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Interaction Between Cationic Gemini and Monomeric Surfactants: Micellar and Surface Properties

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Attraction effects in the mixed micelle of gemini (C₁₆-12-C₁₆, 2Br⁻) and monomeric surfactants i.e. cetyltrimethylammonium bromide (CTAB), cetyltriphenylphosphonium bromide (CTPB) and cetyltributylphosphonium bromide (CTBuPB) mixtures in aqueous solution were investigated by conductivity and surface tension measurements. The attractive interaction of surfactants in the mixed micelle leading to non-ideality has theoretically treated by Clint’s and Rubingh’s model in the light of regular solution theory. The experimental critical micelle concentration (cmc) values were lower than predicted from ideal mixture theory. The negative values of interaction parameters (βᵐ and βˢ) for mixed micelle formation indicate the attractive interaction for all the systems. The Motomura’s theory was used to determine the composition of each compound in mixed micelles (Xₐₐₑₐ). The excess free energy of the mixed systems was also calculated and the obtained negative values for all the mixed systems studied gave an indication that the mixed micelles are thermodynamically more stable relative to the individual component.


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1. INTRODUCTION

Micelle formation in mixtures of surfactants is of considerable interest from both fundamental and practical points of view\(^1,2\). Surface-active compounds used in commercial applications typically consist of a mixture of surfactants because they can be produced at a cost relatively lower than that of pure surfactants\(^3-5\). In addition, in practical fields, mixed surfactants work better than single surfactants\(^6,7\); the composition and concentration can be optimized for each practical application. Since different types of surfactants exist, various kinds of combinations are possible, with different properties and application fields. The interactions among surfactant molecules in aqueous solution have been extensively investigated because of their technological relevance in interfacial systems allowing for a better control of stability, flotation and rheology of dispersed systems in different technological processes\(^8-10\). Many hypotheses have been developed in order to predict the ideal behavior of surfactants in aqueous solution regarding equilibrium surface tension and adsorption at the fluid interface. The micellar systems consisting of the mixtures of surfactants of variable structures are of a high theoretical and industrial interest.

Various theoretical models are available to describe the formation of mixed micelles. The first approach proposed by Clint\(^11,12\) is based on the pseudo-phase separation model and assumes an ideal mixing of the surfactant molecules. The treatment of non-ideal mixing was proposed by Rubingh\(^13\) based on the regular solution theory. Using first principle of thermodynamics, Motomura et al.\(^14, 15\) have derived equations in terms of excess thermodynamic quantities. According to Holland and Rubingh\(^5, 16\), mixed micelle or surfactant systems are encountered in nearly all practical applications of surfactants. It has been known for a long time that surfactant mixtures can show a very different behavior from that of their components.

Gemini surfactants are constituted by two hydrophilic groups and two hydrophobic groups per molecular unit rather than one hydrophilic group and one hydrophobic group in conventional surfactant systems. They possess unique properties, such as lower critical micellar concentration (cmc), greater efficiency in lowering the surface tension, lower Kraft temperature, and better solubilization in comparison with conventional surfactants, which is due to the great difference of molecular structures between gemini surfactants and conventional surfactants\(^17-19\). These unusual characteristics of gemini surfactants made a very interesting topic of research. Many gemini surfactants have been synthesized, and their unusual physicochemical properties,
including their high surface activity, unusual changes of viscosity, unusual micelle structure, and aberrant aggregation behavior\textsuperscript{20, 21} have been investigated. Cationic gemini surfactants have applications in skin care formulations\textsuperscript{22, 23}, the construction of high-porosity materials\textsuperscript{24, 25}, templates for the synthesis of nanoparticles\textsuperscript{26-28}, nanorods\textsuperscript{29}, biomedical application including gene delivery\textsuperscript{30-32}, drug entrapment/release\textsuperscript{33} and antimicrobial activity\textsuperscript{34, 35} etc. The performances exhibited by the surfactant mixtures are attributed to the intermolecular interactions which can be predominantly antagonistic or synergistic depending on the nature of the surfactants\textsuperscript{36}.

Recently, Saha et al.\textsuperscript{37} have studied the aggregation behavior and thermodynamics of mixed micellization of gemini surfactants with a room temperature ionic liquid in water and water-organic solvent mixed media. Banipal et. al.\textsuperscript{38} have studied the mixed micellization behavior of \textit{m-2-m} gemini surfactants with some conventional surfactants in aqueous and aqueous polyethylene glycol (PEG) solutions at different temperatures using conductometric and viscometric methods. They observed that all the combinations (except 12-2-12 + CTAB) were found to behave nonideally with mutual synergism which decreases by increasing the temperature. Micellization in the aqueous binary mixtures of n-decanoyl N-methylglucamide, MEGA 10, and alkanediyl-\textit{α,ω}-bis(dodecyldimethylammonium) bromide, 12-s-12 (with \textit{s} = 7, 9, 11), have been investigated at 303 K by Moya and coworkers\textsuperscript{39}.

In our previous paper, we have studied the mixed micellization of gemini (16-10-16 and 16-4-16) and monomeric surfactants in aqueous and aquo-ethylene glycol solution\textsuperscript{40-41}. All the binary mixtures showed a synergic interaction behavior. In this present investigation, we have used gemini (16-12-16) and monomeric surfactants (CTAB, CTPB and CTBuPB) [Scheme I]. The results have been analyzed in the light of physicochemical concepts and proposed theories.
Cetyltrimethylammonium bromide (CTAB)

Cetyldiphenylphosphonium bromide (CTPB)

Cetyltributylphosphonium bromide (CTBuPB)

Gemini surfactant \([\text{C}_{16-12}-\text{C}_{16}], 2\text{Br}^-\)

Scheme I Structure of some cationic monomeric and gemini surfactants

2. EXPERIMENTAL DETAILS

2.1 MATERIALS

The gemini surfactants were synthesized as previously reported\(^ {41, 42}\). CTPB and CTBuPB were obtained from Caldon chemicals, Canada (distributors of Lancaster, Synthesis of England). CTAB was purchased from Sigma-Aldrich. All the chemicals were used without further purification. All solutions were prepared in triple distilled water.
2.2 Conductivity Measurements

Conductivity measurements were carried out with a Systronics direct reading conductivity meter (Type 306). The conductivity cell was calibrated with KCl solutions in the appropriate concentration range. Accuracy of measured conductance was within ±0.5%. The critical micelle concentrations (cmc) of single and mixed surfactants were determined by conductivity measurements at 300 K. The pure surfactant solutions were prepared by diluting the concentrated stock solution. The mixed solutions were prepared by mixing two pure solutions and were kept for at least 12 hrs for equilibrium. The conductivity at each mole fraction was measured by successive addition of concentrated solution of surfactant mixture in pure water.

2.3 Surface Tension Measurement

The surface tension of aqueous solutions of surfactants at various concentrations were determined with a surface tensiometer (Jencon, India) using a platinum ring by the ring detachment technique. The tensiometer was calibrated against distilled water. Platinum ring was thoroughly cleaned and dried before each measurement. The ring was hung to the balance, dipped into the solution and then pulled out. The maximum force needed to pull the ring through the interface was measured and correlated to the surface tension. Each experiment was repeated several times until good reproducibility was achieved. The results were accurate within ±0.1 mN m⁻¹.

3. RESULTS AND DISCUSSION

We have studied the cmc values of three binary systems (16-12-16 + CTAB, 16-12-16 + CTPB, 16-12-16 + CTBuPB) using conductivity and surface tension measurements. For each system, the cmc values of these binary mixtures with mole fractions ranging from 0.0 to 1.0 (0.0, 0.2, 0.3, 0.5, 0.7, 1.0) were determined. As discussed above, all the conductivity and surface tension measurements were made at 300 K.

The intramicellar interactions in the surfactant mixture are studied at the critical micelle concentration, where these effects on mixed micelle formation can be measured. Break points in the specific conductivity (κ) versus molar concentration plots were taken to represent critical micelle concentrations (see Figure 1(a)). Table I lists the cmc values obtained at variable mole ratios at 300 K, as well as the composition of each mixed system. Figure 1(b) shows the surface
**Table I.** Critical micelle concentration (cmc) of binary combinations at 300 K in aqueous solution.

<table>
<thead>
<tr>
<th>ω_{Mono.}</th>
<th>CTAB/16-12-16</th>
<th>CTPB/16-12-16</th>
<th>CTBuPB/16-12-16</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cmc (mM)</td>
<td>cmc (mM)</td>
<td>cmc (mM)</td>
</tr>
<tr>
<td>0.0</td>
<td>0.024 0.022 0.023</td>
<td>0.025 0.025 0.025</td>
<td>0.025 0.025 0.025</td>
</tr>
<tr>
<td>0.2</td>
<td>0.027 0.026 0.026</td>
<td>0.028 0.028 0.028</td>
<td>0.028 0.028 0.028</td>
</tr>
<tr>
<td>0.3</td>
<td>0.032 0.030 0.031</td>
<td>0.032 0.031 0.032</td>
<td>0.035 0.035 0.035</td>
</tr>
<tr>
<td>0.5</td>
<td>0.034 0.032 0.033</td>
<td>0.036 0.036 0.036</td>
<td>0.052 0.054 0.053</td>
</tr>
<tr>
<td>0.7</td>
<td>0.060 0.058 0.059</td>
<td>0.174 0.170 0.172</td>
<td>0.200 0.200 0.205</td>
</tr>
<tr>
<td>1.0</td>
<td>1.000 1.000 1.000</td>
<td>0.3</td>
<td>0.025 0.025 0.025</td>
</tr>
</tbody>
</table>

S.T. = Surface Tension, Cond. = Conductivity, Av. = Average

**Fig. 1.** Dependence of the specific conductivity and surface tension on surfactant concentration for CTBuPB + C_{16}-12-C_{16}2Br binary system, with solution X_{CTBuPB} = 0.7.
tension (γ) versus log (C) (i.e., C is the surfactant concentration) plots for gemini surfactant at 300 K. The surface tension initially decreases with increasing concentration of surfactants and then reaches a plateau region, indicating that micelles are formed and the concentration of the break point corresponds to the critical micelle concentration. The cmc values as determined by both methods are the same; however, the trend of increasing cmc values with increasing the mole fraction of monomeric surfactants is observed in Table I. The average cmc values, determined by tensiometric and conductometric methods (plots are shown in Figure 2 and others in Supporting Information), of pure and binary mixtures of gemini with conventional surfactants are presented in Table I.

3.1 Surface Properties

The amount of surfactant adsorbed per unit area of the surface can be calculated with the help of Gibbs adsorption Eq. The packing densities of surfactants at the air−water interface are important to the interpretation of the surface activities of surfactants. The surface areas occupied by the surfactant molecules should reflect their packing densities. The surface excess concentration, Γ\text{max} and the surface area, A\text{min} at the air−water interface can be calculated using the Gibbs adsorption Eq.

\[ \Gamma_{\text{max}} = \frac{1}{2.303 n R T} \left[ \frac{d\gamma}{d \log C} \right]_{T, P} \]  

(1)

where, γ denotes the surface tension, R is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), T is the absolute temperature, C is the surfactant concentration, \((d\gamma / d \log C)\) is the slope of the γ vs log C plot taken at the cmc. The constant (prefactor) n takes the values 2 for a conventional surfactant where the surfactant ion and the center line are univalent and \(n = 3\) for a gemini surfactant made up of a divalent surfactant ion and two univalent counterions.

The area occupied per surfactant molecule (A\text{min}) at the air−water interface has been obtained by using Eq. (2)

\[ A_{\text{min}} = \frac{1}{N} \Gamma_{\text{max}}. \]  

(2)

The value of the surface pressure at the cmc (\(\pi_{\text{cmc}}\)) was obtained from Eq. (3),
Table II. Critical micelle concentration (cmc_{ideal}), the maximum surface excess (Γ_{max}), the minimum surface area per molecule (A_{min}), Surface pressure at the cmc (π_{cmc}), packing parameter (P), Gibbs free energy of micellization (ΔG^{°}_{m}), the standard Gibbs energy of adsorption (ΔG^{°}_{ads}), and the free energy at the air/water interface (G^{°}_{min}) values of single and mixed cationic gemini and monomeric surfactant.

<table>
<thead>
<tr>
<th>α_{Mono.}</th>
<th>cmc_{ideal}</th>
<th>Γ_{max} \times 10^6 mol.m^{-2}</th>
<th>A_{min} \times 10^{20} m^2</th>
<th>π_{cmc} mN.m^{-1}</th>
<th>P</th>
<th>ΔG^{°}_{m} kJ/mol</th>
<th>ΔG^{°}_{ads} kJ/mol</th>
<th>G^{°}_{min}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.024</td>
<td>0.82</td>
<td>203</td>
<td>26.2</td>
<td>0.21</td>
<td>-80.9</td>
<td>-112.8</td>
<td>56.24</td>
</tr>
<tr>
<td>0.2</td>
<td>0.026</td>
<td>1.24</td>
<td>133</td>
<td>27.7</td>
<td>0.32</td>
<td>-58.1</td>
<td>-80.5</td>
<td>35.64</td>
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<tr>
<td>0.3</td>
<td>0.029</td>
<td>1.08</td>
<td>153</td>
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<td>0.28</td>
<td>-57.1</td>
<td>-81.4</td>
<td>42.38</td>
</tr>
<tr>
<td>0.5</td>
<td>0.039</td>
<td>0.92</td>
<td>180</td>
<td>24.2</td>
<td>0.24</td>
<td>-56.0</td>
<td>-82.3</td>
<td>52.03</td>
</tr>
<tr>
<td>0.7</td>
<td>0.056</td>
<td>0.88</td>
<td>186</td>
<td>22.2</td>
<td>0.23</td>
<td>-54.7</td>
<td>-79.9</td>
<td>56.01</td>
</tr>
<tr>
<td>1.0</td>
<td>0.174</td>
<td>1.51</td>
<td>109</td>
<td>19.2</td>
<td>0.39</td>
<td>-52.5</td>
<td>-65.3</td>
<td>34.79</td>
</tr>
<tr>
<td>0.2</td>
<td>0.027</td>
<td>1.05</td>
<td>157</td>
<td>26.2</td>
<td>0.27</td>
<td>-58.3</td>
<td>-83.3</td>
<td>43.49</td>
</tr>
<tr>
<td>0.3</td>
<td>0.030</td>
<td>1.04</td>
<td>159</td>
<td>25.5</td>
<td>0.26</td>
<td>-56.7</td>
<td>-81.3</td>
<td>44.72</td>
</tr>
<tr>
<td>0.5</td>
<td>0.039</td>
<td>0.91</td>
<td>180</td>
<td>24.0</td>
<td>0.24</td>
<td>-55.2</td>
<td>-81.6</td>
<td>52.25</td>
</tr>
<tr>
<td>0.7</td>
<td>0.058</td>
<td>0.89</td>
<td>186</td>
<td>21.8</td>
<td>0.23</td>
<td>-52.8</td>
<td>-77.3</td>
<td>56.46</td>
</tr>
<tr>
<td>1.0</td>
<td>1.69</td>
<td>97</td>
<td>15.4</td>
<td>0.44</td>
<td>-51.3</td>
<td>-60.4</td>
<td>33.18</td>
<td></td>
</tr>
</tbody>
</table>

CTAB

CTPB

CTBuPB
\[ \pi_{\text{cmc}} = \gamma_o - \gamma_{\text{cmc}} \]  

(3)

where \( \gamma_o \) and \( \gamma_{\text{cmc}} \) are the values of surface tension of water and the surfactant solution at the cmc, respectively. The surface excess \( \Gamma_{\text{max}} \) is an effective measure of adsorption at air/water interface. It measures how much the air/solution interface has been changed by surfactant adsorption and depends on the molecular structures of surfactants. The value of the surface excess concentration (\( \Gamma_{\text{max}} \)) in each case has been calculated and is given in Table II. Adsorption behavior at the air/solution interface of gemini surfactants affect other characters such as wetting, emulsification, bubbling, foaming, and so on, since coherently packed interfacial films have very different properties than that of noncoherent loosely packed ones. The minimum area per molecule is higher in mixed surfactant systems for the conventional monomeric surfactants but lower than the pure cationic gemini surfactant. The low values of \( \Lambda_{\text{min}} \) suggest that the orientation of the surfactant molecule at the interface is almost perpendicular to the interface.  

As proposed by Israelachvili et al., the micellar shape is mainly governed by the geometry of the surfactant and its packing. The surface area of amphiphiles in mixed micelles and micellar growth (spherical- nonspherical) can be used to find out the packing parameters, \( P \),

\[ P = \frac{V_0}{\Lambda_{\text{min}} l_c} \]  

(4)

where \( V_0 \) is the volume of exclusion per monomer in the aggregate, given by Tanford’s formula \( V_0 = [27.4 + 26.9 (n_c-1)]2 \ \text{Å}^3 \), \( l_c = [1.54 + 1.26 (n_c-1)] \ \text{Å} \), is the maximum chain length and \( n_c \) is the number of carbon atoms in the hydrocarbon chain. The \( \Lambda_{\text{min}} \) refers to a property related to the surfactant monolayer at the air/water interface and in reality, different from the required value at the micellar surface. The packing parameter determines the geometry of micelles and indicates minimum sized aggregates in solution, which minimizes the Gibbs free energy of micellization.  

It is worth noting that one of the Gibbs energy contributions to micellization is the deformation Gibbs energy of the surfactant tail. This contribution, which is positive, increases when the packing parameter increases for a given hydrophobic chain length. Therefore, a decrease in \( P \) favors micellization. It is interesting to point out that differences in the shape of micelles not only affect the mixtures within the micellar core, but also the electrostatic interactions at the mixed micelles (among other contribution to the Gibbs energy of micellization). This would mean that the nonideality is observed when the difference in the packing parameter of the components increases and this will be the result of hydrophobic as well
as electrostatic interactions between the two surfactants present in the mixed micelles. Table II shows the values of the packing parameter for the binary mixtures studied in this work. The $P$ values corresponding to the pure components of the system differ substantially, co-micellization will result in significant $P$ variations. Changes in the formation of Gibbs energy contribution will follow and as a consequence, nonideal behavior is expected for these binary systems. Taking this into account, one would expect that the nonideality of the binary systems would increase when difference in the packing parameters of the two components of the mixture increases. Packing parameter is higher in mixed systems for single gemini surfactants, but lower than the single monomeric surfactants (shown in Table II).

3.2 Thermodynamics of Micellization and Interfacial Adsorption Phenomena.

The standard free energy of micellization per mole of monomer unit ($\Delta G^\ominus_m$) for the binary combinations in the case of ionic gemini surfactant is related to cmc through Eq. (5)  

\[
\Delta G^\ominus_m = 2(1.5 - \alpha) \text{ RT } \ln X_{\text{cmc}}
\]  

where $X_{\text{cmc}}$ is the cmc in mole fraction units and $\alpha$ is the degree of micellar ionization. The $\Delta G^\ominus_m$ values (Table II) reveal that all the binary systems have considerable spontaneity of micellization. The adsorption of single cationic gemini, monomeric surfactants and their binary mixtures at the air/water interface can be calculated according to the Gibbs adsorption isotherm Eq. (7),

\[
\Delta G^\ominus_{\text{ad}} = \Delta G^\ominus_m - \left(\pi_{\text{cmc}}/\Gamma_{\text{max}}\right)
\]

where $\pi_{\text{cmc}}$ is the surface pressure at cmc. Both $\Delta G^\ominus_m$ and $\Delta G^\ominus_{\text{ad}}$ are negative and their magnitudes reveal the latter to be more spontaneous due to hydrophobicity of amphiphiles leading them toward air/water interface. From this, it is concluded that micelle formation is secondary and less spontaneous compared to adsorption.

The synergism/attraction in the mixed adsorbed monolayer formation can also be quantified in terms of another thermodynamic quantity, known as free energy of a surface at equilibrium ($G^s_{\text{min}}$) 

\[
G^s_{\text{min}} = A_{\text{min}} \cdot \gamma_{\text{cmc}} \cdot \text{NA}
\]

where $\gamma_{\text{cmc}}$ is the surface tension of the surfactant system at equilibrium. $G^s_{\text{min}}$ is a measure of evaluation of synergism and is defined as free energy change accompanied by transition from the
bulk phase to the surface phase of solution or work needed to make an interface per mole. The lower is the value of free energy, the more thermodynamically a stable surface is formed, which is a measure of evaluation of synergism. The low magnitudes of $G^{s}_{\min}$ values (Table II) of pure monomeric, pure gemini surfactants and their mixtures indicate that thermodynamically stable surfaces are formed by these systems. The $\Delta G^{s}_{\min}$ values are listed in Tables II. In case of mixtures, these values increase with increasing mole fractions of monomeric surfactant. The value of $\Delta G^{s}_{\min}$ is maximum for gemini surfactant whereas the minimum value is obtained for CTBuPB.

3.3 Clint Model

Clint equation\textsuperscript{11, 12} has been used to understand the behavior of mixed micelle formation by varying the mole fractions to relate the experimental cmc of the pure components with the ideally mixed cmc (i.e. cmc\textsubscript{ideal}) as

$$\frac{1}{\text{cmc}_{\text{ideal}}} = \frac{\alpha f_1}{\text{cmc}_1} + \frac{1 - \alpha f_2}{\text{cmc}_2}$$

where $\alpha$ is the mole fraction of surfactant 1 in the total mixed solute, $f_1$ and $f_2$ are the activity coefficients of surfactants 1 and 2, respectively, and cmc\textsubscript{1} and cmc\textsubscript{2} are the cmc values of surfactants 1 and 2, respectively.

In the case of ideal behavior, $f_1 = f_2 = 1$. Hence, Eq. (9) can be written as:

$$\frac{1}{\text{cmc}_{\text{ideal}}} = \frac{\alpha}{\text{cmc}_1} + \frac{1 - \alpha}{\text{cmc}_2}$$

Inspite of inherent limitations, Eq. (10) is useful for comparison between ideal and nonideal mixtures. Critical micelle concentrations (cmc\textsubscript{ideal}), calculated from Clint Eq.\textsuperscript{11}, have been plotted against the stoichiometric mole fraction for various binary surfactant mixtures (Figures 2 and S1). The deviation of cmc\textsubscript{exp} from cmc\textsubscript{ideal} indicates nonideality in the mixed micelles. A nonideal mixing behavior is expected for the present binary mixtures due to various structural dissimilarities. All the Figures show that the cmc values of each mixture vary nonlinearly with respect to the change in bulk mole fraction, and that the cmc\textsubscript{exp} values are lower than the cmc\textsubscript{ideal} for all the binary mixtures. It is to be mentioned here that a lower value of cmc\textsubscript{exp} than the corresponding cmc\textsubscript{ideal} value indicates mixed micellization due to some sort of attractive
interactions operating between the unlike components. Due to the presence of dimeric head groups in combination with those of monomeric surfactants in the Stern layer of the mixed micelles, a nonideal behavior is expected in the mixed state. A quantitative interpretation of the results can be carried out by considering the regular solution approximation. This theory allows for the calculations of the micellar mole fraction as well as the interaction parameter by using equations, respectively.

### 3.4 Micellar Composition and Molecular Interaction Parameter ($\beta^m$)

#### 3.4.1 Rubingh Model

Most of the theories dealing with the binary mixtures of surfactants are based on the regular solution theory, and they have been applied to the phase separation model for the micelles in order to estimate the interaction parameter $\beta^m$ in various systems and the synergistic/attraction effects in mixed micelle formations. The molecular interaction parameter, $\beta^m$, for mixed micelle can be evaluated, among other things, using the equation derived by Rubingh $^{16}$.

$$\frac{(X_1)^2 \ln(\alpha_1 C_{mix} / X_1 C_1)}{(1-X_1)^2 \ln[(1-\alpha_1) C_{mix} / (1-X_1) C_2]} = 1$$  \hspace{1cm} (11)

Here $C_1$, $C_2$ and $C_{mix}$ denote the experimental cmc values of the surfactants 1, 2 and their binary mixtures, respectively, $X_1$ being the micellar mole fraction of surfactant 1 in the mixed micelle.

The micellar mole fraction of the ideal state ($X_{ideal}$) can also be evaluated by applying Motomura’s theory $^{14, 15}$, which is based upon excess thermodynamic quantities, and the related Eq. is

$$X_{ideal} = \frac{\alpha_1 C_2}{(\alpha_1 C_2 + (1 - \alpha_1) \times C_1)}$$  \hspace{1cm} (13)

It is found that $X_1$ (micellar mole fraction calculated from Rubingh equation) is lower than $X_{ideal}$ (Figures 3 and S2) in the case of $C_{16-12-C_{16}}/CTAB$, $C_{16-12-C_{16}}/CTPB$, and $C_{16-12-C_{16}}/CTBuPB$; this indicates the presence of nonideality in the mixed micelles. The results are shown in Table III.
Fig. 2. Variation of the cmc (mM) with the mole fraction $\alpha$ of (a) $C_{16-12}$-CTAB (b) $C_{16-12}$-CTPB systems. Solid line indicates the cmc$_{exp}$, and dotted line indicates the cmc$_{ideal}$. 
The interaction parameter, $\beta^m$, given by
\[
\beta^m = \frac{\ln(\alpha_i C_{\text{mix}/i} / X_i C_i)}{(1 - X_i)^2}
\] (12)

$\beta^m$ is an indicator of the degree of interaction between two surfactants in mixed micelles relative to the self interaction of two surfactants under similar conditions before mixing and accounts for deviation from ideality. A negative value implies an attractive interaction, a positive value to incompatible surfactant species and repulsion among mixed species while zero value indicates ideal mixing. The $\beta^m$ values are negative at all mole fractions of the mixed system, suggesting that the interaction between the two components is more attractive in the mixed micelle than the self-interaction of two components before mixing. From Table III, it is clear that the $\beta^m$ values are negative for all gemini and monomeric mixed surfactant systems indicating attractive interactions and hence synergism in the systems. The larger the negative value of $\beta^m$, the stronger the attractive interaction between two surfactant molecules. As reported in Table III, 16-12-16 + CTAB systems show the greater interaction at $\alpha = 0.5$ in comparison with other mixed systems. The average $\beta^m$ values for the three systems are -2.45 (CTAB/16-12-16), -1.5 (CTPB/16-12-16) and -1.04 (CTBuPB/16-12-16). This synergistic/attraction and hence nonideality lead to a polymorphism by interplaying between geometric packing and electrostatic interaction. The existence of synergism in mixtures containing surfactants depends not only on the strength of interaction but also on the relevant properties of individual surfactants of the mixture. For dimeric and monomeric surfactants, mixed systems significantly affect the electrostatic interaction at micellar surface along with size and shape of the micellar aggregate, which, in turn, can affect the hydrophobic interactions within the micellar core. The interactions between surfactants in binary mixtures are the result of two contributions: (i) electrostatic interactions in the micellar core and (ii) electrostatic interactions between head groups of both surfactants at the interface.

3.4.2 Rosen model

This model considers the interaction between the amphiphiles in a mixed surfactant solution at the air/solution interface. The micellar mole fraction of the surfactant 1 ($\chi^\alpha_1$) at the mixed adsorbed film can be calculated iteratively from the Rosen model solving the Eq.,
Fig 3. Micellar mole fraction, $X_m^1$ and $X_m^{ideal}$, versus mole fraction $\alpha$ of (a) C$_{16}$-12-C$_{16}$ + CTAB (b) C$_{16}$-12-C$_{16}$ + CTPB, binary mixtures. Solid line indicates the $X_1$, and dotted line indicates the $X_{ideal}$. 
Table III. Micellar mole fraction ($X_1$, $X_1^*$, $X_{\text{ideal}}^*$ and $X_{\text{ideal}}^*$) interaction parameter ($\beta^m$ and $\beta^\sigma$), activity coefficients ($f_1$, $f_2$, $f_1^*$ and $f_2^*$) and excess Gibbs free energy ($\Delta G^E$) for binary surfactant (CTAB/16-12-16, CTPB/16-12-16 and CTBuPB/16-12-16) system at 300 K in aqueous solution.

<table>
<thead>
<tr>
<th>$\alpha_{\text{Mon.}}$</th>
<th>$X_1^*$</th>
<th>$X_{\text{ideal}}^*$</th>
<th>$\ln(C_1^m/C_2^m)$</th>
<th>$\beta^m$</th>
<th>$f_1$</th>
<th>$f_2$</th>
<th>$\Delta G^E$ J/mol</th>
<th>$X_1^*$</th>
<th>$X_{\text{ideal}}^*$</th>
<th>$\ln(C_1^o/C_2^o)$</th>
<th>$\beta^\sigma$</th>
<th>$f_1^*$</th>
<th>$f_2^*$</th>
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<td></td>
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<td></td>
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\[
\frac{(X^\sigma)^2 \ln \left( \frac{\alpha_1 C_{\text{mix}}}{X^\sigma C_1^0} \right)}{(1 - X^\sigma)^2 \ln \left( \frac{(1 - \alpha_1) C_{\text{mix}}}{(1 - X^\sigma) C_2^0} \right)} = 1
\]  

(14)

where \(C_{\text{mix}}\), \(C_1^0\) and \(C_2^0\) are the concentrations of the mixture, pure surfactant 1 and 2 respectively at a fixed \(\gamma\) value, \(\alpha_1\) is the stoichiometric mole fraction of surfactant 1 in solution. The \(X_1^\sigma\) value was then used to evaluate the interaction parameter \((\beta^\sigma)\) at the air/solution interface using,

\[
\beta^\sigma = \frac{\ln \left( \frac{\alpha_1 C_{\text{mix}}}{X^\sigma C_1^0} \right)}{(1 - X^\sigma)^2}
\]

(15)

The values of \(\beta^\sigma\) and \(X_1^\sigma\) of the mixtures are presented in Table III. The \(X_1^\sigma\) values calculated by using the Eq. (14) and as shown in Figure S3, were found to be higher than \(X_1^m\) values, suggesting that more surfactant is present in mixed monolayer as in the mixed micelles. The calculated values of surface interaction parameters \((\beta^\sigma)\) are negative with the respective average values being -3.093, -2.135, -1.71 for CTAB+16-12-16, CTPB+16-12-16 and CTBuPB+16-12-16 and order is: CTAB+16-12-16 > CTPB+16-12-16 > CTBuPB+16-12-16. The negative value of \(\beta^\sigma\) shows the attractive interaction in mixed monolayer formation. In mixtures containing two amphiphiles, the existence of synergism has been shown to depend not only on the strength of interaction between them (measured by the values of the \(\beta\) parameter) but also on the relevant properties of the individual amphiphile components of a mixture. The conditions for synergism in surface tension reduction efficiency (when the total concentration of mixed surfactant required to reduce the surface tension of the solvent to a given value is less than that of individual amphiphile) are the following: (a) \(\beta\) (\(\beta^\sigma\) and \(\beta^m\)) must be negative and (b) \(|\beta| > |\ln (C_1/C_2)|\) where \(C_1\) and \(C_2\) are the molar concentrations of amphiphile 1 and 2, respectively, required to achieve the conductivity and surface tension value. The data show that there is very good synergism in surface tension reduction efficiency for the gemini surfactant/monomeric surfactant mixtures (Table III).

\(\beta^\sigma\) values are more negative than the \(\beta^m\) values in all the systems, which may be due to the difficulty of incorporating tightly packed chains into micelle. The \(\beta^\sigma\) and \(\beta^m\) values for the two mixed systems are listed in Table III and average value of interaction parameters are given in
Table IV, respectively \((\beta^\sigma > \beta^m)\). The comparative plots \((X_{\text{mono.}} \text{ vs } \beta)\) are shown in Figure 4. Both \(\beta^\sigma\) and \(\beta^m\) values are negative, suggesting that the interaction between the two surfactants is more attractive in the mixed monolayer and mixed micelle than the self-interaction of two surfactants before mixing. The comparison of average values reveals that \(\beta^\sigma\) and \(\beta^m\) values are higher for CTAB/16-12-16 surfactants while it is least for 16-12-16/CTBuPB combinations. Consequently, the attraction between the different surfactants in the mixed adsorbed layer is greater than in the mixed micelle. This is because the interaction between polar groups of the two surfactants is more effective on a flat surfactant solution–air surface than on the curved surface of a micelle\(^{58}\).

In addition, at the surfactant solution–air interface, the attraction between hydrocarbon fragments of two different surfactants caused by van der Waals forces will also be greater than on the volume of the micelle.

With the knowledge of the micellar interaction parameters \((\beta)\) for the mixed micelles, it is possible to determine the activity coefficients of surfactants in the mixed micelles. Using the nonideal solution theory, the activity coefficients \(f_1\) and \(f_2\) of gemini and monomeric surfactants, respectively, in mixed micelles\(^{13}\) are related to \(\beta\) by the following relations:

\[
f_1 = \exp\left[\beta \cdot (1 - X_1)^2\right]
\]
\[ f_2 = \exp [\beta \cdot (X_1)^2] \] \hspace{1cm} (17)

The values of activity coefficients, \( f_1 \) and \( f_2 \) are obtained from the Eqs. 16 and 17. For mixed micelles, \( f_1 = f_1^m \), whereas for a mixed monolayer, \( f_1 = f_1^\sigma \). From Table III, it is evident that the values of \( f_1^m \) and \( f_1^\sigma \) for monomeric amphiphiles are low signifying nonideal behavior whereas for gemini, \( f_2^m \) and \( f_2^\sigma \) are close to unity. This manifests molecular activity phenomenon between gemini and monomeric surfactants in the mixed micelles. It is clear from Eqs. 16 and 17 that the activity coefficients are directly related to both \( \beta \) and \( X_1 \). As the attractive or repulsive forces between various molecules in the mixed systems increase, the activity coefficients deviate from ideality (where activity coefficients should be unity). From Table III, it is evident that the values of \( f_1^m \) and \( f_2^m \) are less than unity which signifies nonideal behavior and thus attractive interactions between gemini and monomeric surfactants in the mixed micelles.

**3.4.3 Gibbs Excess Energy of Mixing (G\(_E\)):** Activity coefficients can be used to calculate excess free energy of mixing by the relation\(^{25}\)

\[ \Delta G_E = RT \left[ X_1 \cdot \ln f_1 + (1-X_1) \cdot \ln f_2 \right] \] \hspace{1cm} (18)

where \( R \) and \( T \) have their usual meanings. The negative \( \Delta G_E \) values, presented in Table III and Figure 5, suggest that mixed micelles are more stable than the micelles of pure surfactants. From a careful observation (Table III), it can be calculated that an increase in mole fraction of monomeric surfactant makes micelles more stable. The average values of \( \Delta G_E \) are -621.7, -634.5 and -293.3 (Jmol\(^{-1}\)) for CTAB / 16-12-16, CTPB / 16-12-16 and CTBuPB / 16-12-16 systems respectively. Average values of \( \Delta G_E \) are given in Table IV.
Fig. 5. Mole fraction of monomeric surfactant versus $\Delta G^E$.

Table IV. Average values of interaction parameters ($\beta$) and $\Delta G^E$.

<table>
<thead>
<tr>
<th>Surfactant Systems</th>
<th>$\beta^m_{av.}$</th>
<th>$\beta^e_{av.}$</th>
<th>$\Delta G^E$ J/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>16-12-16+ CTAB</td>
<td>-2.45</td>
<td>-3.09</td>
<td>-621.7</td>
</tr>
<tr>
<td>16-12-16+ CTPB</td>
<td>-1.57</td>
<td>-2.14</td>
<td>-634.5</td>
</tr>
<tr>
<td>16-12-16+ CTBuPB</td>
<td>-1.04</td>
<td>-1.71</td>
<td>-293.3</td>
</tr>
</tbody>
</table>
4. **SUMMARY**

In this paper, conductometric and surface tension studies of the binary mixtures of gemini and monomeric (CTAB, CTPB and CTBuPB) surfactants were presented. The surface properties (cmc, $\Gamma_{max}$, and $A_{min}$) have been evaluated. The results of our study show that experimental cmc values of all the binary mixtures are lower than the ideal cmc determined from the Clint’s equation. A negative deviation from the ideal behavior in the mixed micelle formation indicates the nonideal behavior. Both $\beta^{\sigma}$ and $\beta^{m}$ are more negative for the CTAB/16-12-16 mixture than that for other mixed systems; furthermore, the $\beta^{m}$ is less negative than $\beta^{\sigma}$ in all the mixed systems. The interaction parameters in the micelle as well as at interface are negative, indicating synergistic interaction of mixed systems. The negative values of the Gibbs free energy ($\Delta G^{\circ}_{m}$, $\Delta G^{\circ}_{ads}$, and $\Delta G^{E}$) indicate that the micelle formation takes place spontaneously and thereby stabilization of the micelles. These observations may be of interest in practical applications of gemini and monomeric surfactants combinations. The experimental results obtained in the present study may be useful for the selection of mixed surfactant systems.

**Acknowledgement**

Financial support of this work by the CSIR, New Delhi [Project No: 02/(0063)/12/EMR-II] is gratefully acknowledged. N.B. and P.Q. thank Compagnia di San Paolo for a grant (Progetti di Ricerca di Ateneo 2011-Linea 1A, project ORTO11RRT5).

**References and Notes**

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(c) P. Quaglìotto, N. Barbero, C. Barolo, K. Costabel, L. Marchese, S. Coluccia and K.G. Kalyanasundaram, Dyes and Pigments 82, 124 (2009).


Fig. Caption

**Scheme I.** Structure of some cationic monomeric and gemini surfactants

**Fig. 1.** Dependence of the specific conductivity and surface tension on surfactant concentration for CTBuPB + C_{16}-12-C_{16}2Br’ binary system, with solution X_{CTBuPB} = 0.7.

**Fig. 2.** Variation of the cmc (mM) with the mole fraction α of (a) C_{16}-12-C_{16} + CTAB (b) C_{16}-12-C_{16}+ CTPB systems. Solid line indicates the cmc_{exp}, and dotted line indicates the cmc_{ideal}.

**Fig 3.** Micellar mole fraction, X_{\text{m}} and X_{\text{ideal}}, versus mole fraction α of (a) C_{16}-12-C_{16} + CTAB (b) C_{16}-12-C_{16}+ CTPB, binary mixtures. Solid line indicates the X_{1}, and dotted line indicates the X_{\text{ideal}}.

**Fig. 4** Comparative plots of α_{mono.} vs β^{m}, β^{σ}.

**Fig. 5.** Mole fraction of monomeric surfactant versus ΔG_{E}. 
Scheme I Structure of some cationic monomeric and gemini surfactants

Cetyltrimethylammonium bromide (CTAB)

Cetyltriphenylphosphonium bromide (CTPB)

Cetyltributylphosphonium bromide (CTBuPB)

Gemini surfactant [C_{10}-12-C_{12}], 2Br⁻
Fig. 1. Dependence of the specific conductivity (a) and surface tension (b) on surfactant concentration for CTBuPB + C_{16-12}-C_{16,2}Br⁻ binary system, with solution X_{CTBuPB} = 0.7.
Fig. 2. Variation of the cmc (mM) with the mole fraction $\alpha$ of (a) $C_{16}$-12-$C_{16}^+$CTAB (b) $C_{16}$-12-$C_{16}^+$ CTPB systems. Solid line indicates the cmc$_{exp}$, and dotted line indicates the cmc$_{ideal}$. 
Fig 3. Micellar mole fraction, $X^m_1$ and $X^m_{\text{ideal}}$, versus mole fraction $\alpha$ of (a) C$_{16}$-12-C$_{16}$+CTAB (b) C$_{16}$-12-C$_{16}$+ CTPB, binary mixtures. Solid line indicates the $X_1$, and dotted line indicates the $X_{\text{ideal}}$. 
**Fig. 4** Comparative plots of $\alpha_{\text{mono.}}$ vs $\beta^m$, $\beta^\sigma$.

**Fig. 5.** Mole fraction of monomeric surfactant versus $\Delta G^E$. 
Table Caption

Table I. Critical micelle concentration (cmc) of binary combinations at 300 K in aqueous solution.

Table II. Critical micelle concentration (cmc_{ideal}), the maximum surface excess (Γ_{max}), the minimum surface area per molecule (A_{min}), Surface pressure at the cmc (π_{cmc}), packing parameter (P), Gibbs free energy of micellization (ΔG^°_m), the standard Gibbs energy of adsorption (ΔG^°_{ads}), and the free energy at the air/water interface (G^s_{min}) values of single and mixed cationic gemini and monomeric surfactant.

Table III. Micellar mole fraction (X_1, X_1^{ideal}, X^{ideal} and X^{ideal}) interaction parameter (β^m and β^σ), activity coefficients (f_1, f_2, f_1^σ and f_2^σ) and excess Gibbs free energy (ΔG^E) for binary surfactant (CTAB/16-12-16, CTPB/16-12-16 and CTBuPB/16-12-16) system at 300 K in aqueous solution.

Table IV. Average values of interaction parameters (β) and ΔG^E.
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<th>$\alpha_{\text{Mono}}$</th>
<th>CTAB/16-12-16</th>
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Table I. Critical micelle concentration (cmc) of binary combinations at 300 K in aqueous solution.
Table II. Critical micelle concentration ($\text{cmc}_{\text{ideal}}$), the maximum surface excess ($\Gamma_{\text{max}}$), the minimum surface area per molecule ($A_{\text{min}}$), Surface pressure at the cmc ($\pi_{\text{cmc}}$), packing parameter ($P$), Gibbs free energy of micellization ($\Delta G^\circ_m$), the standard Gibbs energy of adsorption ($\Delta G^\circ_{\text{ads}}$), and the free energy at the air/water interface ($G^s_{\text{min}}$) values of single and mixed cationic gemini and monomeric surfactant.

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<tr>
<th>$\alpha_{\text{Mono.}}$</th>
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<th>$A_{\text{min}} \times 10^{20}$</th>
<th>$\pi_{\text{cmc}}$</th>
<th>$P$</th>
<th>$\Delta G^\circ_m$ (kJ/mol)</th>
<th>$\Delta G^\circ_{\text{ads}}$ (kJ/mol)</th>
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S.T. = Surface Tension, Cond. = Conductivity, Av. = Average
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Table III. Micellar mole fraction ($X_1$, $X_\sigma$, $X_{ideal}$ and $X_{\sigma ideal}$) interaction parameter ($\beta^m$ and $\beta^\sigma$), activity coefficients ($f_1$, $f_2$, $f_1^\sigma$ and $f_2^\sigma$) and excess Gibbs free energy ($\Delta G^E$) for binary surfactant (CTAB/16-12-16, CTPB/16-12-16 and CTBuPB/16-12-16) system at 300 K in aqueous solution.

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Table IV. Average values of interaction parameters ($\beta$) and $\Delta G^E$.

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**Fig. S1.** Variation of the cmc (mM) with the mole fraction $\alpha$ of C$_{16}$-12-C$_{16}$+CTBuPB systems. Solid line indicates the cmc$^{\text{exp}}$, and dotted line indicates the cmc$^{\text{ideal}}$.

**Fig. S2.** Micellar mole fraction, $X^\text{m}_1$ and $X^\text{m}_\text{ideal}$, versus mole fraction $\alpha$ of C$_{16}$-12- C$_{16}$+CTBuPB, binary mixtures. Solid line indicates the $X^\text{m}_1$, and dotted line indicates the $X^\text{m}_\text{ideal}$.
Fig. S3. Micellar mole fraction, $X_1^{\sigma}$ and $X_{\text{ideal}}^{\sigma}$, versus mole fraction $\alpha$ of (a) $\text{C}_{16-12}$-$\text{C}_{16}$+CTAB (b) $\text{C}_{16-12}$-$\text{C}_{16}$+CTPB (c) $\text{C}_{16-12}$-$\text{C}_{16}$+CTBuPB, binary mixtures.