

Research Article

Thermodynamic and Interfacial Properties of DTABr/CTABr Mixed Surfactant Systems in Ethanolamine/Water Mixtures: A Conductometry Study

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Mixed-micelle formation in the binary mixtures of dodecyltrimethylammonium bromide (DTABr) and cetyltrimethylammonium bromide (CTABr) surfactants in water-ethanolamine mixed solvent systems has been studied by conductometric method in the temperature range of 298.1 to 313.1 K at 5 K intervals. It was observed that the presence of ethanolamine forced the formation of mixed micelle to lower total surfactant concentration than in water only. The synergistic interaction was quantitatively investigated using the theoretical models of Clint and Rubingh. The interaction parameter β_{12} was negative at all the mole fractions of DTABr in the surfactant mixtures indicating a strong synergistic interaction, with the presence of ethanolamine in the solvent system resulting in a more enhanced synergism in micelle formation than in water only. The free energy of micellization ΔG_M values was more negative in water-ethanolamine mixed solvent system than in pure water indicating more spontaneity in mixed micelle formation in the presence of ethanolamine than in pure water.

1. Introduction

Mixed micelles are widely recognized and employed in numerous fields ranging from biological systems to technical applications such as in detergency, cosmetic, pharmaceuticals, enhanced oil recovery, and as flotation agents. This is because they provide a direct and convenient approach to improve physical stability as well as better chemical and surface active properties over the individual surfactant; hence little quantity is required for any application [1–4]. The physicochemical properties of these systems are dependent on environmental conditions such as the presence of additives, with different additives behaving differently in mixed surfactant systems.

In a given medium (usually, water or binary mixtures of either two nonaqueous solvents or nonaqueous solvent with water), amphiphilic molecules self-aggregate together

to minimize the unfavorable interaction with the solvent (medium) and form different types of aggregates (depending on their properties and the other physicochemical conditions which are experienced by them). Hydrophobic or, more generally, solvophobic interactions play an important role in raising the above situation and, therefore, several studies have been made by altering the medium (solvent) properties either by the incorporation of additives [5–10] or by mixing with other solvents [11–19].

The effects of different kinds of additives including glycols, hydrazine, and formamide on the micellization of single surfactants have been widely studied [20–23]. These solvents are known to have high cohesive energies and considerable hydrogen bonding ability which favor aggregation of surfactant monomers to form micelle. Notwithstanding the recognition of the importance of “water structure” in the micelle formation in aqueous surfactant solutions, no

significant attempt seems to have been made to investigate the role of “structuredness” which may exist in many polar organic solvents due to the presence of one or more potential hydrogen bonding centers in their molecules. Addition of alcohols and amine has been reported to have a drastic effect on the micellization of surfactants resulting in a significant change in the critical micelle concentration [22]. Ethanolamine combines the properties of amine and alcohol; it exhibits the unique capability of undergoing reactions common to both groups [23]. It is therefore worthwhile to consider the effect of an organic molecule that combines the properties of alcohol and amine as a single entity on the mixed micelle formation. A literature survey shows that considerable efforts have been made on the study of mixed surfactant systems [24–26] to characterize micelles and their formation in water.

In this work, results of the conductometric study of the physicochemical properties such as micellar composition, counterion binding, interaction parameter, thermodynamic parameters of mixed micelle formation of mixed cationic surfactants in ethanolamine-water binary system using dodecyltrimethyl ammonium bromide (DTABr) and cetyltrimethyl ammonium bromide (CTABr) are presented. The results have been analyzed in light of the existing theories of Clint’s for ideal mixing and Rubingh model for nonideal mixing [2, 27]. It may be mentioned that although comprehensive studies on binary mixtures of cationic surfactants are reported in the literature, fundamental investigations on the effect of ethanolamine on micellization have not been mentioned.

2. Experimental

2.1. Materials. Cetyltrimethylammoniumbromide (CTABr) and dodecyltrimethylammonium bromide (DTABr) ethanolamine were purchased from Sigma-Aldrich (USA). All the products were used without further purification. All solutions were prepared in doubly distilled water and the experiment was performed between 298.1 and 313.1 K.

2.2. Electrical Conductivity Measurements. The conductivity measurements were made on a DDS-307 conductivity meter (Shanghai Precision Scientific Instrument Co., Ltd.). The conductivity (κ) measurements were made as a function of total surfactant concentration at different mole fraction of DTABr in the DTABr-CTABr mixtures. The mixed solutions were prepared by diluting the concentrated stock solutions and were kept for at least 30 min for equilibration before measuring the conductivity. The conductivity meter was calibrated with different concentrations of solutions of potassium chloride KCl (Merck, purity > 99%). Electrodes were inserted in double walled glass cell containing the solution. The cell constant of the cell used was 1 cm^{-1} . The measurement of conductivity was carried out with an absolute accuracy up to $\pm 3\%$. The conductivity measurements were made at different temperatures from 298.1 to 313 K for the mixed surfactant/ethanolamine/water system.

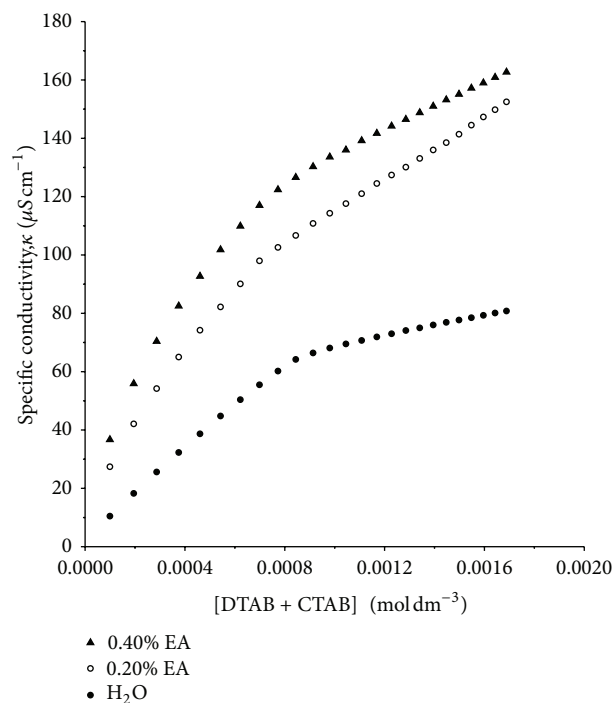


FIGURE 1: Plots of specific conductivity against concentration of DTABr/CTABr in ethanolamine + water mixtures at 298.1 K.

3. Results and Discussion

3.1. Critical Micelle Concentration (CMC). The determination of the CMC and the degree of counter-ion dissociation (binding) for each solvent composition and at different temperatures was carried out from the conductivity-surfactant concentration curve. A number of these plots are shown in Figure 1.

As shown in Figure 1, it is well known that the location of the break point appearing in the plot of specific conductivity versus concentration gives the CMC, while the ratio of the slopes of the plot above and below the CMC gives the degree of dissociation [28]. However, as the concentration of ethanolamine and temperature increased, there appeared a curvature around CMC making the precise determination of CMC difficult. Similar observations are reported in the literature and in most cases have been addressed by either carrying out a nonlinear fit of the raw conductivity-surfactant data or by the analysis of the plots of differential conductivity. This latter approach is adopted in this work, which is based on the assumption that the first derivative of the specific conductivity-concentration curve is well-described by the Boltzmann-type decreasing sigmoid given by [29]

$$\frac{d\kappa}{dc} = A_1 + \frac{A_1 - A_2}{1 + e^{(c-cmc)/d}}, \quad (1)$$

where κ is the specific conductivity, c is the total concentration of mixed DTABr-CTABr, A_1 and A_2 are the upper and lower limit of the sigmoid, respectively, the CMC value is the center of the sigmoid, and d is the time constant, which is directly related to the independent variable range, where

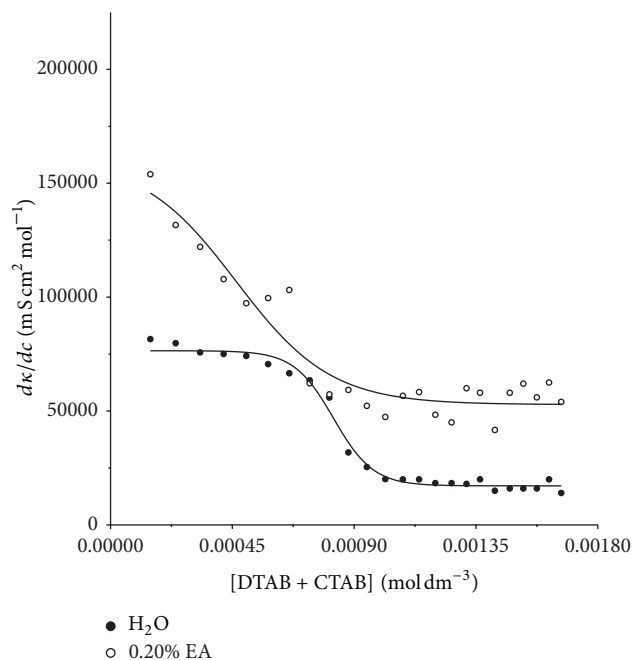


FIGURE 2: Plot of the differential conductivity versus the average concentration of DTABr/CTABr binary system in ethanolamine + water mixture at 298.1 K.

the sudden change of the dependent variable occurs. Typical plots of differential conductivity versus average surfactant concentration are shown in Figure 2.

3.2. Effects of Ethanolamine on Micellar Behaviour in DTABr-CTABr Mixtures. The critical micelle concentration of the surfactant mixtures at different mole fraction of DTABr in the presence of ethanolamine was found to be significantly lower than the values in pure aqueous system as can be seen in Tables 1, 2, and 3. Also, the values decreased with increase in ethanolamine concentrations from 0.2% to 0.4% at any given mole fraction of DTABr, though the CMC increases along this trend as depicted by Figure 3. This observation can be explained in terms of the reinforcement of water structure through extensive intermolecular hydrogen bond formation due to the presence of the amino nitrogen atom; this of course increases the hydrophobic effect favouring micellization. Hence, a concomitant decrease in CMC was observed in ethanolamine and this increases with increase in concentration of ethanolamine in the mixed solvent systems.

3.3. Surfactant-Surfactant Mixed Micelle in the Absence and in the Presence of Ethanolamine. Like amine additive, addition of ethanolamine may affect micellization of mixed ionic surfactant in two ways. First, the nitrogen atoms bearing lone pair of electron tend to form hydrogen bond with water and break down the "ice-berg" structure formed around the monomer. Secondly, the hydrophobic alkyl portion of the ethanolamine has the tendency to incorporate in micelles, which may also replace some of the water molecules at the surface. This replacement increases the distance between

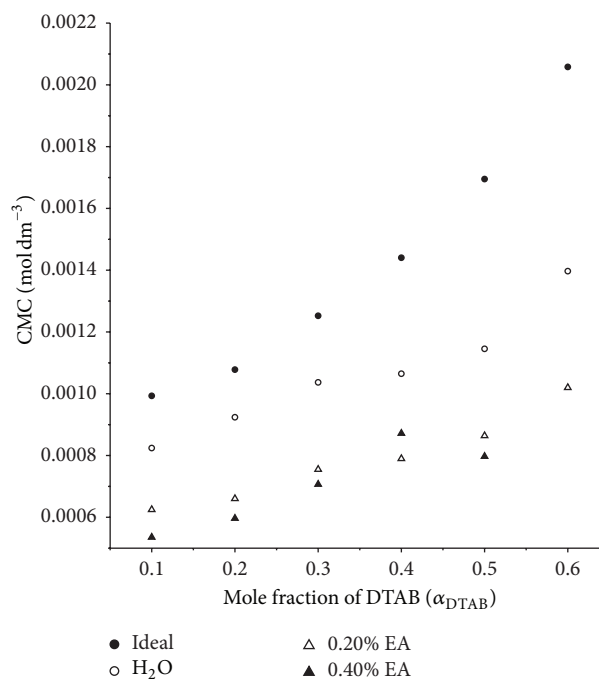


FIGURE 3: The critical micelle concentration of DTABr/CTABr binary system in ethanolamine + water mixture as a function of the mole fraction of DTABr in the mixture.

head group and decreases the charge density of the micellar surface. These effects contribute to the micellization of mixed DTABr-CTABr surfactant in water-ethanolamine medium with concomitants decrease in CMC.

Mixed systems comprising of DTABr and CTABr in water-ethanolamine undergo several physico-chemical changes due to surfactant-surfactant and surfactant-solvent interactions resulting in enhanced micellar properties as compared to pure aqueous system. To investigate the mixing behavior between DTABr and CTABr in this mixed solvent system, the Rubingh's regular solution theory was employed [2]. This model is based on regular solution approach for the treatment of a nonideal mixing, and due to its simplicity, it has been mostly used. The nonideality is introduced with the inclusion of the activity coefficient, f_i , in (2); that is,

$$\frac{1}{\text{cmc}^*} = \sum \frac{\alpha_i}{f_i \text{cmc}_i}. \quad (2)$$

In the case of ideal behavior, $f_{\text{DTAB}} = f_{\text{CTABr}} = 1$ and (2) can be reduced to the form (for binary surfactant systems)

$$\frac{1}{\text{cmc}^*} = \frac{\alpha_1}{c_{\text{DTABr}}} + \frac{(1 - \alpha_1)}{c_{\text{CTABr}}}, \quad (3)$$

as proposed by Clint's [27] for ideal mixed micelle.

TABLE 1: The degree of counterion binding, thermodynamic function, micellar composition, interaction parameters, and critical micelle concentration of the DTABr + CTABr in aqueous medium.

Temp (K)	α_{DTABr}	β	ΔG^E (J/mol)	ΔH_M (J/mol)	ΔS_M (J/mol·K)	ΔG_M (J/mol)	χ_1	β_{12}	f_{DTABr}	f_{CTABr}	cmc* (mM)
298.1	0.1	0.79	-1081.9	-1081.9	3.17	-2010.9	0.124	-4.02	0.046	0.940	0.824
	0.2	0.68	-893.1	-893.1	3.27	-1867.5	0.134	-3.11	0.097	0.946	0.923
	0.3	0.67	-818.2	-818.2	3.46	-1851.0	0.147	-2.64	0.146	0.944	1.003
	0.4	0.59	-1187.4	-1187.4	4.15	-2427.3	0.200	-2.99	0.147	0.887	1.102
	0.5	0.73	-1402.9	-1402.9	4.57	-2767.0	0.239	-3.12	0.166	0.837	1.150
	0.6	0.65	-1282.1	-1282.1	4.74	-2695.3	0.253	-2.71	0.225	0.836	1.401
303.1	0.1	0.75	-714.4	-714.4	2.52	-1479.1	0.090	-3.45	0.058	0.972	0.871
	0.2	0.68	-909.6	-909.6	3.39	-1937.8	0.142	-2.96	0.112	0.942	0.939
	0.3	0.65	-751.9	-751.9	3.34	-1766.0	0.139	-2.50	0.157	0.953	1.053
	0.4	0.72	-898.7	-898.7	3.83	-2061.4	0.173	-2.49	0.183	0.928	1.151
	0.5	0.70	-1299.9	-1299.9	4.48	-2659.3	0.230	-2.91	0.177	0.857	1.181
	0.6	0.69	-1243.8	-1243.8	4.70	-2668.7	0.253	-2.61	0.237	0.846	1.420
308.1	0.1	0.74	-686.0	-686.0	2.52	-1463.4	0.090	-3.25	0.067	0.973	0.885
	0.2	0.68	-595.6	-595.6	2.76	-1444.5	0.103	-2.51	0.131	0.973	0.983
	0.3	0.63	-415.1	-415.1	2.71	-1250.1	0.100	-1.79	0.234	0.982	1.135
	0.4	0.73	-761.1	-761.1	3.64	-1882.2	0.159	-2.22	0.207	0.945	1.193
	0.5	0.71	-1302.8	-1302.8	4.48	-2684.5	0.230	-2.87	0.182	0.859	1.217
	0.6	0.68	-1117.5	-1117.5	4.60	-2533.8	0.242	-2.38	0.254	0.870	1.484
313.1	0.1	0.74	-217.9	-217.9	1.47	-678.1	0.043	-2.01	0.154	0.996	0.954
	0.2	0.68	-331.8	-331.6	2.16	-1009.4	0.073	-1.89	0.196	0.990	1.033
	0.3	0.64	-325.9	-325.9	2.47	-1100.8	0.088	-1.56	0.272	0.998	1.158
	0.4	0.75	-743.7	-743.7	3.59	-1869.9	0.156	-2.17	0.213	0.948	1.201
	0.5	0.73	-698.1	-698.1	4.28	-2041.1	0.212	-1.61	0.368	0.931	1.267
	0.6	0.72	-1116.6	-1116.6	4.58	-2551.4	0.240	-2.35	0.257	0.873	1.493

* Critical micellar concentration.

Jana and Moulik [26] also proposed that the composition of the mixed micelle and the interaction parameter (β_{12}) can be calculated by employing the following equation:

$$\chi_{\text{DTABr}}^2 \ln \left(\frac{\alpha_{\text{DTABr}} \text{cmc}^*}{\chi_{\text{DTABr}} \cdot \text{cmc}_{\text{DTABr}}} \right) = (1 - \chi_{\text{DTABr}})^2 \ln \left(\frac{(1 - \alpha_{\text{DTABr}}) \cdot \text{cmc}^*}{(1 - \chi_{\text{DTABr}}) \cdot \text{cmc}_{\text{CTABr}}} \right), \quad (4)$$

$$\beta_{12} = \frac{\ln (\alpha_{\text{DTABr}} \text{cmc}^* / \chi_{\text{DTABr}} \text{cmc}_{\text{DTABr}})}{(1 - \chi_{\text{DTABr}})^2},$$

where in the binary solution

$$f_{\text{DTABr}} = \exp (\beta (1 - \chi_i)^2), \quad (5)$$

$$f_{\text{CTABr}} = \exp (\beta \chi_i^2).$$

The value of χ_1 , β_{12} , f_{DTABr} , and f_{CTABr} for all the system are presented in Tables 1 to 3. It can be seen from Tables 1 to 3 that the β_{12} values are not constant throughout the concentration range, but they are all negative indicating synergism in mixed DTABr-CTABr system. The larger the negative value of β_{12} , the stronger the attractive interaction between the two different surfactant molecules, and the greater the synergism

in mixed micelle formation between them [30]. As proposed by Maeda [31], apart from electrostatic interactions, the chain/chain interactions play a major role in the formation of mixed micelle especially for the nonsimilar chain length. Since the hydrocarbon chains of these surfactants are different from each other, a nonideal behavior is expected. Figure 1 represents the plot of experimental CMC and the ideal CMC* versus the mole fraction of DTABr. The experimental CMC value deviates from the ideal CMC* value in the whole mixing range indicating a strong synergism exists in the mixed micelle formation process. It was observed that the experimental data of mixed CMC value are always lower than the ideal CMCs obtained from Clint's equation. Similar interaction was reported earlier by several authors [32].

The activity coefficient f_i shows effect and contribution of individual component in the mixed micelle. The f_{DTABr} values of the DTABr which increased linearly with temperature are obviously very low, indicating that the DTABr in the mixed micelle is very far to its standard state.

As depicted in Table 1, the micellar mole fraction (χ_{DTABr}) is lesser and increases linearly in aqueous medium compared with what is obtained in ethanolamine-water mixture, as shown in Tables 2 and 3 with increasing mole fraction of DTABr. This signifies less surface activity of DTABr rather than micellization in the mixed state while in aqueous medium rather than in ethanolamine medium.

TABLE 2: The degree of counterion binding, thermodynamic function, micellar composition, interaction parameters, and critical micelle concentration of the DTABr + CTABr in 0.2% ethanolamine.

Temp (K)	α_{DTABr}	β	ΔG^E (J/mol)	ΔH_M (J/mol)	ΔS_M (J/mol·K)	ΔG_M (J/mol)	χ_1	β_{12}	f_{DTABr}	f_{CTABr}	cmc* (mM)
298.1	0.1	0.67	-2406.7	-2406.7	4.18	-3625.4	0.202	-6.03	0.021	0.783	0.625
	0.2	0.66	-2333.7	-2333.7	4.45	-3660.0	0.227	-5.37	0.040	0.759	0.667
	0.3	0.56	-2091.9	-2091.9	4.58	-3448.8	0.237	-4.67	0.066	0.769	0.755
	0.4	0.54	-2257.3	-2257.3	4.82	-3694.6	0.267	-4.65	0.081	0.718	0.789
	0.5	0.53	-2333.4	-2333.4	5.02	-3830.2	0.292	-4.55	0.102	0.678	0.865
	0.6	0.50	-2262.3	-2262.3	5.17	-3802.6	0.313	-4.25	0.134	0.660	1.019
303.1	0.1	0.75	-2769.9	-2769.9	4.34	-4084.9	0.216	-6.49	0.019	0.739	0.579
	0.2	0.71	-2607.5	-2607.5	4.56	-3988.3	0.237	-5.72	0.036	0.725	0.618
	0.3	0.63	-2577.3	-2577.3	4.75	-4017.9	0.259	-5.33	0.053	0.699	0.667
	0.4	0.71	-2423.0	-2423.0	4.87	-3899.5	0.273	-4.85	0.077	0.697	0.761
	0.5	0.57	-2480.9	-2480.9	5.06	-4013.3	0.297	-4.72	0.097	0.659	0.835
	0.6	0.53	-2296.2	-2296.2	5.17	-3861.9	0.313	-4.23	0.135	0.660	1.021
308.1	0.1	0.73	-3124.3	-3124.3	4.47	-4500.8	0.228	-6.92	0.016	0.697	0.537
	0.2	0.66	-2973.0	-2973.0	4.69	-4416.6	0.251	-6.17	0.031	0.677	0.571
	0.3	0.64	-2760.1	-2760.1	4.80	-4240.4	0.265	-5.54	0.051	0.678	0.641
	0.4	0.62	-3011.7	-3011.7	5.05	-4565.9	0.295	-5.65	0.060	0.611	0.646
	0.5	0.58	-2757.3	-2757.3	5.12	-4335.5	0.306	-5.07	0.087	0.621	0.775
	0.6	0.56	-2488.2	-2488.2	5.21	-4092.4	0.319	-4.47	0.126	0.634	0.971
313.1	0.1	0.70	-2911.6	-2911.6	4.36	-4276.6	0.218	-6.56	0.018	0.732	0.572
	0.2	0.66	-2766.9	-2766.9	4.59	-4203.6	0.241	-5.82	0.035	0.714	0.607
	0.3	0.59	-2700.0	-2700.0	4.77	-4192.6	0.260	-5.39	0.052	0.694	0.660
	0.4	0.61	-2732.6	-2732.6	4.95	-4282.3	0.283	-5.18	0.069	0.661	0.712
	0.5	0.53	-2716.9	-2716.9	5.09	-4313.6	0.303	-4.92	0.091	0.635	0.796
	0.6	-	-	-	-	-	-	-	-	-	-

*Critical micellar concentration.

3.4. *Thermodynamic of Micellization.* The regular solution theory (RST) was used to compute the thermodynamic function of mixing which assumes that the excess entropy of mixing is zero. According to this theory, the excess free energy, excess enthalpy, and enthalpy of micellization, ΔH_M are given by

$$G^E = H^E = \Delta H_M = RT\chi_{\text{DTABr}} \ln f_{\text{DTABr}} + (1 - \chi_{\text{DTABr}}) \ln f_{\text{CTABr}}. \quad (6)$$

The excess free energy of micellization represents the deviation from the ideal behavior ($G^E = \Delta G_M - \Delta G_M^{\text{ideal}}$). For an ideal mixing, the free energy of micellization can be given by

$$\Delta G_M^{\text{ideal}} = RT(\chi_{\text{DTABr}} \ln \chi_{\text{DTABr}} + (1 - \chi_{\text{DTABr}}) \ln (1 - \chi_{\text{DTABr}})). \quad (7)$$

The nonideal free energy of micellization is given by

$$\Delta G_M = RT(\chi_{\text{DTABr}} \ln (\chi_{\text{DTABr}} \cdot f_{\text{DTABr}}) + (1 - \chi_{\text{DTABr}}) \ln ((1 - \chi_{\text{DTABr}}) \cdot f_{\text{CTABr}})). \quad (8)$$

Using the values of enthalpy and free energy of micellization, entropy of micellization can be obtained from

$$\Delta S_M = \frac{\Delta H_M - \Delta G_M}{T}. \quad (9)$$

As reported in Tables 1 to 3, the free energy of micellization (ΔG_M) is all negative and becomes more negative as ethanolamine concentration in the mixed solvent increases over the temperature range of study, suggesting that micellization process occurs less spontaneous in aqueous medium compared with the mixed solvent.

The negative value of ΔH_M implies micellization of DTABr-CTABr in water, and ethanolamine-water mixture is an exothermic process and the tendency becomes more negative with enhanced temperature. Indication from this result shows that the total energy change including translational energy loss by individual and the heat released by the interaction among hydrocarbon bonds is less than the energy absorbed when the iceberg structure of water was destroyed during micellization.

In Tables 1 to 3, the values of ΔS_M are all positive as temperature increases, indicating that the degree of disorderliness increases due to micellization and the entropy change is favorable to the formation of mixed micelle. In aqueous medium, as shown in Table 1, ΔH_M is much less than $T\Delta S_M$, indicating that the enthalpy change contribution to the Gibbs energy of micellization is smaller. This confirmed that the micellization process is entropy driven, while in ethanolamine medium, $-T\Delta S_M$ is less than ΔH_M , indicating that the process is enthalpy driven in the mixed micelle.

TABLE 3: The degree of counterion binding, thermodynamic function, micellar composition, interaction parameters, and critical micelle concentration of the DTABr + CTABr in 0.4% ethanolamine.

Temp (K)	α_{DTABr}	β	ΔG^E (J/mol)	ΔH_M (J/mol)	ΔS_M (J/mol·K)	ΔG_M (J/mol)	χ_1	β_{12}	f_{DTABr}	f_{CTABr}	cmc* (mM)
298.1	0.1	0.78	-3040.6	-3040.6	4.47	-4374.2	0.229	-4.95	0.016	0.694	0.535
	0.2	0.72	-2716.1	-2716.1	4.62	-4094.0	0.244	-5.94	0.033	0.702	0.596
	0.3	0.71	-2329.3	-2329.3	4.66	-3720.3	0.249	-5.03	0.058	0.732	0.706
	0.4	0.63	-1917.7	-1917.7	4.64	-3308.1	0.247	-4.14	0.097	0.774	0.797
	0.5	0.55	-2586.2	-2586.2	5.09	-4106.4	0.303	-4.94	0.091	0.635	0.872
	0.6	—	—	—	—	—	—	—	—	—	—
303.1	0.1	0.67	-3194.3	-3194.3	4.51	-4562.3	0.233	-7.09	0.015	0.680	0.520
	0.2	0.65	-3233.4	-3233.4	4.79	-4685.5	0.263	-6.62	0.027	0.632	0.524
	0.3	0.62	-2513.2	-2513.2	4.72	-3946.2	0.256	-5.24	0.054	0.709	0.679
	0.4	0.58	-2525.1	-2525.1	4.90	-4012.8	0.277	-5.00	0.073	0.681	0.738
	0.5	0.57	-2490.2	-2490.2	5.05	-4023.5	0.297	-4.73	0.097	0.658	0.833
	0.6	—	—	—	—	—	—	—	—	—	—
308.1	0.1	0.71	-3733.6	-3733.6	4.63	-5160.9	0.245	-7.87	0.011	0.623	0.451
	0.2	0.69	-3616.1	-3616.1	4.88	-5121.7	0.275	-7.09	0.024	0.586	0.478
	0.3	0.57	-2879.2	-2879.2	4.84	-4372.2	0.269	-5.71	0.048	0.660	0.620
	0.4	0.54	-3006.2	-3006.2	5.04	-4559.9	0.295	-5.64	0.061	0.611	0.647
	0.5	0.51	-2864.9	-2864.9	5.14	-4451.6	0.310	-5.22	0.083	0.604	0.750
	0.6	—	—	—	—	—	—	—	—	—	—
313.1	0.1	0.75	-3627.1	-3627.1	4.63	-5075.6	0.245	-7.54	0.014	0.636	0.481
	0.2	0.64	-3114.6	-3114.6	4.72	-4591.7	0.255	-6.30	0.030	0.664	0.559
	0.3	0.63	-2764.0	-2764.0	4.79	-4263.8	0.263	-5.48	0.051	0.685	0.660
	0.4	0.61	-2237.9	-2237.9	4.76	-3730.5	0.260	-4.47	0.087	0.739	0.711
	0.5	—	—	—	—	—	—	—	—	—	—
	0.6	—	—	—	—	—	—	—	—	—	—

*Critical micellar concentration.

4. Conclusion

Mixed micellization of DTABr and CTABr was investigated in aqueous and ethanolamine-water mixed solvent systems, and the results of the study allow us to conclude the following.

- (1) The observed CMC values of DTABr-CTABr mixture obtained by Rubingh model are lower than those predicted from Clint's model, indicating the presence of nonideality in the mixed micelle formation.
- (2) It was observed that changing the mole fraction (α_{DTABr}) over the temperature of studies, the CMC increases, signifying the dependence of CMC of mixed DTABr-CTABr on temperature.
- (3) The higher cohesive energy of ethanolamine in relation to water justifies the higher aggregation of DTABr-CTABr, as the concentration of ethanolamine in the solvent system increases.
- (4) The negative value of excess free energy (G^E) and interaction parameter (β_{12}) obtained for the binary combination of DTABr and CTABr at different temperature indicate the synergistic behavior and also signify evidence of significant degree of interaction in mixed-micelle formation, which increases as the amount of ethanolamine in the water-ethanolamine mixed solvent system increases.

- (5) The negative value of ΔH_M and positive value of ΔS_M over the temperature of studies both in aqueous and ethanolamine medium signify exothermic process and increase degree of disorderliness indicating that entropy change is favorable to the formation of mixed micelle. The ΔG_M values become more negative in the mixed solvent systems than in pure aqueous system indicating that the micellization process is more spontaneous in the mixed solvent system than in the pure aqueous system.

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