cationic triphenylmethane-based dye "Victoria Blue-B (VBB)". The study was conducted using ionic surfactants viz. Cetyltrimethylammonium Bromide (CTAB), Sodium Dodecyl Sulphate (SDS), and Sodium Docusate (SD). The behavior of dye in micellar media at concentration ranges of the surfactants mentioned above was monitored by UV-vis absorption spectroscopic study. The solubilization parameters to reveal the interaction of cationic dye in micellar media were assessed. The mathematical calculations of partition constant (K_c), partition coefficient (K_x), binding coefficient (K_b), Gibb's free energy for partition (ΔG_p) and binding (ΔG_b) were derived from UV-Vis absorption data. The presence of anionic surfactants caused more bathochromic shifts in the maximum absorption of the dye, which was indicative of strong interactions as compared to the cationic surfactant.

Keywords: Absorption spectroscopy, Ionic Surfactants; Micellization behavior, Partitioning coefficients, Solubilization parameters; Victoria Blue-B

Introduction

Surface active Surfactants show amphiphilic properties and hence facilitate the process of solubilization of molecules of additive/drug/dye between the intermolecular micellar and bulk phases, obeying the partitioning mechanism. The formation of colloidal-sized nanoaggregates is a characteristic property of surfactants that occurs at a specific concentration, i.e. critical micellar concentration (CMC) [1-2]. Micelles have a great potential to serve as solubilization indicators of additives, drug carriers, and emulsifying agents [1]. Micelle formation in aqueous solutions of the ionic surfactants profoundly affects the solubilization of sparingly water-soluble organic substances. The solubilization behavior provides comprehensive information on partitioning trends of dye molecules at the junction of micellar and inter-micellar bulk interfaces [3-5]. Extensive investigation of the significant properties of surfactants has attracted and encouraged researchers to work to explore their characteristic behaviors in biological and industrial processes [6-10]. Previously, many researchers have reported the solubilization behavior of dyes and metal complexes in the presence of surfactants [12-23]. Still, much less work is done on the cationic dyes and their interactions.

There are many techniques used for the study of interactions of Dye-surfactants, including UV-

visible spectroscopy, conductometry, potentiometry, tensiometry, and NMR. Absorption spectroscopy is the most widely used and established method for exploring interactions of various compounds and surfactants [11-16]. The appearance of new absorption bands, shifting of bands, and variations in the intensity of absorption bands occur due to the chemical interactions of surfactants and dyes [1]. If the dye and surfactants are oppositely charged, there arises an electrostatic interaction between them, which in turn leads to ion-pair formation in the solution.

Spectral changes due to dye-surfactant interactions of the dye at varying concentrations of surfactants may lead to (i) equilibrium attainment between the monomers of surfactant and the corresponding micelles; (ii) Formation of dye/surfactant complex at sub-micellar concentrations; (iii) Penetration of dye molecules into the micelles; (iv) Ion-pairs formation between oppositely charged molecules of the dye and surfactant; (v) Self-aggregation of additives in the micellar media [17-23]. Thus, it is the most widely and commonly used method to explore the behavior of surfactants and their self-aggregation in the presence of additives. Victoria blue colorants are relatives of methyl violet dyes, except they contain a naphthylamino group. Victoria blue-B dye is widely

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used in nuclear staining during cytological and histochemical application and is also used for quantitative analysis of phospholipids [24].

In continuation of our earlier reported work on the micellization and solubilization of synthetic dyes in various ionic and nonionic micellar media [20-23], we herein report the solubilization phenomenon of a Victoria Blue cationic dye using absorption spectroscopy. We report an interactional study of dye in micellar media of cationic and anionic surfactants using absorption spectroscopy. The structure of the surfactants and dye is represented in Figure 1.

Experimental

Materials

The surfactants received from Sigma Aldrich Chemicals were used without any additional purification. Sodium Dodecyl Sulfate (SDS: CAS 151-21-3); Sodium Docusate (SD: CAS 577-11-7); Cetyltrimethylammonium bromide (CTAB: CAS 57-09-0). The primary stock solution of the dye (VBB) [$C_{33}H_{32}ClN_3$; CAS Number: 2580-56-5] was prepared in doubly distilled water.

Aqueous and micellar solutions

Stock solutions of the dye (2 mM) were prepared in distilled water and afterwards used in the preparation of micellar solutions of various concentrations (post-micellar, micellar, and pre-micellar concentrations). The concentration range was 16-7 mM for SDS and 3.2-2.2 mM for SD.

The maximum absorbance (λ_{max}) of an aqueous solution of the dyes was observed at 614 nm [24]. The absorbance was measured in the micellar media of both surfactants at their critical micellar concentrations. The change in absorbance significantly towards a redshift in the case of SDS and SD possibly indicated the interaction of dye molecules with surfactants. At the same time, a very minor wavelength shift was observed in the case of CTAB. Further investigation was conducted to determine the extent and type of interactions with anionic surfactants.

UV-Visible absorption spectroscopy

UV-visible spectroscopy, being the most valuable technique to detect the interactions between the dyes and surfactants, was chosen for this study. A double-beam UV-visible spectrophotometer (Perkin Elmer-USA) was used for measuring spectroscopic data of the aqueous and micellar solutions. Maximal absorbances of the dye aqueous and micellar media were recorded. The lambda max of the anionic micellar solution of dye was observed to shift towards a higher value. Absorption values during Simple and differential UV-Vis spectroscopic analysis were recorded at room temperature (298K) with an accuracy control of $\pm 0.5K$. The reference in simple absorption was distilled water, while the aqueous solution of surfactant was used in differential absorption. Ternary solution dye and surfactant in water was taken as a sample in both cases. The samples were kept overnight to attain equilibrium before analysis [21-24].

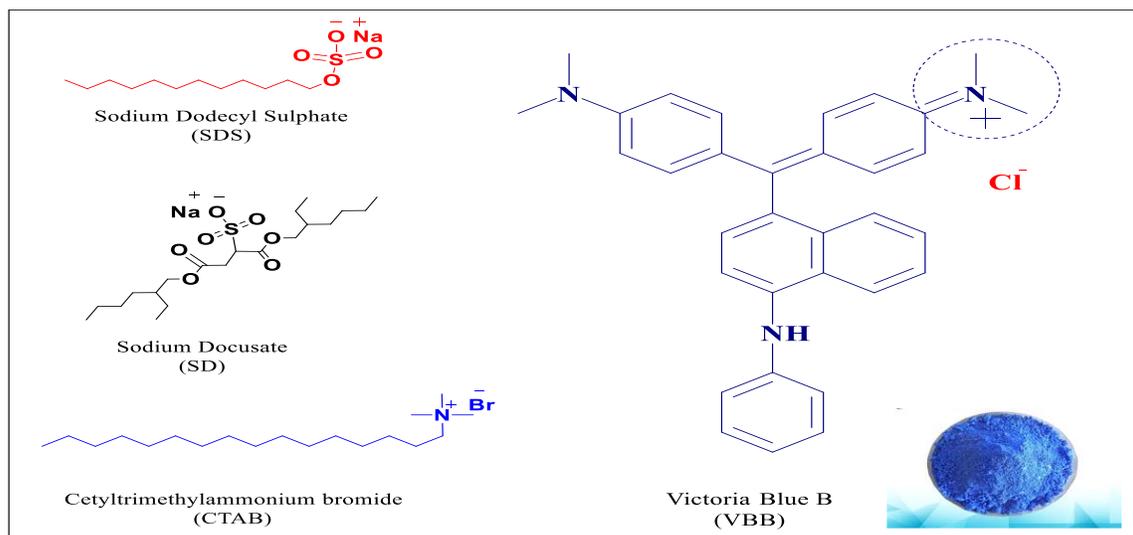


Fig. 1: Structural models of cationic dye and surfactants.

Estimation of partitioning and binding parameters

The estimation of binding and partitioning parameters from the observed absorption data was calculated using the mathematical expressions given in equations 1-5 [25].

I. Partition constant (K_c)

$$\frac{1}{\Delta A} = \frac{1}{K_c \Delta A_\infty (C_d + C_s^{m^o})} + \frac{1}{\Delta A_\infty} \quad (\text{Eq. 1})$$

II. Partition coefficient (K_x)

$$K_x = K_c n_w \quad (\text{Eq. 2})$$

The differential absorption (ΔA) is a useful tool to calculate the binding constant followed by its use to compute the partition coefficient K_x (Eq. 1 & 2) [26].

III. Change in Gibb's free energy of partition (ΔG_p)

$$\Delta G_p = -RT \ln K_x \quad (\text{Eq. 3})$$

IV. Binding constant (K_b)

$$\frac{C_s C_d}{\Delta A} = \frac{C_s}{\Delta \epsilon l} + \frac{1}{K_b \Delta \epsilon l} \quad (\text{Eq. 4})$$

V. Change in Gibb's free energy of binding (ΔG_b)

$$\Delta G_b = -RT \ln K_b \quad (\text{Eq. 5})$$

In the equations shown above the terms represent C_d = concentration of the dye; ΔA_∞ = differential absorbance at infinite dilutions. The relationship in equation 1, [$C_s^m = C_s - \text{CMC}_0$]; is showing CMC of the surfactants in water as CMC_0 , C_s = surfactant concentration. In equation 2, n_w = No. of moles of water.

Results and Discussion

Absorption Spectroscopic study

Surfactant/Dye absorption

Micellar solubilization represents a dynamic process which affected by any minor fluctuations in the media [27-28]. The interactions result from the effect of non-covalent attractive forces among the molecules of dye and surfactant. Figure 2 shows simple absorption trend of VBB in the aqueous and micellar media of SDS, SD, and CTAB. The absorption maxima of the dye matched its literature reported value of 614 nm shifted to

higher value of 641 nm in micellar media of SDS and moved to 634 nm in the SD due to significant interactions while interacting to a lesser extent in the presence of CTAB and shifted to 620 nm.

The change in the wavelength towards red shift resulted when the dye interacted with anionic surfactants versus with cationic surfactants. These wavelength shifts indicated a strong and predominant host-guest type association, electrostatic and hydrophobic interactions. This shift was due to a change in the microenvironment in the vicinity of the dye molecules especially while migration from polar aqueous layers to less polar micellar layers [12-19, 27-29].

Figure 3 represents the absorption plots of dye versus concentrations of surfactants and increasing trend in the absorbance was observed until the CMC was reached. Once the dye molecules attained maximum threshold of incorporation in the micelles, the CMC became constant. The anionic surfactants and the cationic dye will have electrostatic interactions due to their oppositely charged groups. The phenomenon occurred primarily due to the maximum and optimum incorporation of the dye molecules inside the micelles of anionic surfactants (SDS and SD). Due to similar charges in the case of CTAB, there was a very slight variation in absorbance and maximum absorbance showed less redshift as compared to SDS and SD. The microenvironment around dye molecules was continuously changing from lower micellar concentration to CMC when there was maximum incorporation of dye molecules within micelles; no further significant change in the environment was observed [12-18].

The cumulative effect of hydrophobic and electrostatic interactions was the driving force which aided the dye molecules to incorporate into surfactant micelles in the case of SDS, whereas the molecules tended to remain in the outer edges of micelles due to repulsive interactions of oppositely charged head groups. The CMC shifted from 8.23 mM to 9.58 mM in case of SDS while very minimal variation from 2.39 mM to 2.67 mM was observed in SD. The well-organized aqueous structures got disturbed due to the structure breaking effect of the cationic dye which in turn led to a rise in the CMC [11-18, 24, 30].

The hydrophilic end of the dye molecules remained on the surface, while the hydrophobic ends were partially extended towards the hydrophobic region of surfactant micelles. Partitioning of excipient molecules between aqueous bulk and the micellar phases is directly linked to the hydrophilic-lipophilic balance (HBL). Thus, the attractive interactions between surfactants and dye kept the dye molecules near the micellar surfaces [31].

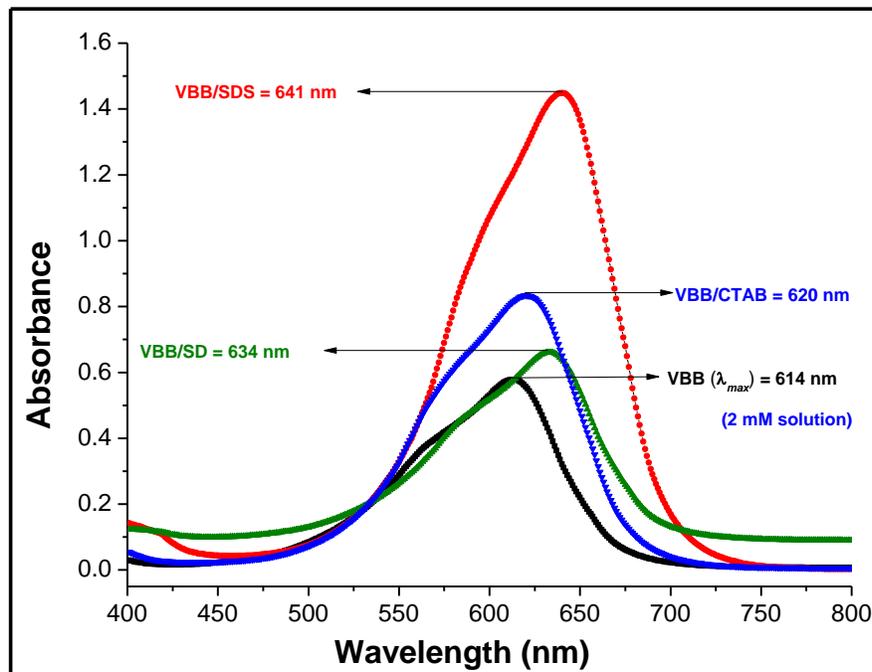


Fig. 2: Comparison of shifts in absorption of dye in aqueous and micellar media.

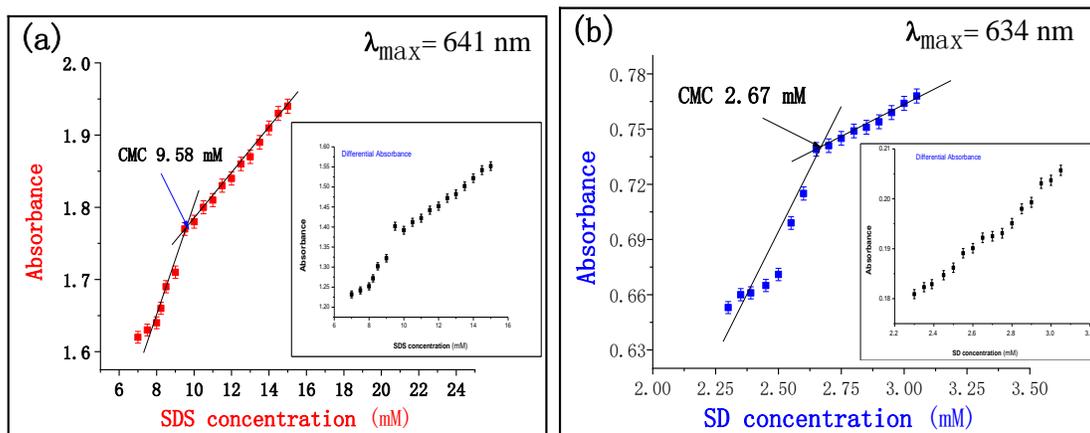


Fig. 3: Graphical representation of simple and differential absorption of the dye in (a) SDS (b) SD.

Differential absorption

The differential spectroscopy provided a convenient way to get substantial information about the interactions of synthetic dyes in micellar solutions [31]. The figure represents the differential absorption of the dye plotted against surfactant concentration. It shows a change in Gibb's free energy of binding and partition constant. There was a gradual rise in differential absorption with increasing concentration of surfactants, which was indicative of continual movement of the cationic dye molecules within the micelles. Differential absorption protocol was devised using the Kawamura model to estimate the partitioning coefficient [25].

The spectroscopic study unveiled the interactions between dye and SDS micelles. Dye molecules partitioned themselves spontaneously from the aqueous phase towards the micellar phase. The experimental results revealed greater interaction of VBB dye in SDS media due to the greater electrostatic interactions as compared to that of SD. The overall behavior of the dye with both anionic surfactants was comparable, but there was a slight variation in the solubilization parameters. This was due to the similar head groups, and the variation was possible due to the chain length of the non-polar tails, which were different in both cases.

The solubilization behavior was evaluated using partitioning and binding constant and their respective Gibb's free energies using absorption spectroscopy. Experimental results of K_c , K_x , and K_b for micellar systems of VBB in SDS and SD are summarized in Table 1. Negative magnitudes of Gibb's free energy of partition (-31.18 kJ/mol) in the VBB/SDS system, when compared to that of VBB/SDS (-26.08 kJ/mol), show the spontaneous nature of partitioning, binding, and stability of the SDS than the SD system [30]. Figure 4 represents the partition coefficients of VBB in micellar media.

Process of Solubilization and Interaction of VBB dyes with anionic surfactants

Solubilization is a very useful process to get an *in-vitro* insight into various drug and bio-membrane interactions. Such interactions and events play pivotal

roles in biological as well as industrial processes. Micelle formation is a very distinctive attribute of surfactants, which facilitates them in solubilizing partially soluble dyes or drug molecules in solution [16-19]. At pre-micellar concentrations, there forms dye-surfactant ion. In the first step, there is an interaction of cationic molecules of VBB (D^{n+}) and anionic micelles of SDS (S^-) which lead to the formation of Dye-Surfactant ion-pairs (DS). In the second step, there occur self-aggregations of DS ion-pairs (nDS). This step is followed by micellar engulfment (M), which finally lead dye-surfactant complex formation (DM). This self-aggregation phenomenon occurs specifically at post-micellar concentrations due to adsorption and penetration of the dye molecules onto micelles. The ion-pair formation and location of dye in micellar regions is shown in Fig. 6.

Table-1: Solubilization parameters of Victoria Blue in micellar media.

System	K_c $\times 10^{-2} (\text{dm}^3/\text{mol})$	K_x $\times 10^{-3} (\text{dm}^3/\text{mol})$	ΔG_p (kJ/mol)	K_b (dm^3/mol)	ΔG_b (kJ/mol)
VBB/SD	6.73	37.4	-26.08	560	-15.68
VBB/SDS	52.5	292	-31.18	200	-13.13

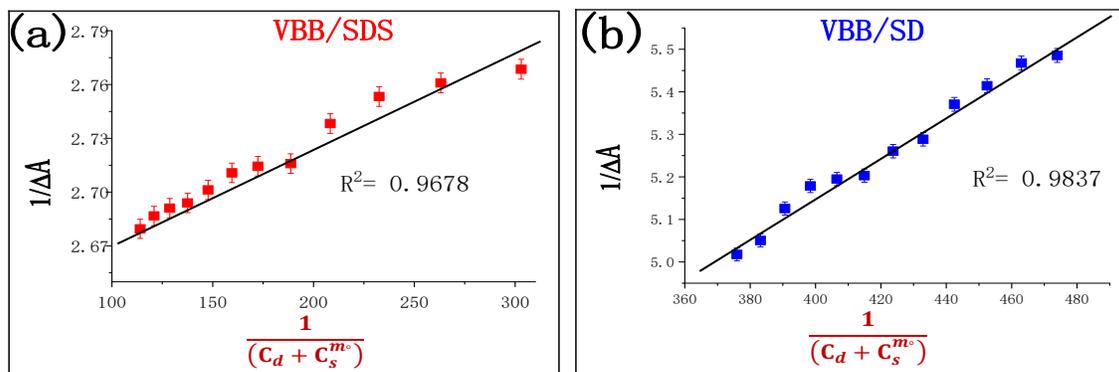


Fig. 4: Plots of partition coefficient (K_x) for (a) VBB/SDS; (b) VBB/SD system.

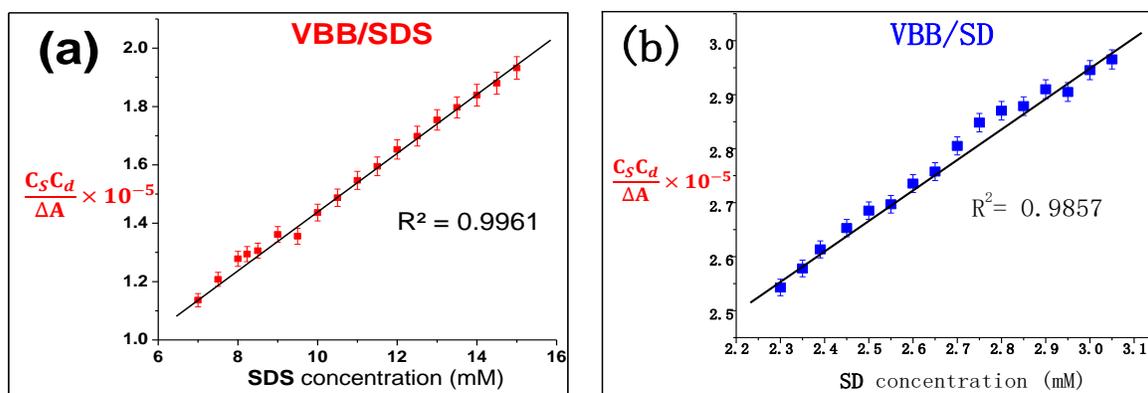


Fig. 5: Plots of binding coefficient (K_b) for (a) VBB/SDS; (b) VBB/SD system.

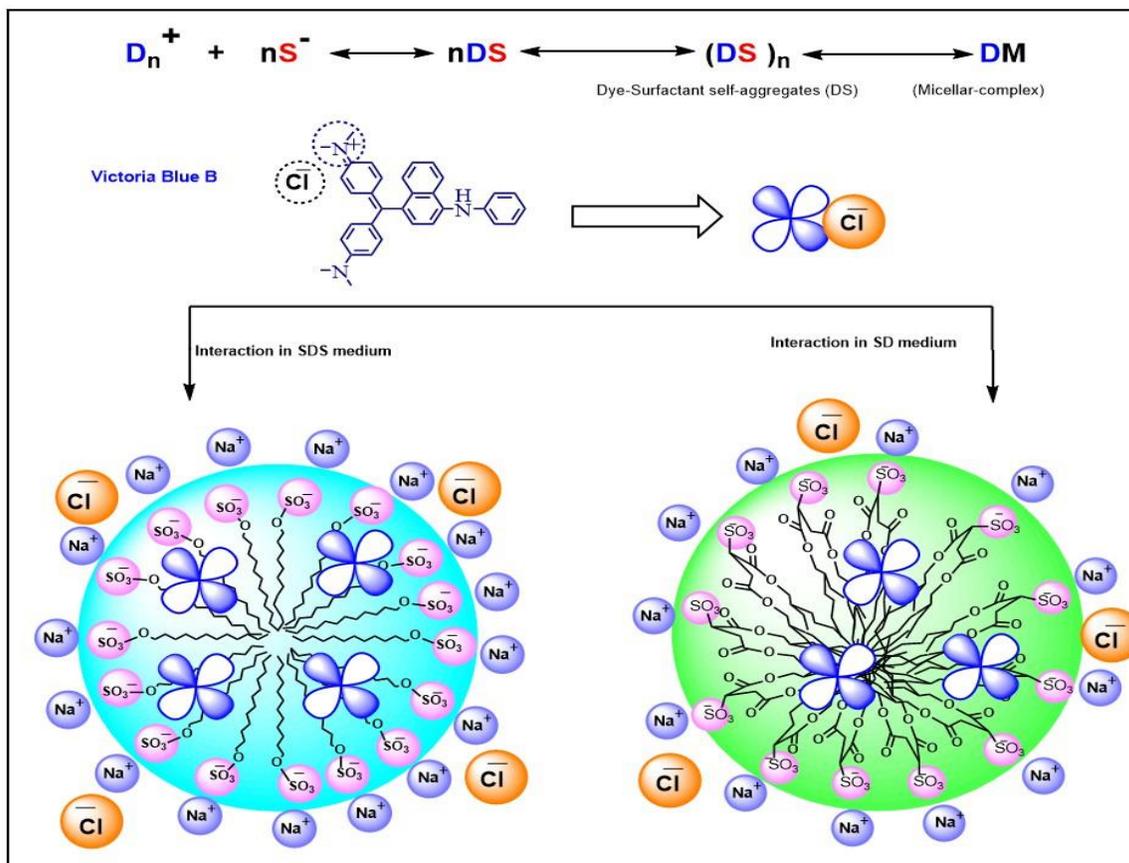


Fig. 6: Plausible partitioning and position of dye in the micelles.

The determination of CMC during this study was very helpful in determining the extent of the interaction of dye in surfactants. The exact mechanism of such interactions is still under debate, but there are some generalizations quoted about the relationship between surfactants and dyes. Ionic surfactants occupy more space due to some enhanced repulsive interactions between negatively charged sulphonate heads in SDS and SD. Greater solubilization was observed in the case of the SDS medium than in SD, as the magnitude of the partition coefficient indicates [11-15] (Table 1).

Conclusion

This research article reported the interactions of triphenylmethane-based dye Victoria Blue-B in the presence of ionic surfactants, including Sodium Dodecyl Sulphate (SDS), Sodium Docusate (SD) and Cetyltrimethylammonium bromide (CTAB). To our knowledge, such an interactional study of Victoria Blue B dye in micellar has not been reported. Partition in the SDS system showed more solubilization in

comparison to SD due to the strong interactions with dye molecules. Higher K_x ($292 \times 10^{-3} \text{ (dm}^3/\text{mol)}$) value in SDS indicated stronger interactions as compared to SD which had lower value of K_x ($37.4 \times 10^{-3} \text{ (dm}^3/\text{mol)}$). The determination of CMC was very helpful in determining the extent and nature of the interaction of dye in the surfactants. The dye VBB did not show any significant interaction with cationic surfactant due to possible repulsive interaction of the oppositely charged head groups.

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