Synergistic Behavior of Mixed Monolayer/Mixed Micelle Formation between Cationic Monomeric and Dimeric Surfactants with PEO-PPO-PEO Triblock Copolymer

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The micellar and surface properties of PEO-PPO-PEO triblock copolymer (Pluronic F-127) with cationic monomeric (hexadecyltrimethylammonium bromide), and gemini or dimeric (Pentanediyl-1, 5-bis (dimethylcetylammonium bromide)) surfactants was investigated using surface tension and conductivity measurements in aqueous solution. Various micellar, interfacial and thermodynamic parameters were evaluated. All the mixtures of binary systems show synergism. The synergistic interactions are found to be more with dimeric surfactant. The copolymer contribution in mixed micelles also increases with gemini surfactant.

1. INTRODUCTION

The interactions between polymers and surfactants in aqueous solutions have gained wide interest because of their extensive industrial applications [1-4]. The addition of polymers to surfactant solutions may alter micellar properties due to the interactions between polymer chains and surfactant micelles [5-9] which results in conformational changes in polymer chains [10]. The triblock copolymers, Pluronics, with general formula PEO_n–PPO_m–PEO_n (where PEO is poly(ethyleneoxide), PPO is poly(propyleneoxide) blocks and n, m are the number of blocks), have been the subject of intense research due to their industrial applications. Use of these pluronics as drug encapsulation/drug delivery systems and in the synthesis of different nanostructures has been well-demonstrated in literature [11-15]. Pluronics are known to form a core-shell micellar structure with hydrophobic core of the PO block and relatively hydrophilic EO blocks as the corona region [16].

In most of their applications, triblock copolymers (TBPs) are used with other surfactants to enhance their properties [17,18]. The presence of two different types of amphiphiles results in complex micro heterogeneous systems. It is essential to understand properties of such systems in detail for their efficient use. The association mechanism and the break-up of TBP micelles upon addition of ionic surfactants have been studied by calorimetry and scattering techniques, cyclic voltametry, time-resolved fluorescence, SANS and NMR [19-22]. It is reported that TBPs form unique assemblies in the presence of sodium dodecylsulfate (SDS) where the hydrophobic chain of the surfactant gets dissolved in the core of the polymer micelle and the charged head group resides at the peripheral region of the core projecting into the hydrated corona region [23].

The interaction of TBPs with nonionic surfactants was investigated by means of differential scanning and isothermal calorimetry, static and dynamic light scattering, and shear viscosity method [20,24,25]. Vieira et al. [26] observed a synergistic interaction between TBP ($EO_{23}PO_{52}EO_{23}$) and ionic surfactants (SDS and DTAB) and a strong repulsive interaction with nonionic surfactant (C_8EO_4). Couderc et al. [27] observed a synergistic interaction in binary mixtures of hexaethylene glycol mono-n-dodecyl ether ($C_{12}EO_6$) and F-127. However, reports on TBP – gemini surfactant interactions are scarce [22,28-33]. Therefore, aim of this study is to investigate the interactions between F-127 and cationic gemini 16-5-16 at the surface and in the solution. A comparison is made with those of the mixtures of F-127 and CTAB. The results are compiled in the form of Tables and Figures.
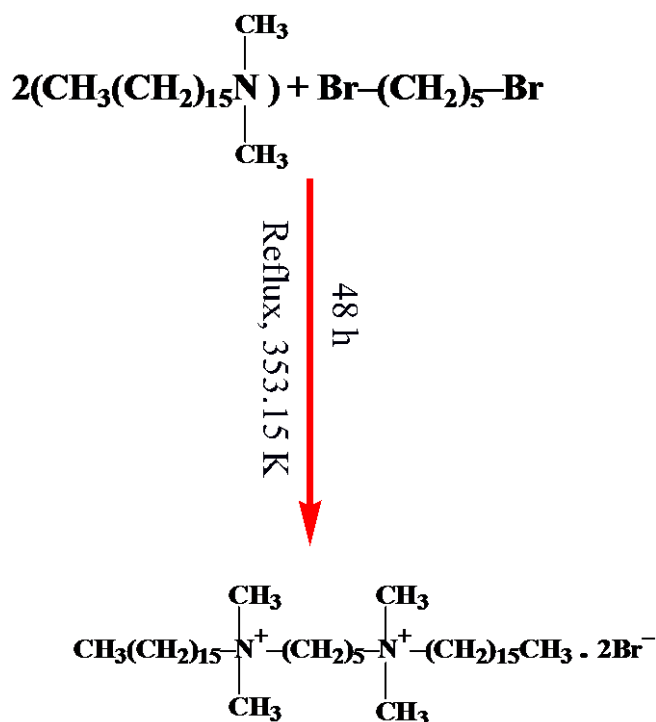
2. EXPERIMENTAL PROCEDURE

2.1 Materials and chemicals

Pluronic F-127 (Sigma, USA), Hexadecyltrimethylammonium bromide (CTAB; Merck, Germany), *N*, *N*-dimethylhexadecylamine (Fluka, Germany), 1, 5-dibromopentane (Fluka, Germany) ethanol absolute (Merck, Germany), ethyl acetate for high performance liquid chromatography and spectroscopy (Sigma, USA) were used and employed as obtained without further purification throughout the study. The double distilled de-ionized water was used in the making of stock solutions of pure and mixed surfactants solutions.

### 2.2 Synthesis of gemini surfactant

The gemini surfactant was synthesized by adopting scheme 1 and procedure outlined in references [34]. A 1:2.1 equivalent of the corresponding 1, 5-dibromopentane with *N*, *N*-dimethylhexadecylamine in dry ethanol was refluxed for 48h. At the end, the solvent was removed under vacuum from the reaction mixture, and the obtained solid was re-crystallized several times from hexane/ethylacetate mixture to obtain the compound in pure form. The overall yield of the surfactants ranged from 70 to 90 %. The synthesized gemini surfactant was checked by proton nuclear magnetic resonance (^{1}HNMR) spectroscopy using deuterated chloroform ($CDCl_3$) as a solvent.

$$2(CH_3(CH_2)_{15}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N}}) + Br-(CH_2)_5-Br$$

Reflux, 353.15 K   48 h

$$CH_3(CH_2)_{15}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N^+}}-(CH_2)_5-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N^+}}-(CH_2)_{15}CH_3 \cdot 2Br^-$$

Scheme 1. Protocol for synthesis of gemini (16-5-16) surfactant.

2.3 Surface tension measurements

The surface tension of pure as well as mixed solution was acquired by using Attension tensiometer (Sigma 701, Germany) at 298.15 K and follows the platinum ring detachment technique [35]. The surface tension of doubly distilled pure water at 298.17 K was used (72 m Nm^{-1}) to calibrate the instrument. A thermostat was used to maintain the temperature (having error ± 0.1 K) of the studied solution.
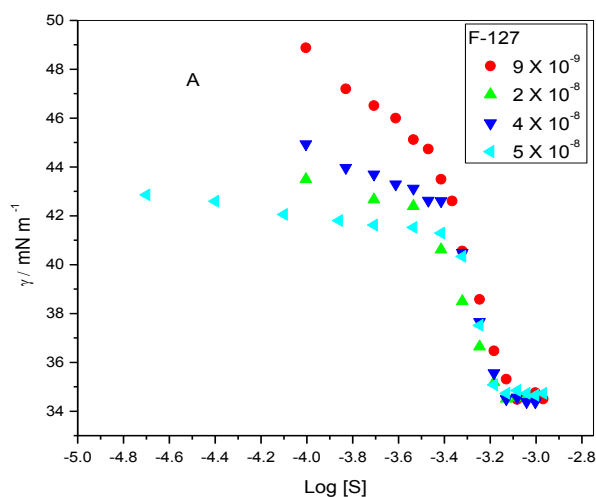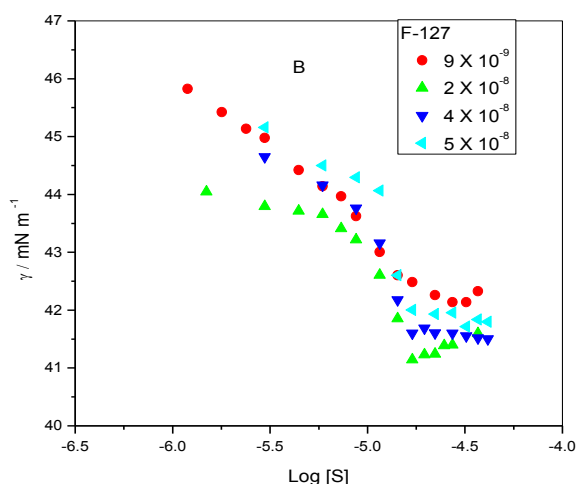
Figure 1. Plots of surface tension versus log of total surfactant molar concentration for (A) F-127+CTAB (B) F-127+16-5-16.

The mentioned instrument works on Du Nouy principle proposed by the French physicist Pierre Lecomte du Nouy [36]. According to Du Nouy principle, the force, required to raise the ring from the liquid's surface is measured and related to the liquid surface tension as:

$$F = 2\pi(r_i + r_a)\gamma \qquad (1)$$

where F is the force, r_i is the radius of the inner ring of the liquid film pulled and r_a is the radius of the outer ring of the film. In the vessel fixed amount of solvent was taken and different aliquot volumes of stock solution were added. After each set of experiment the ring was cleaned on the ethanol flame. The precision of the measurements was around ± 1.0 m Nm^{-1}. The logarithm of surfactant concentration vs. measured surface tension graph (Fig. 1) was used to determine the critical micelle concentration (cmc).
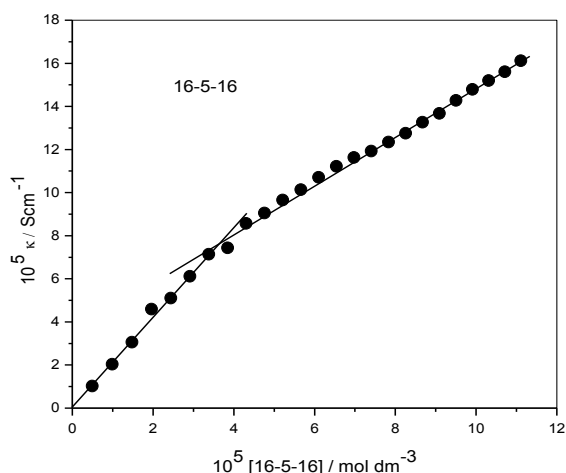
2.4 Conductometry measurement
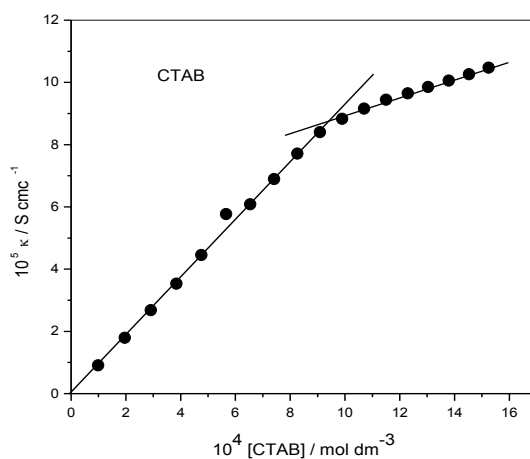
Figure 2. Typical plots of the variation of specific conductivity versus CTAB / [16-5-16] at 298.15 K.

The cmcs of pure conventional and gemini surfactants were estimated by this method. The Equiptronic conductivity meter (EQ 661, India) was used with a temperature probe. The intersection of the two straight lines of the specific conductance (κ) vs concentration graph was used to get the cmc value (Fig. 2).

3. RESULTS AND DISCUSSION

3.1 Interaction in the mixed micelles

Table 1. Different physicochemical parameters for F-127+CTAB/16-5-16 mixtures at 298.15 K.

α_1	$\dfrac{10^4 cac}{(\text{mol dm-}^3)}$	$\dfrac{10^4 cmc}{(\text{mol dm-}^3)}$	$\dfrac{10^4 cmc_{\text{ideal}}}{(\text{mol dm-}^3)}$	X_1^{m}	$10^{-7}\,X_1^{\text{ideal}}$	$-\beta$	$10^{-6}\,f_1^{\text{m}}$	f_2^{m}
			F-127+CTAB					
0		9.48	9.48					
9.0×10^{-9}	3.37	8.34	9.48	0.063	0.681	15.79	0.951	0.939
2.0×10^{-8}	3.52	7.05	9.48	0.104	1.510	17.13	1.077	0.829
4.0×10^{-8}	3.85	6.94	9.48	0.109	3.020	16.53	2.021	0.820
5.0×10^{-8}	4.28	6.76	9.48	0.115	3.780	16.53	2.352	0.805
1.0	0.11	1.25	1.25					
			F-127+16-5-16					
0		0.38	0.38					
9.0×10^{-9}	0.07	0.19	0.38	0.144	0.027	25.16	0.009	0.595
2.0×10^{-8}	0.09	0.17	0.38	0.157	0.061	25.13	0.017	0.538
4.0×10^{-8}	0.10	0.16	0.38	0.168	0.121	25.03	0.029	0.493
5.0×10^{-8}	0.12	0.14	0.38	0.177	0.152	25.49	0.032	0.450
1.0	0.11	1.25	1.25					

The cmcs of pure surfactants were determined by the tensiometric and conductometric techniques. The TBP is non-ionic in nature, so the cmc values of pure and mixed system were only determined by surface tension. The obtained value of cmcs (by conductometric titration) of CTAB (0.935 mM) and 16-5-16 (0.0361 mM) match well with the tensiometric cmc values (Table 1). Interaction between TBPs and ionic surfactants mainly depends on the surfactant tail length, surfactant head-group, polymer hydrophobicity and flexibility [3,37]. Figure 1 shows the plots of surface tension vs. concentration for four different mole fractions of F-127 in F-127 +16-5-16/CTAB mixtures. It is clear from the figures that there are two breaks in F-127 + surfactant plots whereas a single break is present in pure surfactants' plots. Two breaks in presence of polymer indicate that two kinds of aggregation phenomena are taking place in the solution. First break is critical aggregation concentration (cac) where the interaction of polymer chains with surfactant starts. At this concentration polymer supported micelles forms along the polymer chain. A further increase in the surfactant concentration results in second break point which is known as critical micelle concentration (cmc). This is considered as the saturation point above which normal micelles of surfactant coexist with aggregates supported on the polymer backbone. The cmc is, in general, about two to three times higher than the cac (Table 1). It is clear from the table that as the polymer mole fraction increases, cac values increase in both gemini and conventional surfactant systems; the increase is slower with gemini as compared to CTAB. Similar results were obtained by Bakshi [38] with poly(vinyl pyrrolidone) and Sardar et al. [39] with hydroxypropyl methyl cellulose. The cmc values, on the other hand, for both surfactants increase as the polymer mole fraction increases. This may be due to the fact that, as the amount of polymer increases, there is an increase in the binding sites available to the surfactant monomers or micelle-like aggregates (not the true micelles), therefore, a greater amount of the surfactant is required to bind to the polymer. After the total binding sites are occupied, the surfactant becomes free to form micelles [39]. The increase in cmc is also slow in both systems as the amount of added polymer is small. In F-127 + CTAB systems as the cmc values of the mixture fall in between those of pure components mixed micelles are formed due to attractive interactions whereas in F-127 + 16-5-16 systems synergism occurs (the mixture cmc values are lower than those of single components). This difference may be due to the hydrophobicity of the two components. Geminis are more hydrophobic than CTAB; hence, they form micelles more easily both in aqueous systems and in mixtures.

To evaluate and understand the interactions among mixed systems, Clint [40] proposed a model which depends upon the cmc values of single amphiphile. The relevant equation for this model is:

$$\frac{1}{cmc_{ideal}} = \frac{\alpha_1}{cmc_1} + \frac{1-\alpha_1}{cmc_2} \qquad (2)$$

where α_1 is the mole fraction of F-127, cmc_1 and cmc_2 are the cmc values of F-127 and surfactants respectively. The cmc_{ideal} is the cmc at ideal condition. These values are provided in Table 1 along with cac values. As the mole fraction of polymer is very small its effect on mixed micelles would be small. This is clear from the data as cmc_{ideal} is equal to that of cmc of CTAB or 16-5-16. cmc_{ideal} is always greater than cmc values of the mixtures suggesting attractive/synergistic interactions among polymer and surfactant in mixed micelles.

As mixed micelles are formed by the contribution of two components, Rubingh [41] proposed a model to obtain the fraction of both components in the mixed micelles. It is an iterative algorithm and the equation is:

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

where X_1^m is the micellar mole fraction of F-127 and cmc is the mixture's experimental cmc value. The obtained values are provided in Table 1, X_1^m values are close to 0.1 in CTAB + polymer systems and close to 0.15 in 16-5-16 + polymer systems. The mole fraction of polymer is small so its contribution in the mixed micelles is also expected to be low. Also polymer has a large structure and accommodation of these chains in mixed micelles is difficult. Therefore, its contribution remains low.

Motomura [42] proposed an equation to calculate the value of mole fraction of mixed components at ideal condition (X_1^{ideal}).

$$X_1^{ideal} = \alpha_1 \, cmc_2/(\alpha_1 cmc_2 + (1-\alpha_1) \, cmc_1) \qquad (4)$$

X_1^{ideal} values are smaller than X_1^m values and increases slightly with the increase in α_1. Ideally the mole fraction of TBP in the mixed micelles should be very low.

Rubingh's model evaluates not only the contribution of mixed components, but also gives the strength and nature of interaction among them. β^m, the interaction parameter, is given by the equation:

$$\beta^m = \frac{\ln(cmc\alpha_1/cmc_1 X_1^m)}{(1-X_1^m)^2} \qquad (5)$$

If β^m comes out to be positive the interactions between the two components are antagonistic; if it is zero, then there is no net interaction among the mixed components. Negative values of β^m indicate attractive or synergistic interactions. Larger the magnitude of β^m stronger is the interactions, either attractive or repulsive. In our systems β^m values are large in magnitude and negative, suggesting synergism in the systems. Within a system magnitude increases with the increase in α_1. Also, with gemini the magnitude is greater as for CTAB.

These values can be used to calculate the values of activity coefficients, f_1^m and f_2^m, of the two components in mixed micelles.

$$f_1^m = \exp\{\beta^m(1-X_1^m)^2\} \qquad (6)$$
$$f_2^m = \exp\{\beta^m(X_1^m)^2\} \qquad (7)$$

At all mole fraction values $f_1^m < f_2^m$ and values for gemini are lower than for CTAB. This means that surfactants (both conventional and gemini) are closer to their standard state (for which activity coefficient should be 1). This is understandable as the amount of polymer in the solution as well as in the mixed micelles is small.

3.2 Interaction at the air–water interface

Amphiphiles, in general, adsorb at the interfaces before forming aggregates. The mole fraction of the two components can be evaluated using Rosen's model [43] which is analogous to Rubingh's

model. In this model instead of cmc values, concentration of mixture and pure components at a particular γ (surface tension) value is taken.

$$\frac{(X_1^\sigma)^2 \ln[C_{Exp}\alpha_1/C_1 X_1^\sigma]}{(1-X_1^\sigma)^2 \ln[C_{Exp}(1-\alpha_1)/C_2(1-X_1^\sigma)]} = 1 \qquad (8)$$

$$\beta^\sigma = \frac{\ln(C_{Exp}\alpha_1/C_1 X_1^\sigma)}{(1-X_1^\sigma)^2} \qquad (9)$$

where C_{Exp}, C_1 and C_2 are the concentration of the mixture, F-127 and surfactant respectively. X_1^σ is the mole fraction of F-127 and β^σ is the interaction parameter at the interface (Table 2).

Table 2. Different physicochemical parameters for F-127+CTAB/16-5-16 mixtures at 298.15 K.

α_1	$10^4 C_{exp}$ (mol dm^{-3})	$10^4 C_{ideal}$ (mol dm^{-3})	X_1^σ	$10^{-6} X_1^{\sigma ideal}$	$-\beta^\sigma$
		F-127+CTAB			
0	5.45				
9.0×10^{-9}	4.40	5.45	0.092	0.412	15.21
2.0×10^{-8}	3.45	5.45	0.144	0.916	16.95
4.0×10^{-8}	3.36	5.45	0.152	1.830	16.42
5.0×10^{-8}	0.81	5.45	0.274	2.290	25.39
1.0	0.12				
		F-127+16-5-16			
0	0.24				
9.0×10^{-9}	0.24	0.24	0.015	0.018	14.02
2.0×10^{-8}	0.14	0.24	0.150	0.041	21.71
4.0×10^{-8}	0.15	0.24	0.141	0.082	20.12
5.0×10^{-8}	0.17	0.24	0.119	0.103	18.47
1.0	0.12				

The calculated values of surface interaction parameters are negative with respective average value being F-127+16-5-16 > F-127+CTAB. The average negative values, in the case of gemini is more than CTAB indicate the large synergistic interaction. The van der Waals interaction between hydrophobic tails is, therefore, the prevailing factors over electrostatic repulsion. For F-127+CTAB system the average negative value of β^σ is higher than β^m, means the interaction between the components of adsorbed monolayer is higher than that of between the components in micellar phase. While in case of F-127+CTAB the opposite trend is obtained.

The amount of amphiphile adsorbed at the interface or mixed interface can be evaluated by Gibbs adsorption isotherm [44].

$$\Gamma_{max} = -\frac{1}{2.303nRT}(\partial\gamma/\partial \log C) \qquad (10)$$

where $(\partial\gamma/\partial \log C)$ is the slope of γ vs. concentration curve, R and T have their usual meanings. Γ_{max} is the maximum surface excess concentration at cmc and n is the number of species whose concentration at the interface changes with concentration. For CTAB, n is taken as 2; for 16-5-16, n is

taken as 3; and for F-127, n is taken as 1. For mixtures, n is calculated using the relation $n = n_1 X_1^{\sigma} + n_2(1 - X_1^{\sigma})$. Equation 10 can be used to calculate minimum surface area per amphiphile molecule (A_{min}).

$$A_{min} = 1/(N_A \Gamma_{max}) \qquad (11)$$

where N_A is Avogadro number. The values of Γ_{max} and A_{min} are given in Table 3.

Table 3. Interfacial and thermodynamic parameters for F-127+CTAB/16-5-16 mixtures at 298.15 K.

α_1	$10^6 \Gamma_{max}$ (mol m^{-2})	A_{min} (nm)	A_{ideal} (nm)	γ_{cmc} (mNm-1)	$_{cmc}\Pi$ (mNm-1)	$-\Delta G_m^o$ (kJmol-^{1})	$-\Delta G_{ad}^o$ (kJmol-^{1})	$-\Delta G_{ex}$ (kJmol-^{1})
				F-127+CTAB				
0	2.29	0.72		36.11	33.89	27.20	41.96	
9.0×10^{-9}	2.37	0.69	0.92	34.43	35.57	27.51	42.49	2.31
2.0×10^{-8}	2.94	0.56	1.03	34.47	35.53	27.93	40.02	3.97
4.0×10^{-8}	2.24	0.74	1.05	34.46	35.54	27.97	43.83	3.99
5.0×10^{-8}	2.65	0.62	1.32	34.81	35.18	28.04	41.28	4.16
1.0	0.57	2.89		38.83	31.17			
				F-127+16-5-16				
0	0.73	2.27		39.17	30.83	35.17	77.36	
9.0×10^{-9}	0.94	1.76	2.28	42.20	27.80	36.83	66.28	7.66
2.0×10^{-8}	0.63	2.62	2.36	41.14	28.86	37.12	82.72	8.24
4.0×10^{-8}	0.46	3.59	2.36	41.58	28.42	37.36	98.83	8.67
5.0×10^{-8}	0.27	6.15	2.35	42.56	27.44	37.62	139.19	9.19
1.0	0.57	2.89		38.83	31.17	32.22	86.61	

As the two parameters have inverse relationship we will discuss only A_{min}. As expected, A_{min} values for single components are in the order: F-127 >16-5-16 > CTAB. TBPs have long PEO chains and hence TBPs acquire higher A_{min} values. On the other hand CTAB has a single ammonium head group and its A_{min} value is lowest among the three amphiphiles. In 16-5-16 gemini there are two ammonium head groups and a spacer, therefore, its A_{min} value is greater than that of CTAB. In TBP – surfactant systems, in general, the values are lower than those of single amphiphiles. Due to the small amount of TBP in the solution its effect on A_{min} also remains insignificant and with the increase in α_1 A_{min} changes slightly. Presence of TBP in micelles of cationic surfactant decreases the repulsion among head groups and A_{min} values decrease. Table 3 also lists the ideal mixing values, A_{ideal} calculated from the equation

$$A_{ideal} = X_1^{\sigma} A_1 + X_2^{\sigma} A_2 \qquad (12)$$

where X_1^{σ} and X_2^{σ} are the micellar molar fraction of components 1 and 2 at the interface, respectively. We found that the ideal values are higher than the corresponding experimental values in the case of F-127 + CTAB which reveal attractive interaction between two components at studied mole fractions. For the F-127 + 16-5-16 mixed system the ideal values are lower than experimental values. This indicates that the area occupied by the surfactant head is greater than the ideal state as a result of the loose monolayer formation by binary mixtures.

The surface pressure (π_{cmc}) is the difference between the interfacial tension of water (γ_o) and interfacial tension at the cmc (γ_{cmc}). The effectiveness of interfacial tension reduction is measured by the surface pressure. The π_{cmc} values were calculated for various systems and recorded in Table 3.

These are found to increase with the addition of TBP with CTAB and decrease with the addition of TBP with 16-5-16 for the present binary systems.

3.3 Thermodynamics of micellization and interfacial adsorption

For mixed micellar systems, the theoretical models are based on the equilibrium between the micelles and the monomer in solution. Phase separation and mass action are the two models that commonly explain the micellization phenomenon. The mixed aggregate as a separate phase is considered in the phase separation approach, which considers the mixed aggregate to be a separate phase, whereas in the mass action model the process of aggregation is treated as a set of reversible reactions in which the reactants are monomers and the products are aggregates with different sizes. Considering the negligible degree of counterion dissociation of the Pluronic F-127 + surfactants mixed systems, the standard free energy of micellization is calculated from RST (Regular Solution Theory) using [45–49]

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

The cmc in mole fraction units is shown by the term X_{cmc} and obtained from surface tension studies. The calculated values of ΔG_m^o are given in Table 3. The negative values of ΔG_m^o signify the spontaneity of the aggregation formation. The standard Gibbs free energy of adsorption was calculated from ΔG_m^o and through surface tension data using the equation [50–52]

$$\Delta G_{ad}^o = \Delta G_m^o - \frac{\pi_{cmc}}{\Gamma_{max}} \qquad (14)$$

In our systems, high and negative values of ΔG_{ad}^o were obtained, thus interfacial adsorption of molecules is favored, suggesting no phase separation occurs in the mixed adsorbed monolayers and confirming that a miscible monolayer exists. The ΔG_{ad}^o is found to be more negative as compared with ΔG_m^o, revealing that the adsorption is the primary process compared to micellization.

By using activity coefficients, the excess free energy of mixing (ΔG_{ex}) can be computed using the relation [53–62]:

$$\Delta G_{ex} = \left[X_1^m \ln f_1^m + \left(1 - X_1^m\right) \ln f_2^m \right] RT \qquad (15)$$

Table 3 lists the values of ΔG_{ex}. It is concluded that the micelles formed by the pure single amphiphiles are less thermodynamically stable than the micelles formed by the mixed system, as confirmed by the negative values of the ΔG_{ex}.

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