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Mixed Micellization of Cationic Surfactant Cetyltrimethylammonium p-tolunesulfonate (CTAT) with Anionic Zwitterionic Gemini Surfactant in Aqueous Medium

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Abstract

In this work mixed micellar system containing an anionic gemini surfactant with charged (cationic) surfactant has been studied by using surface tension method under standard condition in aqueous medium. The Clint approach was employed to determine various parameters like critical micelle concentration (cmc), surface excess concentration (Γ_{excess}), surface pressure at cmc (π_{cmc}), minimum area per molecule (A_{min}) etc as well as different thermodynamic parameters. The properties of the mixtures indicate spontaneous formation of thermodynamically stable micelles.

Key words: gemini surfactant, surface tension, Clint approach, cmc

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1. Introduction

Surfactants are a special type of compounds bearing physicochemical properties at the interfaces and in the bulk of the solution. Interactions between different surfactant molecules in solution have been extensively investigated because of their relevance in allowing for a better control of stability, flotation and rheology of dispersed systems. A complex balance of intermolecular forces between them is responsible for the formation of mixed micellization (synergistic effect). Mixed micelles are used in pharmaceutical formulations, in enhanced oil recovery, in industrial preparations, etc., depending upon surfactants, their compositions as well as temperature, solvents, additives, etc. [1].

Mixed micelles can exhibit better solution properties than single surfactants from the viewpoint of fundamental technologies, pharmaceutical and biological considerations [2]. Various theoretical models have been given and used to interpret the experimental results of binary combinations [3–14]. Mixed micelles formed by surfactant combinations such as nonionic/nonionic [15,16], anionic/nonionic [17,18], cationic/nonionic [16,19], cationic/ anionic [20–22], cationic/cationic [19,23] and anionic/anionic [16,18] have been studied in detail by several workers. Now-a-days biodegradable gemini surfactants are gaining considerable attention in both academic and industrial research laboratories as these surfactants are much more surface active compared to their conventional counterparts due to presence of two hydrophobic tails and two hydrophilic head groups covalently attached to a spacer [24]. Binary mixtures of gemini

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surfactants with single tail surfactants have greater probability of exhibiting synergism although the degree of synergism is governed by the head group variations and also by chain length variations [25]. Taking cognizance of their potential use (as already shown by better performance on micellar front), mixed micellization of cationic surfactants, cetyltrimethylammonium p-toluenesulfonate (CTAT) and Zwitterionic Gemini surfactant 1,2-bis[N-methyl-N-carboxymethyl tetradecylammonium] ethane (referred as $C_{14}Ab$) has been focused herein. Their structures are given in Figure 1.

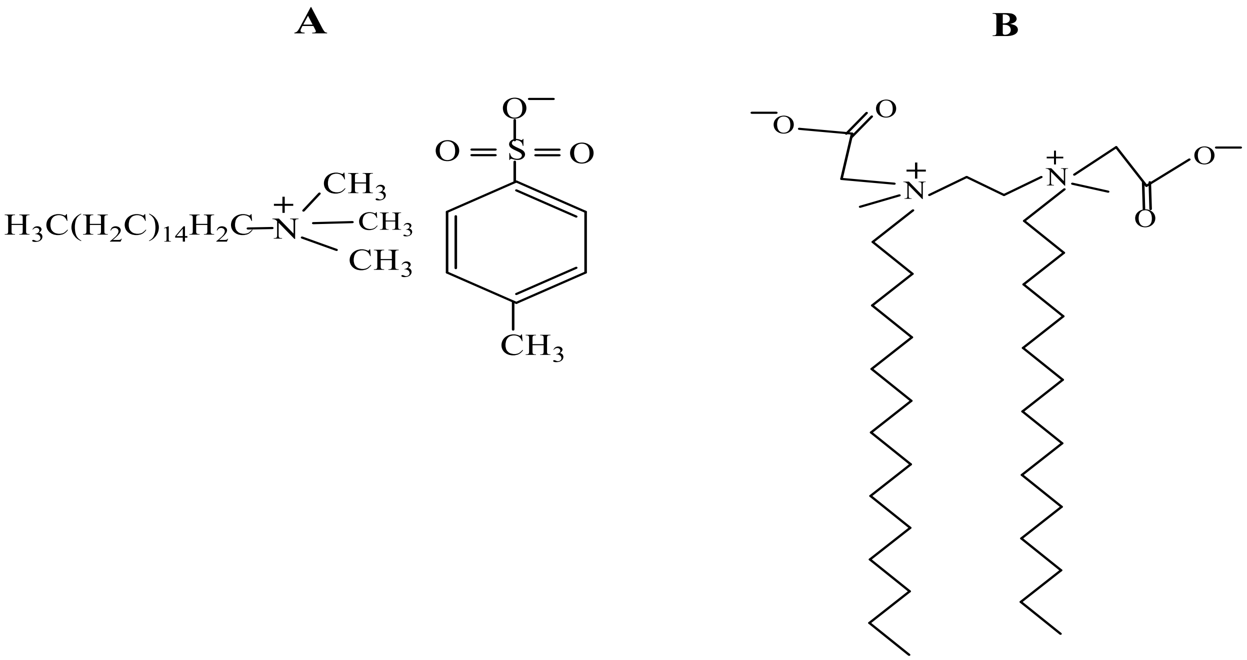

Figure 1. Chemical structure of (A) Cetyltrimethylammonium p-toluenesulfonate (CTAT), (B) 1,2 - bis [N-methyl-N-carboxymethyl tetradecylammonium] ethane ($C_{14}Ab$)

2. Materials and methods

Hexadecyltrimethylammonium p-toluenesulfonate (CTAT) (purity ≥ 98%) were purchased from Merck, India. The gemini was synthesized in the laboratory by the method discussed in the literature [26]. All the solutions were prepared in triple distilled water.

Tensiometry

For surface tension measurements, it was used Krüss (Germany) tensiometer applying ring detachment method. Concentrated stock solution of surfactants in aqueous medium at a particular mole fraction of CTAT was added to water with a Hamilton micro syringe taking 5 min time for equilibration before each measurement. All measurements were done for three times to check reproducibility. The accuracy of the method was ± 0.1 mN.m^{-1}. To get the *cmc*, surface tension (γ) vs. log [surfactant] was plotted and from the breaks in the plot, *cmc* (at this stage surface tension remains almost unchanged) was obtained (Figure 2).

3. Results and discussion

In aqueous medium, the surfactant solutions of low concentration behave as simple electrolytic solutions and most of the surfactant molecules exist as free monomers. However, above a certain concentration, known as critical micelle concentration (cmc), micelles start to form through aggregation of monomers. In a homologous series, the cmc of surfactants is related to the number of carbon atoms in the hydrophobic chain. An increase in the length of hydrophobic chain releases more water molecules causing an increase in entropy. Hence micelle formation becomes easier, i.e., cmc value decreases. However, effect of head group and counter ion on cmc is comparatively lesser. In case of gemini surfactants, two hydrophobic chains break the water structures and thus enhance the tendency to form micelles more in comparison to single chain surfactants, hence cmc values are lower for gemini surfactants [27]. An aqueous solution containing surfactant mixtures also forms aggregates, but the tendency of aggregation can be different from that of the pure surfactants. In binary mixtures, the cmc values decrease with the increase in mole fraction of the gemini surfactant. The results indicate that the added geminis assist conventional surfactants in the micelle formation and partition in micelles of monomeric surfactants; whereas the opposite is not true, i.e., conventional surfactants do not penetrate into gemini micelles. As mole fraction of conventional surfactant CTAT increases in the mixture cmc of mixtures increases gradually. For binary systems, *cmc** (critical micellar concentrations of the mixture) can be calculated by using Eq. (1) where α_1 is the mole fraction of surfactant 1 (CTAT), α_2 is the mole fraction of surfactant 2 (C_{14}Ab), and cmc_1 and cmc_2 are the cmc values of pure surfactants

$$\frac{1}{cmc*} = \frac{\alpha_1}{cmc_1} + \frac{\alpha_2}{cmc_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Along with the experimentally evaluated cmc values of binary mixtures, Table 1 records the *cmc** (ideal cmc of the mixtures) values, calculated in the light of Eq. (1). The difference in cmc and cmc* indicates non-ideality. A smaller cmc value corresponding to $cmc*$ is attributed to the mixed micelle formation due to attractive interactions between the unlike monomers, i.e., synergism in the system. It can be seen from Table 1 that the cmc values for CTAT/C_{14}Ab mixtures are higher than that for C_{14}Ab. Greater hydrophobicity of gemini molecules enhances the process of micellization and hence micelle formation occurs at concentrations lower than the ideal concentrations, which is clear from the curves shown in Figure 2. Interaction of hydrophobic chains in surfactant mixture, can be considered as an ideal process and free energy of the system decreases when the surfactant chain moves from monomeric phase to micellar phase. However, interactions between head groups may be considered as a nonideal process.

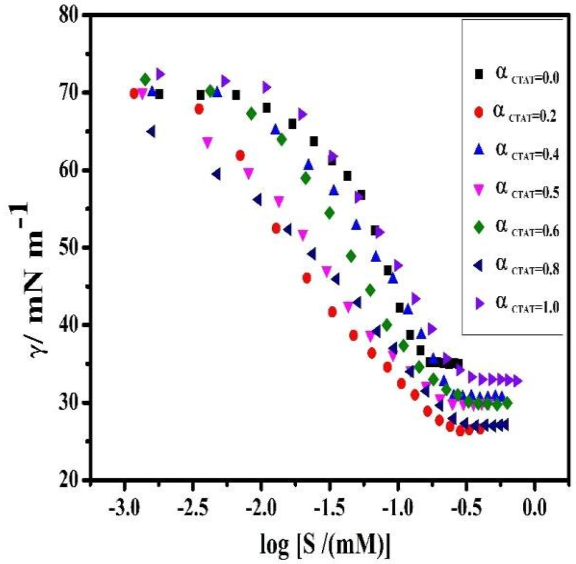

Figure 2. Plots of surface tension (γ) *vs* log [S/(mM)] at different mole fraction of CTAT in water at 298.15 K.

Adsorption behaviour

The surface tension of pure or mixed solution decreases when amphiphiles adsorb at the air–water interface. The breakdown of hydrogen bonds at the surface is responsible for the reduction in surface tension. On increasing the concentration of amphiphiles after the saturation at the interface, the amphiphilic molecules start to aggregate into nanostructured assemblies called as the micelle. After this association, the surface tension remains constant (Figure 1). The Gibbs adsorption isotherm can be used to calculate the amount of adsorbed amphiphiles per unit area at various concentrations by the fundamental Gibbs adsorption equation [28].

$$\Gamma_{max} = -\frac{1}{2.3031nRT}\, lim_{C\rightarrow cmc}\frac{d\gamma}{dlogC} \ldots\ldots\ldots\ldots\ldots \quad (2)$$

where R, T, and c are the gas constant (8.314 J·mol⁻¹·K⁻¹), the temperature in Kelvin and concentration in mol·kg⁻¹ respectively; n is the number of ionic species whose concentration at interface varies with the change in the [amphiphile] in the solution. For CTAT, n is taken as 2, and for gemini n is taken as 1. For mixtures, n is calculated by using the relation $n = X_1n_1 + X_2n_2$. The surface excess is a measure of the effectiveness of the surfactant adsorption at the interface. The packing and tightness of molecules at the interface depends on the value of Γ_{max}, higher value of corresponds to maximum packing and strong surfactant molecules at the interface. The physico-chemical properties like foaming, wetting, and emulsification can be determined by the adsorption effectiveness. The surfactant concentration required to reduce the surface tension by 20 mN·m⁻¹ is a useful measure of efficiency a surfactant. It is a negative logarithm of C_{20} values, $pC_{20} = -\log C_{20}$. The pC_{20} for pure CTAT is lower than the mixtures, indicates that the concentration required to decrease the surface tension of water in 20 mN·m⁻¹ is lower in the presence of CTAT (Table 1).

The efficiency increase with increasing length of the gemini surfactant. The values of minimum area per molecule (A_{min}) for all the studied mixed systems were calculated using the equation:

$$A_{min} = \frac{10^{18}}{N_A\Gamma_{max}} \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

The Γ_{max} and A_{min} values are recorded for these systems in Table 1. The data shows that the Γ_{max} of C_{14}Ab is more than that of the CTAT. The lower Γ_{max} values in the case of gemini are due to the fact that these molecules, having two hydrophilic head groups covalently bonded with the help of a spacer and thus occupy more area. Moreover, with the increase in chain length of these surfactants, the data recorded in Table 1 reveals that the CTAT has higher surface adsorption (less A_{min}), while the adsorption tendency of CTAT molecule in the binary mixtures decreases. The balance between hydrophilicity and hydrophobicity of a particular amphiphile is responsible for the surface activity of that surfactant. The adsorbed molecules at solution–air interface occupy more at lower values of the Γ_{max} (higher A_{min}), due to the lower compactness. The Table 1 data show that the area occupied per molecule in the mixtures is more than those taken by CTAT, which confirmed that the interacting components are loosely packed at the interface. The obtained outcomes also advocate that the gemini surfactants somewhat engaged in the adsorption on the surface.

The areas occupied by the amphiphiles heads are greater than the ideal state, as a result of loose monolayer formation by binary mixtures. The difference between the interfacial tension of water (γ_o) and interfacial tension at cmc (γ_{cmc}) is known as surface pressure (π_{cmc}). It is a measure of the effectiveness of interfacial tension reduction. It can be expressed as

$$\pi_{cmc} = \gamma_0 - \gamma_{cmc} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

The π_{cmc} values of mixtures are larger than CTAT (Table 1), which indicates a significant reduction in the effectiveness of the amphiphiles in lowering the surface tension.

Table 1. Experimental Critical Micellar Concentrations (*cmc*), Calculated ideal Critical Micellar Concentrations according to Clint equation (Eqn no. 1) and other surface and thermodynamic parameters at 298.15 K.

α_{CTAT}	cmc_{exp} (mM)	cmc^* (mM)	Γ_{max} x 10^6 mol m^{-2}	A_{min} nm^2/molecule	π_{cmc} (mN m^{-1})	pC_{20}	γ_{cmc} mN m^{-1}	$-\Delta G^o_m$ kJ mol^{-1}	$-\Delta G^o_{ads}$ kJ mol^{-1}	G_{min}
0	0.169		2.336	0.710	34.9	0.772	35.2	30.045	47.462	11.682
0.2	0.185	0.187	2.642	0.628	44.2	0.617	26.7	30.473	46.425	11.290
0.4	0.207	0.210	3.237	0.512	40.7	0.589	30.6	30.593	44.245	8.246
0.5	0.218	0.224	3.480	0.477	42.1	0.596	29.8	29.788	41.280	9.452
0.6	0235	0.240	3.738	0.444	42.5	0.569	30.7	30.319	41.699	8.226
0.8	0275	0.279	4.883	0.339	40.7	0.521	27.3	30.433	38.784	6.270
10	0.334		8.428	0.196	40.0	0.476	32.9	31.477	35.618	4.176

Here the surface pressure = π_{cmc} , minimum area per molecule = A_{min} , efficiency of interfacial adsorption = pC_{20}, standard free energy of micellization = ΔG^o_m , standard free energy of interfacial adsorption = ΔG^o_{ads} , surface tension at *cmc* = γ_{cmc}

Thermodynamics of micellization

The standard Gibbs free energies of micellization and adsorption have been calculated as per the following equations [29, 30]:

$$\Delta G^{o}_{m} = RT \, In X_{cmc} \qquad \ldots\ldots\ldots\ldots (5)$$

$$\Delta G^{o} = \Delta G^{o}_{m} - (\pi_{cmc}/\Gamma_{max}) \qquad \ldots\ldots\ldots\ldots\ldots (6)$$

where X_{cmc} is the cmc in mole fraction unit obtained from surface tension studies. The calculated values of ΔG^{o}_{m} are given in Table 1. The ΔG^{o}_{m} are found to be negative for pure amphiphiles as well as mixed amphiphiles, indicating that the process of micellization is spontaneous. The adsorption process can be measured as a distribution between the bulk and surface phases. The values of ΔG^{o}_{ad} of the mixtures are more negative than those of pure CTAT, which signify that in the attendance of surfactants molecules are dragged up to the interface more easily. More negative values of the ΔG^{o}_{ad} than ΔG^{o}_{m} confirm that the micellization is secondary in nature as compared to surface adsorption. Sugihara et al. [31] have projected a thermodynamic quantity, G_{min}, for evaluating synergism in mixed systems and given as:

$$G_{min} = A_{min}\gamma_{cmc}N_{A} \qquad \ldots\ldots\ldots\ldots\ldots (7)$$

G_{min} is considered as the work required for making an interface or the free energy change accompanied by the transition from bulk phase to the interface of the components in the solution. In other words, the lower the value of G_{min}, the more thermodynamically stable surface is formed. The value of G_{min} also measures the evaluation of synergism in the mixed systems. It is clear from the Table 1 that the values G_{min} are lower in magnitude. It means thermodynamically stable surfaces are formed with synergistic interaction.

4. Conclusions

The mixed micellization and thermodynamic properties of the Cetyltrimethylammonium p-toluenesulfonate (CTAT) and cationic gemini surfactants (C_{14}Ab) have been studied. The cmcs of the mixed amphiphiles were measured by surface tension measurement. The results suggested that the two components formed mixed micelles and mixed monolayer. The values of experimental cmc (cmc_{exp}) are lower than that of the ideal cmc (cmc^{*}) which suggests that the mixed micelles were formed due to electrostatic interactions. The spontaneity of the current systems is confirmed by the negative values of the standard free energy of micellization (ΔG^{o}_{ad}). Values of free energies indicate that the process of adsorption at the interface is primary whereas micellization is secondary.

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