CHAPTER – II

POLYMER – MICELLES INTERACTIONS : PHYSICAL ORGANIC ASPECTS
2.0 INTRODUCTION

Interactions between polymer and micelle-forming surfactants in aqueous solution are currently attracting much interest. Various micelle-forming surfactants associate with nonionic water-soluble polymers in aqueous solution forming polymer-bound micelles. Polymer-micelle complexes have found applications in many industrial products, such as paints and coating, laundry detergents, and cosmetic products, and they also play a role in tertiary oil recovery.

Several aspects of polymer-micelle interaction have been investigated, and a model for the morphology of the complex has emerged, which is almost generally accepted. According to this model, the polymer segments are thought to reside at, and stabilize the interface between the micellar hydrocarbon core and water. The aggregation number of polymer-bound micelles is smaller and the counterion binding is lower, compared to that of free micelles. Usually, the polymer asserts a stabilizing influence on the micelles, which is reflected in a lower value for the critical micelle concentration (cmc).

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Nagarajan and Ruckenstein have suggested that the bulky size of the usual cationic and nonionic surfactant impairs the presence of polymer segments at the core water interface.

More systematic studies on the polymer/surfactant mixtures are needed, however, in order to map out general trends and, ultimately to arrive at a more detailed molecular understanding of their behaviour. The basic understanding of solution and interfacial behaviour of surfactants is necessary for the art of management of their surface chemical application and its properties as a reaction medium.

Micellar properties of both anionic and cationic surfactants are significantly influenced by the presence of additives. They provide vital information about the solute-solvent and solute-solute interactions in surfactant solutions, and hence, have lead to extensive structural, kinetic and thermodynamic studies. The properties of surfactant solutions can be effectively tuned to a desired range and application by altering (i) the tendency to form micelles, as reflected by the critical micelle concentration (CMC) and (ii) the structure and shape of the micelles by changing the additive conditions. Studies involving the physicochemical properties of surfactant mixtures have proved powerful to optimize these properties by just changing the
solution composition. Therefore, a thorough understanding of underlying physics and chemistry of such systems is highly desirable.

The investigation of interfacial and thermodynamic properties of surfactants in solutions, both in the presence and in the absence of additives, can provide a wealth of information about solute-solute and solute-solvent interactions of the surfactant in solutions.

In the present study, two types of additives viz., solvent and polymer have been used. From the conductivity data, the CMC and the counterion dissociation constant of the cationic (CTAB, CPB and CPC) and anionic (SDS) surfactants have been determined in the non-ionic polymers like polyethylene glycol (Mol wt. – 600 and 20,000) and in the binary mixtures of ethylene glycol (EG-H2O), dimethylformamide (DMF-H2O), methanol (MeOH-H2O) and acetonitrile (ACN-H2O).

The solution properties of surfactants are evaluated in terms of surface tension lowering ability, CMC, the degree of counterion dissociation ($\beta$), and interfacial adsorption parameters ($\tau_{\text{max.}}$, $\pi_{\text{cmc}}$ and $A_{\text{min.}}$).

These parameters are all simultaneously or synergistically
reflected from surfactant ions comprising various combinations of hydrophobic tail with hydrophilic head group and from counterion species.

Recently, polymer–surfactant systems are under extensive investigation \(^{88-103}\) due to their wide industrial applications. Moreover, the additive effect of repeating units will affect the nature of interactions responsible for micelle formation. A major question that remains to be solved in order to fully understand polymer–micelle interaction is the role of surfactant charge on the tendency to associate with polymers.

This chapter describes a systematic studies of the physical properties such as surface tension and conductance on aqueous solutions of some ionic and non–ionic surfactants and the relevant results have been discussed in terms of molecular characteristics of surfactants viz. non–polar chain length, polar head group size and counterion.

In this chapter, following aspects have been discussed:

(I) Micelle formation in mixed systems
(II) Properties at the air/water interface
(III) Determination of critical micelle concentration (CMC)
2.1 EXPERIMENTAL

Materials

The following surfactants were used without any further purification: cetyltrimethyl ammonium bromide; CTAB; (SIGMA), cetyltrimethyl ammonium chloride; CTACl; (FLUKA), cetylpyridinium bromide; CPB; (SRL), cetylpyridinium chloride; CPC; (SRL), cetyltrimethyl ammonium p – Toluene sulphonate; CTATs; (FLUKA), cetyltrimethyl ammonium p-Toluene sulphonate; CTATs; (FLUKA), cetyltrimethyl ammonium p – Toluene sulphonate; CTATs; (FLUKA), benzyltrimethyl ammonium chloride; BTAC; (SIGMA), benzylhexadecyl ammonium chloride; BHAC; (SIGMA), sodium dodecyl sulphate; SDS; (SIGMA), sodium deoxycholate; NaDC; (SIGMA), dodecylbenzene sulphonic acid sodium salt; DDBS; (FLUKA), di – octyl sodium sulphosuccinate; AOT; (S.D.Fine), polyoxyethylene (23) lauryl ether; BRIJ – 35; (SIGMA), polyethylene glycol tertocetyl phenyl ether; TX – 100; (S.D.Fine), polyoxyethylene (10) cetyl ether; BRIJ – 56; (SIGMA), polyoxyethylene (2) isoocetyl phenyl ether; IGEPAL CA – 210; (ALDRICH).

Methanol (CH₃OH), dimethyl formamide (DMF), ethylene glycol (EG) and acetonitrile (CH₃CN) were generally of spectral purity grade obtained from E. Merck and Qualigens.

Polyethylene glycol with a molecular weight of 600 and 20,000
(PEG – 600 and 20,000; SIGMA) was used for the surfactant / polymer mixed systems. Surfactant solutions of a definite concentration were always freshly prepared by weighing out a certain amount of surfactant and diluting it up to the required volume with double distilled water.

Methods

**Surface Tension**

The surface tension of aqueous solutions of surfactant at various concentrations in water as well as in presence of additives were determined by drop number method using stalagmometer. All measurements were carried out at 27°C. The CMC values were determined at sharp break points in surface tension against log surfactant concentration plots. The surface tension of the individual solutions was then calculated from known values of surface tension of water, densities and weight of solution and water.

**Conductance**

Digital direct reading conductivity meter Systronics (Type 304) used for conductance measurements.
2.2 RESULTS AND DISCUSSION

The specific conductivity is linearly related to the surfactant concentration in both the pre-micellar and post-micellar regions. A break in plot of specific conductance versus surfactant concentration indicates micelle formation (CMC) and the ratio of the slopes of this plot in the post-micellar region to that in the pre-micellar region gives the degree of counterion dissociation, $\beta$. The values of CMC and $\beta$ of CTAB and SDS in various solvents are given in Table - 2.1. Some typical plots of the conductance data from which the CMC and $\beta$ were derived are shown in Figures - 2.1 - 2.8. It is clear from Table - 2.1 that the CMC of CTAB and SDS surfactants increase with increasing composition of solvents. Our observation can be explained in terms of the two interactions responsible for the micellization, i.e., hydrophobic interactions and the break up of the water structure. Generally, the structure of water of liquid water is considered in terms of three-dimensional hydrogen bonded “flickering clusters” which retain much of the ordered structure of ice. Surfactant monomers with a long hydrocarbon chain increase the orderliness of water by formation of “Frank–Evan iceberg” around the hydrocarbon chain, resulting in a decrease in the entropy of the system. However, aggregation of the amphiphile monomer by formation of spherical micelles (due to hydrophobic interaction) breaks the icebergs and
### TABLE 2.1

VALUES OF CMC AND $\beta$ (DEGREE OF COUNTERION DISSOCIATION) OF SURFACTANTS IN VARIOUS SOLVENT SYSTEMS (CONDUCTOMETRIC METHOD), TEMP. = 27°C

<table>
<thead>
<tr>
<th>SOLVENTS</th>
<th>VOL / VOL (%)</th>
<th>CMC x 10$^{-3}$ / mol. dm$^{-3}$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CTAB</td>
<td>SDS</td>
</tr>
<tr>
<td>MeOH</td>
<td>0</td>
<td>0.99</td>
<td>7.90</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.80</td>
<td>12.1</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>3.00</td>
<td>25.0</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>10</td>
<td>1.90</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>3.80</td>
<td>40.0</td>
</tr>
<tr>
<td>DMF</td>
<td>10</td>
<td>2.50</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>7.00</td>
<td>30.0</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>10</td>
<td>1.40</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>2.71</td>
<td>14.5</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>4.80</td>
<td>23.5</td>
</tr>
</tbody>
</table>
FIG. 2.1: PLOTS OF SPECIFIC CONDUCTIVITY ($\kappa$) Vs CONCENTRATION OF CTAB IN CH$_3$OH - WATER MIXTURE

FIG. 2.2: PLOTS OF SPECIFIC CONDUCTIVITY ($\kappa$) Vs CONCENTRATION OF CTAB IN CH$_3$CN - WATER MIXTURE
FIG. 2.3: PLOTS OF SPECIFIC CONDUCTIVITY [$\kappa$] Vs CONCENTRATION OF CTAB IN DMF-WATER MIXTURE

FIG. 2.4: PLOTS OF SPECIFIC CONDUCTIVITY [$\kappa$] Vs CONCENTRATION OF CTAB IN ETHYLENE GLYCOL-WATER MIXTURE
thereby increases the entropy; therefore hydrophobic interaction is an entropy directed process. Addition of solvents decreases the polarity (lowers the dielectric constant) of the medium as a result of which the hydrophobicity of the hydrocarbon tails decreases. Hence, the CMC is observed at a higher concentration of surfactant.

2.21 MICELLE FORMATION IN MIXED SYSTEMS

CMC in EG and PEG−H₂O mixtures

Ethylene glycol is one of the weakest organic denaturants and is also highly associative solvents. The molecule is small and forms hydrogen−bonded networks having mainly two−dimensional cooperative domains, similar in nature to that of water. The CMC values of CTAB and SDS increase non−linearly with increasing concentration of EG are given in Figures−2.4 and 2.8, (Table−2.1). The degree of counterion−binding, also decreases regularly in each case. The above result can be explained on the basis of structure breaking properties of EG, which may disturb the dissolved hydrophobic group, causing increase of CMC. On the other hand the preferential solvation of EG, which results in the association of spherical micelles in order to form the rod−like micelles may also be responsible for the increase of CMC. A decrease in the dielectric
FIG. 2.5: PLOTS OF SPECIFIC CONDUCTIVITY $|\kappa|$ Vs CONCENTRATION OF SDS IN CH$_3$OH - WATER MIXTURE

FIG. 2.6: PLOTS OF SPECIFIC CONDUCTIVITY $|\kappa|$ Vs CONCENTRATION OF SDS IN CH$_3$CN - WATER MIXTURE
FIG. 2.7: PLOTS OF SPECIFIC CONDUCTIVITY ($\kappa$) Vs CONCENTRATION OF SDS IN DMF-WATER MIXTURE

FIG. 2.8: PLOTS OF SPECIFIC CONDUCTIVITY ($\kappa$) Vs CONCENTRATION OF SDS IN ETHYLENE GLYCOL-WATER MIXTURE
constant of the aqueous phase would result in an increase in the repulsion between the ionic head groups, leading to a delayed micellization. The formation of pre-aggregates before the CMC would also increase the CMC.

It can be observed from Tables 2.2 and 2.3 that both PEG-600 and PEG-20,000 increase the CMC of cationic (CTAB, CPB and CPC) and anionic (SDS) surfactants at all concentration levels. Representative illustrations are presented in Figures 2.9-2.12. The quantitative modeling of polymer/surfactant mixture is most difficult problem. The dimensions of the surfactant micelles are normally small compared to the radius of gyration of the polymer, but they are large compared to the polymer thickness. The additives PEG-600 and 20,000 form hydrogen bonds with water molecules. The favourable hydrogen bonding ability of these additives lead to poorer contribution to the hydrophobic interactions, which is driving force for micellization, and hence the higher CMC values. The increase in the number of repeating units does not have any significant influence on the CMC.

2.22 PROPERTIES AT THE AIR/WATER INTERFACE

Amphiphiles orient at the air–water interface and decrease
### TABLE 2.2

VALUES OF CMC AND $\beta$ (DEGREE OF COUNTERION DISSOCIATION) OF SURFACTANTS IN POLYMER SYSTEMS (CONDUCTOMETRIC METHOD), TEMP. = 27°C

<table>
<thead>
<tr>
<th>ADDITIVES</th>
<th>VOL / VOL (%)</th>
<th>CMC $\times 10^3$ / mol. dm$^{-3}$</th>
<th>CTAB</th>
<th>SDS</th>
<th>CTAB</th>
<th>SDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG - 600</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.52</td>
<td>10.0</td>
<td>0.28</td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>2.31</td>
<td>-</td>
<td>0.29</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>4.80</td>
<td>-</td>
<td>0.46</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>7.00</td>
<td>20.0</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>PEG - 20,000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.40</td>
<td>9.10</td>
<td>0.37</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.82</td>
<td>-</td>
<td>0.44</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>2.30</td>
<td>-</td>
<td>0.59</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>2.50</td>
<td>13.0</td>
<td>-</td>
<td>0.46</td>
<td></td>
</tr>
</tbody>
</table>
FIG. 2.9: PLOTS OF SPECIFIC CONDUCTIVITY $[\kappa]$ Vs CONCENTRATION OF CTAB IN POLYMERS [10% (v/v)]

FIG. 2.10: PLOTS OF SPECIFIC CONDUCTIVITY $[\kappa]$ Vs CONCENTRATION OF CPB IN POLYMERS [10% (v/v)]
TABLE - 2.3
VALUES OF CMC AND \( \beta \) (DEGREE OF COUNTERION DISSOCIATION) OF CATIONIC SURFACTANTS IN POLYMER SYSTEMS (CONDUCTOMETRIC METHOD), TEMP. = 27°C

<table>
<thead>
<tr>
<th>ADDITIVES</th>
<th>VOL / VOL (%)</th>
<th>CMC ( \times 10^3 ) / mol dm(^{-3} )</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG - 600</td>
<td>0</td>
<td>0.96 0.90</td>
<td>0.31 0.36</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.40 1.93</td>
<td>0.33 -</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.91 2.50</td>
<td>0.29 0.42</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>3.40 -</td>
<td>0.17 -</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>4.81 -</td>
<td>- -</td>
</tr>
<tr>
<td>PEG - 20,000</td>
<td>10</td>
<td>0.96 0.90</td>
<td>0.43 0.48</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.40 -</td>
<td>- -</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1.91 1.05</td>
<td>0.39 0.44</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>3.40 1.20</td>
<td>- 0.46</td>
</tr>
</tbody>
</table>

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FIG. 2.11: PLOTS OF SPECIFIC CONDUCTIVITY (κ) Vs CONCENTRATION OF SDS IN POLYMERS [10% (v/v)]

FIG. 2.12: PLOTS OF SPECIFIC CONDUCTIVITY (κ) Vs CONCENTRATION OF SURFACANTS IN PEG - 600 [10%(v/v)]
surface tension. The amount of their adsorption per unit area of the surface at various concentrations can be calculated with the help of the Gibb's adsorption equation. For surfactant mixtures in water, the Gibb's surface excess is related to the surface pressure \( \pi \) by using the

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

relation, where \( \gamma_o \) is the surface tension of pure water and \( \gamma_{\text{cmc}} \) is the surface tension of solution at CMC.

Surface excess concentration (\( \tau \)) values, a measure of amount of surfactant adsorbed at the air–water interface were calculated using the Gibb's adsorption equation, where \( n \) is the number of particles per molecule of the surfactant whose surface concentration varies with the surfactant bulk phase concentration (\( C \)). In the case of anionic surfactants, \( n \) is equal to 2, since each of these behaves like univalent electrolyte before CMC. \( R \) is the gas constant (8.314 x 10^7 erg K^{-1} mole^{-1}) and \( T \) is the absolute temperature, \( (-d \gamma / d \log C) \) is the slope of \( \gamma \) versus \( \log C \) plot before CMC (\( T_2 \) to \( T_3 \) in the case of surfactant systems). The results are presented in Tables 2.4–2.6.
<table>
<thead>
<tr>
<th>SYSTEMS</th>
<th>$\tau \times 10^{-10}$ mol cm$^{-2}$</th>
<th>$A_{\text{min.}}$ nm$^2$</th>
<th>$\pi_{\text{CMC}}$ mNm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexadecyl trimethyl ammonium p-toluene sulphonate (CTATs)</td>
<td>0.78</td>
<td>2.12</td>
<td>43.9</td>
</tr>
<tr>
<td>Hexadecyl trimethyl ammonium bromide (CTAB)</td>
<td>2.00</td>
<td>0.83</td>
<td>41.1</td>
</tr>
<tr>
<td>Hexadecyl pyridinium bromide (CPB)</td>
<td>1.30</td>
<td>1.27</td>
<td>44.8</td>
</tr>
<tr>
<td>Hexadecyl pyridinium chloride (CPC)</td>
<td>2.17</td>
<td>0.76</td>
<td>40.2</td>
</tr>
<tr>
<td>Hexadecyl dimethyl ethyl ammonium bromide (CDEAB)</td>
<td>1.40</td>
<td>1.18</td>
<td>40.8</td>
</tr>
<tr>
<td>Benzyl dimethyl hexadecyl ammonium chloride (BHAC)</td>
<td>0.67</td>
<td>2.47</td>
<td>43.1</td>
</tr>
<tr>
<td>Benzyl dimethyl tetradecyl ammonium chloride (BTAC)</td>
<td>1.14</td>
<td>1.45</td>
<td>43.4</td>
</tr>
<tr>
<td>SYSTEMS</td>
<td>$\tau \times 10^{-10}$ mol cm$^{-2}$</td>
<td>$A_{\text{min}}$ nm$^2$</td>
<td>$\pi_{\text{CMC}}$ mN m$^{-1}$</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>--------------------------------------</td>
<td>------------------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>Sodium dodecyl sulphate (SDS)</td>
<td>1.63</td>
<td>1.01</td>
<td>37.4</td>
</tr>
<tr>
<td>Sodium deoxy - cholate (NaDC)</td>
<td>0.66</td>
<td>2.48</td>
<td>30.8</td>
</tr>
<tr>
<td>Di-octyl sodium sulphosuccinate (AOT)</td>
<td>0.60</td>
<td>2.72</td>
<td>47.1</td>
</tr>
<tr>
<td>Dodecyl benzene sulphonic acid sodium salt (DDBS)</td>
<td>1.75</td>
<td>0.94</td>
<td>43.9</td>
</tr>
</tbody>
</table>
TABLE - 2.6

SURFACE EXCESS CONCENTRATION ($\tau$), MINIMUM AREA PER MOLECULE ($A_{\text{min}}$) AND SURFACE PRESSURE AT CMC ($\pi_{\text{CMC}}$) FOR NON-IONIC SURFACTANTS IN WATER

<table>
<thead>
<tr>
<th>SYSTEMS</th>
<th>$\tau \times 10^{10}$ mol cm$^{-2}$</th>
<th>$A_{\text{min}}$ nm$^2$</th>
<th>$\pi_{\text{CMC}}$ mN m$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly oxyethylene (23) lauryl ether (Brij – 35)</td>
<td>1.69</td>
<td>0.98</td>
<td>27.8</td>
</tr>
<tr>
<td>Polyethylene glycol tertocetyl phenyl ether (Triton – X 100)</td>
<td>0.45</td>
<td>3.68</td>
<td>43.7</td>
</tr>
</tbody>
</table>
The minimum area per molecule of a surface active compound \( (A_{\text{min}}) \)

\[
A_{\text{min}} = 10^{14} / N \tau
\]

can be estimated from the relations \( 10^6 - 10^9 \), where \( N \) is the Avogadro number.

2.23 DETERMINATION OF CRITICAL MICELLE CONCENTRATION (CMC)

The concentration at which micelles first appear in solution is termed the critical micelle concentration. Its determination is an important physico-chemical exercise for self-organising surfactant solution. Experimentally the CMC is determined from the inflection point of plots of some physical property of the solution as a function of concentration. Representative illustrations are presented in Figures - 2.13 – 2.22. The comprehensive results for cationic, anionic and non-ionic surfactants are presented in Tables 2.7 – 2.9. Both the methods (conductance and surface tension) have yielded comparable CMC values; method dependent variations are apparent.

Micellar driven reaction depends upon micellization of surfactant in reaction condition. Kinetics of cleavage of carboxylate
### TABLE 2.7
CRITICAL MICELLE CONCENTRATION OF CATIONIC SURFACTANTS DETERMINED BY SURFACE TENSION AND CONDUCTOMETRIC METHOD, TEMP. = 27°C

<table>
<thead>
<tr>
<th>SYSTEMS</th>
<th>AQUEOUS MEDIUM (SURFACE TENSION)</th>
<th>AQUEOUS MEDIUM (CONDUCTANCE)</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexadecyl trimethylammonium p-toluene sulphonate (CTATs)</td>
<td>1.58</td>
<td>1.90</td>
<td>-</td>
</tr>
<tr>
<td>Hexadecyl pyridinium chloride (CPC)</td>
<td>0.60</td>
<td>0.90</td>
<td>0.36</td>
</tr>
<tr>
<td>Hexadecyl pyridinium bromide (CPB)</td>
<td>1.00</td>
<td>0.96</td>
<td>0.31</td>
</tr>
<tr>
<td>Benzyldimethyl hexadecyl ammonium chloride (BHAC)</td>
<td>1.00</td>
<td>0.48</td>
<td>0.59</td>
</tr>
<tr>
<td>Benzyldimethyl tetradecyl ammonium chloride (BTAC)</td>
<td>1.00</td>
<td>1.90</td>
<td>0.44</td>
</tr>
<tr>
<td>Hexadecyl trimethylammonium bromide (CTAB)</td>
<td>1.40</td>
<td>0.99</td>
<td>0.29</td>
</tr>
<tr>
<td>Hexadecyl dimethyl ethyl ammonium bromide (CDEAB)</td>
<td>1.58</td>
<td>0.96</td>
<td>-</td>
</tr>
<tr>
<td>Tetradecyl trimethylammonium bromide (TTAB)</td>
<td>-</td>
<td>4.00</td>
<td>-</td>
</tr>
</tbody>
</table>
FIG. 2.13 PLOTS OF SPECIFIC CONDUCTANCE Vs log (M) • AND SURFACE TENSION Vs log (M) • FOR CMC OF CTATs

FIG. 2.14 PLOTS OF SPECIFIC CONDUCTANCE Vs log (M) • AND SURFACE TENSION Vs log (M) • FOR CMC OF CTAB
FIG. 2.15: PLOTS OF SPECIFIC CONDUCTANCE Vs log (M) • AND SURFACE TENSION Vs log (M) • FOR CMC OF CPC

FIG. 2.16: PLOTS OF SPECIFIC CONDUCTANCE Vs log (M) • AND SURFACE TENSION Vs log (M) • FOR CMC OF BHAC

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## TABLE 2.8

**CRITICAL MICELLE CONCENTRATION OF ANIONIC SURFACTANTS DETERMINED BY SURFACE TENSION AND CONDUCTOMETRIC METHOD, TEMP. = 27°C**

<table>
<thead>
<tr>
<th>SYSTEMS</th>
<th>AQUEOUS MEDIUM (SURFACE TENSION)</th>
<th>AQUEOUS MEDIUM (CONDUCTANCE)</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium dodecyl sulphate (SDS)</td>
<td>7.90</td>
<td>7.90</td>
<td>0.30</td>
</tr>
<tr>
<td>Sodium deoxycholate (NaDC)</td>
<td>3.00</td>
<td>4.00</td>
<td>-</td>
</tr>
<tr>
<td>Dodecyl benzene sulfonic acid sodium salt (DDBS)</td>
<td>1.40</td>
<td>1.90</td>
<td>0.25</td>
</tr>
<tr>
<td>Di-octyl sodium sulphosuccinate (AOT)</td>
<td>3.40</td>
<td>3.80</td>
<td>-</td>
</tr>
</tbody>
</table>
FIG. 2.17: PLOTS OF SPECIFIC CONDUCTANCE Vs \( \log (M) \) • AND SURFACE TENSION Vs \( \log (M) \) • FOR CMC OF DDBS

FIG. 2.18: PLOTS OF SPECIFIC CONDUCTANCE Vs \( \log (M) \) • AND SURFACE TENSION Vs \( \log (M) \) • FOR CMC OF NaDC
FIG. 2.19: PLOTS OF SPECIFIC CONDUCTANCE Vs log (M) ■ AND SURFACE TENSION Vs log (M) ● FOR CMC OF CDEAB

FIG. 2.20: PLOTS OF SPECIFIC CONDUCTANCE Vs log (M) ■ AND SURFACE TENSION Vs log (M) ● FOR CMC OF TX - 100
TABLE 2.9
CRITICAL MICELLE CONCENTRATION OF NON-IONIC SURFACTANTS DETERMINED BY SURFACE TENSION AND CONDUCTOMETRIC METHOD, TEMP. = 27°C

<table>
<thead>
<tr>
<th>SYSTEMS</th>
<th>AQUEOUS MEDIUM (SURFACE TENSION)</th>
<th>AQUEOUS MEDIUM (CONDUCTANCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyoxyethylene (23) lauryl ether (Brij-35)</td>
<td>0.05</td>
<td>0.09</td>
</tr>
<tr>
<td>Polyethylene glycol tertocyl phenyl ether (Triton-X-100)</td>
<td>1.58</td>
<td>0.40</td>
</tr>
</tbody>
</table>
FIG. 2.21: PLOTS OF SPECIFIC CONDUCTANCE Vs log (M) and SURFACE TENSION Vs log (M) FOR CMC OF AOT

FIG. 2.22: PLOTS OF SURFACE TENSION Vs log (M) FOR CMC OF SDS
and phosphate esters by the hydroxamate ions have been studied in chapter - IV. It is important to determine the micellization behaviour of surfactant in reaction condition. Hence, at variable pH, CMC of CTAB and CTACl surfactants were determined (Table - 3.0).

A large number of techniques\textsuperscript{110} can be used for the determination of CMC, viz. surface tension\textsuperscript{111-112}, conductance\textsuperscript{113-115}, viscosity\textsuperscript{116-117}, fluorescence\textsuperscript{118}, sound velocity\textsuperscript{119-120}, dye solubilization\textsuperscript{121}, light scattering\textsuperscript{122} and small angle neutron scattering\textsuperscript{123-125}.

In the present investigation conductometric method has been employed to determine CMC. The conductivity is linearly correlated to the surfactant concentration in both pre-micellar and 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 (\(\alpha = 1 - \beta\)).

Surface tension of various solution was measured by means of stalagmometer. Different surfactant solution were prepared in polymer and solvent solution\textsuperscript{126 - 128}. The range of surfactant concentrations was chosen sufficiently above and below the normal values of CMC.
**TABLE - 3.0**

**CRITICAL MICELLE CONCENTRATION OF CATIONIC SURFACTANTS DETERMINED AT DIFFERENT CONDITIONS, TEMP. = 27°C**

<table>
<thead>
<tr>
<th>CONDITION</th>
<th><strong>CMC X 10^3 / mol dm^-3</strong></th>
<th><strong>SURFACE TENSION</strong></th>
<th><strong>CONDUCTANCE</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CTAB</td>
<td>CTACI</td>
</tr>
<tr>
<td>Normal</td>
<td>1.0</td>
<td>1.0</td>
<td>0.96</td>
</tr>
<tr>
<td>pH 9.16</td>
<td>0.1</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>pH 11.0</td>
<td>0.1</td>
<td>0.1</td>
<td>0.48</td>
</tr>
</tbody>
</table>
in pure water. Number of drops was counted carefully for all the surfactant solutions. Weights of all surfactant solutions were determined by means of pyknometer. Finally weight of pure water and number of drops were determined.

The surface tension of each solution was evaluated by using equation (1).

\[
\gamma_2 = \frac{d_2 n_1}{d_1 n_2} \times \gamma_1 \quad - \quad (1)
\]

where,
\[
\gamma_2 = \text{surface tension of surfactant solutions}
\]
\[
\gamma_1 = \text{surface tension of pure water at that temperature}
\]
\[
d_2 = \text{density of surfactant solutions}
\]
\[
d_1 = \text{density of pure water at that temperature}
\]
\[
n_2 = \text{number of drops for surfactant solutions}
\]
\[
n_1 = \text{number of drops for pure water}
\]

A graph was plotted in between log [surfactant] Vs surface tension. The point of inflection in the graph corresponds to the value of CMC.

2.3 CONCLUSION

In the present investigation CMC of some important class of
surfactants were determined, both in normal and at reaction conditions. It is concluded that CMC gets lowered by increasing the hydrophobicity of surfactants. The nature of counterions have little effect on the magnitude of CMC.

Micellar properties of surfactants are significantly influenced by the presence of additives. They provide vital information about the solute–solvent interactions in surfactant solutions and hence, have lead to extensive structural, kinetic and thermodynamic studies.

This chapter provides information on how the properties of surfactants vary with structural components (non–polar hydrocarbon chain, polar head and counterion).
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