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Application of anionic-nonionic mixed micellar system for solubilization of methylene blue dye

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ABSTRACT

Present study highlights the interaction of methylene blue (MB), a cationic dye, with anionic surfactant, sodium dodecyl sulfate (SDS), and its mixed micelles with a nonionic surfactant Triton X-114 (TX-114). The results obtained from UV–visible spectrophotometry were used to obtain the degree of solubilization in terms of binding constant (K_b) and partition coefficient (K_x) of dye in single and mixed micellar systems (MMS). Gibb's free energies of partitioning and binding were also calculated for both systems. Specific conductance was measured to determine the CMC of single and mixed micellar media at five different temperatures, T = (293.15 – 333.15) K. Temperature-dependent thermodynamic parameters like Gibb's free energy of micellization (ΔG^o_{mic}), enthalpy of micellization (ΔH^o_{mic}), and entropy of micellization (ΔS^o_{mic}) were calculated using data of specific conductance measurements. Effect of concentration of TX-114 on K_x and K_b values of the MB in MMS is also investigated. Spectroscopic and conductometric results revealed that the anionic-nonionic mixed micellar system was better and more effective for the removal and solubilization of MB from aqueous system as compared to anionic micelles only. However, it has been observed that after a critical concentration an increase of non-ionic surfactant concentration has a reverse effect on solubilizing power of ionic-nonionic mixed micellar system. This indicates that the dye-surfactant interaction became weaker due to possible decrease in ionic character of mixed micelles when the high fraction of TX-114 was used.

1. Introduction

Surfactants are organic compounds having both hydrophilic and hydrophobic parts in their structure. They have ability to reduce the interfacial tension between liquid/liquid or liquid/gas interface [1]. Based on the charges present on their head groups, surfactants are of four different types namely; cationic, anionic, nonionic, and zwitterionic [2]. During recent years, another emerging class of surfactants named as gemini surfactants [3] has gained the attention of many researchers [3–7] due to their very low CMC and greater solubilization power compared to conventional surfactants [8–10]. Surfactants are amphiphilic molecules having a hydrophilic head and a hydrophobic tail. Hydrophilic head group is charged in ionic surfactants whereas it does not contain any apparent charge in nonionic surfactants. Hydrophilic-lipophilic balance (HLB) is a parameter used to compare the hydrophilicity and lipophilicity of an amphiphilic molecule. HLB specifies the use of a particular surfactant in a specific application. Another important property of surfactants is their ability to form self-assembled aggregates called micelles at a specific concentration called critical micelle concentration, CMC [11]. Micelles can be spherical, rod like, cylindrical, ellipsoid, unilamellar vesical or planar. Particular shape of a micelle depends on many factors like concentration of surfactant, temperature, and polarity of a solvent [12]. It is reported in literature [13–15] that MMS can be used for the removal of dyes from aqueous phase. Mixed micelles show synergistic effects to remove the dye efficiently from aqueous media and have higher degree of solubilization. The solubilization power can be changed by changing the concentration ratio of surfactants in MMS [16,17]. It is worth mentioning that MMS have got lower CMC values, possess better surface properties [18,19] and enhanced dye solubility compared to single micellar media [13].

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Dyes are unsaturated organic compounds showing absorbance in the range of 400 – 800 nm. Dyes are industrially significant as they are widely used in textile, rubber, paper and pulp, tannery, cosmetics, and food industries as coloring agents [20,21] . A Dye consists of two main parts: chromophores and a matrix. Chromophores are responsible for color effects [21]. Chromophores consist of conjugated systems having resonance in their structure. Auxochrome affects the color of chromophore because auxochromes contains electron-withdrawing groups. The auxochromes may be (–CO_2H), (–NH_3), (-SO_3H), and/or (–OH) groups [22].

The color of a dye is due to the presence of certain groups of atoms (chromophoric groups) present in dyes. Each dye has a specific chemical structure and hence a unique color. Chromophoric groups include: alkenes (–C═C-), imines (-C═N-), carbonyl (-C═O-), azo (-N═N-) and/or nitro (–NO_2) [23]. Different structural varieties of dyes including disperse, azo, reactive, basic, diazo, anthraquinone dyes and almost eight thousand chemical products are available in market for their use in different dying processes [24]. After their usage in the industries, these dyes need to be removed from waste water because some dyes are naturally carcinogenic and pose potential risk to the human beings and other living creatures. The removal of dyes from industrial waste requires huge volume of chemicals for wet processing and hence the industrial wastewater containing dye effluents is released without subsequent processing. The chemical industries using dyes approximately produce 9 billion tons of waste per year [25].

Surfactants can be used as an effective and efficient tool for the treatment of industrial wastewater containing dye effluents due to their excellent solubilizing power. Solubilization of effluent dyes from wastewater by surfactants directly relies on their ability to form micelles. In the premicellar region, the dye molecules bind with surfactant mostly through the hydrophilic interactions like electrostatic interaction or hydrogen bonding, whereas, in the post micellar region, the dye solubilizes into the micelles mainly due to hydrophobic interactions. The water insoluble and sparingly soluble compounds present in water are more solubilized by micellar media [20,21]. Surfactants are also used in different dyeing baths to fix and adsorb the dye on to the substrate and also to remove the loosely attached dye molecules [26]. In this regard, understanding the interaction of dyes with surfactants in aqueous media is the very useful. Present study provides a detailed insight of interaction of MB with anionic micelles of SDS and anionic-nonionic mixed micelles of SDS and TX-114 in aqueous solutions.

2. Experimental section

2.1. Materials and method

All the chemicals used in the present study were laboratory-grade reagents. The cationic dye methylene blue (MB: $C_{16}H_{18}ClN_3S{\cdot}3H_2O$; M. Weight 373 g/mol) and sodium dodecyl sulfate (SDS: $NaC_{12}H_{25}SO_4$; M. Weight 288.37 g/mol, purity ≥ 99 %) were obtained from Sigma-Aldrich Co., (St. Louis, MO, USA).

Triton X-114 (TX-114, $C_{18}H_{30}O_3$, M. Weight 294.43 g/mol, 2-(2-[4-(1, 1, 3, 3 tetramethylbutyl) phenoxy] ethoxy) ethanol) of high purity was obtained from RHAWN limited, China. All the chemicals were used without any additional purification. Distilled water was used throughout the study as the aqueous phase for the preparation of different solutions. Structures of chemicals used in the present study are given in Fig. 1.

2.1.1. Preparation of solutions

Aqueous solution of 1×10^{-5} M methylene blue is used as a solvent to prepare a series of single and mixed surfactant solutions. The literature value of the CMC of SDS is 8.2 mM [27]. Aqueous solutions of different concentrations (0.8 mM −16 mM) of SDS were prepared in MB dye. The effect of concentration of non-ionic surfactant as part of mixed micelles was checked at four different concentrations of TX-114 (0.11–0.17 mM with 0.02 mM increment scale). The literature value of CMC of TX-114 is 0.2 mM [28].

2.2. Experimental techniques

2.2.1. UV–visible spectroscopy

UV–visible spectroscopy is a very reliable, commonly available and feasible technique to study the interaction of dyes with surfactants. UV–visible spectra were recorded on a computer interfaced, Analytik Jena (Specord 210 Plus), double beam UV–visible spectrophotometer. Quartz cuvettes were used for measuring the simple and differential absorbance at 298.15 K with an accuracy of ±0.10 K. For simple absorbance measurements, distilled water was placed in the reference cell and surfactant solution prepared in MB dye was placed in the sample cell. For differential absorbance, aqueous dye solution was used as reference and aqueous surfactant solution of different concentrations prepared in MB dye were used as sample [29]. Different spectra of simple and differential absorbance were recorded for single and mixed micellar systems. All spectra were recorded in the wavelength (λ) range of 400 – 800 nm.

2.2.2. Quantification of partitioning and binding parameters

Spectroscopic studies are helpful for the determination of interaction parameters like partition co-efficient (K_c), binding constant (K_b) and Gibb's energies of partitioning (ΔG°_p) and binding (ΔG°_b) of dye with surfactant micelles.

Kawamura equation (eq. (1)) was used to quantify the K_c (in dm^3/mol) for interaction of MB with surfactants [30]. The value of K_c was calculated using equation (1):

$$\frac{1}{\Delta A} = \frac{1}{K_c \Delta A_\infty (C_d + C_s^{mo})} + \frac{1}{\Delta A_\infty} \tag{1}$$

where C_d represents concentration of dye in mol/dm^3 (M), ΔA is differential absorbance and ΔA_∞ is the differential absorbance at infinite surfactant concentration. The parameter, K_c, is the water to micelles partition coefficient of the dye. The value of C_s^{mo} is analytical concentration of surfactant being used and is obtained from equation (2):

$$C_S^{mo} = C_S - CMC_o \tag{2}$$

Here C_s is concentration of surfactant and CMC_o is the CMC of surfactant without dye. Equation (3) is used [31] to calculate the dimensionless partition coefficient K_x as:

$$K_x = K_c n_w \tag{3}$$

where n_w represents the number of moles of water per dm^3 (55.5 mol/dm^3).

The standard free energy change for partitioning of dye (ΔG°_p) between aqueous and micellar phase can be measured using equation (4):

$$\Delta G^o{}_p = -RTlnK_x \tag{4}$$

where R is the general gas constant and T is the absolute temperature.

Benesi-Hildebrand equation (eq. (5)) can be used to calculate the binding constant, K_b, of dye with ionic micelles [32]. The value of K_b was determined from the values of slope and intercept of a linear plot between $\frac{dC_d}{\Delta A}$ and $\frac{1}{C_s^{mo}}$ using equation (5):

$$\frac{dC_d}{\Delta A} = \frac{1}{K_b \Delta\varepsilon (C_s^{mo})} + \frac{1}{\Delta\varepsilon} \tag{5}$$

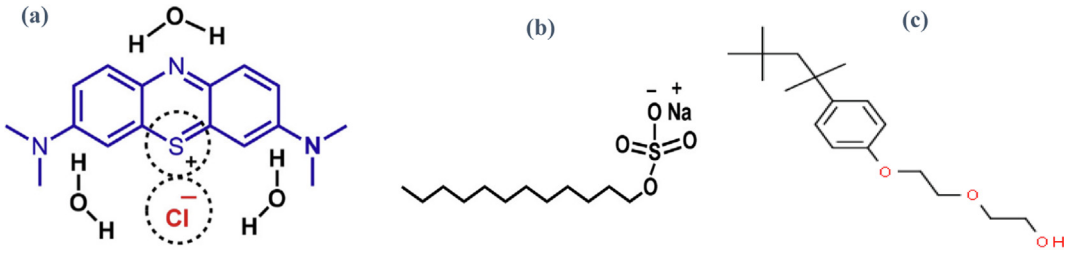

Fig. 1. Molecular structure of (a) MB dye (b) SDS and (c) TX-114.

where C_d is the concentration of dye, d represents the optical path length (1.0 cm) of the sample solution and ΔA is the difference of absorbance between the MB-Surfactant complex and MB. Δε is difference in absorption coefficient of complex and dye (Δε = ε - $ε_o$).

The Gibb's free energy change of the dye binding to surfactant ($ΔG°_b$) can be calculated using K_b [33] according to eq. (6):

$$\Delta G_b^o = -RTlnK_b \tag{6}$$

2.2.3. Specific conductance

Specific conductance (κ) is a sensitive, reliable and simple technique to detect the changes in the medium when ionic additives interact with a surfactant in aqueous solutions. Specific conductance was employed to determine the CMCs of the single and MMS in the presence and absence of MB. Various thermodynamic parameters of micellization were evaluated by measuring specific conductance at five different temperatures (T = 293.15 K – 333.15 K) with an accuracy of ± 0.10 K. Data was recorded using the InoLab Cond 7110 (WTW, Germany) benchtop conductometer connected with a conductivity cell (KLE 325, WTW Germany) consisting of two graphite electrodes. The cell constant of the conductivity cell was 0.84 cm^{-1}. Standard solution of KCl was used to calibrate the conductivity cell.

2.2.4. Calculations of thermodynamic parameters

The CMC values of micellar systems were determined from the specific conductance versus concentration plots. The abrupt change in κ at a specific concentration (CMC) of surfactant is the indication of onset of micellization. From the obtained CMC values various thermodynamic parameters were calculated [34]. The sudden decrease in the κ value near CMC is due to a decrease in the mobility of ions and the presence of fewer free ions in the solution. Equation (7) is used to calculate the degree of dissociation (α) which is the ratio of the slope of post-micellar region (S_2) to the slope of pre-micellar region (S_1) of plot of κ versus concentration of surfactant. Gibbs free energy of micellization ($ΔG°_{mic}$) of surfactant was calculated from equation (8). Equations (9) and (10) were used to calculate enthalpy ($ΔH°_{mic}$) and entropy change ($ΔS°_{mic}$) of micellization of surfactants in dye solution, respectively.

$$\alpha = \frac{S_2(post-micellarregion)}{S_1(pre-micellarregion)} \tag{7}$$

$$\Delta G^o{}_{mic} = (2-\alpha)RTlnX_{cmc} \tag{8}$$

$$\Delta H^o{}_{mic} = -2.303(2-\alpha)RT^2\frac{\partial(logX_{cmc})}{\partial T} \tag{9}$$

In the above expressions, R is the general gas constant (8.314 J mol^{-1} K^{-1}), T is absolute temperature, X_{cmc} is critical micelle concentration in terms of mole fraction. A plot between the $logX_{cmc}$ and T gives a straight line having slope equal to $\frac{\partial(logX_{cmc})}{\partial T}$ which can be substituted in eq. (9) to determine the value of $\Delta H^o{}_{mic}$. The values of $\Delta G^o{}_{mic}$ and $\Delta H^o{}_{mic}$ can then be used to calculate $\Delta S^o{}_{mic}$ using equation (10) as below:

$$\Delta S^o{}_{mic} = \frac{\Delta H^o{}_{mic} - \Delta G^o{}_{mic}}{T} \tag{10}$$

3. Results and discussion

3.1. Solubilization of MB dye in single micellar system

3.1.1. Simple absorbance of MB and SDS

Figure S1 of supporting information represents the spectrum of 1×10^{-5} M MB in aqueous solution. The spectrum manifests a broad peak showing maximum absorbance ($λ_{max}$) at 665 nm wavelength and a shoulder peak at 609 nm. It is reported in the literature that MB may also exist in dimeric form in aqueous solutions. The peak at 609 nm in spectrum of MB can be assigned to dye aggregates [35].

Simple absorbance spectra of 1×10^{-5} M MB in the presence of varying concentrations of SDS (from 0.8 mM to 16 mM) are shown in Fig. 2. In the presence of SDS the $λ_{max}$ of MB-SDS system was observed at 667 nm. When compared with the $λ_{max}$ of 665 nm for pure dye, the MB-SDS system showed only a slight bathochromic shift. This bathochromic shift can be attributed to the presence of electrostatic forces between the cationic MB dye and anionic SDS surfactant [36].

The absorbance at 667 nm of 1×10^{-5} M MB dye as a function of molar concentration of SDS is shown in inset of Fig. 2. As can be seen in Fig. 2, the CMC of SDS in the presence of 1×10^{-5} M MB dye in aqueous solution is 0.010 M.

3.1.2. Differential absorption spectra of single micellar system

The differential absorbance spectra of single surfactant system were used to investigate the interactions between MB and SDS micelles in terms of binding and partitioning. Using the Benesi-Hildebrand equation (eq. (5)), dye-surfactant binding interaction was checked in terms of K_b. In Fig. 3, the differential spectra of post micellar concentrations of SDS are given. In order to check the linearity of data, the plot was drawn between $\frac{dC_d}{\Delta A}$ and $\frac{1}{C_s^{mo}}$. From the Fig. 4, binding constant values were evaluated and ultimately $ΔG°_b$ values were determined.

The partitioning of dye between micellar media and aqueous phase was determined by partition law, using Kawamura model (eq. (1)) in terms of K_c. The graph was plotted between $\frac{1}{\Delta A}$ and $\frac{1}{(Cd+C_s^{mo})}$ (Fig. 5) and intercept and slope values were used to calculate K_c. From the K_c values, K_x was determined using eq. (3) whereas eq. (4) was used to calculate $ΔG°_p$.

The calculated values of K_b and K_x for MB-SDS system are presented in Table 1. The value of K_b determines the strength of binding of dye with micelle and the value of K_x indicates the extent of partitioning of dye between aqueous and micellar phase. Large val-

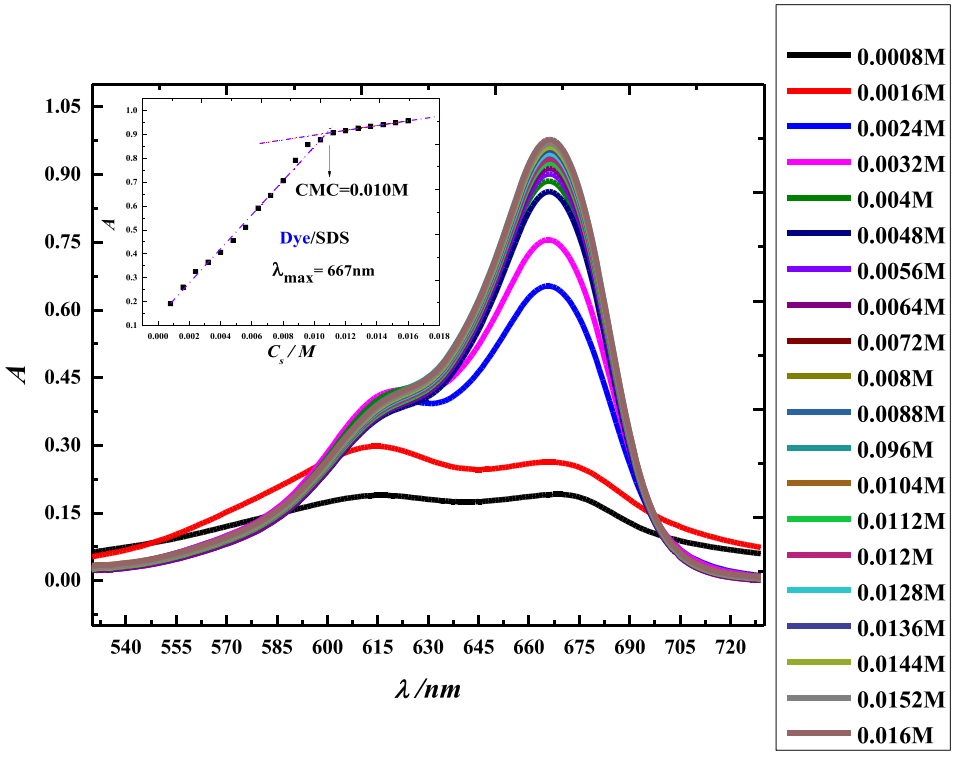

Fig. 2. Simple absorbance spectra of 1×10^{-5} M MB dye at different concentrations of SDS at 298.15 K.

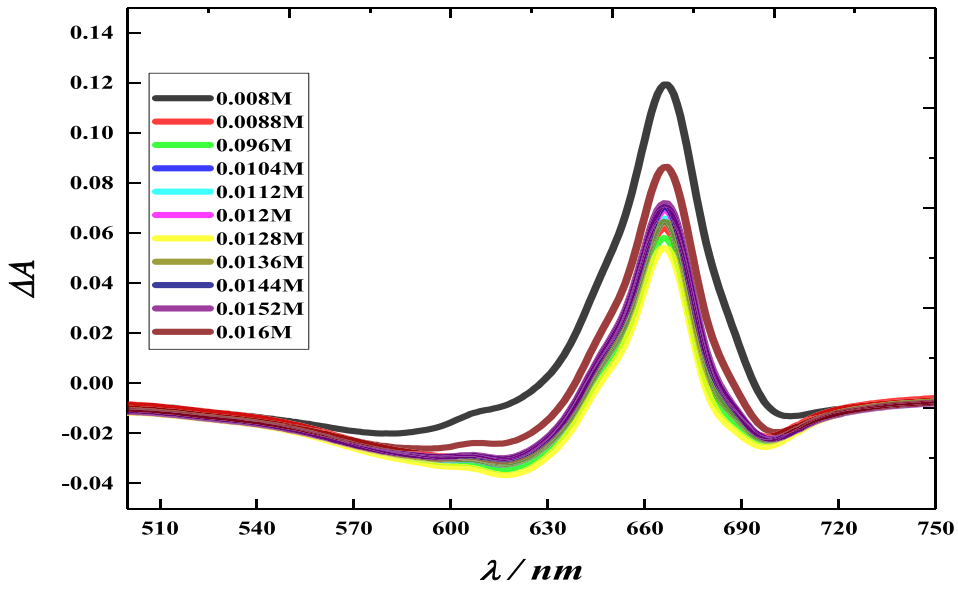

Fig. 3. Differential absorbance spectra of 1×10^{-5} M MB dye at different concentrations of SDS at 298.15 K.

ues of K_b and K_x obtained in present study explain that dye interacts strongly with SDS micelles and hence solubilized effeciently into them. Considering the amphiphilic nature of dye it can be stated that the locus of solubilization of MB in SDS micelles is palisade layer [37]. The negative values of $\Delta G°_b$ and $\Delta G°_p$ denote the spontaneous nature of binding and partitioning of dye in the studied systems.

3.2. Solubilization of MB dye in mixed micellar system (MMS)

The λ_{max} of pure dye in aqueous solution was observed at 665 nm and it was shifted to 667 nm in the presence of SDS. The simple absorbance spectra of MB in the presence of MMS (SDS/TX-114) are shown in Fig. 6. The spectra indicate that the λ_{max} of MB in MMS showed a red shift from 665 nm to 680 nm. This shift in wave-

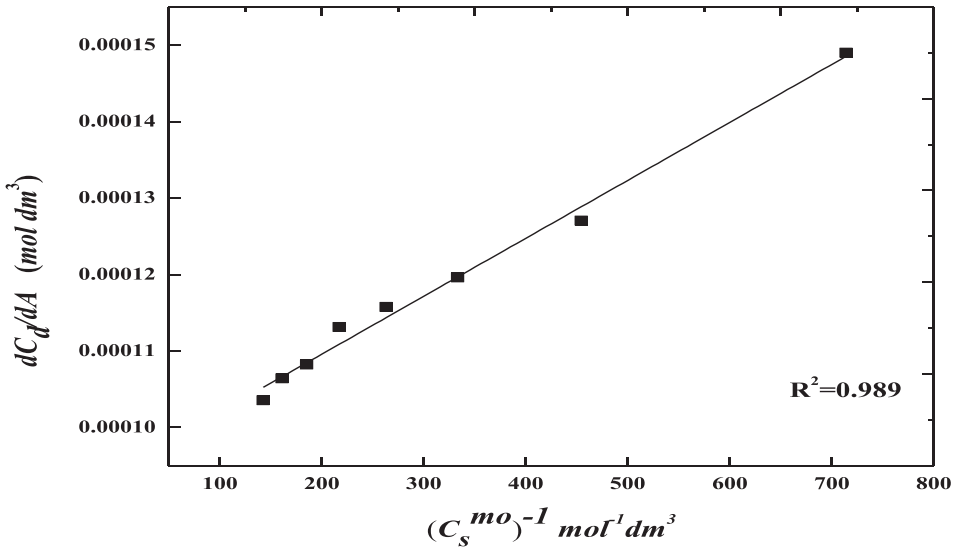

Fig. 4. Plot for calculation of binding constant, K_b, of MB-SDS system.

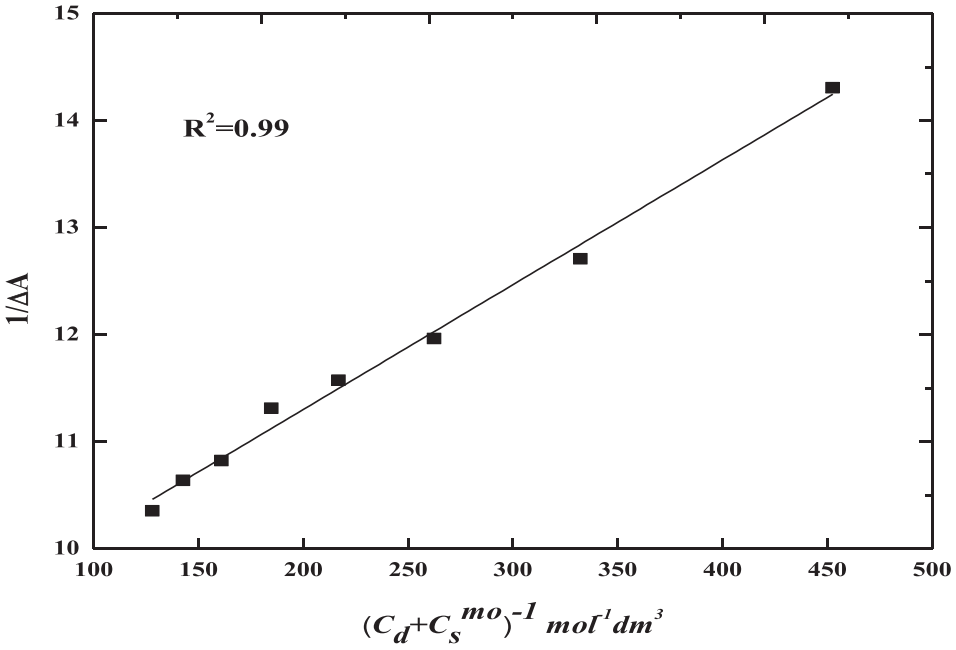

Fig. 5. Plot for calculation of partition coefficient, Kc, for the MB-SDS system.

Table 1
Binding constant (K_b), partition constant (K_c), partition coefficient (K_x), Gibbs energy of binding ($\Delta G°_b$), Gibbs energy of partitioning ($\Delta G°_p$) for MB-SDS and MB-SDS/TX-114 systems.

TX-114 (mM)	K_b (dm^3/mol)	$\Delta G°_b$ (kJ/mol)	K_c (dm^3/mol)	$K_x \times 10^{-3}$	$\Delta G°_p$ (kJ/mol)
0	1240 ± 1	−17.7 ± 0.1	769 ± 2	43 ± 1	−26.4 ± 0.1
0.11	2210 ± 1	−19.1 ± 0.1	2190 ± 2	121 ± 1	−29.0 ± 0.1
0.13	2030 ± 1	−19.8 ± 0.1	2020 ± 2	112 ± 1	−28.8 ± 0.1
0.15	1150 ± 1	−17.5 ± 0.1	1146 ± 2	64 ± 1	−27.4 ± 0.1
0.17	615 ± 1	−15.9 ± 0.1	612 ± 2	34 ± 1	−25.9 ± 0.1

length can be attributed to the changes in the micro-environment of MB. The redshift can also be explained in terms of the solvatochromic effect. According to this effect, when the dye molecules move from highly polar aqueous media to non-polar micellar media, they show either a bathochromic shift (redshift) or a hypsochromic (blue shift) in the λ_{max}. If the former shift is observed, it is known as positive solvatochromic effect and if the latter shift is observed, it is known as negative solvatochromic effect.

During partitioning, the polar solvents stabilize the n and π^* molecular orbitals to a greater extent [36]. The solubilization of

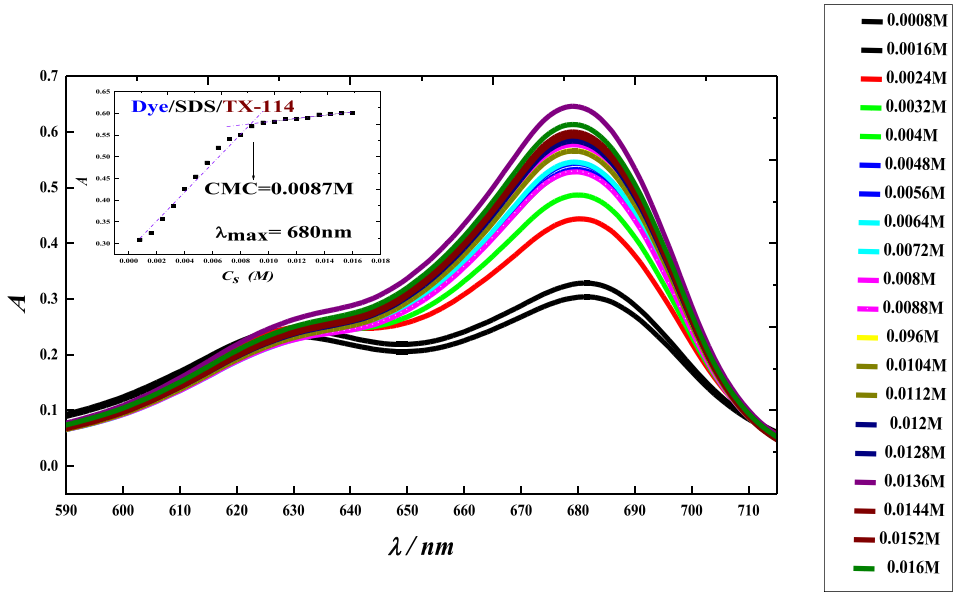

Fig. 6. Simple absorbance spectra of MB at different concentrations of SDS in the presence of 0.17 mM TX-114.

dye molecules from aqueous to micellar phase results in change of polarity of environment of dye molecules which causes rearrangement of energy levels with less energy gaps. The resulting n to π^* transitions would occur at lower wavelengths. This conforms to the observed bathochromic shift in the present study. In the pre-micellar region, the absorbance of dye increases sharply with increasing concentration of SDS up to the CMC as shown in inset of Fig. 6. After CMC (0.0087 M), however, the increase in absorbance is less pronounced.

When non-ionic surfactant, TX-114, was added to the dye solutions containing SDS, a decrease in CMC was observed. This decrease in CMC can be explained by the suppression in the ionic character of SDS as, in presence of TX-114, the repulsion between ionic head groups of SDS lessens.

3.2.1. Differential absorbance of MMS

The binding constant and partition constant values of MMS were calculated from the differential spectroscopy. Effect of concentration of TX-114 on solubilizing power of SDS was investigated at four different concentrations. Differential absorbance spectra of 1×10^{-5} M MB dye at different concentrations (0.11 mM, 0.13 mM, 0.15 mM and 0.17 mM) of TX-114 at 298.15 K are given in Figure S2 of supplementary information. Fig. 7 depicts the plot of differential absorbance at λ_{max} of 1×10^{-5} M MB dye in MMS at different concentrations of SDS.

The plot for calculation of K_b of MB with mixed surfactant systems at four different concentrations of TX-114 (0.11 mM – 0.17 mM) is shown in Fig. S3. The partitioning of MB dye from aqueous to micellar phase of ionic surfactant (SDS) improves in the presence of non-ionic surfactant (TX-114) [37]. Molecules of TX-114 incorporate themselves between the anionic groups of SDS resulting in decreased electrostatic repulsions. Due to this reason, there is an increment in micellar size and hence higher solubilization of dye into the micellar phase which decreases the CMC of MMS [14,38]. The plot for calculation of partition constant (K_c) for mixed surfactant system at four different concentrations of Tx-114 from (0.11 mM – 0.17 mM) is shown in Fig. S4. Spectroscopic parameters which determine the extent of solubilization of MB in MMS in terms of K_c, K_x, K_b, $\Delta G°_b$ and $\Delta G°_p$ are mentioned in Table 1.

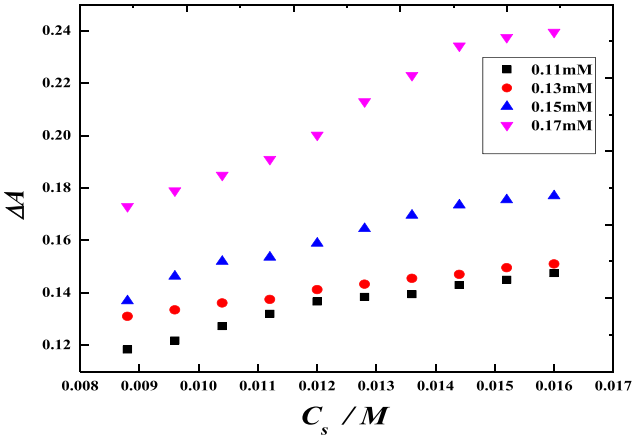

Fig. 7. Plot of differential absorbance of 1×10^{-5} M MB as a function of C_s of SDS at four different concentrations of TX-114.

Noor et al. studied [39] that mixed micellar media of cationic and non-ionic surfactants enhance the solubilization of reactive dyes very efficiently as compared to the single cationic or non-ionic surfactants. Similar results are obtained in the present study. The binding constant (K_b) value increased from 1240 dm^3/mol to 2210 dm^3/mol and 2030 dm^3/mol in the presence of 0.11 mM and 0.13 mM TX-114, respectively, in MB-MMS (Table 1). However, K_b values at 0.15 mM and 0.17 mM TX-114 in MMS are smaller than that of MB-SDS system.

As can be seen in Table 1, the value of K_b of MB with MMS containing 0.17 mM concentration of TX-114 is the smallest compared to the MMS containing 0.11 mM – 0.15 mM TX-114. This indicates that the addition of TX-114 increases the micellar solubilization of MB in MMS up to a specific limit. After that limit further increase in the dose of non-ionic surfactant has a reverse effect on solubilizing power of MMS. It can be inferred from these findings that at higher concentrations of TX-114 the ionic character of MMS decreases and hence the attraction between the micelles and dye also decreases. This leads to the weak interaction of MB dye with MMS [40].

Similar trend, as that of K_b, was observed for the partitioning of MB between aqueous and micellar phase. The value of K_x increased

with addition TX-114 in MB-SDS system. These results indicate that dye is partitioned more favorably in MB-MMS than that of MB-SDS system. The molecules of non-ionic surfactant TX-114 incorporated between the anionic groups of SDS decreased the electrostatic repulsions between them. Due to this reason, there is an increment in micellar size and hence the solubilization of dye into micellar phase is enhanced which decreased the CMC of MMS [14,38].

Above mentioned results (Table 1) elucidate that the ΔG°_{b} values for MB-MMS are more negative than that of MB-SDS system at low concentrations (0.11 mM – 0.13 mM) of TX-114. It indicates that addition of TX-114 at low concentrations (0.11 mM – 0.13 mM) favors the binding of MB with mixed micelles. This conforms to the K_b and K_x results discussed above. The obtained ΔG°_{p} values for MB-SDS and MB-MMS are negative (Table 1). This represents that partitioning of MB between aqueous and micellar phase is spontaneous in nature. Similar to that of K_b, K_x and ΔG°_{b}, the ΔG°_{p} values for MB-MMS are more negative than that of MB-SDS system at low concentration (0.11 mM – 0.15 mM) of TX-114 in MMS. The values of binding and partitioning energies indicate that MB-SDS/TX-114 system is more favorable for solubilization of MB in MMS at 0.11 mM and 0.13 mM concentrations of TX-114.

Detailed analysis of data presented in Table 1 clearly indicates the enhancement in the partitioning of MB dye in mixed micelles of SDS and TX-114 compared to single micellar solutions of SDS. The obtained values of K_c and K_b for MMS at 0.11 mM and 0.13 mM concentrations of TX-114 are significantly high as compared to MB-SDS system. This proves that presence of non-ionic surfactant, TX-114, not only facilitates the transfer of MB dye from bulk water to micelle but also its binding to the micelles. However, it is worth noting that for 0.17 mM TX-114, binding as well as partitioning of MB becomes poorer compared to single micelle systems. This might help to set an upper cut off limit to the amount of TX-114 that can actually be utilized for the enhancement of MB solubilization. Moreover, both solubilization and binding of MB is spontaneous in both MB-SDS and MB-SDS/TX-114 solutions.

3.3. Specific conductance measurements

Specific conductance is very reliable technique to detect the movement of ions in aqueous solutions. Specific conductance, κ, is recorded for different concentrtaions of SDS in the presence of 1×10^{-5} M MB (Fig. 8). It is worth noting that presence of 1×10^{-5} M MB has no appreciable effect onto the CMC of SDS in the studied temperature range [41]. The plot of κ versus various concentrations (C_s) of SDS at five different temperatures is demonstrated in Fig. S5 of supporting information.

The CMC of MB-SDS aqueous system increases with increasing temperature (Fig. 8 & Table 2). This corresponds to the higher thermal motions of surfactant monomers at higher temperatures.

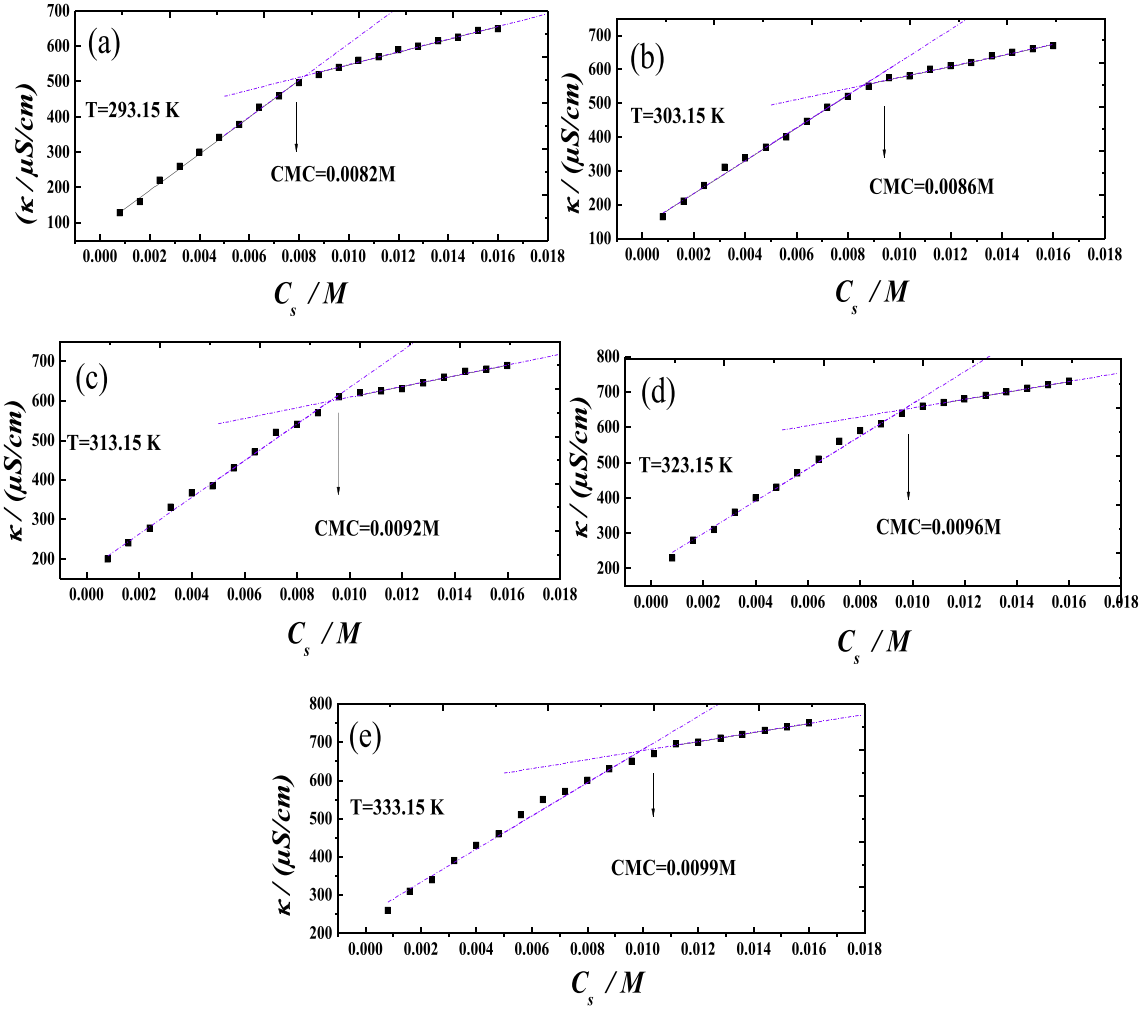

Fig. 8. The plot of specific conductance (κ) as a function of various concentrations of SDS (Cs) in presence of MB (1×10^{-5} M) at different temperatures: (a) 293.15 K, (b) 303.15 K, (c) 313.15 K, (d) 323.15 K, (e) 333.15 K.

Table 2
Critical micelle concentration, CMC, Gibb's energy of micellization, ΔG^{o}_{mic}, enthalpy of micellization, ΔH^{o}_{mic}, entropy of micellization, ΔS^{o}_{mic}, and degree of dissociation, α, for SDS in presence of 1×10^{-5} M MB.

Temperature (K)	CMC (M)	ΔG^{o}_{mic} (kJ/mol)	ΔH^{o}_{mic} (kJ/mol)	ΔS^{o}_{mic} (kJ/K mol)	α
293.15	0.0082	−35.52	−5.97	0.09973	0.34671
303.15	0.0086	−36.74	−6.43	0.10041	0.33735
313.15	0.0092	−38.71	−7.05	0.10082	0.29096
323.15	0.0096	−40.17	−7.59	0.10088	0.27286
333.15	0.0099	−41.28	−8.06	0.10154	0.27254

Standard uncertainties in *T*, *CMC*, ΔG^{o}_{mic}, ΔH^{o}_{mic}, ΔS^{o}_{mic} and α are ± 0.10 K, ±0.0001 M, ±0.03 kJ / mol, ±0.01 kJ / mol, $\pm 2 \times 10^{-5}$ kJ / K . mol and $\pm 5 \times 10^{-5}$ respectively.

The results in Table 2 indicate that with increase in temperature the values of ΔG^{o}_{mic} become more and more negative. This suggests that by increasing the temperature, micellization occurs more easily and effectively. The enthalpy of micellization (ΔH^{o}_{mic}) is the sum of all enthalpies such as enthalpy of counter ion binding to surfactant micelles, enthalpy of hydration of hydrophobic groups and enthalpy of electrostatic and hydrphobic interactions. The negative value of enthalpy of micellization is due to the electrostatic interactions of dye with micellar media and hydration of hydrophilic head groups of the surfactants. A steady rise in the negative values of ΔH^{o}_{mic} is observed from −5.97 kJ/mol (at 293.15 K) to −8.06 kJ/mol (at 333.15 K). Whereas, the ΔS^{o}_{mic} is found to be slightly increasing upon temperature rise i.e. from 0.09973 kJ/K. mol (at 293.15 K) to 0.10154 kJ/K. mol (at 333.15 K). The entropy value is less at 293.15 K, beause more hydrogen bonds are present around the hydrphobic groups which may hinder the vibrations of hydrophobic

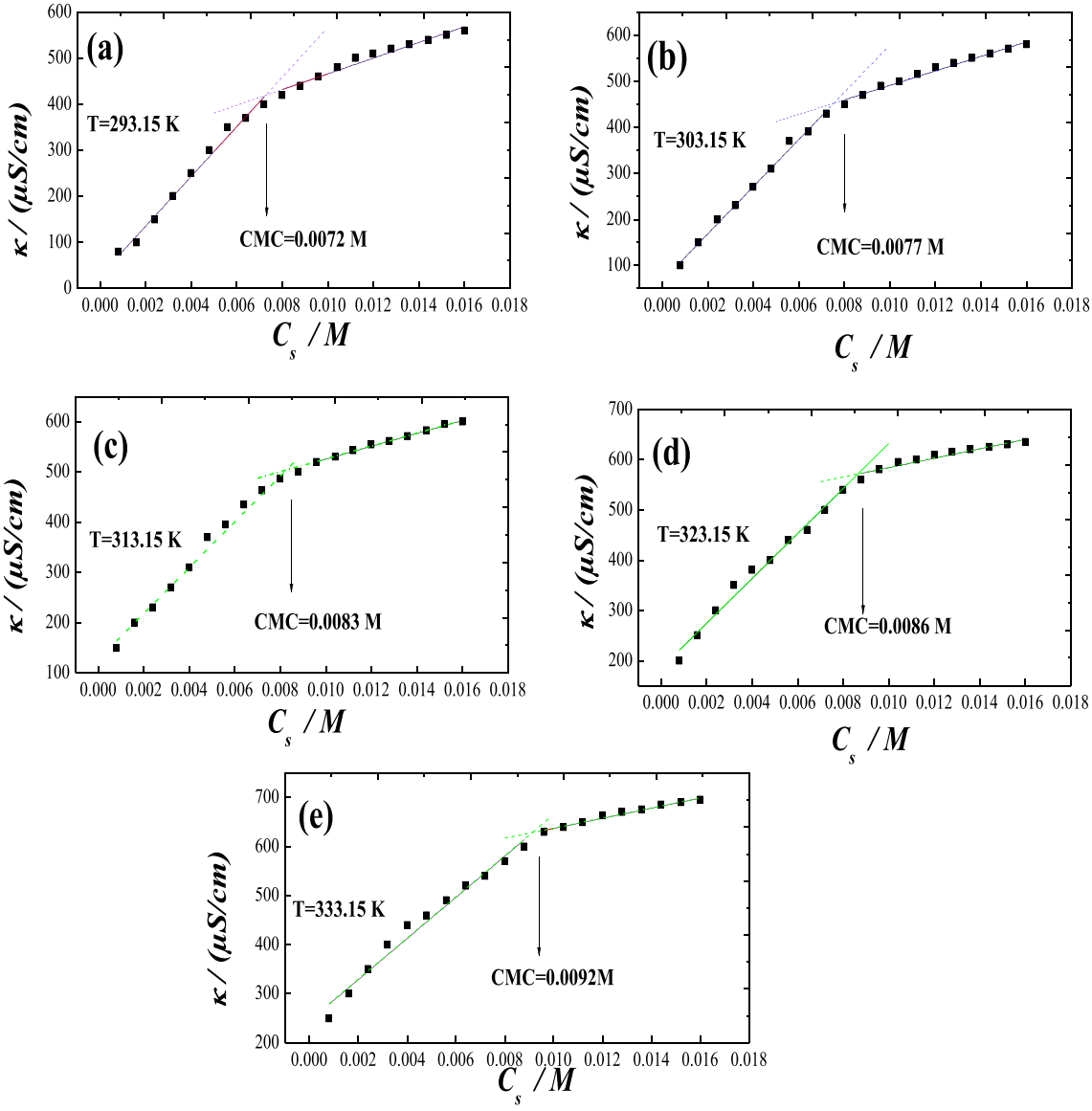

Fig. 9. The plot of specific conductance (κ) as a function of various concentrations of SDS (C_s) in presence of MB (1×10^{-5} M) and TX-114 (0.17 mM) at different temperatures: (a) 293.15 K, (b) 303.15 K, (c) 313.15 K, (d) 323.15 K, (e) 333.15 K.

groups. At higher temperatures, however, increase in entropy is due to the change in the micro-enviornment of dye from the aqueous phase to micellar phase.

3.4. Specific conductance of mixed micellar system

Fig. 9 and S6 of supporting information demonstrate the plot of κ versus various concentrations of SDS at five different temperatures at a fixed concentration (0.17 mM) of TX-114 in the presence of 1×10^{-5} M MB. The determined CMC values of MMS from the κ data at different temperatures have been presented in Table 3. The results reported in Table 3 revealed that the CMCs of the MMS at all studied temperatures are less than the single micellar system (Table 2). In MMS at 293.15 K, the CMC is 0.0072 M while in single micellar system its value at the same temperature is 0.0082 M. Moreover, at 303.15 K, 313.15 K, 323.15 K and 333.15 K temperatures, CMCs are 0.0086 M, 0.0092 M, 0.0096 M and 0.0099 M for single micellar system and in MMS the CMC values at corresponding temperatures are 0.0077 M, 0.0083 M, 0.0086 M and 0.0092 M respectively. The obtained CMC values were used to calculate the different thermodynamic parameters of micellization i.e. ΔG^{o}_{mic}, ΔH^{o}_{mic} and ΔS^{o}_{mic} of MMS in the presence of 1×10^{-5} M MB (Table 3). The comparison of ΔG^{o}_{mic} values of single micelle system (Table 2) with those of MMS (Table 3) at different temperatures indicates that an increase in the temperature increases the ΔG^{o}_{mic} of both systems. However, the ΔG^{o}_{mic} values for MMS are higher than those of single micelle system. Furthermore negative values of ΔG^{o}_{mic} for both systems specify that the micellization of SDS is spontaneous in the presence of MB and MB/TX-114.

The obtained values of ΔH°_{mic} are also negative for MMS (Table 3) similar to those obtained for single micelle system (Table 2). ΔH^{o}_{mic} is positive when the structure of water molecules around hydrophobic groups of surfactant is destructed rather than hydrating the hydrophilic groups of surfactants. The negative values of ΔH^{o}_{mic} indicate that the water molecules show overall structuring around the hydrophilic groups of surfactants by hydrating them. An increase in value of ΔH^{o}_{mic} has been observed with increase in temperature for both systems. A comparison of ΔH^{o}_{mic} of both systems suggests that ΔH^{o}_{mic} of MMS is more exothermic as compared to single micelle system at all temperatures. This indicates that addition of TX-114 to SDS solution in the presence of 1×10^{-5} M MB enhances the hydration of hydrophilic groups of surfactants [42].

The entropy of system could be decreased when water molecules show strong hydrogen bonding due to repulsion of hydropobic groups. This type of interaction lead to restrict the hydrophobic tail to freely vibrate. Thus, the system experiences decrease in entropy of system. From the results of single micelle system (Table 2), it can be seen that the value of ΔS^{o}_{mic} is increased from 0.09973 (kJ / K. mol) to 0.10154 (kJ / K . mol) with an increase in temperature from 293.15 K to 333.15 K respectively. Whereas, the obtained values of ΔS^{o}_{mic} in case of MMS increase from 0.10169 (kJ/K.mol) to 0.99071(kJ / K. mol) with incraese in temparature from 293.15 K to 333.15 K respectively. The higher values of ΔS^{o}_{mic} of MMS as compared to single micelle system at all temperatures can be explained on the basis of strong dehydration of hydrophilic head groups of TX-114 with increase in temperature. The results presented in Tables 2 and 3 specify that the micellization in single and mixed micellar systems is entropically favorable. The entropy of system is increased due to aggregation of surfactant molecules at or above the CMC and movement of dye molecules from the aqueous phase into the micellar phase leaving behind free water molecules. Therefore, this phenomenon lead to an increase in the entropy of system because of desturcturing of water molecules and allowing the vibrational movements of hydrophobic tail [43–45]. From the obtained values of ΔH^{o}_{mic} and ΔS^{o}_{mic} (Tables 2 & 3), it can be concluded that the micellization process for both systems is enthalpy as well as entropy driven.

4. Conclusion

The interaction of MB dye with SDS and MMS (SDS/TX-114) was investigated using UV–visible spectroscopy and conductometric measurements. Partition coefficient, K_c, and binding constant, K_b, were obtained using differential absorbance data of the respective systems. Obtained values of K_c for MMS (at 0.11 mM, 0.13 mM & 0.15 mM TX-114) are higher than that of MB-SDS system. This indicates that compared to MB-SDS system, the encapsulation / solubilization of MB dye significantly improved in presence of non-ionic surfactant TX-114. However, for MMS containing 0.17 mM TX-114 the obtained value of K_c is lower compared to MB-SDS system. Similarly, out of four studied concentrations of TX-114, dye bound better with the micelles of MMS containing 0.11 mM & 0.13 mM TX-114 with corresponding K_b values of 2210 dm^3 mol^{-1} and 2030 dm^3 mol^{-1} respectively. Except for 0.17 mM TX-114, the slightly higher values of ΔG_b and ΔG_p for MMS containing MB dye suggest that MB-SDS/TX-114 systems are thermodynamically more stable as compared to MB-SDS systems. Thermodynamics of micellization of MB-SDS and MB-SDS/TX-114 was investigated using conductometric studies at five different temperatures. From the current thermodynamic study, it can be inferred that micellization is more favorable in MB-SDS/TX-114 as manifested by more negative values of ΔG^{o}_{mic}. Moreover, the negative values for ΔS^{o}_{mic} and ΔH^{o}_{mic} (for both MMS & single micellar media) show that the micellization process is both enthalpy as well as entropy driven.

Data availability

No data was used for the research described in the article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Table 3
Critical micelle concentration, CMC, Gibb's Free energy of micellization, ΔG^{o}_{mic}, enthalpy of micellization, ΔH^{o}_{mic}, entropy of micellization, ΔS^{o}_{mic}, and degree of dissociation, α, for SDS/TX-114 system in presence of 1×10^{-5} M MB.

Temperature (K)	CMC (M)	ΔG^{o}_{mic} (kJ/mol)	ΔH^{o}_{mic} (kJ/mol)	ΔS^{o}_{mic} (kJ/K mol)	α
293.15	0.0072	−36.72	−6.92	0.10169	0.31599
303.15	0.0077	−37.88	−7.44	0.10047	0.30710
313.15	0.0083	−39.41	−8.06	0.10014	0.28057
323.15	0.0086	−42.16	−8.94	0.10280	0.21017
333.15	0.00992	−42.31	−9.32	0.99071	0.24444

Standard uncertainties in *T*, *CMC*, ΔG^{o}_{mic}, ΔH^{o}_{mic}, ΔS^{o}_{mic} and α are ± 0.10 K, ±0.0001 M, ±0.03 kJ/mol, ±0.01 kJ / mol, $\pm 2 \times 10^{-5}$ kJ / K . mol and $\pm 5 \times 10^{-5}$ respectively.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2022.120958.

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