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Micellization and Thermodynamic Properties of Cationic Surfactant Cetyltrimethylammonium Bromide in non-Aqueous Mixture of Lauric Acid

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In this work, the multi technique approach has been utilized to study the intermolecular interactions in lauric acid with the cationic surfactant cetyltrimethylammonium bromide in non aqueous media. The pseudo-phase separation model was used for the calculation of various thermodynamic parameters like standard free energy, ΔG^o_{mic}, enthalpy, ΔH^o_{mic}, and entropy, ΔS^o_{mic}, of micelle formation. The interfacial properties (the maximum surface excess at the air/solvent interface, Γ_{max}, the minimum area per surfactant molecule at air/solvent interface, A_{min}) of mixed system were calculated by using the Gibbs adsorption isotherm. The density data were applied to calculate the apparent molar volumes at infinite dilution, V_ϕ^o, apparent molar volumes at the critical micelle concentration, V_ϕ^{cmc}, and apparent molar volumes upon micellization, ΔV_ϕ^m, at 298.15, 303.15, 308.15 and 313.15 K. The 1H NMR analysis suggested the intermolecular interaction especially in the hydrophilic head and interface region of CTAB with regard to shifting of proton signals.

Keywords: Micellization; Hydrophobic; Lauric acid; CTAB; Thermodynamics

1. INTRODUCTION

The knowledge of the conductometric and volumetric properties of surfactants in presence of different kinds of additives is very important from practical and theoretical points of view. Mostly the additives are added in aqueous media of surfactants but the study in non aqueous media is very attractive in order to observe the mixing behaviour of different constituents. Surfactants show sharp changes in properties at a particular concentration, called cmc, which signifies the essential micelle property of the amphiphilic molecules to self-aggregate in the solution. In addition, for the micelle formation the surfactant structure, medium of solubilization, surfactant concentration and the process employed to prepare self assemblies are well liable for the micelle formation [1]. CTAB is one of the most frequently used surfactants in many industrial processes and everyday life. It is used as an effective antiseptic agent against bacteria and fungi [2]. It has been extensively utilized in the synthesis of gold nanoparticles and is present in many household products [3, 4]. Ethyl alcohol is polar molecule and self-associated through hydrogen bonding and is expected to interact strongly with others fluids by hydrogen-bonding. On the other hand, the recent findings emphasize the attention of using fatty acids as green surfactants with original properties for various applications such as petrochemical, washing, environmental clean-up, material recovery processes, encapsulation and drug delivery. Lauric acid is having the greatest antibacterial activity and in the intestinal tract it discharges the enzyme which stimulates the thyroid hormone [5-8].

Dubey has reported the effect of organic additives on CTAB aggregation in aqueous solutions [9]. Sidim and Acar have studied alcoholic effect on cmc of polysorbate 20 and CTAB mixed solutions [10]. Aggregation properties of the CTAB and TX-100 mixture with ethanol in aqueous media were also investigated by Magdalena and his coworkers [11]. Micellization of CTAB in mixed water alcohol media was also reported by Nazir and co-workers [12]. Although, various studies have been carried out on the CTAB and SDS in aqueous and non aqueous medium to explain the micellization behavior given in literature [13-21]; but the use of non-aqueous media and fatty acid for the micellization has been neglected.

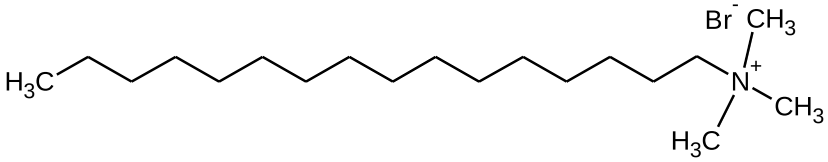
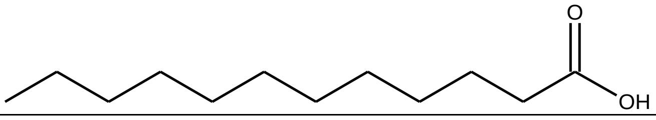
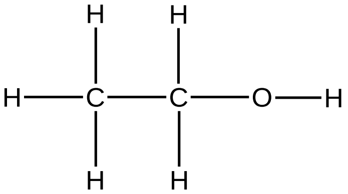
In this paper we report the micellization of CTAB with ethanol and lauric acid mixtures using conductometric, volumetric, tensiometric, and ^{1}H NMR methods. The compounds we choose are interesting as lauric acids (12-carbon atom chain saturated fatty acid, and extremely low solubility in water), which can't self-assemble due to small head group [22]. Moreover, we observe the noticeable deviation of the relative permittivity of different mediums which have an effect on the micellization process because in ionic surfactants the magnitude of cmc increases with decrease in the relative permittivity of medium [23]. It is interesting to note the structure of both lauric acid and CTAB having regions with differing polarity, which show both hydrophilic and hydrophobic characteristic. Thus, it would be interesting to examine the aggregation process of surfactant in non aqueous media.

2. EXPERIMENTAL

2.1 Materials

Cetyltrimethylammonium bromide (CTAB) 99% purchased from Fluka, Lauric acid (LA) 99%, obtained from Merck, Germany, Both CTAB and lauric acid were dried in vacuum over P_2O_5 at room temperature for about 72 h. Ethanol, E-OH 99% (Sigma–Aldrich) was used without further purification. Stock solution of 0.10 mol kg^{-1} of lauric acid was prepared in ethanol and was used as a solvent for the preparation of 1.0, 3.0, 5.0, 7.0, 9.0, 11.0, 13.0, 15.0, 17.0, 19.0 and 21.0 × 10^{-4} mol kg^{-1} CTAB solutions. The entire solutions were prepared freshly and weightings were done by using an electronic balance Shimadzu AY220, Japan, with precision of ± 0.0001 g. All the mixtures were prepared just before use and kept in stopper air tight bottles to avoid evaporation. The chemical structures of CTAB, lauric acid and ethanol have been presented in Table 1.

Table 1. Chemical structures of CTAB, Lauric acid and ethanol.

Materials	**Structure**	**M.W ($g.mol^{-1}$)**
Cetyltrimethylammonium bromide (CTAB)		364.44
Lauric acid		200.31
Ethanol		46.06

2.2 Methods

The conductivity measurement of each sample was measured with a digital conductivity meter (PC 510 Bench/Conductivity Meter (EUTECH instruments). The calibration of the conductivity meter was carried out by measuring the conductivities of 0.01 and 0.10 N solutions of extra-pure KCl (Across Organics purity >99 %). The solutions of KCl were prepared in doubly-distilled, deionised water from alkaline $KMnO_4$ to remove organic matter, if any, with conductivity 1.05 × 10^{-4} S m^{-1} at 298.15 K. The glass cell with two platinum electrodes was dipped in a corning glass tube containing the sample solution, which was immersed in an electronically controlled thermostated water bath. Conductivity measurements were recorded when thermal equilibrium was attained by the solutions. The uncertainty of the conductivity measurements was estimated to ± 0.5 %.The analytical digital density meter DDM 2910 (Rudolph Research, USA) was used to measure densities of the mixtures at different temperatures (298.15-313.15) K. The uncertainties of the measurements were estimated to be better than ± 0.0001 g. cm^{-3}. Proper calibration of densitometer at each temperature was performed at atmospheric pressure using doubly distilled and deionised water.

The surface tension of CTAB + water, and CTAB + lauric acid having different molar ratio were measured with a SD Hardson tensiometer at 303.15 K. The Pt–Fe ring was washed well with distilled water and then rinsed in ethanol prior to use. The ring was then burnt in low ethanol flame. Each measurement was repeated at least thrice and the reproducibility was within 0.1 m Nm^{-1}. The 1H

NMR measurements were made at a temperature of 303.15 K using Bruker Avance NMR spectrometer operating at 300 MHz. The stock solutions of [CTAB] = 1.0×10^{-4} mol kg^{-1} was prepared in D_2O. About 1 ml of each solution was transferred to a 5mm NMR tube and chemical shifts were recorded on the δ ppm scale (reproducibility within 0.01 ppm) with respect to internal reference TMS. 1H NMR signals of pure CTAB and mixtures of CTAB + lauric acid over the whole mole fraction range were studied (while keeping the total surfactant concentration constant).

3. RESULTS AND DISCUSSION

3.1 Conductometric study

The conductance was measured as a function of CTAB in the presence of in LA + E-OH in the concentration range from 0.0001 to 0.0021 mol kg^{-1} respectively, at temperature 298.15, 303.15, 308.15 and 313.15 K. The values of cmc of CTAB in E-OH + LA at different temperatures are presented in Fig. 1.

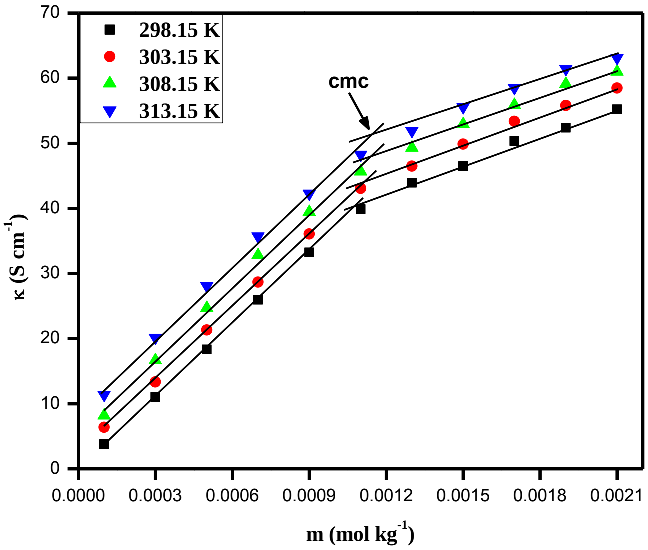


Figure 1. Plot of conductivity, κ, versus concentration of CTAB surfactant in 0.1 m LA + E-OH solution at different temperatures

These values were attained from the intersection point of the two straight lines of the conductivity versus concentration above and below the break points.

The data given in Table 2 reveals that the cmc values increases with increase in temperature. The effect of temperature on the magnitude of cmc values of surfactant is generally analyzed due to the presence of different components present in the mixtures. At relatively higher temperature, the disruption of the ordered molecules surrounds the hydrophobic groups of the surfactant. As LA molecules are insoluble in aqueous medium so in favor of there solubility we prefer the study in non aqueous medium. When E-OH a structure breaker molecule is in contact with LA and CTAB molecules the order in the mixture is destroyed, which results the distraction of H-bond associates in

LA molecules and which in turn surrounds the hydrophobic groups of CTAB, this disfavors micellization, thereby, and an increase in cmc value of the CTAB is examined.

Table 2. The values of cmc, β, ln X_{cmc}, ΔG_m^o, ΔH_m^o and ΔS_m^o of CTAB surfactant at different concentration in 0.1 m LA + E-OH solution at different temperatures

Parameters	T/K			
	298.15	303.15	308.15	313.15
cmc/ (mol kg^{-1})	0.001069	0.001106	0.001138	0.001176
β	0.4455	0.4534	0.4628	0.4730
ln X_{cmc}	-9.8903	-9.8562	-9.8282	-9.7954
	Thermodynamic parameter of micellization			
ΔG_m^o (kJ mol^{-1})	-38.111	-38.420	-38.706	-38.943
ΔH_m^o (kJ mol^{-1})	-7.4092	-7.4671	-7.5107	-7.5432
ΔS_m^o (J mol^{-1} K^{-1})	0.1030	0.1021	0.1012	0.1003
$T\Delta S_m^o$ (J mol^{-1} K^{-1})	30.7094	30.9516	31.1847	31.4089

Moreover, it is convenient that at higher temperatures the thermal motion increase which results the demicellization owing to the distraction of the palisade layer of the micelle, which subsequently enhances the cmc of the surfactants [24]. This is because of the facts that at increasing temperature high solubility of hydrocarbon stabilize the surfactant monomers and, therefore, micelle formation is hindered, results the higher cmc of CTAB [25, 26]. From the Table 2 an increase in cmc values with increasing temperature is possibly due to the other factors such as ion-hydrophobic interactions have capability of forming the close packed ion pairs among the charge centers (N^+-CH_3) group of CTAB together with hydrophilic part of LA molecules.

Thermodynamic parameter plays a vital role in order to understand of the process of micellization. The elucidation of these parameters ΔG_m^o, ΔH_m^o and ΔS_m^o is essential to observe the effects of structural and environmental factors on the cmc values and also to estimate the effects of new structural and environmental deviations in presence of different additives. Pseudo-phase separation model is applied to estimate these parameters because of its wide acceptance for the interpretation of the energetics of micellization.

The standard free energy of micellization was calculated according to the following relation [27]:

$$\Delta G_m^o = (2 - \beta)RT\ In\ X_{CMC} \qquad (1)$$

where X_{cmc}, R and β are the cmc value expressed in mole fraction, gas constant (8.314 JK^{-1}mol^{-1}) and the degree of ionization which can be predicted from the conductance data from the ratio of the slopes of the two linear segments above and below cmc of specific conductivity versus surfactant concentration [28, 29]. The degree of counter ion association, is given as $\alpha = 1 - \beta$. This easy approach is relatively acceptable in providing quantitative evaluation of β, as described in literature [30]. Moreover, Kale et al., Bandyopathyay and Moulik certified the integrity of this method to calculate the values of β through the ion-selective membrane electrode. They found that the values of β thus acquired are in good agreement with those obtained conductometrically [31, 32]. The β values are given in Table 2. It is noticed from Table 2 that both cmc and β values increase with an increase in the temperature. The increased thermal energy because of the rise in temperature enhances the ionization of the CTAB and, thereby, an increase in β with temperature is evident. This specifies strong correlation between the variation of cmc and β. A similar increase in cmc and β values with temperatures in presence and absence of additives in aqueous medium were reported in literature [33]. Yet, an opposite trend in these parameters is observed by Nazir at al. for CTAB in water + ethanol mixtures were there is possibility of the alcohol to penetrate into the micelle [13]. Such penetration would direct the screaming of electrostatic repulsions between ionic head groups of the surfactant thereby promoting micellization i.e. would result in decrease in cmc and increase of β. Hence, in the light of the results acquired in present study, the role of different additives present in the mixture are responsible for deciding the magnitude in cmc and β.

From the temperature-dependent values of ΔG_m^o, the other thermodynamic parameters of micellization can be estimated such as enthalpy, ΔH_m^o and entropy, ΔS_m^o, by applying the following estimated thermodynamic relations.

$$\Delta H_m^o = -RT^2(2-\beta)\frac{d\,In\,X_{CMC}}{dT} \qquad (2)$$

$$\Delta S_m^o = \frac{\Delta H_m^o - \Delta G_m^o}{T} \qquad (3)$$

The values of $\frac{d\,In\,X_{CMC}}{dT}$ were determined by fitting ln Xcmc ~ T with the polynomial function:

$$In\,X_{CMC} = a + b(\mathrm{T/K}) + \mathrm{c}(\mathrm{T/K})^2 \qquad (4)$$

where a, b and c are respective polynomial constants. Then

$$\frac{d\,In\,X_{CMC}}{dT} = b + 2c(T/K) \qquad (5)$$

The results obtained from the thermodynamic parameters calculated from Eqs. (2 to (5) for the studied system at different temperatures are presented in Table 3.

The free energy of micellization ΔG_m^o is the determination of the readiness with which the micelle formation takes place. It is observed the values of ΔG_m^o are negative at all inspected temperatures, become increasingly more negative with an increase in temperature. This signifies the micellization is thermodynamically spontaneous of CTAB in LA + E-OH mixtures and the decreasing trend in the ΔG_m^o values with increasing temperature is recognized as the desolvation of the hydrophilic group of the surfactant [33]. The increasing negative values of ΔG_m^o with rise in temperature obtained from the Eq. (1) are because of the mutual effect of β and $In\,X_{CMC}$, the former quantity is found to increase while the later one decreases with increase in temperature.

Table 3. Density values, ρ, of CTAB surfactant at different concentration in 0.1 m LA + E-OH solution at different temperatures

mol kg^{-1}	CTAB + 0.1 m LA + E-OH solution (ρ / g cm^{-3})			
T / K	298.15	303.15	308.15	313.15
0	0.8075	0.8058	0.8044	0.8032
0.0001	0.8004	0.7965	0.7924	0.7885
0.0003	0.8013	0.7975	0.7935	0.7895
0.0005	0.8038	0.8001	0.7962	0.7921
0.0007	0.8004	0.7961	0.7915	0.7871
0.0009	0.7952	0.791	0.7872	0.783
0.0011	0.7947	0.7904	0.7864	0.7819
0.0013	0.7944	0.7901	0.786	0.7813
0.0015	0.7941	0.7898	0.7855	0.7809
0.0017	0.7935	0.7893	0.7849	0.7804
0.0019	0.7929	0.7888	0.7843	0.7798
0.0021	0.7924	0.7879	0.7839	0.7793

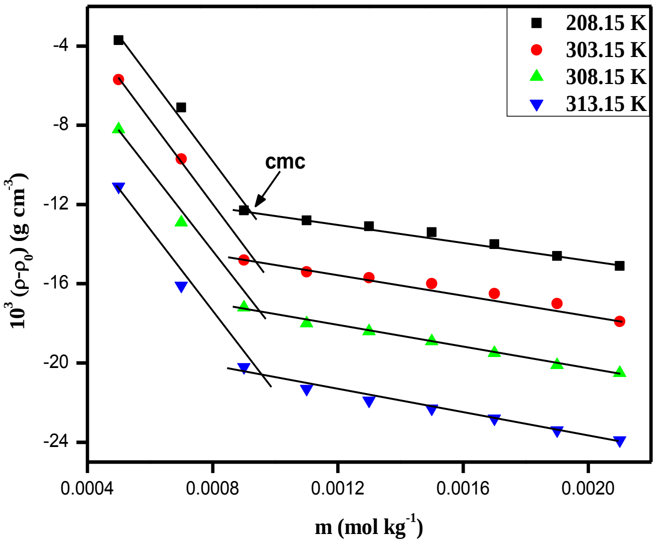


Figure 2. Plot of densities, ρ, versus concentration of CTAB surfactant in 0.1 m LA + E-OH solution at different temperatures

This supports the change in cmc with temperature. An increase in ΔG_m^o values with increase in temperature for CTAB in presence of octan-1-ol and nonan-1-ol mixtures was reported by Dubey [9]. Chauhan and co-workers [34] reported the similar increase in ΔG_m^o and β values of CTAB in leucine + water at different temperatures. It is important to point out the observed ΔG_m^o values of CTAB in LA + E-OH mixtures are -38.70 and -38.94 kJ mol^{-1} at 308.15 K and 313.15 K, respectively, which are smaller than the literatures values -47.59 and -47.86 kJ mol^{-1} at 308.15 K and 313.15 K, respectively, of CTAB in water + E-OH mixtures at the corresponding temperatures, representing that the micellization of CTAB is more favored in water + E-OH mixtures than in LA + E-OH mixtures [35, 36]. This signifies the hydrophobic-hydrophobic interactions among the larger non-polar groups of

CTAB and non-ionic moiety of water are maximum, which results greater negative ΔG_m^o values in presence of water than in the presence of LA + E-OH mixtures. Moreover, ΔH_m^o values are negative and become more negative with rises in temperature. Besides hydrophobic interactions negative ΔH_m^o values may also be because of the electrostatic interactions among the cationic head (N^+-CH_3) group of CTAB and hydrophilic part of LA molecules. It is reported that ΔH_m^o values are not constantly negative, often becomes positive, depending upon the structural and solution aspects prevailing in the surfactant mixture in the presence of different additives. Hence, in the present investigation the micellization of CTAB is dependent on the hydrophilic and hydrophobic nature of additives as well as its quantity in mixed constituents. It is significant to note down the comparison of ΔH_m^o values of CTAB in water + E-OH mixed mixtures are more negative (-13.36 and -13.72 kJ mol^{-1} at 308.15 and 313.15 K]) as that of smaller ΔH_m^o negative values (Table 3) in presence of LA + E-OH mixed mixtures [35]. This shows micellization of CTAB is highly favored in water + E-OH mixtures than in LA + E-OH mixtures. The resultant values are in good agreement with values found in Chauhan et al regarding the micellization parameters (ΔG_m^o and ΔH_m^o values with temperature) for CTAB in water + leucine mixtures [34]. In support of the results discussed above it is observed the increased values of ΔH_m^o are accompanied with increase in $T\Delta S_m^o$ values (Table 3). The increasing values of $T\Delta S_m^o$ than that of ΔH_m^o in the present study signifies that the micellization is generally directed by entropy gain and the driving force for micellization process is in fact the tendency of the hydrophobic group of the surfactant in transferring from the bulk solvent to the interior of the micelle [36]. This is possibly because of the breaking up of the ordered LA molecules by structure breaker ethanol molecules. These LA molecules surround the hydrophobic alkyl group of CTAB when it is shifts from the solvent environment to the interior of the micelle. In addition, this may be due to the increased freedom of hydrophobic chains in the nonpolar interior of the micelle than in the solvent environment [2].

3.2 Volumetric Study

The measured densities, ρ of the of the system CTAB in LA + E-OH system at 298.15, 303.15, 308.15, and 313.15 K are presented in Table 3. Thermodynamic parameters have been estimated which predict the extent of interactions taking place in the mixed systems. The plots of density, which represent cmc of CTAB surfactant in LA + E-OH solution at different temperatures, are presented in Figure 2. The data were used to calculate the apparent molar volumes V_ϕ of CTAB in LA + E-OH mixture at different temperatures by the following equation:

$$V_\phi = \frac{M}{\rho} - \frac{10^3(\rho - \rho_0)}{\rho\rho_0 m} \qquad (6)$$

where M, ρ and ρ_0 are the molar mass of the solute CTAB, densities of the solution and the solvent (LA + E-OH), respectively.

Table 4. Values of critical micelle concentration, m_{cmc}, critical aggregation concentration, apparent molar volumes at infinite dilution, V_{ϕ}^{o}, apparent molar volumes at the cmc, V_{ϕ}^{cmc}, and apparent molar volumes upon micellization, ΔV_{ϕ}^{m}, of CTAB surfactant at different concentration in 0.1 m LA + E-OH solution at different temperatures

cmc/ Volumetric parameters	T/K 298.15	303.15	308.15	313.15
m_{cmc} / (mol kg^{-1})	0.000920	0.000938	0.000955	0.000971
V_{ϕ}° / 10^{-4} (m^3 mol^{-1})	0.6806	0.9565	1.0146	2.2303
V_{ϕ}^{cmc} / 10^{-4} (m^3 mol^{-1})	1.2481	2.671	3.9661	5.8967
ΔV_{ϕ}^{m} / 10^{-4} (m^3 mol^{-1})	0.5675	1.7145	2.9515	3.6664

The values of apparent molar volumes V_{ϕ} at different temperatures are reported in Table 4. The observed apparent molar volume values V_{ϕ}, are positive and the values becomes more positive with rise in the temperature. These values are in agreement with the observations reported for other surfactant systems [37]. The observed increase in the values of V_{ϕ} are generally because of the decreased hydrophobic hydration and electrostriction [38]. In monomeric form it is agreeable that the surfactants act as 1:1 electrolytes in pre-micellar region [39]; hence, partial molar volumes V_{ϕ}^{o} can be estimated by fitting the values of V_{ϕ} to Debye-Huckel limiting law as:

$$V_{\phi} = V_{\phi}^{o} + A_{v} m^{1/2} + B_{v} m + ... \tag{7}$$

where V_{ϕ}^{o}, A_{v} and B_{v} are the apparent molar volume at infinite dilution, Debye-Huckel limiting law coefficient and adjustable parameter which evaluates the deviations from the limiting law. The estimated values of the V_{ϕ}^{o} are presented in Table 4. It is worth to mention the value of V_{ϕ}^{o} (101.46 cm^3 mol^{-1}) of CTAB in LA + E-OH at 303.15 K is lower than the reported value (176.6 cm^3 mol^{-1}) in presence of LA + E-OH at the corresponding temperature [40]. The lowering in values of V_{ϕ}^{o} can be elucidated by considering the size of the additives present in the surfactant systems. Therefore, herein present investigation the size of the additives LA and CTAB are large as in contrast to cavity size of the solvent. Thus, there would be increased positive values of V_{ϕ} due to the poor accommodation of additive molecules in the cavities. Moreover, there may be reduced electrostriction on account of smaller surface charge density [41]. In the micellar region the values of V_{ϕ} were fitted to the equation [39].

$$V_{\phi} = V_{\phi}^{\mathrm{cmc}} + \frac{\Delta V_{\phi}^{\mathrm{m}}(m - cmc)}{[B + (m - cmc)]} \tag{8}$$

where B is an adjustable parameter without physical meaning. V_{ϕ}^{cmc} is the value of apparent molar volume at the cmc and the change in apparent molar volume on micellization. $\Delta V_{\phi}^{\mathrm{m}}$ is taken as the difference between the limiting values of V_{ϕ} and V_{ϕ}^{cmc} and is given by the following relation:

$$\Delta V_{\phi}^{\mathrm{m}} = V_{\phi}^{\mathrm{cmc}} - V_{\phi}^{\mathrm{o}} \tag{9}$$

The values of V_ϕ, $\Delta V_\phi^{\mathrm{m}}$ and V_ϕ^{cmc} were presented in Table 4 at all investigated temperatures. The values of $\Delta V_\phi^{\mathrm{m}}$ are observed positive and increases with increase in temperature. The gradual increase in these values with temperature were recognized due to the raise in thermal energy which results the release of some LA molecules from the solvation layers of the ionic monomer to the bulk solution, making these values more positive. Thus, these features appeared to contribute in the process of micellization in present study.

3.3 Tensiometric Study

Surface tension (γ) measurements have been carried out in the concentration range of 0.0001 to 0.0021 m / mol kg^{-1} at the temperature 298.15, 303.15, 308.15 and 313.15 K.

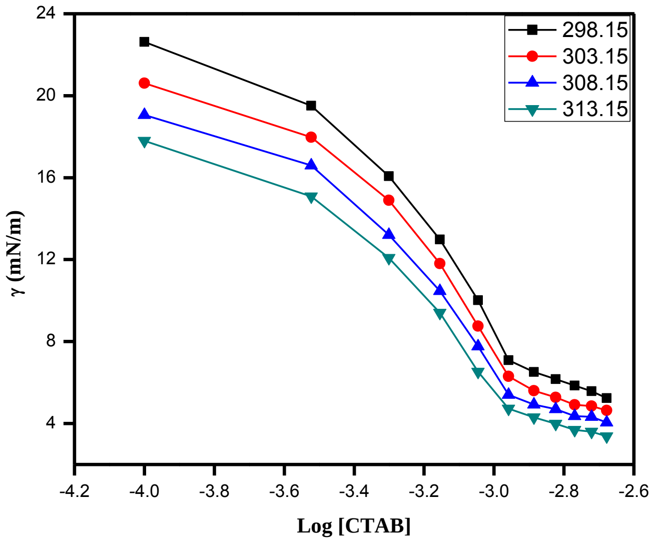


Figure 3. Plots of surface tension, γ, as a function of log concentration of CTAB surfactant in 0.1 m LA + E-OH solution at different temperatures

Fig. 3 presents the variation of surface tension (γ) versus logarithm of CTAB surfactant in 0.1 m LA + E-OH mixtures at different temperatures. In order to make better understanding various interfacial (air-solvent) parameters of the CTAB in E-OH + LA system have been calculated. The air /solvent interface of surfactant mixtures are well occupied by the adsorbed molecules. The surfactant concentration is always more at the interface because of the adsorption as compared to the concentration of the surfactant in the bulk. The excess surface concentration ($\Gamma_{\max}$) was estimated by the Gibbs adsorption equation (Eq. (10)) [42].

$$\Gamma_{\max} = -\frac{1}{2nRT}\left(\frac{\partial \gamma}{\partial \log C}\right)_{T,P} \qquad (10)$$

The minimum area per head group, $A_{\min}$, can be evaluated by Eq. (11)

$$A_{\min} = \frac{10^{18}}{N_A \Gamma_{\max}} \qquad (11)$$

where R is the universal gas constant = 8.314 J mol^{-1} K^{-1}, N_A = Avogadro's number, and n = number of ionic species at the at the interface vary with the surfactant bulk concentration. The value of n was taken as 2 based on previous reports [43]. The Γ_{max} value, the adsorption effectiveness and describes the adsorption tendency of surfactant molecules at the interface. The Γ_{max} and A_{min} are expressed in moles per square meter and square nanometers per molecule, respectively; γ = surface tension, and C = concentration of surfactant in solution.

The values of the surface pressure at the cmc (Π_{cmc}) were obtained by using the following equation:

$$\Pi_{cmc} = \gamma_0 - \gamma_{cmc} \qquad (12)$$

where γ_0 is the surface tension of the solvent and γ_{cmc} is that of the surfactant solution at the cmc. The surface tension data were utilized to calculate the Gibbs free energy of micellization using cmc in mole fraction units (X_{cmc}) by the expression:

$$\Delta G_m^0 = RT \ln X_{cmc} \qquad (13)$$

Finally, the Gibbs energy of adsorption (ΔG_{ads}^0) was determined from:

$$\Delta G_{ads}^0 = \Delta G_m^0 - \frac{\Pi_{cmc}}{\Gamma_{max}} \qquad (14)$$

where the standard state in the surface phase is defined as the surface covered with a monolayer of surfactant at a surface pressure equal to zero. The dependence of surface tension with the logarithm of the molar concentration of CTAB in LA + E-OH mixtures is shown in Fig 3. The values of cmc, Γ_{max}, A_{min}, and ΔG_{ads}^0 are listed in Table 5.

Table 5. Values of different parameters of surface tension measurements of CTAB surfactant at different concentration in 0.1 m LA + E-OH solution at different temperatures

	T/K			
Surface tension parameters	298.15	303.15	308.15	313.15
cmc / (mol kg^{-1})	0.001118	0.001136	0.001157	0.001169
$\Gamma_{max} .10^6$ (mol m^{-2})	1.32	1.20	1.08	1.05
A_{min} (nm^2 mol^{-1})	1.26	1.39	1.54	1.59
Π_{cmc} (mN m^{-1})	13.61	14.23	14.29	14.75
ΔG_{mic} (kJ mol^{-1})	-24.48	-24.85	-25.21	-25.59
ΔG_{ad} (kJ mol^{-1})	-34.77	-36.74	-38.42	-39.69
ΔG_{min} (kJ mol^{-1})	25.71	27.58	28.90	28.34

Table 6. δ(ppm) values of CTAB protons from ^{1}H NMR spectrum in absence and presence of lauric acid under different experimental conditions.

	N^+-(CH_3) or -COOH	**α-CH_2**	**β-CH_2**	**γ–CH_2**	**Bulk-CH_2**	**Terminal-CH_3**
CTAB	3.03	3.25	1.65	1.42	1.24	0.85
Lauric Acid	11.0	2.32	1.66	-	1.32	0.95
CTAB + Ethanol	3.01	3.01	1.56	1.40	1.12	0.75
CTAB + Ethanol + Lauric acid	2.98	3.12	1.55	1.38	1.19	0.81

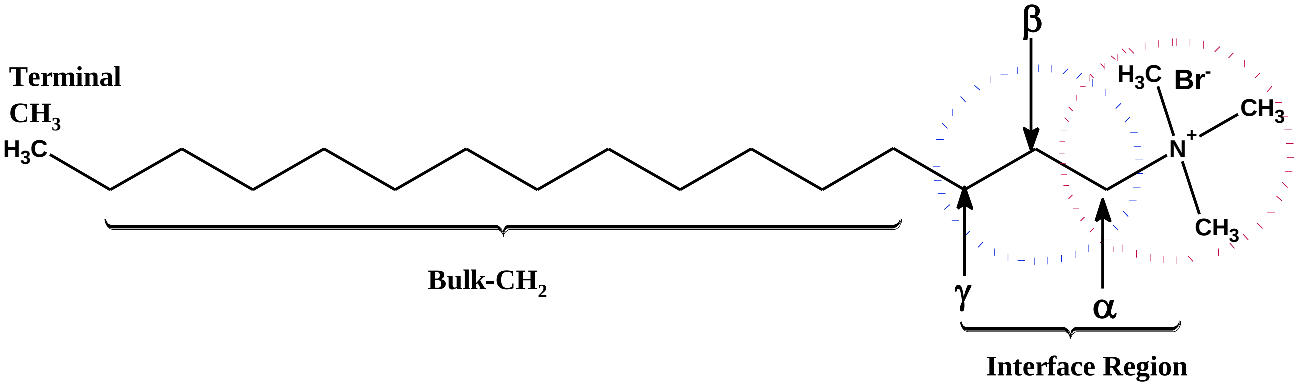


Figure 4. The structural features and substitutions of cationic surfactant CTAB molecule.

The cmc values acquired from the surface tension measurements are in good agreement with those obtained from volumetric and conductometric measurements. It is observed that the higher $\Gamma_{\max}$ values indicate the higher surface activity. The obtained decreased $\Gamma_{\max}$ values in Table 5 suggested of the fact that the system involves both electrostatic as well as hydrophobic interactions [44]. The ΔG^0_{ads} values obtained are negative which indicates the adsorption of amphiphilic molecules at the air/mixture interface takes place spontaneously. The negative trend in ΔG^0_{ads} values becomes more with rise in temperature. This specifies that the dehydration of the hydrophilic group is required for the process of the adsorption to happen. As the surfactant molecule is not so much hydrated and it needs the small amount of energy for the process of adsorption to happen at increasing temperatures [45]. In addition, the observed negative ΔG^0_{ads} values are greater than the corresponding ΔG^0_m values. This signifies that when the micelle is formed work needs to be done to transfer the surfactant molecules in the monomeric form at the surface to the micellar state in the mixed solvent media [46]. The molar Gibbs energy at the maximum adsorption attained at cmc, $\Delta G_{\min}$, is given by:

$$\Delta G_{\min} = \gamma_{cmc} A_{\min} N_A \tag{15}$$

where γ_{cmc} = surface tension at cmc [47]. The lower the value of Gibbs energy of the given surface with fully adsorbed amphiphile molecules. The minimum value of the Gibbs energy indicates that the more thermodynamically stable is the surface formed.

3.4. ^1H NMR spectroscopic data

It is well known that the additives can solubilize and/or penetrate into the various micellar phases hydrophilic (Gouy-Chapman layer, and Stern layer) and hydrophobic (Palisade layer, and core) regions through hydrophobic, hydrophilic, electrostatic, and hydrogen bonding interactions [48]. These interactions depend on the nature and structure of additives. The micellar core behaves like an organic phase and the hydrophobic forces play in important role in the solubilization process [49]. Bunton and his co-workers used NMR technique and suggested that the some of the water solvating the surfactant head group was lost on micellization [50]. The nature of proton and their chemical shift values depends on the chemical environment of the molecules. Therefore, to see in sight into the micellization and /or solubilization of lauric acid with CTAB, a series of ^{1}H NMR spectra were recorded for pure CTAB, lauric acid, CTAB + ethanol, and CTAB + lauric acid + ethanol. The corresponding chemical shifts values are summarized in Table 6. The ^{1}H NMR signals of CTAB (Fig. 4) five different protons (ca. 0.85 , 1.24, 3.25, 1.65, 1.42, and 3.03 ppm to the terminal hydrophobic CH_3-, bulk ($–(CH_2)_{12}–$), α-CH_2-, β-CH_2-, γ-CH_2- and polar head N^+-$(CH_3)_3$, respectively, shifted to the more upfield region (Table 7 in presence of lauric acid (δ= 11.0, 2.32, 1.66, 1.32 and 0.95 ppm for -COOH, α-CH_2-, β-CH_2-, bulk ($–(CH_2)_{82}–$), and terminal CH_3-). These chemical shifts can be attributed in terms of the solubilization of lauric acid into the cationic CTAB micelles. The polar head group (-COOH and/or -COO^-) of lauric acid orients toward the water rich region of micelles, i.e., Stern layer.

4. CONCLUSIONS

The present work investigates the study of interactions and micellization of CTAB in an non-aqueous media, E-OH + LA mixtures. A variety of parameters like $\Gamma_{\max}$, A_{min}, $\Delta G_{\min}$, Π_{cmc}, ΔG^o_{mic}, ΔH^o_{mic}, and ΔS^o_{mic}, the change of the apparent molar volumes at infinite dilution, V_ϕ^o, apparent molar volumes at the cmc, V_ϕ^{cmc}, and apparent molar volumes upon micellization, ΔV_ϕ^m at different temperatures were estimated by tensitometric, volumetric and conductivity measurements.^{1H}NMR data shows that the intermolecular interactions (ion-pair between positive head group (-$N^+(CH_3)_3$) of CTAB and negative -COO^- of lauric acid) exist in the Stern layer (hydrophilic region) of CTAB. An increasing negative trend is observed in ΔG_m^o, and ΔH_m^o values may be due to the electrostatic interactions because of different additives present in mixing environment. $T\Delta S_m^o$ values are greater than the ΔH_m^o values as estimated in the present study suggesting that the process of micellization is generally by the entropy gain. Moreover, V_ϕ, $\Delta V_\phi^{\mathrm{m}}$ and $\Delta V_\phi^{\mathrm{m}}$ values are positive which specifies the poor accommodation of additive molecules in the cavities of solvent. The observed behaviors of these parameters may be attributed in the light of various interactions taking place between the components of the mixtures under the applied experimental conditions.

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Potential Conflicts of Interest

No conflicts of interest among the Authors for financial or non-financial matters.

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