

## Research Article

# Physicochemical Studies on the Interaction between Sodium Dodecyl Sulfate and Methylene Blue in Methanol-Water Mixed Solvent Media

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The surface activity and the process of micellization of sodium dodecyl sulfate (SDS) with methylene blue (MB) in a methanol-water mixed solvent system were investigated by tensiometry and conductometry at 298.15 K. The measurements of surface tension and conductivity of SDS-MB complex were carried up to 0.3 volume fractions of methanol because the resulting complex appeared turbid above 0.3 volume fractions of methanol. The critical micelle concentration (CMC) of the SDS was determined from both tensiometry and conductometry. The CMC of SDS increased with the increasing volume fraction of methanol due to the inclusion of methanol in the micelles and decreased in the presence of methylene blue due to the reduction of electrostatic repulsion within the anionic moiety of SDS by the positive charge of the added dye. Different properties like surface excess concentration ( $\Gamma_{\max}$ ), minimum surface area ( $A_{\min}$ ), Gibbs free energy of micellization ( $\Delta G_m^{\circ}$ ), surface pressure ( $\pi_{\text{CMC}}$ ), efficiency of a surfactant ( $pC_{20}$ ), packing parameter ( $P$ ), and standard free energy interfacial adsorption ( $\Delta G_{\text{ads}}^{\circ}$ ) of SDS in the absence/presence of MB were calculated. On the basis of  $\Delta G_m^{\circ}$  values, it was noticed that the increasing volume fraction of methanol disfavors the micellization of SDS, while the presence of MB increased the efficiency of SDS making the micellization process more spontaneous.

## 1. Introduction

In the present context, industrialization and urbanization increase the contamination of water, which is a serious problem in human life. Dyes that are used in various industries such as paper, pulp, leather, pharmaceuticals, plastic, paint, rubber, and textiles make a significant contribution to this contamination [1]. They damage humans badly as they cause liver dysfunction and have a negative impact on the brain, central nervous system, kidneys, and reproductive system [2]. The removal of dyes from wastewater is, therefore, very important for the ecosystem and human health. Currently, researchers are doing rapid investigations on new methods for developing efficient and cost-effective technologies for removing environmentally harmful dyes from industrial wastewater. Based on this problem, surfactant micelles are one of the most suitable

methods for capturing hydrophobic dyes from wastewater [3]. For the production of many industrial and personal care products such as shower gels, shampoos, and bath additives, concentrated aqueous solutions of anionic surfactants are widely used in a blend with salts and additional additives like dyes and perfumes [4]. In the dye industry, surfactants are frequently used because they can wet and help in the scattering of dyes, particularly which are weakly soluble. The interactions of surfactants with dyes play a crucial role in accomplishing a level of the color [5]. Although much research has been done on dye-surfactant interactions [6–14], studies in this area are still interesting and important for the theory and technology of dyeing [15].

There is a considerable interest in the role of cosolvents for the formation of micelles in surfactant solutions from both fundamental and applied points of view because the use of surfactants in many physicochemical and interface

phenomena largely depends on the interactional behavior of them [16].

The adding of external additives into the aggregate structure of surfactants will change their physicochemical characteristics such as the degree of ionization, reaction rates, and clouding or phase separation [17–20]. In the same way, the critical micelle concentration of ionic surfactants is significantly altered by the addition of a modest quantity of an organic solvent, since the added organic solvent will, in general, break or make the water structure by solvating the hydrophobic tail of the surfactant by its hydrocarbon (hydrophobic) portion [21]. Huang and Ren [22] studied the effect of isopropanol on the micellization behavior of a binary mixture of amphoteric amino sulfonate surfactant (C12AS) with octylphenol polyoxyethylene ether (10) in water/NaCl solution and found that the formation of mixed micelles and the intercalation of C12AS into the mixed micelle is disfavored in the presence of isopropanol. Li et al. [23] studied the effect of short-chain alcohol on the micellization behavior of octadecyltrimethylammonium bromide and found that the presence of alcohol molecule at the air-liquid interface or in the micelle causes the variation in the interfacial or micellization behavior. Ren et al. [24, 25] studied the advantages and disadvantages of isopropanol on the micellization behavior of mixed surfactants based on different thermodynamic parameters which are helpful in designing the surfactant formulas relative to cosolvent.

Methylene blue is a thiazine dye that has an assortment of industrial and scientific applications [26]. The self-association property of methylene blue, a common redox indicator and biological dye, has been studied by several researchers for a long period [27–30].

Sodium dodecyl sulfate is a typical anionic surfactant, and its interactions with chromophores such as ruthenium complexes [31], acridine orange [32], methyl orange, cresol red and methyl red [33], methyl violet [34], methylene blue, C.I. Mordant Black 11, C.I. Mordant Black 17, and C.I. Direct Yellow 50 in aqueous solution [35] have been investigated by researchers.

Several types of interactions between anionic surfactants and cationic dyes are known to occur in solution, including dye-dye dimer formation [27, 29], dye-surfactant interaction (including ion-pair formation and dye-surfactant aggregates), [31, 32, 36], and dye-solvent interactions [30, 37]. Many techniques have been used to qualitatively and quantitatively describe dye-surfactant interactions, i.e., potentiometry [38], conductometry [39], ion-selective electrodes [40], and tensiometry [41, 42]. The most frequently used technique to explore dye-surfactant interactions is spectrophotometry [35, 42–46].

The properties of the formation of complex ion pairs of SDS-methylene blue have been explored by means of surface tension and UV-Vis/fluorescence measurements [41], molecular spectroscopic measurement [47], photoacoustic imaging technique [13], and UV spectroscopic analysis [48, 49] in an aqueous medium, but their interactional properties in alcohol-water mixed solvent media have not yet been examined. We have started to study the interactional properties using lower chain alcohols like methanol,

ethanol, and propanol. However, this work mainly focused on the effect of methanol on the interaction between dye and surfactant. To obtain information on the CMC of the individual surfactants and surfactant-dye complex in a binary solvent, the measurements were carried out by tensiometric and conductometric analysis. This study will provide the basic data for designing surfactant formulations in the presence/absence of dye in mixed solvent systems and will be useful to achieve the applications of these formulations for the industrial sector. Also, it provides a further idea to the researchers to carry out the experiment on dye-surfactant interaction in mixed solvent systems.

## 2. Experimental

**2.1. Materials.** SDS (99% purity) was purchased from Loba Industries, India. Methylene blue (>82% purity) was purchased from Ranbaxy, India, and used as it was brought. All experiments were carried out with analytical reagent grade chemicals using double-distilled water. Methanol was obtained from Merck, India, with the highest purity (99.9%) and was used during the experiment. Methanol-water mixtures were prepared in the research laboratory of the Department of Chemistry, Mahendra Morang Adarsh Multiple Campus, Tribhuvan University, Biratnagar, Nepal.

**2.2. Measurements.** The specific conductance was determined using a digital conductivity meter purchased from Systronics India Ltd. with a dip-type conductivity cell with a cell constant of  $1.002 \text{ cm}^{-1}$ , which was calibrated with KCl solution in the appropriate concentration range with an uncertainty of 0.01%. The surface tension was measured using a Kruss Easy Dyne Tensiometer using the du Nouy's ring method. The calibration data of the tensiometer are stored internally, and after base adjustment, the surface tension of pure methanol and water was measured and found to be  $22.30 \text{ mN} \cdot \text{m}^{-1}$  and  $72 \text{ mN} \cdot \text{m}^{-1}$ , respectively, at 298.15 K which is in good agreement with the literature [50]. The resulting value from measurements has an uncertainty of  $\pm 0.20 \text{ mN} \cdot \text{m}^{-1}$ . Before each measurement, the ring was first cleaned with distilled water and warmed to a red color with a Bunsen burner. Three successive readings were taken for each concentration of SDS, and their mean value was taken into account. The temperature of all measurements was controlled by a jacketed vessel connected to a thermostated water bath. All measurements were carried out at 298.15 K within  $\pm 0.2 \text{ K}$ . SDS was dried for 1 h below its melting point of 479.15 K before preparing solutions. The SDS solution having a concentration of  $0.1 \text{ mol} \cdot \text{L}^{-1}$  was prepared in the double-distilled water ( $\gamma = 72 \text{ mN} \cdot \text{M}^{-1}$ ), and the measurement of surface tension was carried out at each internal dilution at 298.15 K. The CMC was determined to be 8.1 mM which is in very close agreement with the literature [51, 52]. The solution of methylene blue was made in double-distilled water, and absorbance was measured using Labtronics UV Visible Spectrophotometer (Single Beam) at 298.15 K. The peak absorbance was seen at 664 nm which is in agreement with the literature [27, 47, 53, 54].

### 3. Results and Discussion

**3.1. Conductometric Studies.** The CMC values of SDS, calculated from conductivity and surface tension measurements at 298.15 K, are very close to each other and are in close agreement with the literature [55, 56]. From Figure 1, it can be seen that the linear region which is above the CMC has a smaller slope than that of the linear region below the CMC. This is the consequence of higher SDS concentrations, which lowers the ionic mobility [10]. It should also be noted that the micelles that are formed at a higher surfactant concentration, far from the CMC, increase the solubility of the dye in solution, which slows down the conductivity [26].

The presence of a cosolvent reduces micelle formation, and it completely inhibits micellization when its concentration reaches an optimum level [57]. The solution of SDS appeared slightly cloudy at 0.4 volume fraction of methanol and resulted in turbidity in the presence of methylene blue, where the distribution of ions/ion pairs was nonuniform. The turbid solution gave fluctuated data of conductivity and surface tension (result not shown), which makes it difficult to locate the CMC and calculate other parameters; therefore, measurements were not carried at/above 0.4 volume fraction of methanol. The CMC increases with the increasing volume fraction of methanol, which is due to the inclusion of methanol in the micelles, where it breaks down the micelles [58]. It is seen that short-chain alcohols increase the CMC at the higher bulk phase concentrations because they lower the cohesive energy density of the water that increases the solubility of the monomeric form of the surfactant [59]. There is an alternative explanation in the case of ionic surfactants that is based on the dielectric constant of the medium. The short-chain alcohols reduce the dielectric constant of the aqueous phase, which increases the mutual repulsion of the ion heads in the micelle, which would reverse micellization and increase the CMC [60].

In addition to the interaction between methylene blue and SDS, interactions between the cosolvent and water, cosolvent and surfactant, and cosolvent and dye also need to be taken into account. Most often, the alcohol hydroxyl group is hydrogen-bonded to the head group of the surfactant and henceforth reduces the attraction between SDS and the dye. Therefore, to explain the inhibitory impact of cosolvents on the development of molecular complexes, we need to consider the sum of several potential variables, such as varying physicochemical properties of the medium, preferential solvation of dye, and cosolvent–water and cosolvent–surfactant interactions. However, it is difficult to choose and decide which factor shows the most inhibitory effects among all. Most often, all of the above variables contribute less or more in different ways [57].

It is seen that both the conductivity and CMC of SDS decrease with the addition of methylene blue because the dye has a positive charge which reduces the mutual repulsion within the anionic moiety of SDS [61] by binding with the micellar aggregates at the surface [34].

We could estimate the number of SDS molecules per micelle, i.e., the aggregation number ( $N$ ) using relation  $N = 4\pi l_c^2/A_m$  [62, 63], where  $l_c = [1.54 + 1.26n_c]$  is a

hydrophobic tail length,  $A_m$  is the area occupied per surfactant molecule, and  $n_c$  is the number of carbon atoms in the alkyl chain. Taking  $A_m = 62.10$  for the SDS from the literature [56], we get  $N = 56$ , which is in agreement with the literature [64] where the value of  $N$  was detected to be  $55 \pm 5$ . Sachin et al. [63] also have reported the  $N$  value of SDS to be greater than 50.

Thus, for ionic surfactant, the standard Gibbs free energy of micellization,  $\Delta G_m^o$ , is evaluated on the basis of the pseudophase separation model [65] by the relation

$$\Delta G_m^o = (2 - \alpha)RT \ln X_{\text{CMC}}, \quad (1)$$

where  $\alpha$  is the degree of dissociation, which was determined as  $\alpha = S_2/S_1$  [55, 66–68];  $S_2$  is the postmicellar slope,  $S_1$  is the premicellar slope, and  $X_{\text{CMC}}$  indicates the mole fraction of CMC. The CMC and  $\alpha$  values were calculated by conductometric data on the basis of a conventional procedure called Williams' method [69].

The obtained values of  $\Delta G_m^o$  are negative, which indicates the spontaneity of the micellization process. This spontaneity decreases with an increasing volume fraction of methanol, after which micellization is less favorable. The  $\Delta G_m^o$  values of SDS in the absence of dye are in close agreement with the literature [55]. The negative values of  $\Delta G_m^o$  increase when the dye content is added in mixed systems, which indicates that the formation of micelles becomes more feasible with the addition of the dye.

The values of degree of ionization ( $\alpha$ ), CMC (by conductometry and tensiometry), and Gibbs free energy of micellization ( $\Delta G_m^o$ ) of SDS by conductometry with/without methylene blue in different volume fractions of methanol–water at 298.15 K are tabulated in Table 1.

**3.2. Tensiometric Measurements and Surface Properties.** More often, the micelle structure of aqueous SDS micelles is in equilibrium with solution monomers and the surfactant monolayer at the air/water interface. The positively charged methylene blue strongly attracts SDS from the equilibrium solution, interacts with it, and forms complexes that have a higher potential to stay at the air/solution interface [41], thereby, lowering the surface tension.

The activity of surfactant in the micelles is lower in the presence of dye, whereby micelles are formed at lower concentrations. It is well understood that the impurity (dye) lowers the surface tension significantly below the CMC and then sufficiently solubilized in micelles or forms a dye-surfactant ion pair after an intermediate minimum (CMC), which leads to a higher surface tension [70]. Thus, a slight increment in the surface tension values is seen after CMC (Figure S1).

The oppositely charged dye-surfactant ion pair acts as a nonionic surfactant and has a greater affinity for the air-water interface, which occupies a larger surface. Thus, the ion pair surfactant has higher efficiency and a lower CMC [71] than the corresponding pure anionic surfactants, as observed in Table 1.

The variation in the slope ( $dy/d\log C$ ) of SDS in the absence/presence of methylene blue with a volume

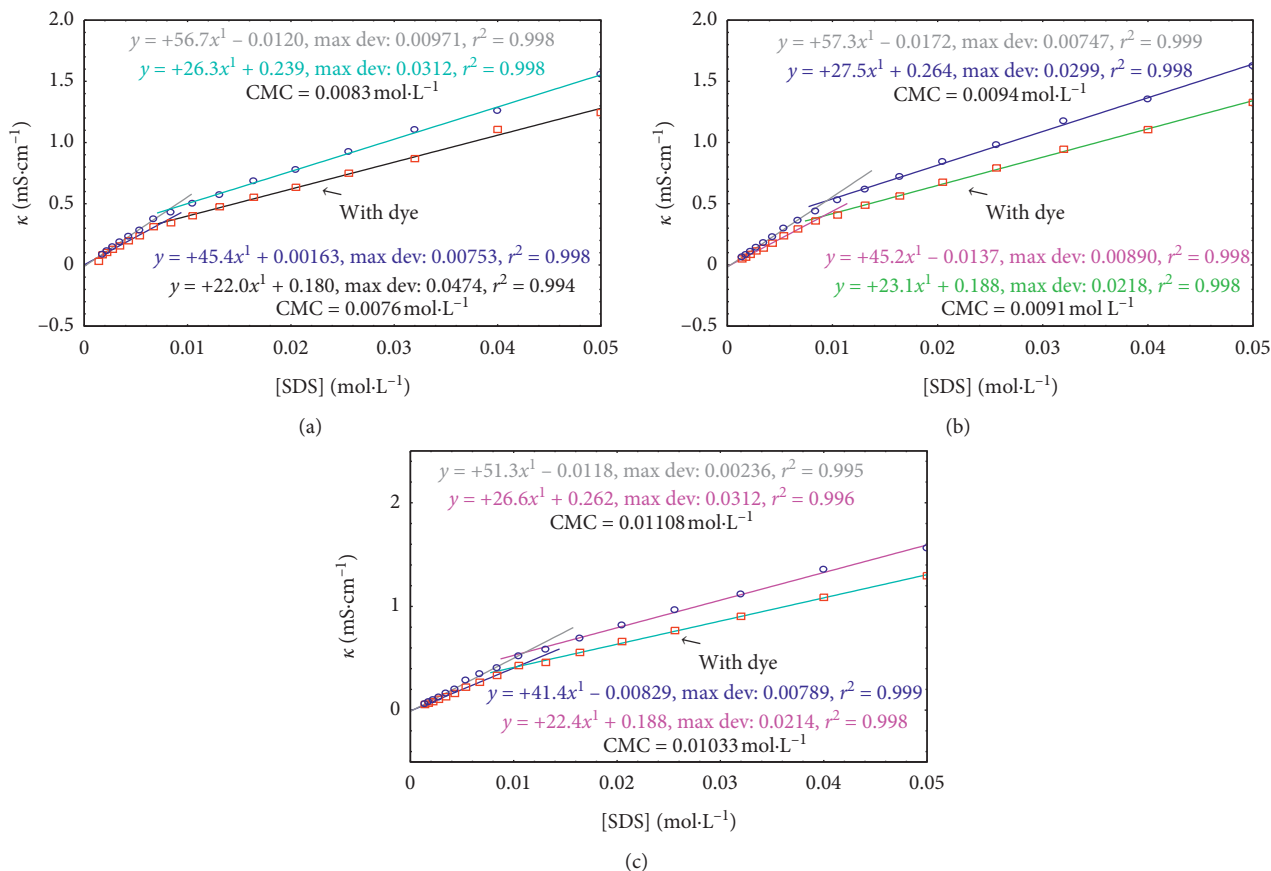


FIGURE 1: Variation of specific conductance of SDS with concentrations in the absence (○) and presence (□) of methylene blue in (a) 0.1, (b) 0.2, and (c) 0.3 volume fraction of methanol in aqueous medium at 298.15 K.

fraction of methanol in water is shown in Figure 2. The negative value of the slopes decreases with an increasing volume fraction of methanol, which indicates the lower surface activity of the surfactants. This consequence is due to changes in the dielectric constant and the hydrophobicity of the medium [56]. With the help of slope, the maximum surface excess concentration at the air/methanol-water interface  $\Gamma_{\max}$  can be determined by applying Gibb's isotherm [72]:

$$\Gamma_{\max} = -\frac{1}{2.303nRT} \left[ \frac{d\gamma}{d\log C} \right]_{T,P}, \quad (2)$$

where  $\gamma$  signifies the surface tension,  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \cdot \text{K}^{-1}$ ),  $T$  denotes the absolute temperature,  $C$  is the surfactant concentration, and  $(d\gamma/d\log C)$  is the slope of the  $\gamma$  versus  $\log C$  plot taken at CMC. The constant  $n$  is known as a prefactor that takes the value equivalent to 2 for the traditional surfactant, where the surfactant ion and the centerline are univalent.

The area occupied per surfactant molecule ( $A_{\min}$ ) at the air/methanol-water interface [73] has been obtained using

$$A_{\min} = \frac{1}{N_A \Gamma_{\max}}, \quad (3)$$

where  $N_A$  is Avogadro's number.

Dissolution of the surfactant molecules leads to the most extreme decrease in surface tension, which is indicated by a parameter  $\pi_{\text{CMC}}$  known as surface pressure.  $\pi_{\text{CMC}}$  is a measure for the effectiveness of the surfactant to lower the surface tension of the solvent [60] and is calculated using

$$\pi_{\text{CMC}} = \gamma_o - \gamma_{\text{CMC}}, \quad (4)$$

where  $\gamma_o$  and  $\gamma_{\text{CMC}}$  are the values of surface tension of water and the surfactant solution at the CMC, respectively.

According to the data, the surface excess concentration,  $\Gamma_{\max}$ , decreases with an increasing volume fraction of methanol. This result is due to the lowering of the dielectric constant of the medium and an increase in the hydrophobic effect. Because of these components, the population of surfactant molecules decreases from the surface of the solvent and is dispersed in the bulk [74]. Because of the smaller population of SDS molecules on the superficial or surface region, the minimum surface area,  $A_{\min}$ , increases and the surface pressure,  $\pi_{\text{CMC}}$ , decreases with an increasing volume fraction of methanol [56].

The  $\Gamma_{\max}$  values of SDS have been found to decrease in the presence of dye. Subsequently, the  $A_{\min}$  increases by approximately 11.4%, 11.9%, and 29.5% in the 0.1, 0.2, and 0.3 volume fractions of methanol, respectively, in the presence of dye. This indicates that the dye-surfactant ion

TABLE 1: Values of the degree of ionization ( $\alpha$ ), CMC (by conductometry and tensiometry), and Gibbs free energy of micellization ( $\Delta G_m^\circ$ , by conductometry) of SDS in different volume fractions of methanol-water at 298.15 K.

Volume fraction of methanol	Degree of ionization ( $\alpha$ )		CMC (mM) by conductometry		CMC (mM) by tensiometry		$\Delta G_m^\circ$ (kJ·mol <sup>-1</sup> ) by conductometry		CMC (mM) by conductometry [55]		CMC (mM) by tensiometry [56]	
	a	b	a	b	a	b	a	b	a	b	a	b
0.1	0.464	0.485	8.30	7.60	8.50	7.60	-33.31	-34.30	8.50	8.50	9.20	9.20
0.2	0.479	0.511	9.40	9.10	9.50	9.0	-32.29	-32.79	9.60	9.60	10.30	10.30
0.3	0.518	0.541	11.08	10.33	11.4	10.56	-30.62	-31.42	~11.0	~11.0	11.70	11.70

a = calculated value in the absence of methylene blue. b = calculated value in the presence of methylene blue.

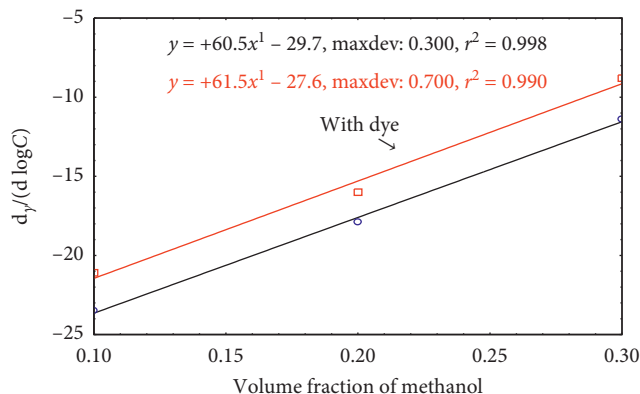


FIGURE 2: Variation in the slope ( $dy/d \log C$ ) of SDS in the absence (o) and presence ( $\square$ ) of methylene blue with different volume fractions of methanol at 298.15 K.

pair occupies more surface area at the air/alcohol-water interface than the surfactant alone. In addition to this, the dye-surfactant ion pair, which is formed by electrostatic interaction, is identical to the new nonionic surfactant with a larger head group, and as a result, a larger surface area per surfactant leads to a lower CMC of the ion-pair surfactant [71]. The values of  $\pi_{\text{CMC}}$  increased in the presence of the dye, which suggests that the dye-surfactant ion pair (DSIP) is more effective in lowering the surface tension.

At the air/saturated monolayer interface, the standard free energy interfacial adsorption ( $\Delta G_{\text{ads}}^{\circ}$ ) can be calculated from [75]

$$\Delta G_{\text{ads}}^{\circ} = \Delta G_{\text{m}}^{\circ} - \frac{\pi_{\text{CMC}}}{\Gamma_{\text{max}}}. \quad (5)$$

A higher negative value of  $\Delta G_{\text{ads}}^{\circ}$  indicates a higher efficiency of the surfactant to be adsorbed, that is, spontaneous adsorption at the surface. In this experiment, the  $\Delta G_{\text{ads}}^{\circ}$  values were found to be less negative with an increasing volume fraction of methanol, which indicates low spontaneity of adsorption of surfactant molecules on the surface. However, the values of  $\Delta G_{\text{ads}}^{\circ}$  become more negative in the presence of dye, indicating that the adsorption process is substantially more spontaneous than in the absence of dye.

$pC_{20}$  is an important parameter for describing the efficiency of a surfactant to reduce the surface tension and is defined in terms of the negative logarithm of  $C_{20}$ , where  $C_{20}$  denotes the concentration of surfactant that is required to reduce the surface tension of the pure solvent by  $20 \text{ mN}\cdot\text{m}^{-1}$ . The value of  $pC_{20}$  has been calculated using  $\pi_{\text{CMC}}$  and  $\Gamma_{\text{max}}$  [76] from

$$pC_{20} = \frac{\pi_{\text{CMC}} - 20}{2.303nRT\Gamma_{\text{max}}} - \log \text{CMC}. \quad (6)$$

The  $pC_{20}$  values that are calculated from (6) are in good agreement with  $-\log C_{20}$  (result not shown), where  $C_{20}$  is the practical concentration of surfactant solution whose corresponding surface tension value is reduced by  $20 \text{ mN}\cdot\text{m}^{-1}$  than that of the methanol-water mixed solvent and can be taken from the plot of Figure S1. Higher adsorption

efficiency is indicated by the larger  $pC_{20}$  value, which depends on the hydrophobicity of the medium [67]. On increasing the volume fraction of methanol, the  $pC_{20}$  value decreases; that is, the adsorption at the interface decreases with the increasing population of surfactants in the bulk phase [75]. The efficiency of surfactants is found to be higher with the addition of dye, which is due to the formation of close-packed dye-surfactant ion pairs (DSIP). DSIP behaves like a nonionic surfactant, which usually has higher efficiency than ionic surfactants [60].

According to Israelachvili [77], there is one important parameter called the packing parameter,  $P$ , which predicts the geometry of the micellar aggregate and can be evaluated by the relation

$$P = \frac{V_o}{A_{\text{min}}l_c}, \quad (7)$$

where  $V_o$  is the volume of exclusion per monomer in the aggregate, as described in Tanford's formula [68, 78].  $V_o = [27.4 + 26.9n_c] \text{ \AA}^3$ ,  $l_c = [1.54 + 1.26n_c] \text{ \AA}$  is the maximum chain length, and  $n_c$  is the number of carbon atoms in the alkyl chain.

The structure of the micelle will be spherical, non-spherical, vesicles, and inverted structures when  $P < 1/3$ ,  $1/3 < P < 1/2$ ,  $1/2 < P < 1$ , and  $P > 1$ , respectively. From Table 2, it can be seen that the values of  $P$  are less than  $1/3$  in both (with/without dye) systems; therefore, the shapes of all the aggregates with/without dye in the mixed solvent are spherical in nature. On increasing the volume fraction of methanol in water, the  $P$  values get decreased. This indicates that micellar aggregates get smaller with the addition of methanol [66]. The  $P$  values also decrease upon the addition of dye, which might be due to the formation of a dye-surfactant ion pair that has smaller aggregates than the surfactant alone. The  $\Gamma_{\text{max}}$ ,  $A_{\text{min}}$ ,  $\pi_{\text{CMC}}$ , and  $P$  values of SDS in the absence of dye are in close agreement with the literature [56].

Table 2 displays the values of  $\Delta G_{\text{m}}^{\circ}$ ,  $\Gamma_{\text{max}}$ ,  $A_{\text{min}}$ ,  $\pi_{\text{CMC}}$ ,  $P$ ,  $\Delta G_{\text{ads}}^{\circ}$ , and  $pC_{20}$  of SDS in the absence/presence of methylene blue in different volume fractions of methanol at 298.15 K.

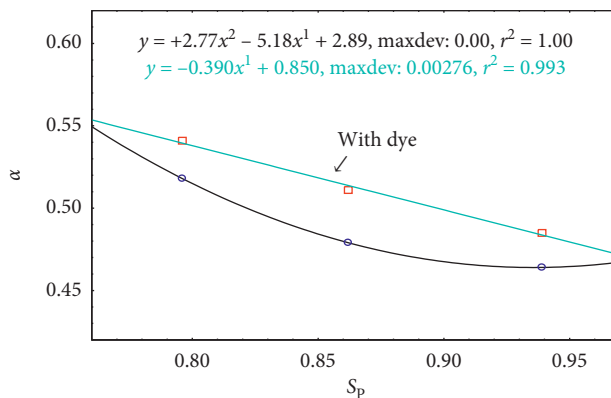
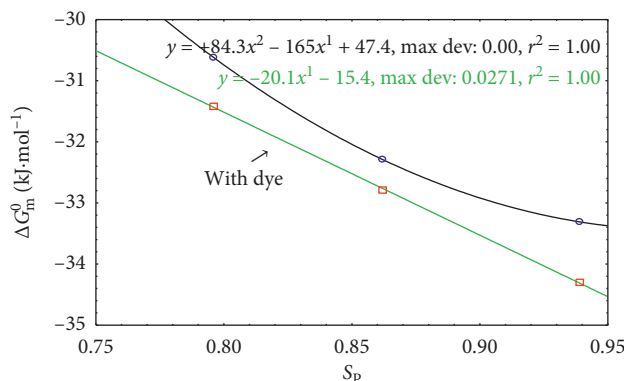
TABLE 2: Surface properties of SDS in different volume fractions of methanol-water at 298.15 K.

Volume fraction of methanol	$\Gamma_{\max}$ $10^6$ ( $\text{mol}\cdot\text{m}^{-2}$ )		$A_{\min}$ ( $\text{\AA}^2$ molecule $^{-1}$ )		$\pi_{\text{cmc}}$ ( $\text{mN}\cdot\text{m}^{-1}$ )		$P$		$\Delta G_{\text{ads}}^{\circ}$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )		$\text{pC}_{20}$	
	a	b	a	b	a	b	a	b	a	b	a	b
0.1	2.06	1.85	80.68	89.86	19.1	21.2	0.28	0.25	-42.59	-45.77	2.03	2.18
0.2	1.57	1.40	105.92	118.5	13.5	16.75	0.21	0.19	-40.9	-44.74	1.66	1.84
0.3	1.01	0.77	166.31	215.45	7.5	10.2	0.14	0.11	-38.13	-44.65	0.85	0.86

a = calculated value in the absence of methylene blue, b = calculated value in the presence of methylene blue.

TABLE 3: Various physicochemical parameters of the mixed solvent (methanol-water) at 298.15 K.

Volume fraction of methanol	Gordon parameter ( $G/J \cdot m^{-3}$ )	Coefficient of viscosity ( $\eta_o/mPa \cdot s$ ) [74]	Reichardt's parameter ( $E_T/kcal \cdot mol^{-1}$ ) [74]	Solvophobic parameter ( $S_p$ ) [79]
0.1	1.91	1.0844	62.33	0.939
0.2	1.53	1.3106	61.56	0.862
0.3	1.27	1.4712	60.79	0.796

FIGURE 3: Plot of variation of  $\alpha$  with solvophobic parameter ( $S_p$ ).FIGURE 4: Plot of variation of  $\Delta G_m^o$  with solvophobic parameter ( $S_p$ ).

3.3. *Correlation of  $\Delta G_m^o$  with Solvent Parameters.* The counterion binding influences  $\Delta G_m^o$ ; therefore,  $\Delta G_m^o$  is the appropriate thermodynamic parameter for ionic surfactants. Here, we correlate  $\Delta G_m^o$  with different solvent parameters, namely, viscosity,  $\eta_o$  (Figure S2a), Gordon parameter,  $G$  (Figure S2b), and Reichardt's parameter,  $E_T(30)$  (Figure S2c). The  $E_T(30)$  and  $\eta_o$  values were taken from the literature [74], and  $G$  values were calculated by us using [75]

$$G = \frac{\Upsilon_{sol}}{V_m^{1/3}}, \quad (8)$$

where  $\Upsilon_{sol}$  is the surface tension of the methanol-water mixed solvents and  $V_m$  is a molar volume of the mixed solvent.

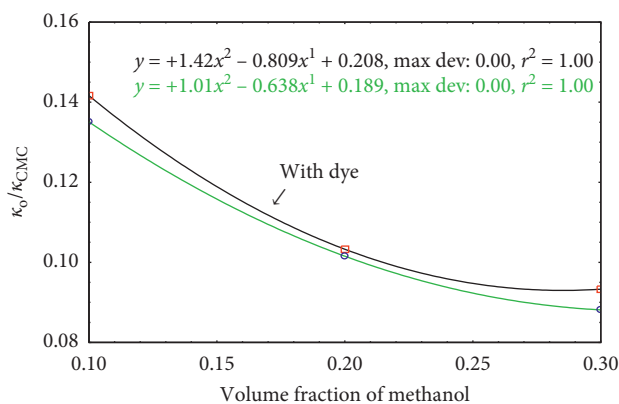
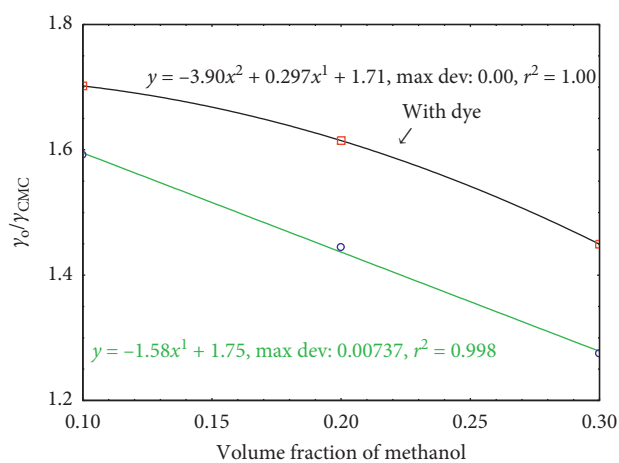
The  $E_T(30)$  values which are depicted in the literature [74] were estimated by the relation

$$E_T(30) = \frac{hc N_A}{\lambda_{max}}, \quad (9)$$

where  $h$  is a Planck's constant,  $c$  is the speed of light,  $N_A$  is Avogadro's constant, and  $\lambda_{max}$  is the wavelength of the maximum absorption band in the visible/near-IR region.

All these three parameters ( $\eta_o$ ,  $G$ ,  $E_T$ ) produced curvilinear correlations with  $\Delta G_m^o$  in the absence of dye, as obtained by Pan et al. [68], while the above parameters produced linear correlations with  $\Delta G_m^o$  in the presence of dye. However, further exploration is necessary in this area with different surfactants and dyes in nonaqueous as well as mixed solvents. The development of a database on the solution behavior of surfactants and their interaction with dyes in mixed solvent media, thereby showing quantitative correlations of the results with different solvent parameters, should be a worthwhile research effort in the future.



FIGURE 5: Plot of variation of  $\kappa_o/\kappa_{CMC}$  with volume fraction of methanol.FIGURE 6: Plot of variation of  $\gamma_o/\gamma_{CMC}$  with volume fraction of methanol.

3.4. Correlation of  $\alpha$  and  $\Delta G_m^o$  with the Solvophobic Parameter ( $S_p$ ). The interaction of alkyl chains with solvents was measured by the solvophobic parameters. A smaller  $S_p$  value reflects a stronger interaction between the hydrocarbon and solvent. The values of  $S_p$  were taken from the literature of Wang et al. [79], which was calculated using (10) mentioned by Abraham et al. [80] as

$$S_p = 1 - \frac{M(\text{solvent})}{M(\text{hexadecane})}, \quad (10)$$

$$S_p = 1 + \frac{M}{4.2024}, \quad (11)$$

where  $M(\text{hexadecane}) = -4.2024$ ,  $M(\text{solvent})$  is the slope value obtained from the plot of  $\Delta G_t^o$  versus  $R_T$  as given by

$$\Delta G_t^o = MR_T + D, \quad (12)$$

where  $\Delta G_t^o$  refers to the transfer of a series of solutes from water to a given solvent,  $R_T$  is a solute parameter, and  $M$  and  $D$  characterize the solvent.

It is seen that the  $S_p$  value decreases linearly with an increasing volume fraction of methanol (Table 3). This means that the hydrophobic interaction between hydrocarbon and water molecules is maximum at a 0.3 volume

fraction of methanol in our study, and this hydrophobic interaction affects the ionization degree of SDS and SDS-MB aggregates in a way that the  $\alpha$  values decrease with increasing  $S_p$  values (Figure 3). The value of  $\alpha$  decreases in the curvilinear path in the case of the SDS alone and linearly in the case of the SDS-MB ion pair, respectively. This suggests that the formation of aggregates is favored by increasing the solvophobic power of hydrocarbon chains in a solvent. However, the linear decrease in  $\alpha$  with increasing  $S_p$  values indicates a higher efficiency of aggregation in the presence of the dye.

Further, from Figure 4, it can be noticed that the  $\Delta G_m^o$  values of SDS decrease in the curvilinear path with increasing  $S_p$  values but decrease linearly in the case of SDS-MB aggregates. The higher negative value of  $\Delta G_m^o$  at higher  $S_p$  values suggests that micellization is more spontaneous at lower interactions between hydrocarbons and solvent. However, micellization is more spontaneous in the presence of the dye than the surfactant alone.

3.5. Correlation of  $\kappa_o/\kappa_{CMC}$  and  $\gamma_o/\gamma_{CMC}$  with Volume Fraction of Methanol. Mukhim and Ismail [81] had developed a concept of the ratio of the solvent surface tension to the limiting surface at the CMC ( $\gamma_o/\gamma_{CMC}$ ) to describe the

solvophobic effect. Sachin et al. [42] also used the same ratio to study the solvent effects. In the same way, the concept of the ratio of the solvent conductance to the conductance at the CMC ( $\kappa_o/\kappa_{\text{CMC}}$ ) has been developed by our researchers to observe the efficiency of surfactants [82, 83]. Figure 5 shows the curvilinear variation of  $\kappa_o/\kappa_{\text{CMC}}$  with volume fraction of methanol. Figure 6 shows the variation of  $\gamma_o/\gamma_{\text{CMC}}$  with volume fraction of methanol. The plot is linear in the absence of dye and is curvilinear in the presence of dye. The  $\kappa_o/\kappa_{\text{CMC}}$  and  $\gamma_o/\gamma_{\text{CMC}}$  value decreases with an increasing volume fraction of methanol, which suggests that the micellization is inhibited by the cosolvent, which might be due to interaction between methanol and methylene blue.

#### 4. Conclusions

The CMC of SDS increases, while  $\Delta G_m^o$ ,  $\Gamma_{\text{max}}$ , and  $\pi_{\text{CMC}}$  values decrease, with an increasing volume fraction of methanol in both the absence and presence of the dye. The  $\Delta G_{\text{ads}}^o$  values become less negative and the  $\text{pC}_{20}$  value decreases with an increasing volume fraction of methanol. The  $P$  values decrease with an increasing volume fraction of methanol in both the absence and presence of the dye. In the presence of dye, the value of  $\Delta G_{\text{ads}}^o$  becomes more negative, indicating the spontaneous process of adsorption, and the value of  $\pi_{\text{CMC}}$  increases, indicating a higher efficiency of lowering the surface tension. The increase in positive  $\text{pC}_{20}$  and negative  $\Delta G_m^o$  values suggests that the micellization process is more feasible and spontaneous in the presence of dye. The  $\Gamma_{\text{max}}$  values of SDS decreased and  $A_{\text{min}}$  increased in the presence of dye. The value of the packing parameter,  $P$ , of all aggregates with/without dye is less than 1/3, indicating that aggregates are spherical in shape.

#### Data Availability

The data used in the present study are available from the corresponding authors upon reasonable request.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

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#### Supplementary Materials

Figure S1: tensiometric profiles of SDS without methylene blue (o) and with methylene blue (□) in (a) 0.1, (b) 0.2, and (c) 0.3 volume fraction of methanol in aqueous medium at 298.15 K. Figure S2: plot of variation of  $\Delta G_m^o$  with (a) viscosity ( $\eta_o$ ), (b) Gordon parameter ( $G$ ), and (c) Reichardt's parameter ( $E_T(30)$ ). (Supplementary Materials)

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