Research Article

Interfacial and Micellization Behavior of Cetyltrimethylammonium Bromide (CTAB) in Water and Methanol-Water Mixture at 298.15 to 323.15 K

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The micellization behavior of cetyltrimethylammonium bromide (CTAB) in water, 0.1, 0.2, 0.3, and 0.4 volume fractions of methanol at 298.15, 308.15, 318.15, and 323.15 K were investigated by surface tension measurements. The effect of methanol on values of critical micelle concentration (cmc), free energies of micellization (ΔG_m^0), and surface properties viz. maximum surface excess concentration ($\Gamma_{\max}$), area occupied by per surfactant molecule ($A_{\min}$), surface pressure (π_{cmc}), solution surface tension (γ_{cmc}), solvent surface tension (γ_o), free energies of adsorption (ΔG_{ads}^0), the efficiency of adsorption (pC_{20}), effective Gibbs free energy (ΔG_{eff}^0), and free energy of surface at equilibrium ($G_{\min}$) were investigated using surface tension values. Other parameters such as the packing parameter (P), aggregation number (N), concentration of surfactant in the bulk phase (C_{20}), relation between $A_{\min}$ and π_{cmc} , and correlation of slopes ($dc/d \log C$), γ_o/c_{cmc} , $\Gamma/\Gamma_{\max}$, cmc/C_{20} , $\Delta G_{\text{ads}}^0/\Delta G_m^0$, and cmc/pC_{20} with the volume fraction of methanol are calculated and discussed in the light of the experiment done.

1. Introduction

Surfactants are a group of organic compounds with a hydrophilic head and a hydrophobic tail (hence known as amphiphiles) due to which they reduce surface tension and are also known as surface-active agents. They are used in almost all areas of applications because of their unique properties. It is well-known that the head part shows the hydrophobic nature and tail shows hydrophilic nature. As a result, the molecules are oriented on the surface of the water, tail aligning towards the air. This behavior is very common to all classes of surfactants. With the increase in the concentration of surfactant, amphiphiles start aggregating in the bulk to form aggregates. The concentration at which this occurs is known as critical micelle concentration (cmc) [1]. The stability of micelle in solution is due to soft interactions between amphiphile molecules. The main soft interactions acting in the amphiphilic self-assembly are hydrogen bonding, hydrophobic effects, electrostatic interaction, and

van der Waals forces. Moreover, such interactions are so flexible that a minor disturbance in the system causes significant changes in the physicochemical and surface properties of the surfactant solution [2]. Some factors that directly affect the physicochemical properties and surface properties of the micellar system are additives, temperature, and solvent composition [3–17].

In this study, we explore the effects of solvent composition and temperature on the surface properties of the surfactants. By adding suitable organic cosolvents such as alcohol, there is a measurable change in the hydrophobicity of the medium, which eventually reforms the surface and physicochemical properties of the surfactants [18–22]. By increasing the temperature of the surfactant system, an increase in the cmc can be noticed [20].

Also, we have seen that the surface tension of the surfactant at first decreases with increasing concentration of surfactant and then followed by a sigmoidal curve between surface tension (γ) and $\log$ (surfactant). There is a formation

of the visible break on the sigmoidal curve after which the surface tension remains approximately constant. This concentration is called cmc [23]. A comprehensive investigation of the effect of methanol on such variations at different temperatures has not found in the literature [24, 25].

Kumar et al. investigated the thermodynamic parameters of SDS and CTAB by measuring the conductivity. They reveal that alcohol plays a vital role in these properties. They concluded that the observed changes in the properties of SDS and CTAB are mainly due to different structural consequences of interactions between molecules of surfactant in mixed solvent media [26]. Bielawska et al. studied the influence of methanol, ethanol, and 1-propanol on CTAB monomeric and aggregated forms. However, detailed investigations of the tensiometric approach are lacking [27]. Zdziennicka and Janczuk measured the surface tension of CTAB in methanol and ethanol. The concentration of CTAB was in the premicellar range (1×10^{-5} M to 1×10^{-3} M). They compared the isotherm of surface tension with those obtained from Szyszkowski and Connors equations. They found that alcohol decreased cationic surfactant adsorption at the water-air interface at low concentration. However, at a concentration close to cmc, the cationic surfactant decreases the adsorption of alcohol considerably [28].

Apart from a conventional surfactant, alcohol as a cosolvent shows substantial variations in micellization in a mixed surfactant system. Isopropanol shows the synergistic effect on mixed micellization of a binary mixture of aminosulfonate amphoteric surfactant with octadecyltrimethyl ammonium bromide in an aqueous medium. The effect is understood by interaction behavior between surfactant molecules in terms of hydrophobic effect [29].

According to the investigation done by Li et al. [22], the presence of short-chain alcohols alters the hydrophobic effect and the electrostatic interaction among amphiphiles and cause the variation in interfacial or micellization behavior. In this study, it was also reported that methanol can fully assist as cosolvent and indicates decent hydrophobicity, which encourages the solubility of surfactant in the aqueous medium. This drew out attention to investigate surface properties of CTAB in the presence of methanol.

In our previous article [30], thermodynamic investigations of DTAB and CTAB have been already published. This article describes the tensiometric approach to CTAB in mixed solvent media. The mixture of water and the organic solvent was termed the mixed solvent media. By changing the solvent composition, the relative permittivity of the media can be varied.

We aim to investigate the aggregation behavior of CTAB in water and the methanol-water mixture containing 0.1, 0.2, 0.3, and 0.4 volume fraction of methanol at 298.15 to 323.15 K in detail.

2. Experimental

2.1. Materials and Methods. Methanol (99.0% pure) was purchased from Merck, India. The methanol had a density of 0.7872 g/cm^3 and a coefficient of viscosity of $0.5440 \text{ mPa}\cdot\text{s}$ at

298.15 K; these values are also seen in the literature [31]. The cationic surfactant CTAB was purchased from Aldrich Chemical Company, Inc., USA. CTAB was highly pure ($>99.0\%$) and used after drying for 1 h. The cmc of CTAB was measured at 298.15 K. The observed cmc of CTAB by conductivity is 0.9 mM , which was matched with the literature [32]. The methanol-water mixtures were prepared up to 0.4 volume fraction of methanol at 298.15 K by maintaining a constant temperature in a thermostat [18] by using triply distilled water. The concentration range of the CTAB solution was $1 \times 10^{-2} \text{ M}$ to $5 \times 10^{-4} \text{ M}$.

The specific conductivity measurement of triply distilled water was measured by a digital conductivity meter with a cell constant of 1.002 cm^{-1} with an uncertainty of 0.01% . KCl solution (0.1 M and 0.01 M) was used for calibration of conductivity cell at 298.15 K [33]. Our purpose of using conductivity meter was to check the conductivity of triply distilled water which was $<0.6 \mu\text{S/cm}$ at 298.15 K. The uncertainty of the measurements was within $\pm 3.0\%$.

In the surface tension method, a concentrated solution of CTAB was prepared in water and mixed solvents of the methanol-water mixture at 298.15 K. The solutions of CTAB were diluted by the internal dilution method with the help of a microsyringe to vary the concentration of CTAB. Each concentration of the CTAB solution was placed in a wide mouth dish with the platinum ring [31]. After each addition, the surface tension of the solution was measured (after thorough mixing and temperature equilibration) using a calibrated Kruss K20S force tensiometer, using the technique of ring detachment [34].

The measurements were triplicated. Measurements were made at 298.15 to 323.15 K in a thermostated water-bath maintained within $\pm 0.01 \text{ K}$. The uncertainty during the experiments was within $\pm 1 \times 10^{-3} \text{ Nm}^{-1}$. To maintain the temperature equilibrium, the tensiometer was connected to a water-flow cryostat.

3. Results and Discussion

3.1. Surface Tension Measurements and Surface Properties. The surface tension of the CTAB solutions in water, 0.10, 0.20, 0.30, and 0.40 volume fractions of methanol-water were plotted against the concentration to get the cmc values at 298.15, 308.15, 318.15, and 323.15 K temperatures. The representative Figure 1 shows the variation in the surface tension of CTAB in water, 0.1, 0.2, 0.3, and 0.4 volume fractions of methanol at 308.15 K. The surface tension of CTAB at first decreases with increasing concentration of CTAB, and a sigmoidal curve observed between the surface tension (γ) and $\log [\text{CTAB}]$ by the distinct break is known as the cmc.

In other words, we can discuss the detailed mechanism of the variation in the surface tension of CTAB with its concentration in the following ways: CTAB adsorbs to the surface only at low concentrations, and then, there is a rapid decrease in the surface tension. When the concentration of CTAB is increased further, the molecules start moving towards bulk instead of getting adsorbed at the surface [35].

FIGURE 1: Plot of surface tension versus concentration of CTAB solution at 308.15 K.

From the plot of surface tension with the concentration of CTAB solution, the following surface properties were calculated [20]. The maximum surface excess concentration at the air/methanol-water interface $\Gamma_{\max}$ was calculated by applying Gibbs isotherm:

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

where γ denotes the surface tension, R is the gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), T is the absolute temperature, C is the surfactant concentration, and $(d\gamma/d \log C)$ is the slope of the γ versus $\log C$ plot taken at cmc. The constant n takes the values 2 for the conventional surfactant where the surfactant ion and the centerline are univalent.

The area occupied per surfactant molecule $A_{\min}$ at the air/methanol-water interface was obtained by

$$A_{\min} = \frac{1}{N_A \Gamma_{\max}}, \quad (2)$$

where N_A is Avogadro's number.

The value of the surface pressure at the cmc (π_{cmc}) is obtained as

$$\pi_{\text{cmc}} = \gamma_o - \gamma_{\text{cmc}}, \quad (3)$$

where γ_o and γ_{cmc} are the values of surface tension of water and the surfactant solution at the cmc, respectively.

The standard Gibbs free energy of micellization, ΔG_m° , is calculated from the following relation:

$$\Delta G_m^\circ = (2 - \alpha)RT \ln X_{\text{cmc}}, \quad (4)$$

where X_{cmc} is the mole fraction of cmc and α is the degree of dissociation which is calculated from the ratio of premicellar and postmicellar slopes of the plot of conductivity and concentration.

Since temperature variation is done here, we can try to evaluate free energy by the Van't Hoff method, which is given by the following equation:

$$\left[\frac{\partial \{\Delta G_m^\circ / T\}}{\partial (1/T)} \right]_P = \Delta H_m^\circ. \quad (5)$$

Equation (5) is fulfilled when the entropy is constant in the studied range of temperature.

The standard free energy interfacial adsorption at the air/saturated monolayer interface can be evaluated from the following relation:

$$\Delta G_{\text{ads}}^\circ = G_m^\circ - \frac{\pi_{\text{cmc}}}{\Gamma_{\max}}. \quad (6)$$

The surface area of amphiphiles in mixed micelles and micellar growth (spherical-nonspherical) can be used to find out the packing parameters P :

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

where V_o is the volume of exclusion per monomer in the aggregate, as in Tanford's formula.

$V_o = [27.4 + 26.9(n_c - 1)]2\text{\AA}^3$, $l_c = [1.54 + 1.26(n_c - 1)]\text{\AA}$ is the maximum chain length, and n_c is the number of carbon atoms in the hydrocarbon chain. $A_{\min}$ refers to the property associated with the surfactant monolayer at the air/water interface. P determines the geometry of micelles and denotes the minimum sized aggregates in solution, which reduces the Gibbs free energy of micellization.

The maximum surface excess concentration at the air/methanol-water interface $\Gamma_{\max}$, area occupied per surfactant molecule ($A_{\min}$) at the air/methanol-water interface, surface pressure at the cmc (π_{cmc}), standard free energy interfacial adsorption ($\Delta G_{\text{ads}}^\circ$), and packing parameters (P) of CTAB solutions in water, 0.10, 0.20, 0.30, and 0.40 volume fractions of methanol-water at 298.15, 308.15, 318.15, and 323.15 K, were calculated, and the values are displayed in Table 1.

Chakraborty et al. [36] calculated the cmc (mM) of CTAB at 25°C by (0.959) conductivity and by (0.883) tensiometry with $\gamma_{\text{cmc}} = 33.1$. Our data of CTAB at 25°C in water regarding cmc is 0.97 mM from tensiometry with $\gamma_{\text{cmc}} = 33.4$, which almost matched with literature [36].

Similarly, Shah et al. [21, 37] calculated the cmc of CTAB at 298.15 K in water (0.97 mM) by tensiometry, $\Delta G_m^\circ = -49.90 \text{ kJ} \cdot \text{mol}^{-1}$, $\Gamma_{\max} \times 10^6 = 3.01 \text{ (mol} \cdot \text{m}^{-2})$, $A_{\min} = -54.98 \text{ \AA}^2 \text{ molecule}^{-1}$, $\pi_{\text{cmc}} = 33.59$, packing parameter (P) = 0.38, and $(\Delta G_{\text{ads}}^\circ) = -61.02 \text{ kJ} \cdot \text{mol}^{-1}$. These data almost matched with our system (Table 1). When the temperature was increased, the cmc increased from 0.97 mM at 298.15 K to 1.14 mM at 308.15 K (Table 1). The increase in cmc with temperature is due to the smaller probability of hydrogen bond formation [38].

The relative permittivity of the medium decreases when methanol is added to water because methanol has a lower relative permittivity than pure water and a lower relative

TABLE 1: Critical micelle concentration (cmc), maximum surface excess concentration ($\Gamma_{\max}$), area occupied by surfactant molecule ($A_{\min}$), surface pressure at the cmc (π_{cmc}), packing parameters (P), and free energy of adsorption ($\Delta G_{\text{ads}}^{\circ}$).

T (K)	Volume fractions of methanol	cmc (mM)	$\Gamma_{\max} 10^6$ (mol·m ⁻²)	$A_{\min}$ (Å ² molecule ⁻¹)	π_{cmc} (m·Nm ⁻¹)	P	$\Delta G_{\text{ads}}^{\circ}$ (kJ·mol ⁻¹)
298.15	0.0	0.97	3.01	54.98	33.59	0.38	-63.40
	0.1	1.22	2.10	78.73	18.09	0.26	-57.01
	0.2	1.78	1.72	96.33	10.23	0.21	-51.46
	0.3	3.55	0.94	175.71	8.07	0.11	-47.32
	0.4	6.43	0.77	213.26	4.32	0.09	-39.02
308.15	0.0	1.14	2.83	58.49	32.91	0.36	-63.9
	0.1	1.42	1.82	91.14	18.07	0.23	-57.55
	0.2	1.88	1.55	107.07	11.50	0.19	-52.16
	0.3	4.45	0.76	217.96	8.75	0.09	-48.63
	0.4	7.34	0.62	267.33	5.06	0.07	-40.42
318.15	0.0	1.22	2.22	74.65	33.52	0.28	-64.22
	0.1	1.71	1.72	96.33	20.04	0.21	-57.93
	0.2	2.56	1.41	117.62	12.82	0.17	-52.54
	0.3	5.66	0.68	243.45	8.45	0.08	-47.07
	0.4	7.81	0.52	315.62	6.03	0.06	-41.60
323.15	0.0	1.32	2.17	76.39	33.79	0.27	-64.37
	0.1	1.91	1.60	103.78	21.87	0.20	-58.66
	0.2	2.73	1.22	136.08	14.05	0.15	-53.02
	0.3	5.89	0.57	288.61	9.29	0.07	-49.31
	0.4	7.32	0.43	382.66	6.89	0.05	-42.30

permittivity decreases the hydrophobic interaction and increases the cmc [20].

The data show that $\Gamma_{\max}$, as well as π_{cmc} values, decreases with an increase in the volume fraction of methanol at a particular temperature indicating less population of surfactant molecules at the interface with the addition of methanol. Our decrease in data of $\Gamma_{\max}$ with the addition of methanol was matched with the literature [25]. With the increase in temperature, $\Gamma_{\max}$ values decrease (Table 1). The reason may be due to the enhanced molecular thermal agitation at higher temperatures [39]. Such trends were also observed in the previous study [20].

With the increasing temperature, π_{cmc} is increased. The reason may be that π_{cmc} is a measure of the efficiency of the surfactant to lower γ of water [40].

However, $A_{\min}$ values increase with the addition of methanol that denotes the surfactant molecules occupy more surface areas at the air/methanol-water interface. Such a trend was also observed by Mandal et al. in 2019 [25].

With the increase in temperature, $A_{\min}$ increases (Table 1). The reason may be due to the thermal molecular motion at high temperatures [41].

Negative values of $\Delta G_{\text{ads}}^{\circ}$ indicate that the adsorption of surfactant molecules on the surface is spontaneous, and this phenomenon is more spontaneous than micellization due to a larger negative value than $\Delta G_{\text{m}}^{\circ}$. The values of $\Delta G_{\text{ads}}^{\circ}$ became less negative with the increase in the volume fraction of methanol at a particular temperature that shows less spontaneity of adsorption of surfactant molecules on the surface.

On increasing the temperature, $\Delta G_{\text{ads}}^{\circ}$ values become more negative, which indicates the higher spontaneity of adsorption of CTAB molecules on the surface. Such trends were also observed in the literature [20].

Equation (5) is used to describe the temperature dependence of $\Delta G_{\text{m}}^{\circ}$. The plot of $\Delta G_{\text{m}}^{\circ}/T$ with $1/T$ shows the linear variation in water, 0.10, 0.20, 0.30, and 0.40 volume fractions of methanol-water (Figure 2). Here, $\Delta G_{\text{m}}^{\circ}$ has been taken from the earlier calculations [37]. Negative value $\Delta G_{\text{m}}^{\circ}$ indicates that micellization is spontaneous. This spontaneity decreases with an increase in the volume fraction of methanol; subsequently, micellization is less favorable. The molecular interactions between the amphiphiles needed to micelle are agitated by the presence of methanol, which becomes more pronounced with the addition of the volume fraction of methanol.

3.2. Variation in the Slope ($d\gamma/d\log C$) of Surface Tension Curve with the Volume Fraction of Methanol. The slope ($d\gamma/d\log C$) of the surface tension curve (Figure 3), where C is the concentration of the CTAB solution in water and the methanol-water mixture at 298.15 to 323.15 K, gives various information about the surface properties of the surfactant solution [23]. It is seen that the slopes increase with the increase in methanol and also increase with temperature. As it is mentioned in equation (1) that $\Gamma_{\max}$ is calculated from the slope $d\gamma/d\log C$, the more negative the value of the slope, the larger the values of surface properties. Figure 3 shows that, with the increase in methanol content, values of slope are becoming less negative. Additionally, this slope indicates how pronounced the cmc can be located in the plot of $\log C$ vs γ . In the case of the aqueous solution, the value of the slope is maximum, indicating that it is very easy to locate the cmc, whereas in the case of 0.4 volume fraction of methanol-water, the slope is minimum, indicating that it is difficult to locate the cmc. This makes the limitation of our work up to 0.4 volume fraction of methanol only [37]. As methanol

FIGURE 2: Plot of $\Delta G_m^0/T$ with $1/T$ of CTAB solution in pure water and different volume fractions of methanol-water.

FIGURE 3: Variation in slope $dy/(d \log C)$ with volume fractions of methanol for CTAB solutions.

increases, the formation of the micelle is very difficult to predict due to the solubilization of micelles [34, 42]. However, in a mixed surfactant system of cationic rich and anionic rich, 0.3 volume fraction of methanol was limited due to solubilization of micelles [43].

3.3. Correlation of γ_o/γ_{cmc} with the Volume Fraction of Methanol. In 2012, Mukhim and Ismail [44] assumed that the ratio γ_o/γ_{cmc} can be utilized to discuss the solvophobic effect [45]. Figure 4 shows variation in γ_o/γ_{cmc} with the volume fraction of methanol for CTAB at 298.15 to 323.15 K. The values of γ_o/γ_{cmc} decrease with the increase in methanol and but increase with temperature. The curves indicate that the solvophobic effect decreases with increasing in methanol content.

FIGURE 4: Variation in γ_o/γ_{cmc} CTAB solution with the volume fraction of methanol: square (298.15 K), triangles (308.15 K), closed circles (318.15 K), and closed squares (323.15 K).

3.4. Correlation of ΔG_{ads}^0 with Temperature. Gibbs energies of adsorption of CTAB in water and in a mixture of methanol-water show unique variation at different temperatures (Figure 5). It can be seen from Table 1 that the values of ΔG_{ads}^0 are all negative, indicating adsorption of amphiphiles is spontaneous at all investigated temperatures and volume fractions of methanol. However, the presence of methanol makes the adsorption less easy because methanol acts as a cosolvent and reduces the surface tension by adsorbing on the air/water interface [20]. ΔG_{ads}^0 linearly decreases with the increase in temperature whereas it increases with the increase in methanol. It was found that there is a systematic variation in the slopes with temperatures. Therefore, it will be easier for us to calculate the standard Gibbs energies of adsorption. Such variation in ΔG_{ads}^0 with solvent composition was also seen in the literature [38].

3.5. Correlation of pC_{20} with the Volume Fraction of Methanol. When we plot γ versus $\log C$, the minimum concentration of the surfactant can be obtained. The bulk liquid phase concentration of surfactant required to lower the surface tension of the solvent by 20 mN/M is a good measure of the efficiency of the adsorption of the surfactant (or surfactant efficiency). Hence, the negative logarithm of the concentration of surfactant in the bulk phase necessary to make a 20 mN/M diminution in γ of the solvent is the efficiency of adsorption (pC_{20}).

The standard adsorption Gibbs free energy change, ΔG_{ads}^0 , involved in the transfer of the surfactant molecule from the interior of the bulk liquid phase to the interface. We have the relation of pC_{20} by use of the Langmuir and Szyszkowski equations [46] as

$$pC_{20} = - \left(\frac{\Delta G_{ads}^0}{2.303RT} + 1.74 + \frac{20}{2.303RT\Gamma_{max}} \right). \quad (8)$$

FIGURE 5: Variation in $\Delta G_{\text{ads}}^{\circ}$ of CTAB solution with temperature.

The value of pC_{20} at 25°C calculated using equation (8) is 7.43, which does not match with the literature values of 3.67 [47] and 3.15 [46]. According to equation (8), pC_{20} is calculated using the values of $\Delta G_{\text{ads}}^{\circ}$ and Γ_{max} at a constant temperature. Likewise, $\Delta G_{\text{ads}}^{\circ}$ is calculated using the value of $\Delta G_{\text{m}}^{\circ}$, and the latter quantity depends on the degree of ionization (α) and cmc. For example, $\alpha = 0.56$ and $\text{cmc} = 0.00095 \text{ M}$; then, $\Delta G_{\text{m}}^{\circ}$ turns out to be $-27.42 \text{ kJ}\cdot\text{mol}^{-1}$, and obviously, we can determine $\Delta G_{\text{ads}}^{\circ}$. However, Niranjana et al. in 2011 [48] calculated $\Delta G_{\text{ads}}^{\circ}$ without using π_{cmc} [46] obtained as $-37.05 \text{ kJ}\cdot\text{mol}^{-1}$ which is on the right trends in comparison to their $\Delta G_{\text{m}}^{\circ}$. By using $\Delta G_{\text{ads}}^{\circ}$ and Γ_{max} , we obtained the value of pC_{20} from equation (9) equal to 3.11, which is almost matched with the literature value of 3.15 for CTAB at 25°C [48].

It was surprising for us, so the data of $\Delta G_{\text{ads}}^{\circ}$ and Γ_{max} were taken randomly from the recent work of Zhang et al. [47] and used in equation (8). The value of pC_{20} was calculated to be 7.44 which was high in comparison to other literatures and searched more details on the work of Zhang et al. [47] and found that $\alpha = 0.38$ and $\text{cmc} = 0.00084 \text{ M}$ and then $\Delta G_{\text{m}}^{\circ} = -47.04 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta G_{\text{ads}}^{\circ} = -59.6 \text{ kJ}\cdot\text{mol}^{-1}$ which matched with our data. Therefore, we used the equation from the same literature [47] as

$$pC_{20} = \frac{\pi_{\text{cmc}} - 20}{2.303nRT\Gamma_{\text{max}}} - \log \text{cmc}, \quad (9)$$

and found the value 3.43 of pC_{20} for CTAB at 25°C which matched almost with the literature. For CTAB at 25°C, Javadian et al. [49] calculated the value of $pC_{20} = 0.8$, using $\alpha = 0.30$ without using $\Delta G_{\text{ads}}^{\circ}$. This invigorated us to use equation (9) for the calculation of values of pC_{20} .

Thus, we can conclude that equation (8) is valid only if α is high and $\Delta G_{\text{ads}}^{\circ}$ is less negative, whereas equation (9) is applicable if α is low and $\Delta G_{\text{ads}}^{\circ}$ is more negative. Moreover, equation (9) is even useful if we do not have $\Delta G_{\text{ads}}^{\circ}$, but there is the necessity of π_{cmc} and cmc.

The plot pC_{20} of CTAB in water and methanol-water mixed solvent media (Figure 6) gives very interesting

FIGURE 6: Variation in pC_{20} CTAB with the volume fraction of methanol: squares (298.15 K), circles (308.15 K), triangles (318.15 K), and closed circles (323.15 K).

information. Data show that pC_{20} has a maximum value in the water at 298.15 K which decreases with increasing volume fractions of methanol at the same temperature. This signifies that the adsorption efficiency decreases in the presence of methanol, which is attributed due to a decrease in the solvophobicity of the medium.

The values of pC_{20} are least for 0.4 volume fraction of methanol-water at the respective temperatures. It is interesting to note that, in the case of 0.4 volume fraction of methanol, change in surface tension is in a narrow range (as shown in Figure 1). In such case, adsorption efficiency is least significant. This is further justified by the fact that the formation of micelles at 0.4 and beyond the volume fraction of methanol is not significant enough to discuss surface properties [34].

pC_{20} of CTAB in the water at 298.15 K shows higher values in comparison with higher temperatures and methanol-water mixed solvent media. This suggests that elevated temperature is not favorable for micellization, corresponding to the cmc trends [50]. The convex nature of the curves decreases for 298.15 K and 308.15 K with the addition of methanol, whereas the convex nature of the curves decreases and looks almost linear for 318.15 K and 323.15 K with the addition of methanol (Figure 6).

3.6. Correlation of $\Delta S_{\text{ads}}^{\circ}$ with the Volume Fraction of Methanol. As we know from the literature [51], the standard entropy of adsorption ($\Delta S_{\text{ads}}^{\circ}$) can be calculated if the standard Gibbs free energy of adsorption is known:

$$\Delta G_{\text{ads}}^{\circ} = \Delta H_{\text{ads}}^{\circ} - T\Delta S_{\text{ads}}^{\circ}, \quad (10)$$

$$\Delta S_{\text{ads}}^{\circ} = -\left(\frac{\partial \Delta G_{\text{ads}}^{\circ}}{\partial T}\right). \quad (11)$$

If standard enthalpy of adsorption ($\Delta H_{\text{ads}}^{\circ}$) is constant over the temperature range studied, $\Delta G_{\text{ads}}^{\circ}$ is calculated using equation (6) and the values are presented in Table 1. It is

reported that, for ionic surfactants, the $\Delta H_{\text{ads}}^{\circ}$ values determined based on $\Delta G_{\text{ads}}^{\circ}$ values by using $\Delta S_{\text{ads}}^{\circ}$ calculated from equation (11) are almost less possible. Therefore, $\Delta H_{\text{ads}}^{\circ}$ values are determined using $\Delta G_{\text{ads}}^{\circ}/2$ [52, 53], and $\Delta S_{\text{ads}}^{\circ}$ values are calculated using equation (10). Figure 7 shows that the values of $\Delta S_{\text{ads}}^{\circ}$ are all positive under all conditions. $\Delta S_{\text{ads}}^{\circ}$ increases with the increase in methanol, and the concave variation in $\Delta S_{\text{ads}}^{\circ}$ with the volume fraction of methanol was observed (Figure 7). The increase in the positive values of $\Delta S_{\text{ads}}^{\circ}$ with the increase in the volume fraction of methanol indicates that the surfactant molecules prefer more scattered forms.

3.7. Correlation of $\Delta H_{\text{ads}}^{\circ}$ with the Volume Fraction of Methanol. Figure 8 shows that the values $\Delta H_{\text{ads}}^{\circ}$ are all negative except 0.4 volume fractions of methanol. This shows that adsorption is exothermic. $\Delta H_{\text{ads}}^{\circ}$ increases with the increase in methanol, and the concave variation of $\Delta H_{\text{ads}}^{\circ}$ with the volume fraction of methanol was observed. The addition of methanol decreases the cohesive energy of the solution. The decrease in the cohesive energy is maximum in the case of 0.4 volume fraction of methanol. Therefore, the dispersion of surfactant molecules takes place. The variation in the curve is similar to the variation in the curve of $\Delta S_{\text{ads}}^{\circ}$ with the volume fraction of methanol (Figure 7).

3.8. Correlation of Packing Parameter with the Volume Fraction of Methanol. The value of the packing parameter (P) gives the shape of the micelle. When P values are within 0–0.33, then the shape of the micelle is spherical, whereas for the cylindrical shape of the micelle, the values of P should be between 0.33 and 0.5. In some cases, we can find the lamellar shape of the micelle; under such conditions, the values of P will be between 0.5 and 1.

In aqueous solution, CTAB forms cylindrical micelles. The variation in the packing parameter of CTAB with the volume fraction of methanol shows a unique variation. The P values of CTAB monotonously decrease like a concave curve with the addition of methanol, whereas for the temperatures (308.15 K and 323.15 K), the P values of CTAB decrease sharply in linear fashion, as shown in Figure 9. In all systems, the P values of CTAB decrease with temperature. This may be because of inducing vibrational, rotational, and translational oscillations with wakening of the binding forces of the CTAB system [39]. Such behavior was also noticed in a previous study [20]. The P values of CTAB decrease with the addition of methanol because of leading to a decrease in the solubilization capacity [54]. Such behavior was also seen in the literature [55].

3.9. Correlation of $\Delta G_{\text{eff}}^{\circ}$ with the Volume Fraction of Methanol. The difference between $\Delta G_{\text{ads}}^{\circ}$ and ΔG_m° is called the effective Gibbs free energy ($\Delta G_{\text{eff}}^{\circ}$). The curve of $\Delta G_{\text{eff}}^{\circ}$ sharply increases with convex variation with the addition of methanol and becomes a linear curve for CTAB at 323.15 K. With the increase in temperature, the curve of $\Delta G_{\text{eff}}^{\circ}$ decreases, as shown in Figure 10. It is also observed that the values of $\Delta G_{\text{eff}}^{\circ}$ decrease with an increase in the head group

FIGURE 7: Variation in $\Delta S_{\text{ads}}^{\circ}$ with volume fraction of methanol.

FIGURE 8: Variation in $\Delta H_{\text{ads}}^{\circ}$ with volume fraction of methanol.

polarity of CTAB, indicating that aggregation is more favored than the adsorption process and also less energy is required for the aggregation process [56].

3.10. Correlation of N with the Volume Fraction of Methanol. The number of molecules present in a micelle once the cmc is reached is called an aggregation number (N) [57].

146 was the aggregation number for CTAB in water at 25°C in the literature [58]. It was also noticed that the reported value of N was higher because Goddard found $N = 89$ at 20°C [59].

Similarly, Hartley [60] in his classical monograph mentioned spherical-shaped micelles with aggregation numbers in the range of 50 to 100 for CTAB solutions.

We know that the shape of a micelle is related to its size. The size is usually expressed in terms of an aggregation number that can be determined in different ways like light scattering [61, 62] and diffusion [63] and sedimentation rates in ultracentrifugation [64, 65]. Other scattering techniques [66, 67] such as X-ray scattering, quasielastic light scattering,

FIGURE 9: Variation in P with the volume fraction of methanol: squares (298.15 K), circles (308.15 K), triangles (318.15 K), and closed circles (323.15 K).

FIGURE 10: Variation in $\Delta G_{\text{eff}}^{\circ}$ with the volume fraction of methanol: squares (298.15 K), circles (308.15 K), triangles (318.15 K), and closed circles (323.15 K).

and neutron scattering have also been used for the determination of aggregation numbers. Lindman used NMR techniques [68, 69] to determine aggregation numbers of ionic and nonionic surfactants. The use of fluorescence probes which was a relatively convenient technique became popular [61]. Till now, both static and dynamic fluorescence techniques can be used to obtain aggregation numbers, and the latter is considered to be superior to the former [61].

The aggregation number is generally estimated experimentally by NMR and fluorescence measurements, and they are involved in concentration determination or the number of micelles together with the total amount of surfactants in the micellar form which is used to estimate the aggregation number [70]. However, we have determined here the aggregation number by using the simple equation with varying A_{min} described in the literature [71] as

$$N = \frac{4\pi l_c^2}{A_{\text{min}}}, \quad (12)$$

where A_{min} is the area occupied by per surfactant molecule and $l_c = 20.44 \text{ \AA}$ (hydrophobic tail length).

Our aggregation number almost matched with the literature [72] for CTAB in water at 25°C. It is interesting to see the variation in N with the volume fraction of methanol (Figure 11). N of CTAB varies concave curve on decreasing monotonously with the addition of methanol. On increasing temperature from 298.15 K to 308.15 K, the concave curves are observed, and further increasing temperature, the curve tends to change into a lower value somehow linearly by decreasing sharply with the volume fraction of methanol (318.15 K and 323.15 K). The reason for the decrease in N with increase in temperature may be due to the dissociation of the intra-micellar excimers play the role for the complete interpretation of the results at high temperature [73].

3.11. The Relation between A_{min} and π_{cmc} . π_{cmc} is a measure of the cohesive force in the surfactant film, whereas A_{min} describes the “orientation” of the surfactant’s molecule in an aqueous solution. π_{cmc} decreases with increasing temperature and methanol (Table 1), whereas A_{min} increases with increasing temperature and methanol (Table 1). With the increase in A_{min} , the π_{cmc} value of CTAB decreases sharply in linear fashion with the addition of methanol up to 0.2 volume fraction and then decreases monotonously until 0.4 volume fraction of methanol for 318.15 K and 323.15 K. With the temperatures 298.15 K and 308.15 K increase in A_{min} , the π_{cmc} value of CTAB decreases sharply in linear fashion with the addition of methanol up to 0.2 volume fraction and then decreases monotonously until 0.3 volume fraction of methanol and then decreases sharply up to 0.4 volume fraction of methanol (Table 1). The pattern of our variation in π_{cmc} versus A_{min} looks like the curve of π_{cmc} versus A_{min} of SDCS in the absence and presence of polymer [74]. The same pattern of the curve of CTAB was observed in the literature [75].

We also plot the curve of $\pi_{\text{cmc}} A_{\text{min}}$ with π_{cmc} : the highest curve is at temperature 323.15 K and then decreases for 318.15 K, 308.15 K, and 298.15 K simultaneously (Figure S1). With the increase in methanol, at first, the curve increased to 0.1 volume fraction of methanol and then decreased until 0.2 volume fraction of methanol and again increases continuously (Figure S1).

The plot of area (A_{min}) against $1/\pi_{\text{cmc}}$ gives interesting results (Figure S2). At 298.15 K and 308.15 K, the curves increase with convex nature with the addition of methanol, whereas for 318.15 K and 323.15 K, the curves increase with concave nature. The highest curve is at temperature 323.15 K and then decreases for 318.15 K, 308.15 K, and 298.15 K simultaneously (Figure S2).

3.12. Correlation of $\Gamma/\Gamma_{\text{max}}$ with Volume Fraction of Methanol. Applying the Frumkin isotherm equation provided in the literature [46], it confirmed the concentration value at which γ of water is minimized by 20 mN/m, and the

FIGURE 11: Variation in N CTAB with the volume fraction of methanol: triangles (298.15 K), circles (308.15 K), squares (318.15 K), and circles (323.15 K).

ratio of the Gibbs surface excess concentration (Γ) to the maximal ($\Gamma_{\max}$) is within 0.84 to 0.999.

We have calculated the $\Gamma/\Gamma_{\max}$ values for CTAB systems from the equation used in the literature [46]:

$$\pi_{\text{cmc}} = -RT\Gamma_{\max} \ln \left(1 - \frac{\Gamma}{\Gamma_{\max}} \right). \quad (13)$$

Our values of $\Gamma/\Gamma_{\max}$ for the CTAB system perfectly matched within the range of the literature [46].

On adding methanol, the values of $\Gamma/\Gamma_{\max}$ decrease sharply for the CTAB system at 298.15 K and 308.15 K and monotonously decrease at 318.15 K and 323.15 K up to 0.2 volume fraction of methanol (Figure S3).

The values of $\Gamma/\Gamma_{\max}$ increase sharply for the CTAB system at 298.15 K and 308.15 K and monotonously increase at 318.15 K and 323.15 K up to 0.3 volume fraction of methanol (Figure S3), and finally, the curves decrease sharply for the CTAB system at 298.15 K and 308.15 K and monotonously decrease at 318.15 K and 323.15 K (Figure S3). The highest curve is for 323.15 K, and the lowest is for 298.15 K (Figure S3). But the values of $\Gamma/\Gamma_{\max}$ for water, 0.1, 0.2, 0.3, and 0.4 volume fraction of methanol are more than 0.9 for all investigated temperatures. The exceptional case is for 298.15 K of 0.4 volume fraction of methanol.

3.13. Correlation of cmc/C_{20} with the Volume Fraction of Methanol. When the surface is saturated and γ of the solvent is minimized by 20 mN/M, then for the linear portion of the plot, the Gibbs adsorption equation becomes [46] as

$$\pi_{\text{cmc}} \approx 20 + 2.3nRT\Gamma_{\max} \log \left(\frac{\text{cmc}}{C_{20}} \right). \quad (14)$$

This equation shows that $\Gamma_{\max}$ and cmc/C_{20} are in a parallel fashion. This means if one increases, then others also increase, or if one decreases, then others also decrease. By doing so, a reduction in effectiveness of surface tension

exists. Sometimes, we can see the large values of ratio cmc/C_{20} which may be due to steric barriers associated with the packing of these bulky chains into the micelle. One can observe that the value of C_{20} plays a vital role in the increment or decrement of cmc/C_{20} .

If the value of C_{20} is increased more than the cmc, then the cmc/C_{20} value is decreased, or vice versa. Also, from the above discussion, cmc/C_{20} is a measure of the tendency to form micelles relative to the tendency to adsorb at the air/water interface [76].

There is a decrease or an increase in cmc/C_{20} . A decrease in cmc/C_{20} indicates that the micellization facilitated more than adsorption, whereas the increase in cmc/C_{20} indicates that the adsorption facilitated more than micellization. Therefore, the ratio cmc/C_{20} provides information about the adsorption and micellization processes.

In our system, the decrease in cmc/C_{20} with the volume fraction of methanol indicates that the micellization facilitated more than adsorption (Figure S4). Generally, ionic surfactants with a single straight chain hydrophobic group in an aqueous system show low cmc/C_{20} ratios of 3 or less [46]. We also observed the value of cmc/C_{20} more than 2 and less than 4 for water and methanol-water mixtures at the investigated temperatures (Figure S4).

Variation in the curves for CTAB with the volume fraction of methanol looks concave.

The interesting nature of the curve for CTAB at 323.15 K is that, at first in water, the value of cmc/C_{20} is the highest but decreases with the addition of methanol, whereas the value of cmc/C_{20} is the lowest for CTAB at 298.15 K in water, but decreases with the addition of methanol and finally becomes the highest (Figure S4).

3.14. Correlation of $\Delta G_{\text{ads}}^{\circ}/\Delta G_m^{\circ}$ with the Volume Fraction of Methanol. The observed $\Delta G_{\text{ads}}^{\circ}$ values are higher than $\Delta G_{\text{min}}^{\circ}$ values indicating that adsorption at the air-solution interface is more favorable than the formation of micelles in the bulk solution [77]. The ratio of $\Delta G_{\text{ads}}^{\circ}/\Delta G_m^{\circ}$ is found to be <1.5 (Figure S5) for CTAB in water and water-methanol mixture. The variation in the curves decreases for CTAB at 298.15 K and 308.15 K with the volume fraction of methanol and look concave, whereas the variation in the curve for CTAB at 318.15 K and 323.15 K with the volume fraction of methanol looks linear with the monotonous decrease in the addition of methanol (Figure S5). The curve for CTAB at 323.15 K is the highest, whereas at 298.5 K, the curve of CTAB has been observed the lowest.

3.15. Correlation of cmc/pC_{20} with the Volume Fraction of Methanol. The ratio cmc/pC_{20} is an interesting study. Such type of work was observed by Niranjana and Upadhyay in 2010 [78].

The variation in the curves for CTAB increases sharply with the volume fraction of methanol and looks concave for 298.15 to 323.15 K, whereas the variation in the curve for CTAB at 323.15 K with the volume fraction of methanol looks the highest and the lowest at 298.15 K (Figure S6).

3.16. Correlation of C_{20} with the Volume Fraction of Methanol. C_{20} is the concentration of surfactant in the bulk phase that produces a minimization of 20 mN/M in γ of solvent. C_{20} is not only a measure of the efficiency of adsorption of the liquid-gas interfaces but also a measure of the efficiency of γ minimization by the surfactant [46]. Our calculation of C_{20} for CTAB at 298.15 K is close to the literature [79].

The variation in the curves for CTAB sharply increases with the volume fraction of methanol (Figure S7), whereas the variation in the curve for CTAB at 323.15 K with the volume fraction of methanol looks the highest and the lowest at 298.15 K.

3.17. Variation in $G_{\min}$ with the Volume Fraction of Methanol. The free energy of the surface at equilibrium is also known as the molar Gibbs energy at cmc for maximum adsorption attained. This is one of the thermodynamic parameters for the evolution of synergism in mixed adsorption films at equilibrium [80] and is calculated as follows:

$$G_{\min} = A_{\min} \gamma_{\text{cmc}} N_A, \quad (15)$$

where γ_{cmc} is the surface tension at cmc and N_A is Avogadro's number. We observed the lowest values of $G_{\min}$ in the CTAB-water system at 298.15 K, whereas the highest value in the 0.4 volume fraction of methanol is at 323.15 K. The observed lower values of $G_{\min}$ ascertain the thermodynamic stability [80].

The variation in the curves for CTAB with the volume fraction of methanol up to 0.2 looks as monotonous increment, whereas the curves increase sharply with the addition of more methanol (Figure S8).

The error limits of cmc, $\Gamma_{\max}$, $A_{\min}$, π_{cmc} , P , and $\Delta G_{\text{ads}}^{\circ}$ are within ± 3 , ± 5 , ± 4 , ± 3 , ± 4 , and $\pm 6\%$, respectively.

The surface properties of CTAB in water and methanol-water mixed solvent media at 298.15 K were matched with the literature [21]. Let us take the equation that has the degree of dissociation (α), critical micelle concentration (cmc), area occupied by per surfactant molecule ($A_{\min}$), and surface pressure (π_{cmc}) [47]:

$$\Delta G_{\text{ads}}^{\circ} = 2.303(2 - \alpha)RT \log \text{cmc} - 0.6023 \cdot \pi_{\text{cmc}} A_{\min}, \quad (16)$$

where $\alpha = 0.21$ from our early studies of CTAB in water at 298.15 K by the conductivity technique [10] and the rest values of $A_{\min}$ and π_{cmc} were taken from Table 1; then, the value of $\Delta G_{\text{ads}}^{\circ}$ becomes $-30.837 \text{ kJ} \cdot \text{mol}^{-1}$. The experimental observed the standard Gibbs energy of adsorption for CTAB at 298.15 is $-63.4 \text{ kJ} \cdot \text{mol}^{-1}$ (Table 1), which is different from literature to literature: $-59.62 \text{ kJ} \cdot \text{mol}^{-1}$ [47] and $-42.01 \text{ kJ} \cdot \text{mol}^{-1}$ [51].

4. Conclusion

The surface properties and micellization of CTAB in water and the presence of different volume fractions of methanol-water were investigated by surface tension measurements. The cmc increases with an increase in the volume fraction of methanol and with an increase in temperature. The presence

of methanol shows significant changes in surface properties such as maximum surface excess concentration ($\Gamma_{\max}$), area occupied by per surfactant molecule ($A_{\min}$), and surface pressure (π_{cmc}). A decrease in $\Gamma_{\max}$ with increasing volume fraction of methanol-water indicates that the air/solvent interface is less populated by amphiphiles, which subsequently increase the values of $A_{\min}$ and decreases the values of π_{cmc} . The effect of methanol on the values of pC_{20} suggests that the efficiency of adsorption decreases with an increase in the volume fraction of methanol-water to such an extent that, at 0.4 volume fraction of methanol-water, pC_{20} is almost undetectable.

In short, it was discovered that, with the addition of methanol, the hydrophobicity of the medium gradually decreases, the soft interaction acting in the self-assembly of amphiphiles such as hydrogen bonding, hydrophobic effects, electrostatic interaction, and van der Waals forces, which are balancing forces required for the formation of a micelle is imbalanced, and micelles start disorganizing.

Data Availability

The data used to support the findings of this study will be available upon request to the corresponding author.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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Supplementary Materials

Figures S1–S8: variation in $\pi_{\text{cmc}} A_{\min}$ with π_{cmc} ; variation in $A_{\min}$ with $1/\pi_{\text{cmc}}$; and variation in $\Gamma/\Gamma_{\max}$, cmc/C_{20} , $\Delta G_{\text{ads}}^{\circ}/\Delta G_m^{\circ}$, cmc/pC_{20} , C_{20} , and $G_{\min}$ with the volume fraction of methanol. (*Supplementary Materials*)

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