CHAPTER - III

MICELLAR PROPERTIES
OF SURFACTANTS IN PURE
AND MIXED STATES
MICELLAR PROPERTIES OF SURFACTANTS IN PURE AND MIXED STATES

3.1 INTRODUCTION

In aqueous medium, surfactants in pure and mixed states form micelles after a critical concentration, called critical micelle concentration. The formation of micelles is a cooperative process. The CMC is the characteristic of the surfactant species and various factors such as temperature, pH, additives and pressure etc. of the solution. The CMC can serve as a measure of micelle stability in a given state, the thermodynamics of micellization can be determined from a study of the temperature dependence of the CMC. Thermodynamics of formation, counterion binding, aggregation number, solubilization property, catalysing functions, etc., are important physicochemical aspects that need detailed and intensive attention for both fundamental understanding and application prospects in kinetics. The basic understanding of solution and interfacial behaviour of surfactants is necessary for the art of management of their surface chemical applications.

Mixed surfactants producing mixed micelles are very often used in industrial preparations and pharmaceutical and medicinal formulations for the purpose of solubilization, suspension and dispersion etc. In practical fields, mixed surfactants work better than a single surfactant. The physicochemical properties and functions of surfactant mixtures in solution are essentially guided by the molecular structures and head group types of amphiphiles and the solvent environments into which they are put in. Similar to the behaviour of individual surfactants on micellization, mixed systems undergo abrupt change in physicochemical properties which can be monitored conveniently using suitable experimental methods. The mixtures of surfactants can achieve great synergisms in various processes by manipulation of the relative tendency to form various aggregated structures. Often, the formation of certain aggregate will inhibit the formation of a less desirable aggregate. For example, addition of nonionic surfactants to anionic surfactants enhances the formation of micelles, resulting in a reduced tendency for the anionic surfactant to precipitate.

Much attention has been directed in recent years toward understanding the detailed behaviours of surfactant mixtures yielding mixed micelles.

Fundamental properties of mixed micelles, have, therefore, been studied by a number of workers, and the relevant theories have been proposed and used.
However, none of the theories are yet adequately perfect to predict the micellization properties on the basis of intra-or intersurfactant interactions including modifications therein by counterions, other additives, solvents, temperature, pressure, and other effective perturbants. The recent molecular thermodynamic theory in this direction is of considerable advancement and needs detailed testing on carefully collected data by different techniques. The dimensions of such investigation have also been extended by workers in this field examining the effects of chain length, and hydrophilic and hydrophobic groups in the surfactant molecules on the micellization and solution behaviours of different kinds of surfactants.

Out of the three types (ionic, nonionic, and zwitterionic) of surfactants, it is known that in the mixed state nonionics show ideal behaviour, while other combinations exhibit non-ideality resulting from synergistic (attractive) or antagonistic (repulsive) interactions between the amphiphiles of different types. The factors guiding the interactions are of various origin, their quantitative accounting remains a matter of continued research interest. It may be mentioned that similarly charged surfactants of different molecular architecture may exhibit both ideal and non-ideal behaviours in solutions forming micelles. A literature survey shows that considerable efforts have been made on the study of mixed surfactant systems to characterize micelles and their formation. The significant contributions of Moulik et al. and Rosen et al. deserve special mention in this context. Extensive investigations on the thermodynamics of micellization and adsorption, counterion binding, polarity, and aggregation number have been reported, but systematic studies are limited. In the present investigation various types of pure surfactants, mixed surfactants, and polymer-surfactant systems have been used for kinetic studies. Before doing kinetics it is necessary to characterize the system. In this presentation, results of the detailed exploration of the physicochemical properties of the following systems have been studied. Conductometric and surface tension methods have been adopted.

I. Pure surfactants.
II. Mixed surfactants (in binary combination)
III. Polymer-surfactant systems

Surfactant molecules are composed of a part that is soluble in water and a part that is soluble in oil. This dual nature is responsible for the ability of the surfactant molecules to organize themselves into various structures in aqueous and non-polar solvents, as well as for their ability to orient themselves at various types of interfaces. In a number of applications of importance to chemical, pharmaceutical, petroleum.
and mineral processing industries, the surfactant molecules are present in solution not alone but along with synthetic and biological macromolecules. The presence of the polymer molecules gives rise to changes in the solution and the interfacial properties of the surfactant compared to the corresponding polymer-free systems. A number of experimental studies have been carried out in recent years to determine these changes induced by the polymer molecule in the solution behaviour of surfactants. These studies show that nonionic polymer molecules associate with anionic surfactant micelles. Because of this association, the CMC which micelles begin to appear is lowered and the micelle sizes are smaller compared to the polymer-free systems. The nonionic polymer molecules appear either not to associate or only weakly associate with nonionic or cationic surfactant micelles. An understanding of how uncharged polymer molecules affect the aggregation behaviour of surfactants is useful for various existing applications. Such an understanding can also lead to a novel approach of controlling aggregation patterns in surfactant solutions through the addition of polymer molecules. Currently, a treatment of the interactions of nonionic polymers with various kinds of surfactant assemblies is not available. It would be useful to develop such a comprehensive treatment utilizing a common theoretical basis. The present study is a preliminary attempt to address this need.

The cultivation of the field is thus important but detailed fundamental studies of surfactant mixtures in solution are not yet adequate. Since different types of surfactants exist, various kinds of combinations are possible giving ample scope for further research. We hope that the comparative and quantitative descriptions of the pure and mixed surfactant systems of diverse characters (taken from literature and obtained from studies in our laboratory) will reveal the scope and limitations of the theoretical models and help in the development of more appropriate future mixed micellar models besides providing a useful guidance in the design and selection of non-ideal surfactant combinations for practical purposes.

3.2 CRITICAL MICELLE CONCENTRATION OF PURE SURFACTANTS

The characteristic features of all the physical measurements employed are distinct breaks in the course of the physical properties (specific conductance and surface tension) with respect to concentration recognized as the CMC's of the surfactants. Representative illustrations are presented in Figures 3.1-3.8. The comprehensive results for some cationic, anionic, non-ionic and zwitterionic surfactants are presented in Table 3.1. It is seen that CMC's of the pure surfactants

\[ \text{CMC} \]
<table>
<thead>
<tr>
<th>Surfactant Name</th>
<th>Chemical Name</th>
<th>Acid Medium (48 h)</th>
<th>Alkaline Medium (48 h)</th>
<th>Alkaline Medium (2 h)</th>
<th>Acid Medium (2 h)</th>
<th>Aqueous Medium (0.35 M HCl)</th>
<th>Aqueous Medium (0.1 M NaOH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB</td>
<td>Cetyltrimethylammonium bromide</td>
<td>0.92</td>
<td>0.98</td>
<td>0.96</td>
<td>0.96</td>
<td>6.03</td>
<td>2.25</td>
</tr>
<tr>
<td>TTAB</td>
<td>Tetradecyltrimethylammonium bromide</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
<td>0.03</td>
<td>0.63</td>
</tr>
<tr>
<td>CPC</td>
<td>Cetylpyridinium chloride</td>
<td>0.94</td>
<td>0.94</td>
<td>0.93</td>
<td>0.93</td>
<td>0.47</td>
<td>0.88</td>
</tr>
<tr>
<td>CPB</td>
<td>Cetylpyridinium bromide</td>
<td>0.18</td>
<td>0.18</td>
<td>0.17</td>
<td>0.17</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>CTAS</td>
<td>Cetyltrimethylammonium-p-toluenesulfonate</td>
<td>0.97</td>
<td>0.97</td>
<td>0.97</td>
<td>0.97</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>BDAB</td>
<td>Benzyltrimethylammonium bromide</td>
<td>1.20</td>
<td>1.05</td>
<td>1.05</td>
<td>1.05</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>NaG</td>
<td>Sodium cholate</td>
<td>8.00</td>
<td>8.00</td>
<td>8.00</td>
<td>8.00</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>NaDC</td>
<td>Sodium deoxycholate</td>
<td>8.00</td>
<td>8.00</td>
<td>8.00</td>
<td>8.00</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>DDBS</td>
<td>Sodium dodecylbenzenesulfonic acid</td>
<td>8.00</td>
<td>8.00</td>
<td>8.00</td>
<td>8.00</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium dodecyl sulfate</td>
<td>8.00</td>
<td>8.00</td>
<td>8.00</td>
<td>8.00</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>TX-100</td>
<td>Polyoxyethylene (23) teroctylphenyl ether</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>DDBS</td>
<td>Sodium dodecylbenzenesulfonic acid</td>
<td>8.00</td>
<td>8.00</td>
<td>8.00</td>
<td>8.00</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>SJ16</td>
<td>Hexadecyl-dimethyl-ammonio-propane-sulfonate</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
<td>0.03</td>
<td>0.03</td>
</tr>
</tbody>
</table>

**CMC, CONC\(\text{eq.}\)\text{mol}, \text{dm}^{-3}\)**

**TABLE 3.1 CRITICAL MICELLE CONCENTRATION OF SURFACTANTS AT 303 K**
FIG. 3.1: PLOTS OF SPECIFIC CONDUCTANCE Vs log (M), AQUEOUS MEDIUM •; SURFACE TENSION Vs log (M), AQUEOUS MEDIUM ■; SURFACE TENSION Vs log (M), ACID MEDIUM ▲ AND SURFACE TENSION Vs log (M), ALKALINE MEDIUM ● FOR CMC OF CTAB

FIG. 3.2: PLOTS OF SPECIFIC CONDUCTANCE Vs log (M), AQUEOUS MEDIUM •; SURFACE TENSION Vs log (M), AQUEOUS MEDIUM ■ AND SURFACE TENSION Vs log (M), ACID MEDIUM ▲ FOR CMC OF TTAB
FIG. 3.3: PLOTS OF SPECIFIC CONDUCTANCE Vs log (M), AQUEOUS MEDIUM ■ AND SURFACE TENSION Vs log (M), AQUEOUS MEDIUM ● FOR CMC OF CPB

FIG. 3.4: PLOT OF SPECIFIC CONDUCTANCE Vs log (M), AQUEOUS MEDIUM ● FOR CMC OF CTAS
FIG. 3.5: PLOTS OF SPECIFIC CONDUCTANCE Vs log (M), AQUEOUS MEDIUM • AND SURFACE TENSION Vs log (M), AQUEOUS MEDIUM ■ FOR CMC OF BHAC.

FIG. 3.6: PLOTS OF SPECIFIC CONDUCTANCE Vs log (M), AQUEOUS MEDIUM • AND SURFACE TENSION Vs log (M), AQUEOUS MEDIUM ■ FOR CMC OF BDAB.
FIG. 3.7: PLOTS OF SPECIFIC CONDUCTANCE Vs log (M), AQUEOUS MEDIUM • ; SURFACE TENSION Vs log (M), AQUEOUS MEDIUM □ ; SURFACE TENSION Vs log (M), ACID MEDIUM ▲ AND SURFACE TENSION Vs log (M), ALKALINE MEDIUM ◆ FOR CMC OF SDS

FIG. 3.8: PLOTS OF SURFACE TENSION Vs log (M), AQUEOUS MEDIUM • AND SURFACE TENSION Vs log (M), ALKALINE MEDIUM ◆ FOR CMC OF Brij-35
agree with literature values. Except for a few, both the methods (conductance and surface tension) have yielded comparable CMC values; method dependent variations are apparent. The CMC of some surfactants have also been determined in reaction conditions (acidic and alkaline medium). Micellization is the result of a delicate balance between repulsive and attractive forces. For the ionic surfactant the repulsive forces originates primarily from electrostatic repulsions between the head groups. For a long time the hydrophobic interaction was thought to be the major attractive force for micelle formation, but recently considerable emphasis has been placed on London-dispersion interactions\textsuperscript{92}. Arguments for the importance of one of the two interactions can only be obtained from comprehensive studies of the thermodynamic properties of the complicated process of micellization in which surfactant's alkyl chains, surfactant's head groups, counterions, and the surrounding medium all play important roles. The conductivity is linearly correlated to the surfactant concentration in both the pre-micellar and in the post-micellar regions, having a slope in the pre-micellar region. The intersection point between the two straight lines gives the CMC and the ratio between the slopes of the post micellar region to that in the pre-micellar region gives the degree of counterion dissociation, (\(\beta\)), and, subsequently, the degree of counterion association (\(\alpha = 1-\beta\)).

### 3.3 THERMODYNAMICS OF MICELLIZATION

All the thermodynamic functions characterizing a surfactant solution undergo changes upon micellization. Knowledge of these changes is important both for the understanding of the forces resulting in the micellization and for predicting the behaviour of a micellar solution upon changes of factors such as additives, temperature and alkyl chain length etc. All physicochemical processes are energetically controlled. The spontaneous formation of micelle is obviously guided by thermodynamic principle. Although micellar colloids are in a dynamic association-dissociation equilibrium, the way to treat micelles theoretically depends on whether a micelle is regarded as a chemical species or a separate phase. Two simple models have long been used in the interpretation of micelle behaviour\textsuperscript{63-65}.

(i) Mass action model
(ii) Pseudophase model

According to the first model, above CMC, the concentrations of monomer and micelle are interdependent. Increase of monomer concentration increases micellar
concentration and vice-versa in accordance with the following equilibrium.

\[ n(S^- \text{ or } S^* \text{ or } S) \rightleftharpoons K_M \rightarrow (S_n^- \text{ or } S_n^* \text{ or } S_n), \]  

where \( S^- \text{ or } S^* \text{ or } S = \) surfactant monomer; \( S_n^- \text{ or } S_n^* \text{ or } S_n = \) micelle; \( n = \) aggregation number and \( K_M = \) micellization constant with free energy of micellization \( (\Delta G_m^o) = RT \ln K_M. \)

At CMC, by conceptual approximation, the free energy of micellization expressed per mole of monomer unit \( (\Delta G_m^o = \Delta G_m^o/M/n) \) is given by the relation, \( \Delta G_m^o = RT \ln CMC. \) In the pseudophase model, the monomer concentration at and above CMC remains nonvariant; with increasing surfactant concentration above CMC, micelles are only formed. The micellar pseudophase on the other hand remains in solution. Based on the phase equilibrium,

\[ nS \rightleftharpoons M_n \]

monomer \rightleftharpoons \text{micelle} \]  

at a constant temperature, chemical potential of surfactant monomer in solution \( (\mu_m) \) is equal to the chemical potential of the monomer in the pseudomicellar phase \( (\mu_m) \) thus,

\[ \mu_m = \mu_m^o \]

Explicitly,

\[ \mu_m^o + RT \ln a_m = \mu_m^o + RT \ln a_m \]

Wherefrom we get the

\[ \Delta G_m^o = RT \ln CMC \]

for nonionic micelle (equation 5), and for ionic micelle (equation 6).

\[ \Delta G_m^o = (1 + f) RT \ln CMC \]

In this equation \( "f" \) is the fraction of counterion bound to a micelle. For nonionic
surfactants, \( f = 0 \). The \( \mu^o_m \) and \( \mu^o_m \) are the standard chemical potentials of monomer and micelle respectively and \( a_m \) and \( a_m \) are their corresponding activities (\( a_m = 1 \), for pseudophase is taken to be pure phase). The two models thus lead to the same interpretation of results. It is to be noted that in the above thermodynamic treatments at the critical micelle concentration the equilibrium concentration of free monomer is considered equivalent to CMC.

Applying Gibbs-Helmholtz and Van't Hoff equations, the standard enthalpy of micellization (\( \Delta H^o_m \)) at constant pressure, \( P \), for nonionic micelles is given by the relation

\[
\Delta H^o_m = -RT^2 \left[ \frac{\partial \ln CMC}{\partial T} \right]_P = R \left[ \frac{\partial \ln CMC}{\partial (1/T)} \right]_P
\]

(7)

The \( \ln CMC \) was plotted against \( T \) and \( (\partial \ln CMC)/\partial T \) was computed at each temperature.

The entropy of micellization (\( \Delta S^o_m \)) follows from the Gibbs equation,

\[
\Delta S^o_m = \frac{\Delta H^o_m - \Delta G^o_m}{T}
\]

(8)

The factor \( (1+f) \) has to be included in the above relations for ionic micelles.

A temperature study was performed on micelle formation of some cationic (BHAC) anionic (NaC, NaDC, DDBS) and nonionic (Brij-35) surfactants. The critical micelle concentration (Table - 3.2) and the degree of counterion binding were determined at three temperatures (308, 318, 328 K) by means of conventional electric conductance measurements. From the temperature dependence of CMC, Gibbs free energy \( \Delta G^o_m \), enthalpy \( \Delta H^o_m \), and entropy \( \Delta S^o_m \) on micelle formation, were deduced for the respective surfactants.

Table 3.2 and Figures 3.9-3.11 shows the critical micelle concentration of pure surfactants at different temperatures. In Table 3.3, the thermodynamic quantities (\( \Delta G^o_m \), \( \Delta S^o_m \) and \( \Delta H^o_m \)) for these surfactants are given. The availability of these parameters at various temperatures can give valuable insight into the principles which govern the formation of micelles. The formation of micelles was always found to be connected with a large, negative change in Gibbs free energy \( \Delta G^o_m \), i.e., the aggregation process is
## TABLE - 3.2
CRITICAL MICELLE CONCENTRATION OF PURE SURFACTANTS AT DIFFERENT TEMPERATURES

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>CMC x 10² / mol. dm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>308K</td>
</tr>
<tr>
<td>Benzyldimethyl-hexadecylammonium chloride (BHAC)</td>
<td>0.53</td>
</tr>
<tr>
<td>Sodium cholate (NaC)</td>
<td>12.6</td>
</tr>
<tr>
<td>Sodium deoxycholate (NaDC)</td>
<td>5.62</td>
</tr>
<tr>
<td>Dodecylbenzene sulfonic acid sodium salt (DDBS)</td>
<td>1.99</td>
</tr>
<tr>
<td>Polyoxyethylene(23) lauryl ether (Brij-35)</td>
<td>0.045</td>
</tr>
</tbody>
</table>
FIG. 3.9: PLOTS OF SPECIFIC CONDUCTANCE Vs log (M), AQUEOUS MEDIUM, AT 308 K •, AT 318 K □ AND AT 328 K ▲ FOR THERMODYNAMICS OF MICELLIZATION OF BHAC.

FIG. 3.10: PLOTS OF SPECIFIC CONDUCTANCE Vs log (M), AQUEOUS MEDIUM, AT 308 K •, AT 318 K □ AND AT 328 K ▲ FOR THERMODYNAMICS OF MICELLIZATION OF NaC.
FIG. 3.11: PLOTS OF SPECIFIC CONDUCTANCE Vs log (M), AQUEOUS MEDIUM, AT 308 K ●, AT 318 K ▲ AND AT 328 K ▼ FOR THERMODYNAMICS OF MICELLIZATION OF NaDC.
<table>
<thead>
<tr>
<th>SURFACTANTS</th>
<th>Temp. (K)</th>
<th>$\Delta G^\circ_n$ (kJmol$^{-1}$)</th>
<th>$\Delta H^\circ_n$ (kJmol$^{-1}$)</th>
<th>$\Delta S^\circ_n$ (JK$^{-1}$mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyldimethyl-hexadecylammonium chloride (BHAC)</td>
<td>308</td>
<td>-37.5</td>
<td>-12.1</td>
<td>82.4</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>-37.2</td>
<td>-12.9</td>
<td>76.5</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>-37.5</td>
<td>-13.7</td>
<td>72.5</td>
</tr>
<tr>
<td>Sodium cholate (NaC)</td>
<td>308</td>
<td>-19.0</td>
<td>16.2</td>
<td>120.8</td>
</tr>
<tr>
<td></td>
<td>318</td>
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<td></td>
<td>328</td>
<td>-21.9</td>
<td>20.7</td>
<td>129.9</td>
</tr>
<tr>
<td>Sodium deoxycholate (NaDC)</td>
<td>308</td>
<td>-24.9</td>
<td>11.3</td>
<td>117.8</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>-26.1</td>
<td>12.0</td>
<td>120.1</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>-28.2</td>
<td>12.8</td>
<td>124.9</td>
</tr>
<tr>
<td>Dodecylbenzene sulfonic acid sodium salt (DDBS)</td>
<td>308</td>
<td>-21.9</td>
<td>27.1</td>
<td>159.4</td>
</tr>
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<td></td>
<td>318</td>
<td>-25.7</td>
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</tr>
<tr>
<td></td>
<td>328</td>
<td>-29.6</td>
<td>30.8</td>
<td>184.1</td>
</tr>
<tr>
<td>Polyoxyethylene(23) lauryl ether (Brij-35)</td>
<td>308</td>
<td>-25.6</td>
<td>14.7</td>
<td>130.9</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>-26.9</td>
<td>15.7</td>
<td>133.9</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>-28.3</td>
<td>16.7</td>
<td>137.1</td>
</tr>
</tbody>
</table>
thermodynamically favoured and spontaneous\textsuperscript{66-69}. The major driving forces for micelle formation are hydrophobic interactions. At room temperature these are due to a large gain in entropy when water molecules in hydration shells around the hydrophobic parts of the monomeric amphiphiles are released during the micellization process. The micellization process in these systems is endothermic and the entropy of micellization is positive. In other words, the system as a whole after micellization is less ordered then the system when only monomers are present. The micellization is due to hydrophobic interaction, though it is hindered by the forces of mutual repulsion acting between hydrophilic parts of the molecule\textsuperscript{66-70}. As micellization itself is the formation of order from the random chaotic movement of monomer molecules and is spontaneous, we presume that the overall structure-breaking of water molecules is rather large, making $\Delta S^o_m$ positive.

3.4 TYPES OF BINARY SURFACTANT COMBINATIONS

In the present investigation the behaviour and physicochemical properties of binary mixtures of some cationic, anionic and nonionic surfactants have been studied. Following types of binary combinations of mixed micelles were chosen.

(i) Cationic - cationic
(ii) Cationic - nonionic
(iii) Anionic - nonionic

All the above combinations were used in an equimolar proportion i.e. (1:1). Mixed surfactants after a critical concentration should also micellize yielding CMC. The tendency is guided by their attractive and repulsive interactions. Physicochemical studies are essential for formulations, uses and basic understanding.

(i) CATIONIC-CATIONIC

The binary combination of the two cationic surfactants, namely, cetyl trimethylammonium bromide (CTAB), $C_{16}H_{33}N^+(CH_3)_3Br^-$ and cetylpyridinium chloride (CPC), $C_{16}H_{33}N^+C_5H_5Cl^-$ have been used. These surfactants have similar hydrocarbon chain but different ionic head groups e.g. trimethylammonium and pyridinium ion respectively for CTAB and CPC.
(ii) CATIONIC - NONIONIC

Following systems have been used:

(a) Cetyltrimethylammonium bromide (CTAB)/Polyoxyethylene (23) lauryl ether (Brij-35), \( \text{C}_{12}\text{H}_{25}( \text{OCH}_2\text{CH}_2)_{23} \text{OH.} \)

(b) Cetyltrimethylammonium bromide (CTAB)/Triton X-100 (Polyethylene glycol tert-octylphenyl ether) \( (\text{CH}_3)_{3}\text{CCH}_2\text{C}(\text{CH}_3)_{2}\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_{9.5} \text{OH.} \)

(c) Tetradecyltrimethylammonium bromide (TTAB) \( \text{C}_{14}\text{H}_{29}\text{N}^+(\text{CH}_3)_{3}\text{Br} / \text{Polyoxyethylene(23) lauryl ether (Brij-35)} \)

(d) Tetradecyltrimethylammonium bromide (TTAB)/Triton X-100.

(e) Cetylpyridinium chloride (CPC) / Brij-35.

(iii) ANIONIC-NONIONIC

In this combination the surfactants used were anionic surfactant of sodium dodecyl sulfate (SDS), \( \text{C}_{12}\text{H}_{25}\text{OSO}_3^- \text{Na}^+ \) and nonionic surfactant of polyoxyethylene (23) lauryl ether (Brij-35).

3.5 MICELLAR SOLUTION PROPERTIES OF BINARY SURFACTANT MIXTURES

The micelles formed from a solution of mixed surfactants generally have a different surfactant composition than the monomer. In modeling the equilibrium between monomer and these mixed micelles the micelle is often considered as a pseudophase\(^{71-74}\) (a thermodynamic phase is equilibrium with the monomer). Because the micelles are considered to be infinitely large, this approach cannot provide information on micelle shape or size. If micelle formation is ideal, the critical micelle concentration (CMC) of the mixture, at which micelles first form, can be determined solely from the CMC values of the pure surfactants comprising the mixture. Nonideal micelle formation is most commonly modeled by regular solution theory\(^{73}\), although other nonideal mixing models have been used\(^{75}\). To implement this approach, the CMC must be experimentally measured for the pure surfactants and for at least one mixture composition to determine CMC values of other mixture...
compositions, as well as to calculate the $\beta$ parameter, a quantitative measure of the interaction between the two surfactant species in the mixed micelle.

In regular solution theory, the nonideality is represented by a term of the form $\beta \alpha (1 - \alpha)$, where $\beta$ is a constant and $\alpha$ is the micelle composition. A negative value of $\beta$ indicates synergism in mixed micelle formation, a positive value indicates antagonism, and if $\beta = 0$, then mixed micelle formation is ideal. The larger the absolute value of $\beta$, the stronger the mixing nonideality and the corresponding synergism. The theoretical validity of using regular solution theory to describe nonideal mixing in mixed surfactant micelles has been questioned. Although regular solution theory assumes that the excess entropy of mixing is zero, calorimetric measurements or calculations of the enthalpy of mixing, combined with mixture CMC measurements, have shown that the excess mixing entropy in some mixed surfactant systems is nonzero. However, calculations of the $\beta$ parameter based on CMC measurements for many types of binary surfactant mixtures, including cationic/nonionic, anionic/nonionic, anionic/anionic, anionic/zwitterionic, and mixtures containing bile salts, demonstrate that $\beta$ can vary widely with solution composition. In spite of these limitations, the pseudophase separation/regular solution theory approach remains a very widely used and convenient method for analyzing experimental CMC measurements of mixed micellar systems.

3.51 THEORIES FOR MIXED SURFACTANTS

When ionic surfactant and nonionic surfactants are mixed together to form mixed micelle, molecules of the nonionic surfactant penetrate between molecules of the ionic surfactant. This makes the surface charge density of the mixed micelle lower than that of the single ionic micelle, leads to the decrease of exclusion between ionic head groups of the ionic surfactant and the increase of the ion-dipole interaction between the ionic and the nonionic surfactants. Thus molecules and ions of surfactants of different types in the mixed micelle are closer, and the Stern layer becomes more compact for ionic surfactants, micelle formation is governed by the balance between the head groups, whereas, for nonionic surfactants the tendency of alkyl chain to avoid contact with water is balanced by the hydration and space requirement of oxyethylene chains. The nonionic surfactants with bulky head groups will favour compact structure and form spherical aggregates whereas, ionic surfactants with small head groups will favour rod like micelles.
The mixed CMC is smaller than that of either individual components. This is because of chain length and molecular weight of nonionic surfactant, which is higher than that of ionic surfactant. Since longer chain length decreases the CMC and in fact nonionic surfactants have low CMC's, it is expected that the effect of nonionic surfactant on cationic surfactant would be substantial compared with the effect of cationic surfactant on nonionic surfactant. Thus radius of mixed micelle is with the proportion of nonionic surfactant in micelle. During the formation of mixed micelles a solubilization process between both surfactants may take place. Theoretical equations based on the regular solution theory have been proposed\textsuperscript{84,85}, in order to calculate the extension of the miscibility between the surfactants. In case of SDS and Brij-35 the mixed micelles may become stabilized primarily through contact with hydrocarbon chains of both surfactants. The SDS polar head groups are located in the ethylene oxide region of the nonionic surfactant in a hydrophilic region (second, third ethylene of the nonionic surfactant).

The results given in Tables 3.1-3.4 shows that the mixing CMC is smaller than that of either individual components. This is because of chain length and molecular weight of nonionic surfactant (Brij-35), which is higher than that of ionic surfactant.

Since longer chain length decreases the CMC and in fact nonionic surfactants have low CMC's, it is thus expected that the effect of Brij-35 on CTAB would be substantial compared with the effect of CTAB on Brij-35. The radius of the mixed micelle with the electrical double layer increases with an increasing concentration of nonionic surfactant. Consequently the degree of ionic dissociation, \( \alpha \) of the mixed micelle increases with the proportion of nonionic surfactant in micelle. During the formation of mixed micelles a solubilization process between the both surfactants take place.

3.52 MOLECULAR MODEL OF MIXED MICELLIZATION

Blankschtein et al.\textsuperscript{46} proposed a model of mixed micellization. The free energy of mixed micellization constitutes a central element in the evaluation of micellar solution properties such as the CMC, the micellar size and composition distribution, and the phase behaviour including phase separation of mixed micellar solutions. In the first step of the process (Scheme - I), the heads, if charged, are discharged along with the counterions. Subsequently, in the second step, the bond between the head and the tail of each surfactant molecule is broken. In the third step, the hydrocarbon tails of surfactants A and B are transferred from water to a mixture of...
TABLE - 3.4

CRITICAL MICELLE CONCENTRATION OF BINARY MIXED SURFACNTANTS (EQUIMOLAR PROPORTION) AT 303 K BY DIFFERENT METHODS

<table>
<thead>
<tr>
<th>MIXED SURFACANT S</th>
<th>CMC x 10^3 / mol. dm^-3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AQUEOUS MEDIUM (CONDUCTANCE)</td>
</tr>
<tr>
<td>CTAB-Brij-35</td>
<td>0.10</td>
</tr>
<tr>
<td>CTAB-TX-100</td>
<td>0.48</td>
</tr>
<tr>
<td>TTAB-Brij-35</td>
<td>0.24</td>
</tr>
<tr>
<td>TTAB-TX-100</td>
<td>0.51</td>
</tr>
<tr>
<td>CPC-Brij-35</td>
<td>0.19</td>
</tr>
<tr>
<td>SDS-Brij-35</td>
<td>0.03</td>
</tr>
<tr>
<td>CTAB-CPC</td>
<td>0.71</td>
</tr>
</tbody>
</table>

a = 0.35 M. HCl
hydrocarbons A and B whose composition is equal to the micellar composition $\omega$. In the fourth step, an hydrocarbon droplet having shape $\alpha$ and core minor radius $\kappa$ is created from the hydrocarbon mixture having composition $\omega$. That is, in this step, an interface separating the hydrocarbon mixture from water is created. Note that within this hydrocarbon droplet the tails are unrestricted and can move freely. However, in a micelle, each tail is bonded to a head and therefore one of the tail ends is restricted to lie in the vicinity of the micellar core-water interface. Accordingly, in the fifth step, this restriction is imposed on the tails. Therefore at the end of the fifth step, the creation of the micellar core has been completed. The creation of the micellar corona of heads follows next. Accordingly, in the sixth steps, the discharged heads are reattached to the tails at the micellar core-water interface. This involves three operations; recreating the bond between the head and the tail, screening part of the micellar core-water interface from contact with water, and introducing steric repulsions between the heads. The free energy change associated with reforming the bond is assumed to be equal and opposite in sign to that associated with breaking the bond in the second step, and consequently these two contributions cancel each other. Finally, in the seventh step, the head if charged, are recharged along with the associated counterions. This completes the creation of the micellar corona and the entire mixed micelle.

Scheme 1: Schematic representation of mixed-micellization
The cationic/non-ionic systems (equimolar concentration) were studied at 30 °C using CTAB + Brij-35, CTAB + TX-100, TTAB-TX-100, CPC + Brij-35. The CMC data for each system are shown in Figures 3.12-3.15 and results are tabulated in Table 3.4. The anionic/nonionic (SDS - Brij - 35) and cationic/cationic (CTAB - CPC & CTAB - TTAB) systems have also been studied. The CMC's determined by surface tension and conductance methods vary, but individually the methods have shown good reproducibility. Usually, the CMC's of mixed surfactants fall in between the CMC's of the individual pure components.

The counterion association (f) properties of the mixed micelles have been evaluated from the ratio of the postmicellar and premicellar slopes obtained from the plots of specific conductance of the surfactant solution at different concentrations. The (f) values of the mixed micelles are lower than the pure micelles. The lower counterion association found in the mixed systems compared to pure micelles means lowering of effective surface charge density in the mixed micelle.

3.53 THERMODYNAMICS OF MIXED MICELLIZATION

Complete sets of thermodynamic data are of great importance since they can be used to test theories and models and to obtain information on the interaction governing the mixed micelles formation. Conductivity and surface tension measurements have been carried out in order to determine the CMC and the degree of counterion dissociation as functions of the mixture composition. The results are given in Table - 3.5. Like pure surfactant at a given surfactant mixture composition, the CMC and the degree of counterion dissociation β were evaluated from the plot of the specific conductance against the total molarity (M) (Figures 3.16 - 3.19). The CMC is given by the intersection point of the trends in the pre- and postmicellar region, while β was calculated from the slopes of these trends. The ΔG_m°, ΔS_m° and ΔH_m° values were computed from CMC values at different temperature for the mixed surfactants. The values are given in Table - 3.6 and are not vastly different in a particular mixture, they have on the whole a mild variation. The formation of the different micelles is energetically comparable. As expected, all the micellization processes end up with a considerable positive entropy change. The ΔH_m° < ΔS_m° results manifest the micellization process to be entropy controlled. Randomness produced by the melting of the icebergs around the nonpolar tail during micelle formation and increased randomness of the tails in the micellar interior act in conjunction for the entropy increase. Partially neutral micelle formation takes place
FIG. 3.12: PLOT OF SPECIFIC CONDUCTANCE Vs $\log (M)$, AQUEOUS MEDIUM • FOR CMC OF CTAB-Bnij-35

FIG. 3.13: PLOT OF SPECIFIC CONDUCTANCE Vs $\log (M)$, AQUEOUS MEDIUM • FOR CMC OF CTAB-CPC
FIG. 3.14 : PLOT OF SPECIFIC CONDUCTANCE VS log (M), AQUEOUS MEDIUM • FOR CMC OF CTAB–TX-100

FIG. 3.15 : PLOT OF SPECIFIC CONDUCTANCE VS log (M), AQUEOUS MEDIUM • FOR CMC OF SDS–Brij 35
### TABLE - 3.5

**CRITICAL MICELLE CONCENTRATION OF MIXED SURFACTANTS AT DIFFERENT TEMPERATURES**

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>CMC x 10³ / mol. dm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>308K</td>
</tr>
<tr>
<td>CTAB-Brij-35</td>
<td>0.10</td>
</tr>
<tr>
<td>CTAB-TX-100</td>
<td>0.45</td>
</tr>
<tr>
<td>CTAB-CPC</td>
<td>0.79</td>
</tr>
<tr>
<td>SDS-Brij-35</td>
<td>0.032</td>
</tr>
</tbody>
</table>
FIG. 3.16  PLOTS OF SPECIFIC CONDUCTANCE Vs log (M), AQUEOUS MEDIUM, AT 308 K •; AT 318 K □; AT 328 K ▲ AND AT 338 K ◆ FOR THERMODYNAMICS OF MICELLIZATION OF CTAB-8/1-35 MIXED SURFACTANTS SYSTEM.

FIG. 3.17  PLOTS OF SPECIFIC CONDUCTANCE Vs log (M), AQUEOUS MEDIUM, AT 308 K •; AT 318 K □; AT 328 K ▲ AND AT 338 K ◆ FOR THERMODYNAMICS OF MICELLIZATION OF CTAB-1X-100 MIXED SURFACTANTS SYSTEM
FIG. 3.18. PLOTS OF SPECIFIC CONDUCTANCE Vs log (M), AQUEOUS MEDIUM, AT 308 K •; AT 318 K ■; AT 328 K ▲ AND AT 338 K ○ FOR THERMODYNAMICS OF MICELLIZATION OF CTAB–CPC MIXED SURFACANTS SYSTEM.

FIG. 3.19. PLOTS OF SPECIFIC CONDUCTANCE Vs log (M), AQUEOUS MEDIUM, AT 308 K •; AT 318 K ■; AT 328 K ▲ AND AT 338 K ○ FOR THERMODYNAMICS OF MICELLIZATION OF SDS–Brij 35 MIXED SURFACANTS SYSTEM.
<table>
<thead>
<tr>
<th>SURFACANTS</th>
<th>Temp. (K)</th>
<th>$\Delta G_m^\circ$ (kJmol$^{-1}$)</th>
<th>$\Delta H_m^\circ$ (kJmol$^{-1}$)</th>
<th>$\Delta S_m^\circ$ (JK$^{-1}$mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB–Brij-35</td>
<td>308</td>
<td>-45.3</td>
<td>90.4</td>
<td>440.5</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>-47.9</td>
<td>96.4</td>
<td>453.9</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>-46.8</td>
<td>102.6</td>
<td>455.4</td>
</tr>
<tr>
<td></td>
<td>338</td>
<td>-50.9</td>
<td>108.9</td>
<td>472.9</td>
</tr>
<tr>
<td>CTAB–TX-100</td>
<td>308</td>
<td>-38.0</td>
<td>15.9</td>
<td>173.7</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>-39.9</td>
<td>16.5</td>
<td>177.3</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>-42.3</td>
<td>17.6</td>
<td>182.5</td>
</tr>
<tr>
<td></td>
<td>338</td>
<td>-44.5</td>
<td>18.6</td>
<td>186.8</td>
</tr>
<tr>
<td>CTAB–CPC</td>
<td>308</td>
<td>-34.8</td>
<td>19.8</td>
<td>177.1</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>-39.1</td>
<td>21.0</td>
<td>189.1</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>-41.1</td>
<td>22.4</td>
<td>193.5</td>
</tr>
<tr>
<td></td>
<td>338</td>
<td>-43.0</td>
<td>23.8</td>
<td>197.5</td>
</tr>
<tr>
<td>SDS–Brij-35</td>
<td>308</td>
<td>-50.0</td>
<td>14.2</td>
<td>208.6</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>-52.8</td>
<td>15.2</td>
<td>213.8</td>
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<td></td>
<td>328</td>
<td>-54.6</td>
<td>16.1</td>
<td>215.7</td>
</tr>
<tr>
<td></td>
<td>338</td>
<td>-56.1</td>
<td>17.1</td>
<td>216.8</td>
</tr>
</tbody>
</table>
due to counterion binding, leading to reduced water/dipole interaction thus, resulting in enhanced entropy. The $\Delta G_m^*$ values indicated that the micellization process was more favourable for the surfactant combinations compared to individual surfactants, i.e., the interaction was more spontaneous at the interface.

### 3.6 POLYMER-SURFACTANT INTERACTIONS

Polymer - Surfactant interactions has been characterized by surface tension and conductance measurements at 303 K. The interactions between the nonionic polymer polyethylene glycol (PEG, Mol. wt. = 400) and cationic, anionic and non-ionic surfactants have been studied. Binding and phase separation phenomena in polymer-surfactant systems depend strongly on the ionic nature of each of the two constituents. For the case of ionic polymers and oppositely charged surfactant ions, binding takes place at very low free surfactant ion concentrations, often characterized by a "critical association concentration". The binding isotherm is normally strongly cooperative, and Coulombic forces are the main factor in determining the strength and the degree of binding, although other effects such as polymer structure and hydrophobicity also play a role.

It is well established that surfactant micellization is often facilitated (more or less strongly) by the presence of polymer, leading to a lowered critical micelle concentration, with surfactant aggregates closely resembling the micelles formed in the absence of polymer. The question of how the precise chemical structure of the surfactant and the morphology of the unperturbed micelle are related to the tendency for association with polymers poses a challenge for chemists. The very limited choice of surfactants as well as dubious generalizations in the study of polymer-micelle interaction certainly obscure this problem. In general it has been observed that the neutral polymers interact with anionic surfactants and show little or no tendency to interact with cationic or nonionic surfactants. However, neutral polymers with some hydrophobicity and surface activity show significant interaction with cationic surfactants. The aggregation number of polymer-bound micelles is smaller and the counterion binding is lower, compared to that of free micelles. An unchanged CMC value of the micelles, does not exclude polymer-micelle association, as is illustrated by the interaction between n-octyl-β-D-thioglucoside (OTG) and poly (propylene oxide) (PPO) or hydroxypropyl cellulose (HPC).

One may anticipate that, in surfactant solutions containing nonionic polymers,
aggregation of the surfactant molecules would occur as in polymer-free solutions with the added feature that these aggregates may be free in solution or be bound by physical interactions to the polymer. The concentration of the surfactant at which the polymer-free and the polymer-bound aggregates come into existence can differ from one another. Each polymer molecule can have one or more aggregates associated with it. Alternatively, more than one polymer molecule could be associated with a single aggregate as well. The relative concentrations of the polymer-free and the polymer-bound aggregates would be determined by the nature of interactions between the polymer and the aggregate. Nagarajan developed a model (Scheme - II) for the association of nonionic polymer with globular micelles.

Scheme-II: Schematic representation of the polymer-micelle association structure

The complex is visualized as consisting of fully formed surfactant micelles interacting with the polymer segments. Specifically, the polymer segments wrap around the aggregate interface shielding a part of the hydrocarbon core of the micelle from being in contact with water. The structural and physicochemical properties of the polymer molecule are assumed to determine the area of mutual contact between the polymer molecule and the hydrophobic surface of the micelle.

The results are shown in Table 3.7 Plots of specific conductance Vs log (M) (Concentration) and surface tension Vs log (M) give break points which were critical aggregation concentration (CAC) and polymer saturation point (PSP) (Figures 3.21-3.26). The plots exhibit three regions, below the CAC, between the CAC and PSP,
TABLE - 3.7
CRITICAL MICELLE CONCENTRATION OF POLYMER-SURFACTANT SYSTEM AT 303 K

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>CMC OF THE PURE SURFACANT</th>
<th>CMC x $10^3$ / mol. dm$^{-3}$</th>
<th>AQUEOUS MEDIUM (CONDUCTANCE)</th>
<th>AQUEOUS MEDIUM (SURFACE TENSION)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG-CTAB</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>PEG-TTAB</td>
<td>1.30</td>
<td>0.56</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>PEG-CPC</td>
<td>0.91</td>
<td>1.58</td>
<td>1.33</td>
<td></td>
</tr>
<tr>
<td>PEG-Brij-35</td>
<td>0.05</td>
<td>-</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>PEG-TX-100</td>
<td>0.03</td>
<td>-</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>PEG-SDS</td>
<td>8.00</td>
<td>1.41</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
FIG. 3.21: PLOTS OF SPECIFIC CONDUCTANCE Vs log (M), AQUEOUS MEDIUM • AND SURFACE TENSION Vs log (M), AQUEOUS MEDIUM • FOR CMC OF PEG-CTAB

FIG. 3.22: PLOTS OF SPECIFIC CONDUCTANCE Vs log (M), AQUEOUS MEDIUM • AND SURFACE TENSION Vs log (M), AQUEOUS MEDIUM • FOR CMC OF PEG-TTAB

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FIG. 3.23: PLOTS OF SPECIFIC CONDUCTANCE Vs \( \log (M) \), AQUEOUS MEDIUM • AND SURFACE TENSION Vs \( \log (M) \), AQUEOUS MEDIUM • FOR CMC OF PEG-CPC

FIG. 3.24: PLOT OF SURFACE TENSION Vs \( \log (M) \), AQUEOUS MEDIUM • FOR CMC OF PEG-TX-100
FIG. 3.25: PLOT OF SURFACE TENSION Vs log (M), AQUEOUS MEDIUM • FOR CMC OF PEG-Brij-35

FIG. 3.26: PLOT OF SPECIFIC CONDUCTANCE Vs log (M), AQUEOUS MEDIUM • FOR CMC OF PEG-SDS
where micelle like aggregates develop and above the PSP where co-existence of dynamic equilibrium of surfactant saturated polymer and regular micelles occur\textsuperscript{49}. It is generally accepted that the polymer - surfactant binding starts at CAC. This binding is similar to micellization but occurs at a relatively lower concentration of surfactant. With the increase in surfactant concentration, a second transition known as CMC of the polymer surfactant complex or polymer saturation point (PSP) is obtained\textsuperscript{49}. The degree of ionization, 'a' of an ionic micelle depends on the method of determination\textsuperscript{100}. It is observed from results (Table-3.7) that the CMC of anionic surfactant (SDS) affected in the presence of polymer. The CMC of SDS is lowered. For the cationic and nonionic surfactants no significant change in CMC have been observed. A reduction of the CMC due to the presence of polymer fails to be the ultimate criterion for polymer-micelle attraction. It indicates polymer-micelle association. However, one should consider the situation that binding of the polymer does not affect the stability of the micelle significantly, but only the polymer is stabilized in the binding process. Micellar charge, whether positive or negative, definitely promotes micelle stabilization upon binding of polymers. Two explanations have been advanced for the origin of the weakness of the interactions between polymers and cationic surfactants: (i) the bulkiness of the cationic head group and (ii) a difference in interaction of cations and anions with the hydration sheath of the polymer. The bulkiness of the head group of most cationic and nonionic surfactants is assumed to hamper the presence of a polymer at the hydrocarbon-water interface. Furthermore, a bulky head group quite effectively shields the hydrophobic core. Thus, the stabilization of the core-water interface by the polymer is less relevant in that case than for micelles having a core less shielded by head groups. Probably the size of the head group and the interaction of the head group with the hydration sheath of the polymer are the main reasons for weak interaction of cationic and non-ionic micelles with polymer. Anionic surfactants generally form small globular micelles\textsuperscript{103} in the absence of the polymer molecules give rise to yet smaller polymer-bound micelles at a substantially lower value of the critical micelle concentration. Anionic surfactants that generate large, polydisperse rod-like micelles associate with the polymer to produce smaller globular micelles that are monodispersed at a significantly lower CMC. In general, for anionic surfactant, the CMC associated with the polymer-bound aggregates is substantially lower than the CMC associated with the polymer-free aggregates. In contrast, nonionic and cationic surfactants may or may not form association structures with nonionic polymer molecules.

Polymer-micelle interaction depends on several properties of the surfactant molecule, such as the chemical nature, geometry, and charge. Unfortunately, an arbitrary combination of these factors is not easily obtained.
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