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Experimental and theoretical investigation of micellization behavior of sodium dodecyl sulfate with cetyltrimethylammonium bromide in aqueous/urea solution at various temperatures

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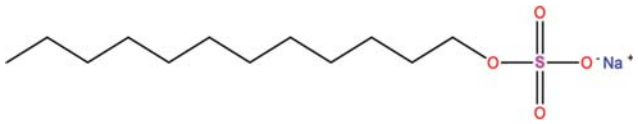
Abstract−Mixed micelle formation behavior of cationic surfactant-cetyltrimethylammonium bromide (CTAB) and anionic surfactant sodium dodecyl sulfate (SDS) in aqueous as well as in urea medium from 303.15 K to 323.15 K at 5 K interval was carried out by conductometric method. The differences between the experimental values of critical micelle concentrations (*cmc*) and ideal critical micelle concentrations (cmc^{id}) illustrate the interaction between the amphiphiles studied. The values of micellar mole fraction (X_1^{Rub} (Rubingh), X_1^M (Motomura), X_1^{Rod} (Rodenas) and X_1^{id} (ideal) of surfactant CTAB determined by different proposed models and outcome indicate high involvement of CTAB in SDS-CTAB mixed micellization, which enhance by means of the augment of mole fraction of CTAB. The negative value of interaction parameter (β) showed an attractive interaction involving CTAB and SDS. Activity coefficients were less than unity in all case, which also reveals the presence of interaction between CTAB & SDS. The negative ΔG_m^0 values imply the spontaneous mixed micellization phenomenon. The attained values of ΔH_m^0 were positive at inferior temperature, while negative at superior temperature. The negative ΔH_m^0 values in urea (NH_2CONH_2) medium illustrate exothermic micellization process. The magnitudes of ΔS_m^0 were positive in almost all cases. The excess free energy of mixed micelle formation (ΔG_{ex}) was found to be negative, which indicates the stability of mixed micelle as compared to the individual's components micelles.

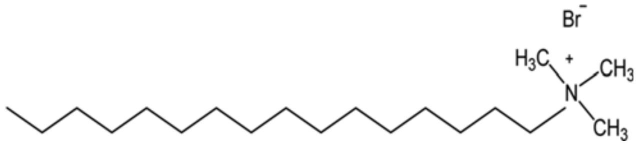
Keywords: Sodium Dodecyl Sulfate (SDS), Mixed Micelle, Interaction Parameter, Activity Coefficient, Thermodynamic Parameter

INTRODUCTION

A delicate balance between hydrophobic and hydrophilic interaction is the prime cause of formation of micellar aggregation of an amphiphilic molecule in a solvent [1]. In H_2O, amphiphilic substances spontaneously form aggregates of definite structure beyond a certain concentration, which is termed as critical micelle concentration (*cmc*) [2,3]. The micelle, micellar aggregates, enhance the solubility of hydrophobic compounds by changing their microenvironment, such as polarity and viscosity [4]. So surfactants are widely used in many processes of interest in different applied field, e.g., industrial, commercial and technological applications [5-10]. In these cases mixed surfactant systems are superior to single surfactant systems because of their stable electrical structure with better micellar property [15-17]. In recent years, different types of mixed micelles formation by the combination of different surfactant for example cationic-cationic [18,19], cationic-anionic [20], cationic-nonionic [21,22], anionic-anionic [23,24], anionic-nonionic [25,26], nonionic-nonionic [27,28] have been studied. Though literature survey reveals the existence of many investigations on the mixed micellization, to the best of our understanding the mixed micellization formation between SDS & CTAB (Scheme 1 and 2) in attendance of aqueous solution of urea at different temperatures has not been studied yet. As a result, in diverse industrial applications of surfactants (pharmaceutical, petrochemical, food industry, etc.), a lesser amount of binary surfactant mixture is needed than the quantity of the more hydrophobic constituent [18-28].



Scheme 1. Molecular structure of sodium dodecyl sulfate (SDS).



Scheme 2. Molecular structure of cetyltrimethylammonium bromide (CTAB).

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The solution possessions of amphiphiles are responsive to the attendance of additives [2,8]. The values of *cmc* are obtained to rely on the kind and environment of additives [8]. To optimize the appliances of amphiphile mixed systems, it is, consequently, significant to understand the interchange of forces that administer the aggregation phenomena in the occurrence of additives [8]. Urea can influence the molecular aggregation of surfactants either by direct or by indirect mechanism [11-13]. In the first case, urea replaces water in the solvent shell around hydrophobic components by forming H-bonding with water and enhanced the solubility of the hydrophobic components. In the second case, urea enhances the solubility of hydrophobic components in the bulk solution by disrupting the three-dimensional network of the water molecules [14]. In most of the studies moderate to high concentration of urea solution (1M-8M) was used as additive. In this study, we performed experiments at lower concentration of urea to investigate the effect of urea on critical micelle concentration (*cmc*), degree of counterion dissociation (g), activity coefficient ($f_1^{Rub}/f_1^{M}/f_1^{Rod}$ and $f_2^{Rub}/f_2^{M}/f_2^{Rod}$), micellar mole fraction ($X_1^{Rub}/X_1^{M}/X_1^{Rod}$), various thermodynamic quantities, e.g., change in standard Gibbs free energy change (ΔG_m^o), standard enthalpy change (ΔH_m^o) and standard entropy change of micellizaiton (ΔS_m^o) as well as excess free energy of micellization (ΔG_{ex}) in absence/presence of different mole fraction of CTAB. The hypothetically proposed models of Clint's, Rubingh's and Rodenas's for micellar mixed systems were used to obtain information about the mixed micellar behavior of SDS and CTAB. The aggregation phenomenon is considerably influenced by the variation of temperature in addition to H-bonding ability of present considered systems.

MATERIALS AND METHODS

1. Materials

Every material employed in this system was of analytical grade and used as procured without further treatment. Sodium dodecyl sulfate (SDS) having purity 0.98 (mass fraction) and cetyltrimethylammonium bromide (CTAB) having purity 0.98 (mass fraction) were purchased from Scharlau Chemie S. A. (E. U.) and BDH (England), respectively. Urea was purchased from Merck (Germany) having purity 0.99 (mass fraction). The entire compounds were dried in a vacuum oven, moreover reserved in vacuum desiccators in the occurrence of P_2O_5 (since it is an excellent H_2O absorbent) for above two days prior to their use. The H_2O content was estimated by the Karl-Fischer technique and was achieved to be below 100 ppm. Double-distilled water having specific conductivity 0.8-1.5 $\mu S\cdot cm^{-1}$ (over temperature range 303.15-323.15 K) was used for every task.

2. Solution Preparation and Conductivity Measurements Technique

We used the conductometric technique for the evaluation of critical micelle concentration (*cmc*) by means of a conductivity meter (model 4510, Jenway, UK), having a dip cell of cell constant 0.97 cm^{-1} (value of cell constant is supplied by company) following the procedure reported in the literature [16,17,19,29-31]. Alternating current (AC) was applied for the conductivity measurements. The precision of conductance measurements via the multimeter was about ±0.5%. At preferred temperature, a 50 $mmol\cdot kg^{-1}$ of SDS solution prepared in water/constant concentration of CTAB/(constant concentration of CTAB+urea) was gradually added to 20 mL of H_2O (in case of without additive)/in attendance of constant concentration of the CTAB/in attendance of (constant concentration of the CTAB+urea) through the help of a high performance micropipette (Glassco, UK). Subsequently, the conductance of the ensuing solution was evaluated following every addition thoroughly mixed properly along with permitting time for becoming constant temperature. The expected temperature of the solution was sustained by means of RM6 Lauda flowing H_2O thermostatted bath of accuracy of ±0.2 K. From the sudden change of the slope in the specific conductivity versus concentration of the surfactant plot the *cmc* of surfactant was obtained. Relative standard uncertainties (u_r) are u_r (C)= 0.02. The relative uncertainty on *cmc* is likely to be around 3%. For all of the calculations and graphical representation in this current study, Microsoft Excel and Origin software were used. Combined expanded uncertainty U_c is $U_c(\kappa)=0.015\ mS\cdot cm^{-1}$ (with 0.95 level of confidence ($k\approx 2$)).

RESULTS AND DISCUSSION

1. *cmc* and *cmc*^{id}

Conductivity measurement is very simple and well known which was employed here to investigate the micellization of pure SDS & CTAB as well as their mixed systems in absence/attendance of NH_2CONH_2 (300 $mmol\cdot kg^{-1}$/700 $mmol\cdot kg^{-1}$). Herein we devised our study in different concentration of urea which is present in human body in order to investigate how these mixtures behave in aqueous/urea medium as well as to get the additional information, e.g., values of thermodynamic quantities for the employed surfactant-surfactant mixtures. The attained outcomes give additional information for amphiphile-amphiphile interaction in order to develop excellent delivery systems in attendance of urea as compared to the aqueous medium. Because, in NH_2CONH_2 medium, *cmc* of individual amphiphiles and their mixed systems further enhances along with spontaneity of studied solution reduces. Surfactant was also used as drug carrier, and also there are many side effects of surfactant due to their concentration employed. By using mixed surfactant as drug carrier we needed at least ten-times less amount of surfactant for that particular propose. Though, there is possibility to precipitate due to coulombic interaction when two oppositely charged surfactants are present at equivalent ratio; for these types of study usually stable mixed micelles are formed when one of the surfactant components is used in excess [32]. The representative specific conductivity versus concentration of surfactant plots in aqueous/300 $mmol\cdot kg^{-1}$ NH_2CONH_2 at 303.15 K are viewed in Fig. 1 for pure SDS and CTAB. The observed *cmc* and *cmc*^{id} values for pure SDS and CTAB and their mixed system in H_2O and aqueous medium of NH_2CONH_2 are presented in Tables 1-3. The obtained value of *cmc* for pure SDS in water was 8.34 $mmol\cdot kg^{-1}$ at 303.15 K, and this value is in fine harmony with previous study [33]. The executed *cmc* value of SDS by Motin et al. [34] with the help of viscosity measurement was 8.50 $mmol\cdot kg^{-1}$ at 303.15 K. Again, Niraula et al. [35] reported the *cmc* value of SDS 9.1 mM and 8.9 mM at 308.15 K by surface tension and viscosity measurement, respectively. The observed *cmc* value of SDS in 300 $mmol\cdot kg^{-1}$ NH_2CONH_2 at 303.15 K was 8.43 $mmol\cdot kg^{-1}$ whereas the re-

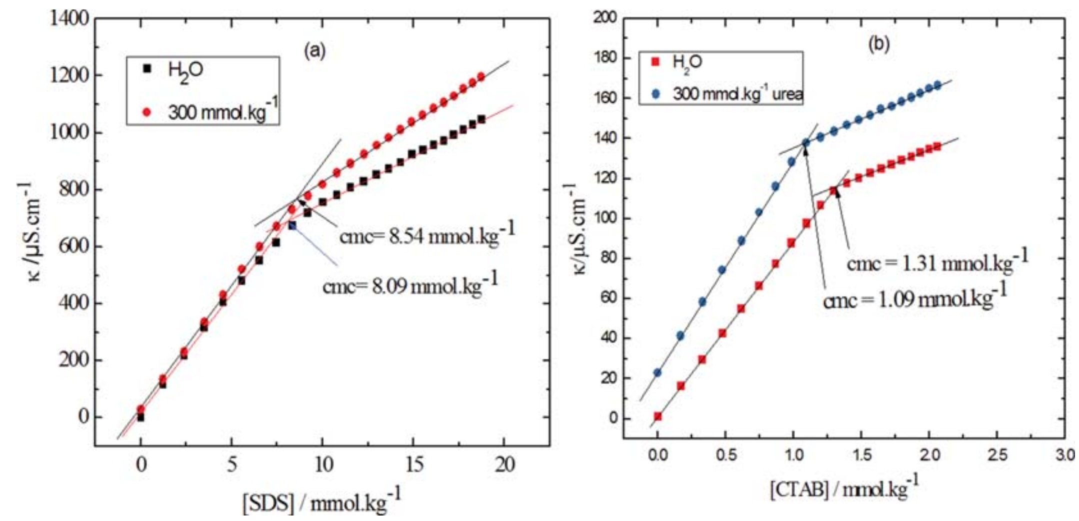

Fig. 1. The representative plots of specific conductivity (κ) versus concentration of surfactant for (a) SDS in aqueous medium and 300 mmol·kg^{-1} (b) CTAB in aqueous medium and 300 mmol·kg^{-1} at 303.15 K.

ported *cmc* value of SDS by Rub et al. was 10.10 mmol·kg^{-1} at same condition [33], and reported values by Ruiz [36] were 8.7 mM and 9.6 mM in 2 M and 4 M urea, respectively. The achieved *cmc* value of pure CTAB in water was 1.31 mmol·kg^{-1} at 303.15 K, and this value is also in good conformity with the values of literature [37-40].

In this study, the obtained *cmc* values of CTAB-SDS mixed system lie between the *cmc* of the individual amphiphiles (Tables 1-3), which suggests an attractive interaction between studied surfactants. Fig. 2 and Tables 1-3 show that *cmc* values of SDS decreased with increasing the mole fraction of CTAB (α_1), indicating that mixed micellization is favored at higher mole fraction of CTAB. Here, the standard uncertainty of the mole faction is dependent on the purity uncertainty and the mass uncertainty (u(α_1)=±0.00001).

The *cmc* values of pure SDS, CTAB and mixtures were observed to be higher in attendance of 300 and 700 mmol·kg^{-1} NH_2CONH_2 solution (Fig. 2 and Tables 1-3). Urea decreases the hydrophobic interaction among the amphiphiles and boosts considerably to be soluble in the hydrocarbon chain in presence of urea and thus tends to enhance the *cmc* value. Again, urea can interact with the hydrophobic part of the surfactant and reduces the hydrophobicity of the surfactant as well as enhances the value of *cmc* [42]. It is also reported that urea breaks up the three-dimensional network of the water, and thus enhances the *cmc* values [41]. The values of *cmc*

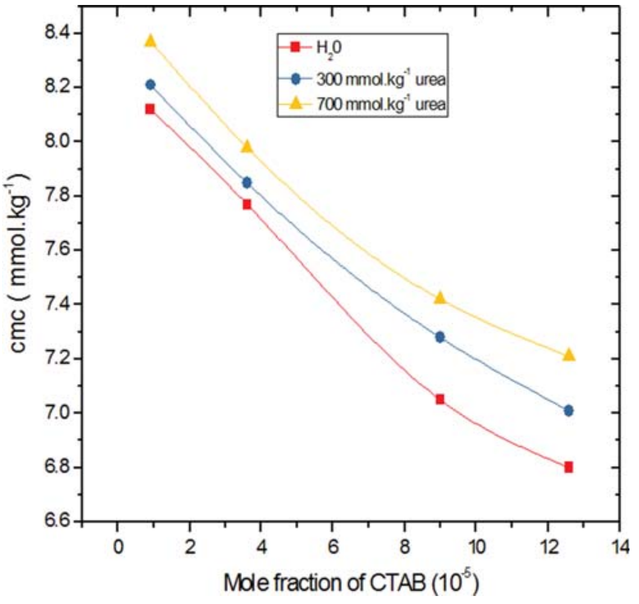

Fig. 2. Representative plot of critical micelle concentration (*cmc*) versus mole fraction of CTAB of SDS-CTAB mixed systems in the absence/attendance of urea at 303.15 K.

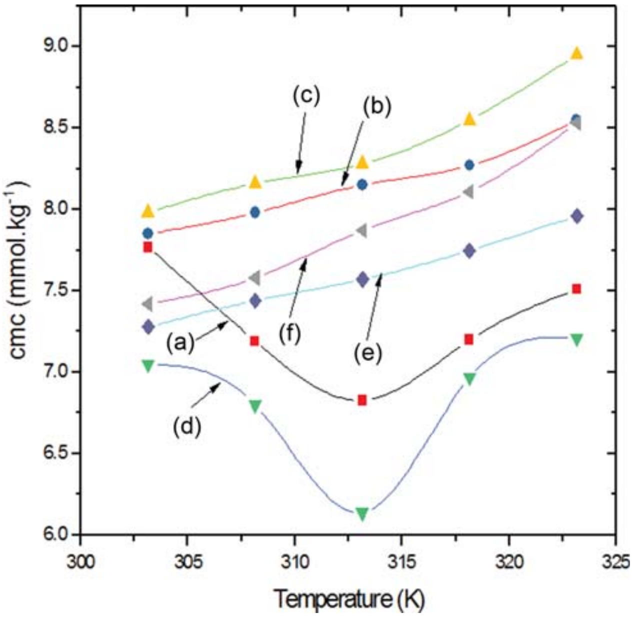

Fig. 3. Variation of *cmc* of SDS + CTAB with temperature at α_1= 3.60×10^{-5} of CTAB in (a) H_2O (b) 300 mmol·kg^{-1} urea (c) 700 mmol·kg^{-1} urea & α_1=8.99×10^{-5} of CTAB in (d) H_2O (e) 300 mmol·kg^{-1} urea (f) 700 mmol·kg^{-1} urea.

for distinct surfactants and their mixture having various mole fractions (α_1) of CTAB at temperature range of 303.15-323.15 K in H_2O and aqueous solution NH_2CONH_2 are listed in Tables 1-3. Normally, the *cmc* of ionic surfactant is reduced at lower temperature and rises at higher temperature [43], and the *cmc* of nonionic surfactant decreases with the rise of temperature [44]. In this current study the *cmc* of pure SDS and SDS-CTAB mixed system in water decreases with the augment of the temperature up to certain level and rises with the further enhancement of temperature (Fig. 3), which is in good harmony with the literature [43]. But we observed that the value of *cmc* of pure surfactants along with their mixtures increases by means of the increase of the temperature in urea (Fig. 3 and Tables 1-3), and such result was also observed in the previous studies [45-47]. The outcome of temperature on the values of *cmc* can be explained through the different modes of hydration surrounding the monomeric amphiphiles as well as pure micelles of amphiphile as well as their mixed micelles. At inferior amphiphile concentration, i.e., at monomeric form of surfactant both

Table 1. The physico-chemical parameters such as critical micelle concentration (*cmc*), ideal values of critical micelle concentration (*cmc*^{id}), degree of dissociation (g), interaction parameter (β), and activity coefficients (f_1 and f_2) for (SDS+CTAB) mixed systems in aqueous solution at various temperatures and concentrations and pressure *p*=0.1 MPa[a]

α_1 (CTAB)	*cmc* (mmol·kg^{-1})	*cmc*^{id} (mmol·kg^{-1})	g	β	$f_1^{Rub}/f_1^{M}/f_1^{Rod}$	$f_2^{Rub}/f_2^{M}/f_2^{Rod}$
T=303.15 K						
0	8.34[b]		0.45			
0.90×10^{-5}	8.12	8.34	0.49	−6.25	0.0026/0.0046/0.0042	0.9966/0.9862/0.9875
3.60×10^{-5}	7.77	8.33	0.46	−6.06	0.0043/0.0042/0.0040	0.9833/0.9840/0.9871
8.99×10^{-5}	7.05	8.32	0.44	−6.48	0.0052/0.0035/0.0037	0.9382/0.9918/0.9834
12.59×10^{-5}	6.80	8.31	0.50	−6.48	0.0061/0.0032/0.0035	0.9197/0.9998/0.9995
1.0	1.23		0.31			
T=308.15 K						
0	8.09		0.47			
0.90×10^{-5}	7.56	8.08	0.55	−7.51	0.0011/0.0046/0.0042	0.9822/0.9451/0.9461
3.60×10^{-5}	7.19	8.07	0.54	−6.95	0.0026/0.0042/0.0040	0.9611/0.9331/0.9348
8.99×10^{-5}	6.80	8.06	0.53	−6.64	0.0046/0.0037/0.0038	0.9347/0.9612/0.9583
12.59×10^{-5}	6.39	8.06	0.56	−6.89	0.0049/0.0033/0.0036	0.9006/0.9717/0.9541
1.0	1.31		0.32			
T=313.15 K						
0	8.16		0.46			
0.90×10^{-5}	7.26	8.15	0.52	−8.51	0.0007/0.0034/0.0031	0.9578/0.9019/0.9032
3.60×10^{-5}	6.83	8.15	0.51	−7.78	0.0018/0.0030/0.0029	0.9278/0.8882/0.8903
8.99×10^{-5}	6.14	8.14	0.51	−7.79	0.0029/0.0024/0.0026	0.8689/0.8961/0.8848
12.59×10^{-5}	6.01	8.13	0.53	−7.58	0.0038/0.0023/0.0025	0.8581/0.9555/0.9318
1.0	1.41		0.34			
T=318.15 K						
0	8.63		0.45			
0.90×10^{-5}	7.66	8.62	0.54	−8.54	0.0006/0.0033/0.0033	0.9564/0.9002/0.9001
3.60×10^{-5}	7.20	8.61	0.52	−7.82	0.0018/0.0029/0.0031	0.9259/0.8871/0.8833
8.99×10^{-5}	5.97	8.60	0.50	−8.47	0.0023/0.0020/0.0026	0.8175/0.8431/0.8032
12.59×10^{-5}	5.81	8.60	0.51	−8.28	0.0031/0.0019/0.0025	0.8035/0.9076/0.8356
1.0	1.49		0.36			
T=323.15 K						
0	8.97		0.45			
0.90×10^{-5}	7.83	8.96	0.55	−8.83	0.0006/0.0053/0.0051	0.9471/0.8801/0.8804
3.60×10^{-5}	7.51	8.95	0.53	−7.83	0.0017/0.0049/0.0049	0.9276/0.8665/0.8668
8.99×10^{-5}	7.21	8.95	0.52	−7.24	0.0035/0.0045/0.0047	0.9082/0.8812/0.8787
12.59×10^{-5}	7.02	8.95	0.54	−7.11	0.0043/0.0043/0.0046	0.8941/0.8958/0.8887
1	1.62		0.37			

[a] Standard uncertainties (u) are u(T)=0.10 K, and u(p)=10 kPa (level of confidence=0.68). Relative standard uncertainties (u_r) are u_r(*cmc*/*cmc*^{id})=±3%, u_r(g)=±3%, $u_r(\beta)$=±3%, $u_r(f_1^{Rub}/f_1^{M}/f_1^{Rod})$=±4% and $u_r(f_2^{Rub}/f_2^{M}/f_2^{Rod})$=±4%

[b] Reference [33]

hydrophobic and hydrophilic hydrations are feasible, whereas only hydrophilic hydration is probable in case of assembled surfactant. These types of hydrations are expected to be decreased by way of enhancing of temperature. The reducing behavior of hydrophilic hydration tends to enhance the aggregation process, whereas lessen hydrophobic hydration through rise of temperature disservices the aggregation of surfactant [4,15]. Thus, the magnitude of both hydration phenomena may decide whether the *cmc* values enhance or reduce at a certain temperature range. In this study the second factor plays a dominating role over the first one within the temperature range studied.

The ideal and non-ideal behavior of the mixture of the amphiphiles can be clarified by pseudo-phase separation model. The ideal *cmc* value (cmc^{id}) of the binary mixture of the amphiphiles can be evaluated by using Clint's equation from the known value of *cmc* of the individual amphiphiles [48]. Clint's equation is as follows:

$$\frac{1}{cmc}=\frac{\alpha_1}{f_1^{Rub}cmc_1}+\frac{\alpha_2}{f_2^{Rub}cmc_2} \quad (1)$$

In Eq. (1), α_1 and α_2 express the mole fraction of CTAB and SDS,

Table 2. The physico-chemical parameters such as critical micelle concentration (*cmc*), ideal values of critical micelle concentration (cmc^{id}), degree of dissociation (g), interaction parameter (β), and activity coefficients (f_1 and f_2) for (SDS+CTAB) mixed systems in aqueous solution of 300 mmol·kg^{-1} urea at various temperatures and concentrations and pressure p=0.1 MPa[a]

α_1 (CTAB)	*cmc*	cmc^{id}	g	β	$f_1^{Rub}/f_1^{M}/f_1^{Rod}$	$f_2^{Rub}/f_2^{M}/f_2^{Rod}$
	(mmol·kg^{-1})					
T=303.15 K						
0	8.43		0.49			
0.90×10^{-5}	8.21	8.42	0.52	−6.03	0.0032/0.0068/0.0059	0.9968/0.9843/0.9859
3.60×10^{-5}	7.85	8.42	0.54	−5.87	0.0052/0.0063/0.0056	0.9834/0.9737/0.9789
8.99×10^{-5}	7.28	8.41	0.53	−6.01	0.0069/0.0056/0.0052	0.9506/0.9747/0.9833
12.59×10^{-5}	7.01	8.41	0.51	−6.06	0.0081/0.0051/0.0051	0.9318/0.9985/0.9985
1	1.02		0.27			
T=308.15 K						
0	8.54		0.48			
0.90×10^{-5}	8.33	8.53	0.52	−6.02	0.0031/0.0064/0.0059	0.9971/0.9861/0.9868
3.60×10^{-5}	7.98	8.52	0.55	−5.85	0.0051/0.0058/0.0056	0.9847/0.9784/0.9799
8.99×10^{-5}	7.44	8.52	0.54	−5.97	0.0069/0.0051/0.0052	0.9549/0.9904/0.9856
12.59×10^{-5}	7.16	8.51	0.51	−6.04	0.0079/0.0047/0.0051	0.936/0.9986/0.9987
1	1.09		0.27			
T=313.15 K						
0	8.82		0.49			
0.90×10^{-5}	8.45	8.81	0.52	−6.71	0.0019/0.0063/0.0058	0.9921/0.9681/0.9689
3.60×10^{-5}	8.15	8.81	0.59	−6.10	0.0044/0.0058/0.0056	0.9801/0.9659/0.9675
8.99×10^{-5}	7.57	8.80	0.57	−6.17	0.0063/0.0051/0.0053	0.9471/0.9715/0.9668
12.59×10^{-5}	7.32	8.80	0.49	−6.17	0.0074/0.0047/0.0051	0.9303/0.9985/0.9848
1	1.15		0.28			
T=318.15 K						
0	9.25		0.50			
0.90×10^{-5}	8.72	9.24	0.56	−7.14	0.0014/0.0058/0.0057	0.9861/0.9531/0.9535
3.60×10^{-5}	8.27	9.23	0.60	−6.63	0.0033/0.0053/0.0054	0.9647/0.9375/0.9365
8.99×10^{-5}	7.75	9.22	0.59	−6.44	0.0055/0.0046/0.0051	0.9337/0.9559/0.9449
12.59×10^{-5}	7.56	9.22	0.50	−6.32	0.0069/0.0044/0.0049	0.9217/0.9935/0.9715
1	1.21		0.29			
T=323.15 K						
0	9.61		0.52			
0.90×10^{-5}	8.98	9.60	0.56	−7.35	0.0012/0.0057/0.0057	0.9824/0.9447/0.9448
3.60×10^{-5}	8.55	9.59	0.61	−6.72	0.0031/0.0052/0.0054	0.9622/0.9323/0.9304
8.99×10^{-5}	7.96	9.59	0.58	−6.58	0.0052/0.0045/0.0051	0.9273/0.9441/0.9301
12.59×10^{-5}	7.75	9.58	0.54	−6.51	0.0063/0.0043/0.0049	0.9111/0.9793/0.9525
1	1.28		0.29			

[a] Standard uncertainties (u) are u(T)=0.10 K, u(urea)=2 mmol·kg^{-1} and u(p)=10 kPa (level of confidence=0.68). Relative standard uncertainties (u_r) are u_r(*cmc*/cmc^{id})=±3%, u_r(g)=±3%, $u_r(\beta)$=±3%, $u_r(f_1^{Rub}/f_1^{M}/f_1^{Rod})$=±4% and $u_r(f_2^{Rub}/f_2^{M}/f_2^{Rod})$=±4%

respectively, in the mixed system. Again, f_1^{Rub} and f_2^{Rub} are the activity coefficients of CTAB & SDS in the mixed micelles.

During ideal mixing, i.e., in case of no net interaction, $f_1^{Rub}=f_2^{Rub}=1$, Clint's equation takes the form as follows [49]:

$$\frac{1}{cmc^{id}}=\frac{\alpha_1}{cmc_1}+\frac{\alpha_2}{cmc_2} \tag{2}$$

Any deviation of the experimentally determined *cmc* values of the mixtures from the ideal *cmc* (cmc^{id}) indicates the mutual interaction between the surfactants. When the deviation is positive, $cmc^{id}<cmc$, interaction is of antagonistic nature and negative variance, $cmc^{id}>cmc$, revealing the synergistic interaction. In this study, the experimental values of *cmc* were obtained to be lower than cmc^{id} (Tables 1-3), which indicates synergistic interactions between the studied amphiphile. The significant reduction in *cmc* is due to enhanced hydrophobicity (interaction between the amphiphiles, SDS and CTAB). The increased electrostatic stabilization of the mixed micelle reduces hydrophilicity. Both combined effects mentioned above reduce HLB (hydrophile-lipophile balance) value significantly for amphiphile mixture. The magnificence of cmc^{id} of the

Table 3. The physico-chemical parameters such as critical micelle concentration (*cmc*), ideal values of critical micelle concentration (cmc^{id}), degree of dissociation (g), interaction parameter (β), and activity coefficients (f_1 and f_2) for (SDS+CTAB) mixed systems in aqueous solution of 700 $mmol\cdot kg^{-1}$ urea at various temperatures and concentrations and pressure p=0.1 MPa[a]

α_1 (CTAB)	*cmc*	cmc^{id}	g	β	$f_1^{Rub}/f_1^M/f_1^{Rod}$	$f_2^{Rub}/f_2^M/f_2^{Rod}$
	($mmol\cdot kg^{-1}$)					
T=303.15 K						
0	8.60		0.51			
0.90×10^{-5}	8.37	8.59	0.55	−6.01	0.0032/0.0071/0.0068	0.9966/0.9837/0.9842
3.60×10^{-5}	7.98	8.59	0.56	−5.88	0.0052/0.0066/0.0065	0.9821/0.9705/0.9712
8.99×10^{-5}	7.42	8.58	0.51	−5.97	0.0073/0.0058/0.0061	0.9504/0.9749/0.9709
12.59×10^{-5}	7.21	8.57	0.49	−5.92	0.0087/0.0052/0.0058	0.9366/0.9983/0.9933
1	0.99		0.28			
T=308.15 K						
0	8.84		0.52			
0.90×10^{-5}	8.52	8.83	0.56	−6.42	0.0023/0.0067/0.0062	0.9941/0.9743/0.9752
3.60×10^{-5}	8.16	8.82	0.58	−6.01	0.0048/0.0061/0.0059	0.9799/0.9671/0.9685
8.99×10^{-5}	7.58	8.81	0.55	−6.08	0.0068/0.0053/0.0055	0.9469/0.9767/0.9714
12.59×10^{-5}	7.32	8.81	0.53	−6.08	0.0081/0.0049/0.0053	0.9296/0.9825/0.9908
1	1.05		0.29			
T=313.15 K						
0	8.96		0.52			
0.90×10^{-5}	8.70	8.95	0.55	−6.19	0.0027/0.0069/0.0064	0.9961/0.9809/0.9816
3.60×10^{-5}	8.28	8.94	0.61	−6.03	0.0046/0.0062/0.0061	0.9803/0.9653/0.9661
8.99×10^{-5}	7.87	8.93	0.55	−5.83	0.0075/0.0056/0.0058	0.9592/0.9894/0.9853
12.59×10^{-5}	7.56	8.93	0.54	−5.93	0.0083/0.0052/0.0056	0.9396/0.9834/0.9951
1	1.11		0.29			
T=318.15 K						
0	9.45		0.52			
0.90×10^{-5}	8.98	9.44	0.56	−6.88	0.0017/0.0068/0.0064	0.9893/0.9599/0.9606
3.60×10^{-5}	8.55	9.43	0.62	−6.41	0.0038/0.0062/0.0061	0.9706/0.9447/0.9454
8.99×10^{-5}	8.11	9.42	0.58	−6.12	0.0066/0.0055/0.0057	0.9471/0.9659/0.9616
12.59×10^{-5}	7.82	9.41	0.56	−6.14	0.0076/0.0051/0.0055	0.9291/0.9874/0.9742
1	1.17		0.30			
T=323.15 K						
0	9.77		0.53			
0.90×10^{-5}	9.31	9.76	0.57	−6.84	0.0017/0.0076/0.0072	0.9902/0.9613/0.9619
3.60×10^{-5}	8.95	9.75	0.62	−6.23	0.0041/0.0071/0.0068	0.9764/0.9508/0.9517
8.99×10^{-5}	8.53	9.75	0.59	−5.95	0.0071/0.0063/0.0065	0.9558/0.9655/0.9631
12.59×10^{-5}	8.21	9.74	0.57	−6.01	0.0079/0.0059/0.0063	0.9373/0.9764/0.9671
1	1.25		0.31			

[a] Standard uncertainties (u) are u(T)=0.10 K, u(urea)=2 $mmol\cdot kg^{-1}$ and u(p)=10 kPa (level of confidence=0.68). Relative standard uncertainties (u_r) are $u_r(cmc/cmc^{id})=\pm3\%$, $u_r(g)=\pm3\%$, $u_r(\beta)=\pm3\%$, $u_r(f_1^{Rub}/f_1^M/f_1^{Rod})=\pm4\%$ and $u_r(f_2^{Rub}/f_2^M/f_2^{Rod})=\pm4\%$

mixed systems is higher in NH_2CONH_2 medium, which further increases with the increase of the concentration of urea.

2. Degree of Counterion Dissociation (g)

Changes of slopes were observed in the specific conductivity versus concentration of surfactant plots for pure and mixed amphiphilic systems. The degree of counterion dissociation (g) was evaluated utilizing the relationship $g=S_2/S_1$, where S_1 and S_2 are the slopes in pre-micellar and post-micellar regions, respectively [40, 50,51]. Tables 1-3 show the values of degree of counterion dissociation (g) for individual surfactants as well as their mixture in H_2O and NH_2CONH_2 medium at different temperatures. Literature surveys revealed the quantitative estimation of g value conductometrically, e.g., Buckingham and co-workers [52] which were well assured by Kale et al. [53] and also by Bandhopadhyay and Moulik [54] who determined g value utilizing ion-selective membrane electrode. Therefore, alike *cmc*, value of counterion dissociation (g) also depends on experimental condition [55]. The value of g is a significant factor in micelles stability [56] and also in the evolution and synergism of spherical- to rod-like micelle structures [57]. Tables 1-3 illustrate that degree of counterion dissociation (g) enhances with the increment of the temperature in almost all cases, and so micellar growth decreases, which is in good agreement with the literature [58,59]. In the current study, we observed that the value of g decreased up to a certain concentration of CTAB and then increased again in aqueous medium, while value of g increased to a certain concentration of CTAB and then decreased again in the presence of urea (Tables 1-3). In presence of urea the value of g increases which confirms that the urea molecules replace water molecules from hydrated polar head portions (Tables 2-3). The mass of NH_2CONH_2 molecules is larger compared to H_2O molecules, so the presence of urea decreases the electrostatic attraction of the counterions at the surface of the micelles. So counterion binding at the surface of the micelles is reduced.

3. Micellar Mole Fraction of the Mixtures Water/Urea Medium

Clint's model neglects the interaction amid the constituents present in the mixed micelle. According to this model, the components are non-interacting and do not influence the micellization of other components. Taking all of the points under consideration, Holland and Rubingh proposed a model for non-ideal mixed systems [60]. Micellar composition of the mixtures can be estimated by solving the subsequent equation iteratively:

$$\frac{(X_1^{Rub})^2\ln[(\alpha_1 cmc/X_1^{Rub}cmc_1)]}{(1-X_1^{Rub})^2\ln[(1-\alpha_1)cmc/(1-X_1^{Rub})cmc_2]}=1 \tag{3}$$

where X_1^{Rub} is the micellar mole fraction of CTAB in the mixed system, and cmc_1, cmc_2 & *cmc* are the experimentally determined values of *cmc* of CTAB, SDS and their mixed system, respectively. The values of X_1^{Rub} were further utilized to get the value of interaction parameter (β) from the following equation:

$$\beta=\frac{\ln(cmc\,\alpha_1/cmc_1X_1^{Rub})}{(1-X_1^{Rub})^2} \tag{4}$$

The non-ideal behavior of the mixed micelle can be estimated from the value of interaction parameter, β. Negative values of β indicate synergistic interaction, whereas positive values indicate antagonistic interaction. When the value of interaction parameter β becomes zero, then there is no interaction between the components that means ideal mixing of the amphiphiles. To compare the value obtained from the Rubingh method, the earlier result was further treated by Motomura's theory [61]. Motomura considers the dissociation of the component and micellization takes place under thermodynamic view of point. According to this model, micellar mole fraction can be calculated from the following equation:

$$X_1^M=\overline{\alpha_1}-\frac{(\overline{\alpha_1}\,\overline{\alpha_2}/\overline{cmc})(\partial\overline{cmc}/\partial\overline{\alpha_1})_{T,P}}{1-\dfrac{\delta\nu_{1,c}\cdot\nu_{2,d}}{\nu_{1,c}\nu_2\overline{\alpha_1}+\nu_{2,d}\nu_1\overline{\alpha_2}}} \tag{5}$$

where $\nu_{1,c}$ indicates that component 1 (CTAB) dissociates into a-ions plus c-ions and $\nu_{2,d}$ implies component 2 (SDS) dissociate into b-ions plus d-ions (where c in addition to d-ions represent the counterparts of the corresponding constituent). Where

$$\overline{cmc}=(\nu_1\alpha_1+\nu_2\alpha_2)cmc, \text{ and} \tag{6}$$

$$\overline{\alpha_i}=\frac{\nu_i\alpha_i}{\nu_1\alpha_1+\nu_2\alpha_2} \quad (i=1, 2) \tag{7}$$

Here $\overline{\alpha_i}$ and ν_i stand for the bulk mole fraction and amount of the ions produced by i^{th} constituent respectively. δ is the Kronecker delta having magnitude 1 (for similar counterions) and 0 (for unlike counterions).

The results were then additionally studied utilizing a different model suggested by Rodenas [62], which is derived from Lange's model [63]. The micellar mole fraction of amphiphiles can be calculated from the known value of *cmc* of the mixture at different stoichiometric mole fraction by utilizing the following reaction:

$$X_1^{Rod}=-(1-\alpha_1)\alpha_1\frac{d\ln cmc}{d\alpha_1}+\alpha_1 \tag{8}$$

The micellar mole fraction in ideal state (X_1^{id}) of CTAB in the mixed systems can be executed utilizing the subsequent Eq. (9):

$$X_1^{id}=\frac{\alpha_1 cmc_2}{\alpha_1 cmc_2+\alpha_2 cmc_1} \tag{9}$$

The values of micellar mole fraction of CTAB, X_1^{Rub}, X_1^M, X_1^{Rod} and X_1^{id} were estimated by all proposed model mentioned above. X_1^{Rub}, X_1^M, X_1^{Rod} and X_1^{id} are noticeably more than respective α_1 of CTAB in all cases studied (Table 4). Herein, the values of X_1^{Rub}, X_1^M, X_1^{Rod} and X_1^{id} of CTAB-SDS mixed systems increase with the increase of CTAB (Table 4). The values of X_1^{id} always increase with the rise of α_1 of CTAB in water as well as in urea (Table 4). The value of X_1^{id} is always less than X_1^{Rub}, X_1^M and X_1^{Rod} which indicates the attractive interaction between the amphiphiles in the mixed micelle. These values (X_1^{Rub}, X_1^M and X_1^{Rod}) do not show any regular trend with temperature (Table 4). The addition of urea in a solution of CTAB and SDS mixture, the X_1^{Rub}, X_1^M as well as X_1^{Rod} values were found to be low comparative to aqueous solution. The reason for the wake of this behavior is owing to the growth in the repulsions among the surfactant (CTAB)-surfactant (SDS) head groups. As a result, interaction amid constituents reduces in presence of urea and is accountable for the increase in the *cmc* as well as reducing the X_1^{Rub}, X_1^M as well as X_1^{Rod} values (Table 4).

Table 4. Values of micellar mole fraction (X_1) of CTAB for SDS+CTAB mixed systems at various temperatures and concentrations and pressure p=0.1 MPa[a]

α_1 (CTAB)	$X_1^{id}\times10^{-4}$	$X_1^{Rub}/X_1^{M}/X_1^{Rod}$	$X_1^{id}\times10^{-4}$	$X_1^{Rub}/X_1^{M}/X_1^{Rod}$	$X_1^{id}\times10^{-4}$	$X_1^{Rub}/X_1^{M}/X_1^{Rod}$	$X_1^{id}\times10^{-4}$	$X_1^{Rub}/X_1^{M}/X_1^{Rod}$	$X_1^{id}\times10^{-4}$	$X_1^{Rub}/X_1^{M}/X_1^{Rod}$
	T=303.15 K		T=308.15 K		T=313.15 K		T=318.15 K		T=323.15 K	
SDS+CTAB mixture in aqueous solution										
0.90×10^{-5}	0.61	0.023/0.013/0.014	0.56	0.049/0.011/0.012	0.52	0.071/0.014/0.015	0.52	0.072/0.014/0.014	0.50	0.079/0.008/0.009
3.60×10^{-5}	2.44	0.053/0.054/0.056	2.22	0.076/0.048/0.049	2.08	0.098/0.058/0.060	2.09	0.099/0.060/0.056	1.99	0.098/0.034/0.034
8.99×10^{-5}	6.09	0.099/0.148/0.141	5.55	0.101/0.123/0.123	5.20	0.134/0.160/0.150	5.21	0.154/0.180/0.139	4.98	0.115/0.088/0.085
12.59×10^{-5}	8.53	0.114/0.215/0.197	7.77	0.123/0.187/0.172	7.28	0.142/0.229/0.210	7.29	0.163/0.258/0.195	6.97	0.126/0.127/0.120
SDS+CTAB mixture in 300 mmol·kg^{-1} aqueous solution of urea										
0.90×10^{-5}	0.74	0.023/0.011/0.012	0.71	0.022/0.011/0.012	0.69	0.034/0.011/0.011	0.69	0.044/0.011/0.011	0.68	0.049/0.011/0.011
3.60×10^{-5}	2.98	0.053/0.044/ 0.049	2.82	0.051/0.045/0.047	2.76	0.057/0.043/0.045	2.75	0.074/0.046/0.045	2.70	0.076/0.046/0.044
8.99×10^{-5}	7.43	0.092/0.114/0.122	7.04	0.088/0.120/0.116	6.89	0.094/0.117/0.112	6.86	0.103/0.124/0.113	6.75	0.107/0.123/0.110
12.59×10^{-5}	10.39	0.108/0.172/0.171	9.86	0.105/0.175/0.163	9.65	0.108/0.169/0.157	9.62	0.114/0.177/0.159	9.45	0.120/0.177/0.153
SDS+CTAB mixture in 700 mmol·kg^{-1} aqueous solution of urea										
0.90×10^{-5}	0.78	0.024/0.011/0.011	0.76	0.031/0.011/0.012	0.73	0.025/0.010/0.011	0.73	0.040/0.010/0.011	0.70	0.038/0.009/0.009
3.60×10^{-5}	3.13	0.055/0.044/0.045	3.03	0.058/0.045/0.047	2.91	0.057/0.043/0.044	2.91	0.068/0.042/0.043	2.81	0.062/0.037/0.037
8.99×10^{-5}	7.80	0.092/0.115/0.111	7.56	0.095/0.122/0.117	7.25	0.085/0.112/0.109	7.26	0.094/0.112/0.108	7.02	0.087/0.096/0.094
12.59×10^{-5}	10.92	0.105/0.173/0.156	10.59	0.110/0.177/0.164	10.15	0.102/0.164/0.152	10.16	0.110/0.162/0.151	9.83	0.104/0.139/0.131

[a] Standard uncertainties (u) are u(T)=0.10 K, u(urea)=2 mmol·kg^{-1} and u(p)=10 kPa (level of confidence=0.68). Relative standard uncertainties (u_r) is $u_r(X_1^{id}/X_1^{Rub}/X_1^{M}/X_1^{Rod})$=±4%

4. Interaction Parameter (β)

The type and measure of interaction between the surfactants existing in the mixed system is determined by means of interaction parameter (β). The negative magnificence of β reveals the synergistic interaction amid the components, while a positive value of β indicates repulsive interaction. Higher the magnitude of the β, higher is the interaction between the components. For ideal mixing of the components the value of β becomes zero. More negative value of β means higher potency of the interaction [50]. The value of β is negative for cationic-anionic surfactant systems as a result of (i) attractive interaction amid the oppositely charged head groups of ionic surfactants, (ii) hydrophobic interaction amid the tail of the surfactants. The β is more negative in absence of urea than that in presence of urea (Tables 1-3), which indicates stronger attractive interaction between the amphiphiles in aqueous medium. With the addition of NH_2CONH_2 the electrostatic attraction amid the oppositely charged head groups reduces as NH_2CONH_2 interacts in the hydrophobic moiety and decrease hydrophobic interaction. Thus the value of *cmc* increases in urea and the β value decreases. In this study, the β values are always negative at all α_1, profiled in Tables 1-3, suggesting that the formation of mixed micelle is owing to the synergistic interaction between both constituents. These values are in fine harmony with the literatures accounted by Molla et al. [50]. Synergism in the mixed micellization attains if *cmc* of the mixed systems is less than that of individual surfactants along with it is validated by subsequent two conditions [8]: (a) β found to be negative and (b) $|\beta|>|\ln(cmc_1/cmc_2)|$. In our study, the first condition mentioned above is satisfied. Thus, it is suitable to say the term "attraction interaction" in spite of "synergism" for the entire studied systems.

5. Activity Coefficients

The activity coefficients ((f_1^{Rub} (CTAB) and f_2^{Rub} (SDS)) of the mixed micelle systems can evaluated using the value of X_1^{Rub} and β by means of Eqs. (10) and (11):

$$f_1^{Rub}=\exp\{\beta(1-X_1^{Rub})^2\} \tag{10}$$

$$f_2^{Rub}=\exp\{\beta(X_1^{Rub})^2\} \tag{11}$$

Motomura and Rodenas models were also utilized to compute the activity coefficients (f_1 and f_2) [64]:

$$f_1=(\alpha_1 cmc)/(X_1^a cmc_1) \tag{12}$$

$$f_2=(1-\alpha_1)cmc/(1-X_1^a)cmc_2 \tag{13}$$

X_1^a is X_1^M for Motomura and X_1^{Rod} for Rodenas model.

The values of activity coefficients give an idea about degree of involvement of each component in the solution mixture. The executed values of f_1^{Rub}, f_1^M and f_1^{Rod} for component 1, CTAB and f_2^{Rub}, f_2^M and f_2^{Rod} for component 2, SDS for the SDS+CTAB mixed systems are viewed in Tables 1-3. The values of f_1 and f_2 were attained to be below 1 (Tables 1-3), which indicates the attractive interaction amid the components. The adding of activity coefficient values (f_1 (CTAB) and f_2 (SDS)) was found to be less than unity, which reveals the existence of attractive interaction among the studied constituents in absence/presence of NH_2CONH_2. The activity coefficients of CTAB (f_1) are much less than that of SDS (f_2). The lesser values of activity coefficient (f_1) for CTAB indicate that CTAB is far away from its standard state in the mixed micelles. Whereas the high values of activity coefficients for SDS signifies that SDS in the mixed micelles are very close to their standard state (Tables 1-3). This behavior is well accounted by Joshi et al. [65]. The values of activity coefficient (f_1^{Rub}, f_1^M and f_1^{Rod}) in aqueous medium are comparatively lower than in the attendance of urea, which signifies that non-ideal behavior of CTAB is reduced in urea.

6. Thermodynamic Parameters of Micellization

The thermodynamic parameters of pure SDS, CTAB and their mixtures in absence/attendance of urea were obtained according to mas action model [50,66,67]. The Gibbs energy of micellization (ΔG_m^0), can be evaluated utilizing the following equation:

$$\Delta G_m^0=(2-g)\,RT\ln(X_{cmc}) \tag{14}$$

where X_{cmc}, R, g and T are the mole fractional of *cmc*, molar gas constant, degree of counter ion dissociation and temperature in Kelvin, respectively. The phenomenon of micellization is one of the main significant features of amphiphile system from theoretical as well as practical purposes, and therefore it is important to be aware of their mechanism (the dynamic force for formation of micelle). An obvious perspective of the phenomena of micellization is essential for rational justification of the outcomes of structural as well as environmental issues on the *cmc* value, furthermore for forecasting the outcomes on it of new structural and environmental deviations. The evaluation of thermodynamic parameters of micellization such as Gibbs energy, enthalpy, and entropy has played a significant role in developing such a perspective. The thermodynamics process to explain the micellization phenomena was earliest suggested by Tanford [68]. Tanford stated that the sum of the Gibbs energies of reactants (surfactant monomers) should be equivalent to the sum of the Gibbs energies of product (micelles). They describe the micellization phenomenon merely based on information concerning the molecular features of materials and circumstances, for instance, temperature, amphiphile concentration, as well as ionic strength.

The standard enthalpy (ΔH_m^0) as well as standard entropy (ΔS_m^0) was estimated by utilizing the following relations:

$$\Delta H_m^0=-(2-g)RT^2\left[\frac{d\ln X_{cmc}}{dT}\right] \tag{15}$$

$$\Delta S_m^0=(\Delta H_m^0-\Delta G_m^0)/T \tag{16}$$

In our current study, the executed values of Gibbs energy of micellization (ΔG_m^0) were found to be negative both for pure and mixed surfactant systems in absence/presence of urea (Table 5), implying that both pure and mixed micellization processes are spontaneous at all temperatures. The value of ΔG_m^0 is more negative at high concentration of CTAB, which indicates that mixed micellization process is more spontaneous at higher α_1 of CTAB. No significant impact of temperature on the value of ΔG_m^0 for SDS-CTAB mixed systems in absence/presence of urea was observed (Table 5). The values of ΔG_m^0 in case of pure SDS and CTAB are in fine conformity with literature [38,39,69]. The negative value of ΔG_m^0 for pure SDS is reduced in urea solution compared to the aqueous medium, which further decreased with the rise of con-

Table 5. The thermodynamic parameters (ΔG_m^0 (kJ mol^{-1}), ΔH_m^0 (kJ mol^{-1}), and ΔS_m^0 (JK^{-1} mol^{-1})) for (SDS+CTAB) mixed systems at various temperatures and pressure p=0.1 MPa[a]

α_1 (CTAB)	$\Delta G_m^0/\Delta H_m^0/\Delta S_m^0$	$\Delta G_m^0/\Delta H_m^0/\Delta S_m^0$	$\Delta G_m^0/\Delta H_m^0/\Delta S_m^0$	$\Delta G_m^0/\Delta H_m^0/\Delta S_m^0$	$\Delta G_m^0/\Delta H_m^0/\Delta S_m^0$
	T=303.15 K	T=308.15 K	T=313.15 K	T=318.15 K	T=323.15 K
SDS+CTAB mixture in aqueous solution					
0	−34.391/7.212/137.236	−34.626/7.356/136.239	−35.383/−11.878/75.063	−35.952/−12.339/74.219	−36.356/−12.730/73.112
0.90×10^{-5}	−33.605/12.910/153.439	−33.067/12.810/148.878	−34.455/13.502/153.145	−34.325/−9.289/78.694	−34.540/−9.517/77.435
3.60×10^{-5}	−34.444/15.167/163.650	−33.483/14.857/156.873	−34.925/15.659/161.531	−35.038/−11.820/72.979	−35.181/−12.112/71.390
8.99×10^{-5}	−35.273/16.472/170.693	−33.922/16.038/162.131	−35.338/16.788/166.458	−35.640/−20.273/48.302	−35.583/−20.636/46.254
12.59×10^{-5}	−34.053/14.154/159.021	−33.459/14.040/154.144	−34.945/14.801/158.859	−35.494/−19.473/50.357	−35.207/−19.685/48.032
1	−45.649/−17.548/92.697	−45.856/−18.024/90.319	−45.728/−18.393/87.291	−45.659/−18.756/84.560	−45.727/−19.232/81.990
SDS+CTAB mixture in 300 mmol·kg^{-1} aqueous solution of urea					
0	−33.462/−7.891/84.351	−34.189/−8.208/84.313	−34.388/−8.421/82.924	−34.517/−8.634/81.355	−34.440/−8.789/79.380
0.90×10^{-5}	−32.896/−5.089/91.729	−33.384/−5.258/91.273	−33.870/−5.430/90.821	−33.361/−5.453/87.720	−33.772/−5.626/87.099
3.60×10^{-5}	−32.617/−4.607/92.395	−32.866/−4.728/91.315	−32.401/−4.748/88.307	−32.631/−4.866/87.270	−32.783/−4.984/86.023
8.99×10^{-5}	−33.119/−4.931/92.986	−33.355/−5.060/91.823	−33.135/−5.118/89.469	−33.106/−5.209/87.685	−33.763/−5.412/87.732
12.59×10^{-5}	−33.712/−5.806/92.052	−34.187/−5.999/91.474	−35.121/−6.279/92.105	−35.318/−6.438/90.774	−34.819/−6.465/87.743
1	−47.546/−147.647/−330.203	−48.036/−152.558/−339.190	−48.293/−156.638/−345.983	−48.549/−160.740/−352.634	−49.054/−165.832/−361.374
SDS+CTAB mixture in 700 mmol·kg^{-1} aqueous solution of urea					
0	−32.944/−7.332/84.488	−33.158/−7.525/83.186	−33.645/−7.771/82.624	−33.973/−8.021/81.573	−34.143/−8.219/80.221
0.90×10^{-5}	−32.159/−5.883/86.677	−32.398/−6.037/85.548	−33.074/−6.277/85.570	−33.249/−6.435/84.283	−33.399/−6.592/82.953
3.60×10^{-5}	−32.110/−6.073/85.888	−32.105/−6.188/84.106	−31.884/−6.256/81.841	−32.043/−6.411/80.568	−32.377/−6.614/79.726
8.99×10^{-5}	−33.498/−7.889/84.476	−33.057/−7.933/81.533	−33.452/−8.192/80.663	−33.170/−8.281/78.231	−33.263/−8.483/76.682
12.59×10^{-5}	−34.057/−7.522/87.531	−33.645/−7.567/84.629	−33.836/−7.761/83.266	−33.776/−7.901/81.330	−33.882/−8.095/79.799
1	−47.401/−15.100/106.550	−47.644/−15.511/104.277	−48.170/−16.019/102.671	−48.416/−16.438/100.514	−48.588/−16.859/98.186

[a] Standard uncertainties (u) are u(T)=0.10 K, u(urea)=2 mmol·kg^{-1} and u(p)=10 kPa (level of confidence=0.68). Relative standard uncertainties (u_r) are $u_r(\Delta G_m^o)$=±3%, $u_r(\Delta H_m^o$=±3%, and $u_r(\Delta S_m^o)$=±4%

centration of urea and that means the micellization of SDS in urea solution is less spontaneous (Table 5). The negative value of ΔG_m^0 for pure CTAB is higher in urea solution, which indicates the micellization of CTAB in urea is more spontaneous than aqueous medium. In almost all cases, for SDS-CTAB mixed systems the negative value of ΔG_m^0 is reduced in urea at all α_1 of CTAB meaning less spontaneity of micellization.

For pure SDS, the ΔH_m^0 values in aqueous medium were found to be positive at lower temperature (endothermic up to temperature 308.15 K) and the sign of ΔH_m^0 values changed from positive to negative on increasing temperatures from 308.15 K to 313.5 K (exothermic at 313.15 K and above), which increased with the increase of temperature. On the other hand, the values of ΔH_m^0 for pure CTAB were found to be negative at all temperatures studied and enhanced with the rise of the temperature, suggesting the micellization process is more exothermic at higher temperatures, and a similar result was reported by Molla et al. [50]. The ΔH_m^0 values for SDS-CTAB mixed system were found to be positive at lower temperatures and then negative at higher temperatures (Table 5). The negative ΔH_m^0 values signify considerable London-Dispersion forces during micellization process [70], whereas positive values reveal the rupturing iceberg structure of waters in the hydrophobic moiety of the amphiphile molecules.

Again the ΔH_m^0 values for pure SDS, CTAB and their mixed system in urea solution are negative and enhanced with the rise of temperature, which suggests that micellization for pure and mixed systems was exothermic and the exothermic behavior was dominant, which is good agreement with the literature [50].

The ΔS_m^0 values for micellization of pure SDS and SDS-CTAB mixture both in absence and presence of urea were positive at all mole fractions of CTAB and temperatures (Table 5), except that the ΔS_m^0 values for micellization of CTAB were negative in 300 mmol·kg^{-1} urea solution (Table 5). The ΔS_m^0 values for pure SDS and SDS-CTAB mixed systems decreased in almost all cases with the rise of temperature. The magnitude of ΔS_m^0 did not follow any specific trend with mole fraction of α_1 (CTAB). The ΔH_m^0 and ΔS_m^0

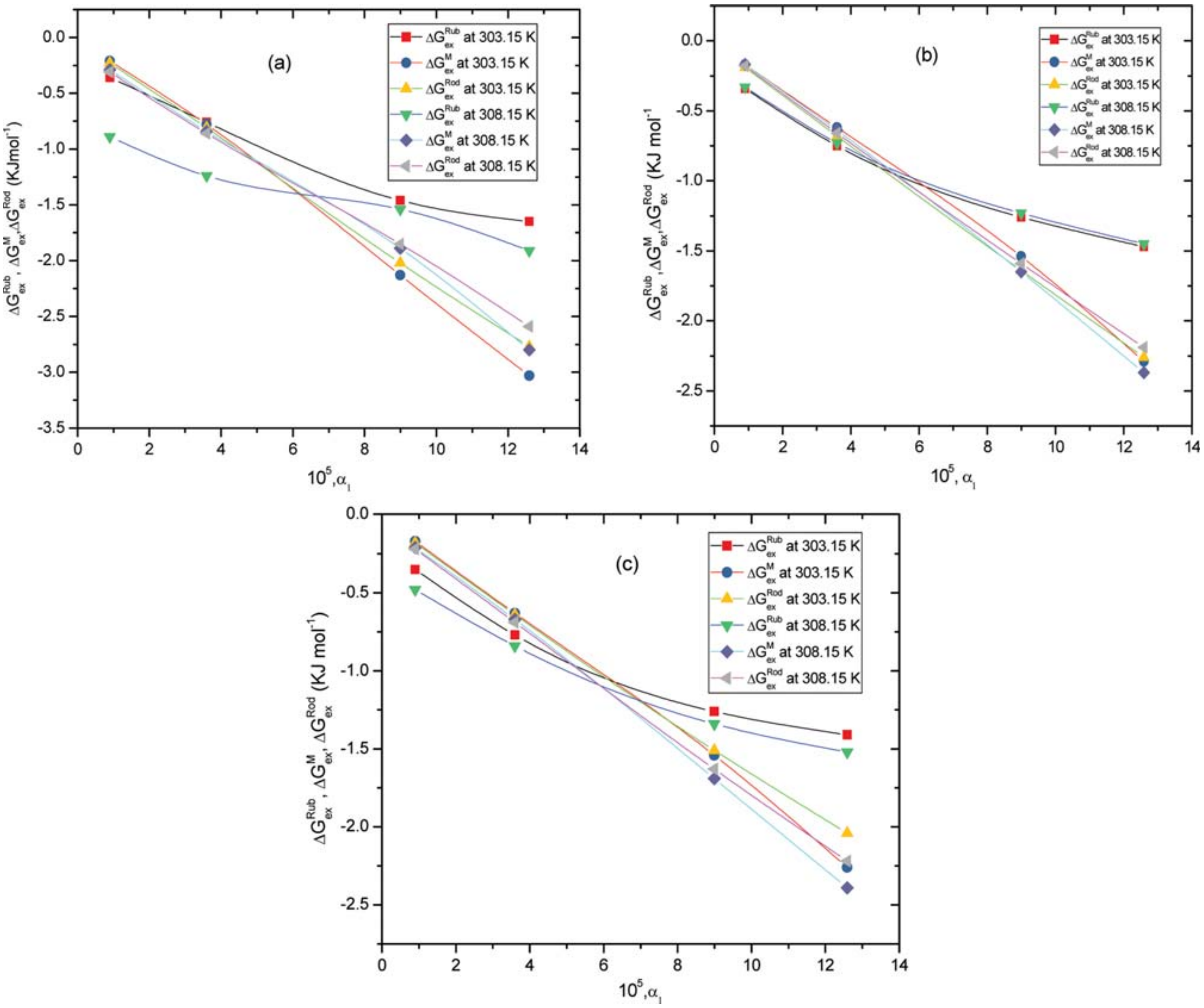

Fig. 4. Variations of ΔG_{ex}^{Rub}, ΔG_{ex}^{M}, and ΔG_{ex}^{Rod} versus mole fraction of CTAB (α_1) in the SDS-CTAB mixed systems in (a) water, (b) 300 mmol·kg^{-1} urea, (c) 700 mmol·kg^{-1} urea at 303.15 K and 308.15 K.

values revealed that the micellization of pure SDS in water was totally entropy directed at inferior temperatures, while that becomes together enthalpy and entropy directed at upper temperatures. The micellization of pure CTAB in water was both enthalpy and entropy subjugated phenomenon over the range of temperature studied. For the SDS-CTAB mixtures, same behavior was obtained as in the case of pure SDS. For pure SDS and SDS-CTAB mixtures in presence of urea (both 300 and 700 $\mathrm{mmol{\cdot}kg^{-1}}$) as well as pure CTAB in 700 $\mathrm{mmol{\cdot}kg^{-1}}$ urea, the micellization was totally enthalpy controlled over the range of temperatures studied. Thus the interactions between pure amphiphiles and their mixtures were hydrophobic in addition to exothermic. In some cases the exothermic contribution was dominant in presence of urea. The large positive value was due to the staving of iceberg structure of water around the hydrophobic moiety of amphiphilic monomer followed by the enhanced randomness in the micelles core [71].

There are different probable interactions among the existing components in the solution; thus complete execution of thermodynamic parameters associated with micellization was not possible as different factors, e.g., charges, polarity, hydrophobicity etc., were associated with them, which is the cause of large uncertainty in the values. Because the technique used (conductivity) in the present study, it was not possible to consider the effect of different factors e.g., polarity, charges, hydrophobicity etc. associated with them to evaluate thermodynamic parameters. From this method we could not evaluate the exact value of various thermodynamic parameters, hence, evaluating the value of the current system is not comparable with values determined by other techniques such as the calorimetric method. Although Ren et al. [72-74] evaluated the thermodynamic parameters by new model, our thermodynamic results are not comparable with models applied by Ren et al. [72-74] probably due to above stated reason.

7. Excess Free Energy

Excess free energy of micellization (ΔG_{ex}) was used to measure the non-ideal behavior of the mixed micelle due to interaction among the studied amphiphiles [50,75-78]. The magnificence of ΔG_{ex} was estimated envisaging different employed models (Rubingh's (ΔG_{ex}^{Rub}), Motomura's (ΔG_{ex}^{M}), as well as Rodenas's (ΔG_{ex}^{Rod}) for SDS-CTAB mixed systems in absence/presence of NH_2CONH_2 are presented in Fig. 4. The executed values of ΔG_{ex} on the basis of different proposed model were negative, which enhanced with augment of α_1 of CTAB, which indicates that mixed micelles formed were extra stable than the stability of micelle of distinct surfactant, and stability of the mixed micelle was enhanced with the increase of the mole fraction of CTAB. In this current study, the negative value of ΔG_{ex} was lower in urea solution compared to urea free solution, which suggests that the mixed micelle formation is more stable in aqueous medium compared to in presence of urea (Fig. 4).

CONCLUSION

We investigated the mixed micellization behavior between anionic surfactant SDS and cationic surfactant CTAB conductometrically in absence and presence of different concentrations of urea from 303.15 K-323.15 K. The obtained result provides the subsequent facts:

- The obtained *cmc* values for (SDS+CTAB) mixed micelle systems are smaller than ideal *cmc* (cmc^{id}) and the values of *cmc* increases in presence of urea.
- Micellar mole fraction (X_1^{Rub}, X_1^{M}, and X_1^{Rod}) values of CTAB are noticeably higher than stoichiometric mole fraction (α_1), suggesting strong participation of CTAB in the mixed micelles. Again, all $X_1 > X_1^{id}$ suggest the non-ideality of the mixed systems.
- Negative value of the interaction parameter (β) of the real binary mixture is a strong indication of attractive interaction between the studied amphiphilic components, SDS and CTAB.
- Activity coefficients for both components (f_1 (component 1, CTAB) and f_2 (component 2, SDS)) were less than unity, which signifies the attractive interaction between the involved constituents.
- The negative magnitudes of ΔG_m^0 illustrate that the micellization is a spontaneous phenomenon, while the negative values of excess free energy (ΔG_{ex}) suggest the high stability of mixed micelle formed as compared to individual ones.
- In case of all mixed systems, the values of standard entropy change (ΔS_m^0) are positive with high magnitude demonstrating the all systems are entropy dominated. Again, both positive and negative values of (ΔH_m^0) in the absence/presence of urea indicate the both hydrophobic and electrostatic interactions among the components present in the mixture.

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LIST OF ABBREVIATIONS

Abbreviation

SDS : sodium dodecyl sulfate
CTAB : cetyltrimethylammonium bromide
cmc : critical micelle concentration
cmc^{id} : ideal critical micelle concentrations
g : degree of counterion dissociation
X_1^{Rub} : micellar mole fraction according to Rubingh model
X_1^{M} : micellar mole fraction according to Motomura model
X_1^{Rod} : micellar mole fraction according to Rodenas model
X_1^{id} : ideal micellar mole fraction
β : interaction parameter
ΔG_m^0 : standard free energy change of micellization
ΔH_m^0 : standard enthalpy change of micellization
ΔS_m^0 : standard entropy change of micellization
ΔG_{ex} : excess free energy of micellization
f^{Rub} : activity coefficient of the component according to Rubingh model
f^{M} : activity coefficient of the component according to Motomura model
f^{Rod} : activity coefficient of the component according to Rodenas model

X_1^{Rub} : micellar mole fraction of CTAB according to Rubingh model
X_1^{M} : micellar mole fraction of CTAB according to Motomura model
X_1^{Rod} : micellar mole fraction of CTAB according to Rodenas model
α_1 : mole fractions of CTAB

REFERENCES

1. J. H. Fendler, *Membrane mimetic chemistry*, Wiley, New York (1982).
2. M. A. Rub, N. Azum and A. M. Asiri, *Russian J. Phys. Chem. B*, **10**, 1007 (2016).
3. G.-H. Li and C.-G. Cho, *Korean J. Chem. Eng.*, **25**, 1444 (2008).
4. S. Roy and J. Dey, *J. Colloid Interface Sci.*, **290**, 526 (2005).
5. W. G. Cutler and E. Kissa, *Detergency: Theory and practice*, Marcel Dekker, New York (1987).
6. J.-C. Kim, *Korean J. Chem. Eng.*, **26**, 1821 (2009).
7. S. E. Friberg, *Food emulsions*, vol. 5, Marcel Dekker, New York (1976).
8. M. J. Rosen, *Surfactants and interfacial phenomena*, 3rd Ed., Wiley, New York (2004).
9. D. Kumar and M. A. Rub, *J. Mol. Liq.*, **240**, 253 (2017).
10. M. A. Rub, N. Azum, F. Khan and A. M. Asiri, *J. Chem. Thermodyn.*, **121**, 199 (2018).
11. D. R. Robinson and W. P. Jencks, *J. Am. Chem. Soc.*, **87**, 2462 (1965).
12. D. B. Wetlaufer, S. K. Malik, L. Stoller and R. L. Coffin, *J. Am. Chem. Soc.*, **86**, 508 (1964).
13. O. Enea and C. Jolicoeur, *J. Phys. Chem.*, **86**, 3870 (1982).
14. A. Chakraborty, M. Sarkar and S. Basak, *J. Colloid Interface Sci.*, **287**, 312 (2005).
15. M. A. Rub, F. Khan, D. Kumar and A. M. Asiri, *Tenside Surf. Deterg.*, **52**, 236 (2015).
16. N. Azum, M. A. Rub, A. M. Asiri and W. A. Bawazeer, *Colloids Surf., A*, **522**, 183 (2017).
17. M. A. Rub, N. Azum and A. M. Asiri, *J. Mol. Liq.*, **218**, 595 (2016).
18. N. Azum, M. A. Rub and A. M. Asiri, *Chinese J. Chem. Eng.*, **26**, 566 (2018).
19. C. Treiner and A. Makayssi, *Langmuir*, **8**, 794 (1992).
20. D. Kumar, M. A. Rub, N. Azum and A. M. Asiri, *J. Phys. Org. Chem.*, **31**, e3730 (2018).
21. T. R. Desai and S. G. Dixit, *J. Colloid Interface Sci.*, **177**, 471 (1996).
22. M. A. Rub, N. Azum, F. Khan and A. M. Asiri, *J. Phys. Org. Chem.*, **30**, e3676 (2017).
23. M. A. Rub, N. Azum and A. M. Asiri, *J. Chem. Eng. Data*, **62**, 3216 (2017).
24. N. Azum, M. A. Rub and A. M. Asiri, *Colloids Surf., B*, **121**, 158 (2014).
25. P. K. Jana and S. P. Moulik, *J. Phys. Chem.*, **95**, 9525 (1991).
26. M. J. Roden, H. Zhu and T. Gao, *J. Colloid Interface Sci.*, **157**, 254 (1993).
27. J. H. Clint, *Surfactant aggregation*, Blackie\Chapman and Hall, Glasgow, New York (1992).
28. M. E. Haque, A. R. Das, A. K. Rakshit and S. P. Moulik, *Langmuir*, **12**, 4084 (1996).
29. J. L. Palous, M. Turmine and P. Letellier, *J. Phys. Chem. B*, **102**, 5886 (1998).
30. M. J. Rosen and D. Murphy, *J. Colloid Interface Sci.*, **110**, 224 (1986).
31. D. Attwood and A. T. Florence, *Surfactant systems: Their chemistry, pharmacy and biology*, Chapman & Hall, New York (1983).
32. P. H. Elworthy, A. T. Florence and G. B. Macfarlane, *Solubilization by surface-active agents and its application in chemistry and biological sciences*, Chapman and Hall, Suffolk (1968).
33. M. A. Rub, N. Azum, S. B. Khan, H. M. Marwani and A. M. Asiri, *J. Mol. Liq.*, **212**, 532 (2015).
34. M. A. Motin, M. A. H. Mia and A. K. M. N. Islam, *J. Saudi Chem. Soc.*, **19**, 172 (2015).
35. T. P. Niraula, S. K. Shah, S. K. Chatterjee and A. Bhattarai, *Karbala Int. J. Modern Sci.*, **4**, 26 (2018).
36. C. C. Ruiz, *Colloid Surf., A: Physicochem. Eng. Aspects*, **147**, 349 (1999).
37. D. Kumar, M. A. Rub, M. Akram and Kabir-ud-Din, *Tenside Surf. Deterg.*, **51**, 157 (2014).
38. F. Akhtar, M. A. Hoque and M. A. Khan, *J. Chem. Thermodyn.*, **40**, 1082 (2008).
39. M. Rahman, M. A. Khan, M. A. Rub and M. A. Hoque, *J. Mol. Liq.*, **223**, 716 (2016).
40. D. Kumar, M. A. Rub, M. Akram and Kabir-ud-Din, *J. Colloid Interface Sci.*, **418**, 324 (2014).
41. R. Jha and J. C. Ahluwalia, *J. Chem. Soc. Faraday Trans.*, **89**, 3465 (1993).
42. S. K. Han, S. M. Lee and H. Schott, *J. Colloid Interface Sci.*, **126**, 393 (1988).
43. G. C. Kresheck, *Water: A comprehensive treatise*, vol. 4, F. Franks (Ed.), Plenum, New York (1975).
44. K. Menguro, Y. Takasawa, N. Kawahashi, Y. Tabata and M. Ueno, *J. Colloid Interface Sci.*, **83**, 50 (1981).
45. Kabir-ud-Din, U. S. Siddique, S. Sanjeev and A. A. Dar, *Colloid Polym. Sci.*, **384**, 807 (2006).
46. C. C. Ruiz, L. Diaz-Lopez and J. Aguiar, *J. Colloid Interface Sci.*, **305**, 293 (2007).
47. C. Das and B. Das, *J. Chem. Eng. Data*, **54**, 559 (2009).
48. S. Paria, *Colloids Surf., A*, **281**, 113 (2006).
49. J. H. Clint, *J. Chem. Soc., Faraday Trans. I*, **71**, 1327 (1975).
50. M. R. Molla, M. A. Rub, A. Ahmad and M. A. Hoque, *J. Mol. Liq.*, **238**, 62 (2017).
51. D. Kumar and M. A. Rub, *J. Mol. Liq.*, **238**, 389 (2017).
52. A. Buckingham, C. J. Garve and G. G. Warr, *J. Phys. Chem.*, **97**, 10236 (1993).
53. K. M. Kale, E. L. Cussler and D. F. Evans, *J. Phys. Chem.*, **84**, 593 (1980).
54. A. Bandhopadhyay and S. P. Moulik, *Colloid Polym. Sci.*, **266**, 455 (1988).
55. Y. Moroi, *Micelles: Theoretical and applied aspects*, Plenium Press, New York (1992).
56. M. A. Rub, A. M. Asiri, J. M. Khan, R. H. Khan and Kabir-ud-Din, *J. Mol. Struct.*, **1050**, 35 (2013).
57. V. Soldi, J. Keiper, L. S. Romsted, I. M. Cuccovia and H. Chaimovich, *Langmuir*, **16**, 59 (2000).
58. R. Zana, *J. Colloid Interface Sci.*, **78**, 330 (1980).
59. N. Gorski and J. Kalus, *Langmuir*, **17**, 4211 (2001).
60. D. N. Rubingh, *Mixed micelle solution*, K. L. Mittal (Ed.), Solution Chemistry of Surfactants, vol. 1, Plenum, New York (1979).

61. K. Motomura, M. Yamanaka and M. Aratono, *Colloid Polym. Sci.*, **262**, 948 (1984).
62. V. Rodenas, M. Valiente and M. S. Villafruela, *J. Phys. Chem. B*, **103**, 4549 (1999).
63. H. Lange and K. H. Beck, *Kolloid Z. Z. Polym.*, **251**, 424 (1973).
64. M. A. Hoque, M.-O.-F. Patoary, M. M. Rashid, M. R. Molla and M. A. Rub, *J. Solution Chem.*, **46**, 682 (2017).
65. T. Joshi, B. Bharatiya and K. Kuperkar, *J. Dispersion Sci. Technol.*, **29**, 351 (2008).
66. Y. Moroi, *J. Colloid Interface Sci.*, **122**, 308 (1988).
67. N. M. van Os, B. Smit and S. Karaborni, *Red. Trav. Chim. Pays-Bas*, **113**, 181 (1994).
68. C. Tanford, *Proceedings of the National Academy of Science*, **71**, 1811 (1974).
69. A. Ali, S. Uzair, N. A. Malik and M. Ali, *J. Mol. Liq.*, **196**, 395 (2014).
70. J. J. H. Nusselder and J. B. F. N. Engberts, *J. Colloid Interface Sci.*, **148**, 353 (1992).
71. D. Kumar and M. A. Rub, *Tenside Surf. Deterg.*, **52**, 464 (2015).
72. Z. H. Ren, Y. Luo and D. P. Shi, *Colloids Surf., A*, **428**, 18 (2013).
73. Z. H. Ren, Y. Luo, Y. C. Zheng, D. P. Shi, P. Mei and F. S. Li, *J. Solution Chem.*, **43**, 853 (2014).
74. Z. H. Ren, *J. Ind. Eng. Chem.*, **20**, 3649 (2014).
75. J. H. Clint and T. J. Walker, *J. Chem. Soc. Faraday Trans. I*, **71**, 946 (1975).
76. N. Azum, M. A. Rub and A. M. Asiri, *J. Dispersion Sci. Technol.*, **38**, 96 (2017).
77. N. Azum, M. A. Rub and A. M. Asiri, *J. Dispersion Sci. Technol.*, **38**, 1785 (2017).
78. M. A. Rub, N. Azum, A. M. Asiri, M. E. M. Zayed and A. O. Al-Youbi, *J. Phys. Org. Chem.*, **29**, 476 (2016).