CHAPTER I

General Introduction

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References
1.1 Introduction

Surfactants form a unique class of surface active chemicals which possess ability to radically alter surface and interfacial properties and to self-associate and solubilize themselves in micelles. These properties enable the use of surfactants in wettability modification, detergency, stabilization and destabilization of dispersions. These in turn lead to frequent appearance of surfactants in diverse fields ranging from routine commercial products: motor oil, pharmaceuticals, detergents, petroleum and flotation agents for beneficiation of ores, to the high technology products: electronics, printing, magnetic recording, biotechnology and microelectronics.\(^1\)\(^-\)\(^7\) Surfactants also constitute an integral part of industry engaged in the formulations of medicines, cosmetics and synthesis of nano-materials.\(^8\)\(^-\)\(^19\) As a consequence, demand for high-performance surfactants is continuously increasing. Besides the commercial need, high performance surfactants are also required for environmental protection since a less amount of surfactant used can contribute in reducing the load on natural purification systems. Self assembly of surfactant systems is therefore an enthralling arena of research that implies for extensive research efforts in designing novel surfactant systems and understanding their self assembly behavior.\(^20\)\(^-\)\(^22\)

Surfactants are the schizophrenic molecules possessing discrete polar and nonpolar entities that helm the surfactant assembly in aqueous solution. Nature of polar entity forms the basis for classification of surfactants into anionic, cationic, nonionic and zwitterionic surfactants. Anionic surfactants possess anionic polar entity like long-

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\textbf{Nonpolar Entity} \hspace{1cm} \textbf{Polar Entity}
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\includegraphics[width=0.5\textwidth]{structure_of_surfactant_monomer.png}
\end{center}

\textbf{Structure of surfactant monomer}

chain fatty acid sulfosuccinates, alkyl sulfates, phosphates and sulfonates. These are the most widely used class of surfactants in industrial applications due to their relatively low cost of manufacture, excellent cleaning properties and high sudsing potential.
Surfactants with cationic polar entity known as cationic surfactants may be protonated long-chain amines or long-chain quaternary ammonium compounds. Cationic surfactants share only a small portion of the surfactant market as ingredients of antibacterials, liquid crystals, gene transfection agents, phase transfer catalysts and crystalline mesoporous materials.\textsuperscript{10,23} Amphoteric surfactants represented by betaines and lecithins being mild in nature are used in personal care products and household cleaning formulations. Nonionic surfactants possess non-dissociable polar entity like polyethylene oxide, alcohol and related polar groups. Most of the cleaning formulations contain nonionic surfactant as an important ingredient that imparts resistance to the hardness in the surfactant systems.

Structural duality in surfactant molecules tends to associate them into well organized supramolecular assemblies called micelles. Organization within these supramolecular assemblies depends upon a complex interplay of molecular geometry, amphiphilic character and charge on the molecules. At low concentration, surfactant monomers are preferentially adsorbed at the air/solution interface that avoids the energetically unfavorable interaction between nonpolar part of surfactant and water dipole. Solvation of surfactant monomer occurs in such a way that the polar head groups are solvated either by dipole-induced dipole or ion-dipole interactions and its non-polar part lies in the air phase. Presence of these molecules on the surface disrupts the cohesive energy at the surface and lowers the surface tension. As the concentration of surfactant increases in the bulk, surface becomes more crowded and eventually gets loaded with amphiphiles to such an extent that further increase in surfactant concentration not leads to decrease in the surface tension. At this concentration, surfactant monomers orient themselves into intelligent arrangements known as micelles
that allow each component to maximally interact with its favored environment. This typical aggregation process prevalent in surfactant systems is referred to as micellization and corresponding concentration is named critical micelle concentration (cmc); a highly temperature-dependent surfactant characteristic.

Micelles are dynamic nanoscopic aggregates possessing variable features in terms of geometry (globular, cylindrical, spherical etc), physicochemical properties, polarity and hydrophobicity. Micellar solutions of different surfactants are frequently used as media in a variety of applications during chemical analysis and synthesis. Size and stability of the micelles are important features that determine their physicochemical properties and applications of a particular surfactant system. Micelles demonstrate considerable affect on the rate of reaction, its equilibrium and stoichiometry of the reactants and products. Exploit of micelles in pharmaceutical formulations is very common as dissolving agent, vehicle and protecting agent. Modulation of micellar properties, therefore, receives constant attention from both the technological as well as ecological viewpoints.

Micellar properties of an aqueous surfactant solution are dependant upon the identity of surfactant and environmental conditions. Surfactant assembly exhibits more or less fixed physicochemical behavior at ambient conditions of concentration and temperature and is difficult to modulate. For the modulation of self-assembly and micellar properties, many approaches have therefore been developed ranging from molecular modifications to the additive introduction. Owing to the inherent difficulty in the preparation of chemically pure surfactants, tailoring of micellar properties of surfactants by using additives has been the underpinning of a great deal of scientific and applied research. Although surfactant science is a reasonably mature discipline, there is still a vast room for designing novel mixed surfactant systems to be used in specific purposes. As the addition of a judiciously selected and environmentally benign substance for behavior modulation is a convenient and preferable in practice, number of external additives like cosolvents, cosurfactants, electrolytes, polar and nonpolar organics etc have been employed for the purpose. Addition of different kinds of additives to surfactant system gives a number of possible surfactant mixtures with better performance characteristics that has been focused in the thesis work.
1.2 Review of Literature

A brief description with detail survey of literature related to different possible surfactant mixtures is given in the thesis under different headings:

1.2.1 Surfactant-Additive Mixed Systems

Probing the micellar, thermodynamic and interfacial properties of surfactants in the presence and absence of additives can provide extensive information about solute-solute and solute-solvent interactions in these systems. Additive modifies environment around the micellar self assembly of surfactant molecule and thereby affects its functionality. Range of possible functional modifications depends upon the nature of surfactant-additive interactions, which might favor or counter the self association process and consequently influence the micellar morphology and physicochemistry. Most studies in literature concentrate on the perspective of favorable association as it provides a way to meet the rising demand of surfactants in industry and fulfills the requirements regarding stringent environmental policies being implemented. Need for such type of studies is also increasing on account of the fact that modern chemical industry engaged in the development of surfactant based formulations often employs surfactant-additive mixed systems to achieve the optimum properties in terms of better cleansing power and foaming capacity with lower skin irritation etc.

Most of the additives in aqueous media decrease the solubility of second component, however, certain additives might exhibit the contrary behavior leading to an enhanced solubility. Terminology used in surfactant chemistry for reduced solubility is ‘salting out’ and ‘salting in’ is the term used for the reverse effect. Additives that enhance aqueous solubility are called hydrotropes or chaotropes. Phenomenon of ‘salting in’ and ‘salting out’ play significant role in numerous practical applications, for instance in separation processes (protein precipitation, isomer separation), development of pharmaceutical formulations and modification of cloud point of surfactant solutions. Assortment of theoretical and experimental efforts aimed at explanation for these effects leads to more than one possible mechanisms. One of these mechanisms assumes a strong interaction between additives and surfactant similar to the complex formation that leads to a higher solubility. Another hypothesis assumes that additive inserts itself
into the water structure and modifies it. This hypothesis imparts specific terminology to the additives depending upon its effect on water structure in terms of structure-breaker or structure-maker. A third alternative available is based on the self association of additives to form aggregates similar to micelles that affects the solubility and properties of other surfactant.\textsuperscript{48} Considering the wide range of additive’s diversity, it is reasonable to ascribe to more than one mechanisms for accounting the changes in the specific property brought about by different kind of additives. Whatomver the hypothesis is employed, enhanced solubility in all the systems results from more favorable solvent-additive interaction compared to pre-existing surfactant-solvent interaction. Influence of additives on the interfacial tension and interaction between different composites in surfactant-additive mixed system has been established in a number of publications.

Zhao and Chen\textsuperscript{49} have studied the clouding phenomena and phase behavior of nonionic surfactants, octylphenol ethoxylate surfactants (Tritons-X-114: TX-114, Triton-X-100: TX-100) in the presence of hydroxyethyl cellulose (HEC) and its hydrophobically modified counterpart (HMHEC). At lower concentration, HMHEC was found to have a stronger lowering effect on the cloud point (CP) of these nonionic surfactants. Difference in clouding behavior observed was attributed to the existence of different kinds of molecular interactions in these systems. Depletion flocculation was reported to be the underlying mechanism in the case of HEC-nonionic surfactant systems, while the chain-bridging effect was responsible for the greater decrease in cloud point observed for HMHEC-nonionic surfactant systems. Composition analyses was also carried out for investigating different macroscopic phases formed so as to support the associative phase separation in HMHEC-nonionic surfactant systems, in contrast to segregative phase separation reported for HEC-nonionic surfactant systems.

Mahajan et al\textsuperscript{50} have investigated the effect of glycols oligomers such as (diethylene glycol: DEG, triethylene glycol: TEG, ethylene glycol monoethyl ether: EGMEE and ethylene glycol monobutyl ether: EGMBE) on the micellar properties of nonionic surfactants (Tween 20 and Tween 80) using small angle neutron scattering (SANS) and turbidity measurements. Shape of Tweens was reported to be oblate ellipsoidal that do not change predominantly in the presence of DEG and TEG. EGMEE and EGMBE were reported to be reducing the aggregation number of Tweens due to the
solubilization of EGMEE and EGMBE in Tween micelle that provides additional hydrophobicity. In another study, they have investigated the additive effect of various glycols: ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), ethylene glycol monomethyl ether (EGMME), ethylene glycol monoethyl ether (EGMEE), ethylene glycol monobutyl ether (EGMBE) and polyethylene glycols (PEG) with average molecular weight 200, 400, 600, 4,000 and 6,000 on the clouding behavior of nonionic surfactants: Tween 20 and Tween 80. They have reported depression in the cloud point of Tween 20 and Tween 80 in the presence of these additives. Among different glycol based oligomeric additives investigated, ethylene glycol monobutyl ether reduced the cloud point to the maximum extent. An increase in repeating units of polymeric glycol additives lead to more decrease in cloud point.

Rodrıguez et al have investigated the effects of glycols (ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol and tetraethylene glycol) on the thermodynamic and micellar properties of tetradecyltrimethylammonium bromide (TTAB) by conductivity and fluorescence techniques. They found that addition of these glycols to aqueous TTAB solutions causes an increase in the critical micelle concentration (cmc) as well as micellar ionization degree. However, effect on Gibbs energies of micellization ($\Delta G_m$) of TTAB was identical and an increase in the glycol content has been reported to cause decrease in the interfacial Gibbs energy contribution to $\Delta G_m$ and average aggregation number. Ability of the TTAB micelles present in the water-glycol mixtures as catalysts has been examined from the study of the reaction of methyl naphthalene-2-sulfonate + Br$^-\"$ in the water-glycol TTAB micellar solutions and found that the reaction was faster in water-glycol TTAB micellar solutions than in water.

Sharma et al have reported the effect of various electrolytes and nonelectrolytes on the cloud point of nonionic polyethoxylated alkyl ether surfactants: $C_{12}EO_6$, $C_{12}EO_9$ and $C_{12}EO_{10}$. Clouding of $C_{12}EO_{10}$ exhibited minimum variation with concentration of additive. Sucrose, glucose, potassium chloride, potassium bromide, sodium chloride, sodium iodide, tetra methyl ammonium bromide and tetra butyl ammonium iodide changed the cloud point (CP) to a larger extent. It was reported that sodium iodide and potassium iodide have different effect on the CP from that of sodium chloride, sodium bromide, potassium chloride and potassium bromide. Difference in the
effect of tetrabutylammonium iodide and tetramethylammonium bromide on the CP was explained on the basis that the mixed micelle formation of tetra butyl ammonium iodide with nonionic surfactant predominates over water structure formation. It has been reported that electrolytes and nonelectrolytes affect the CP of nonionic surfactants by modifying their water structure and hydrophilicity.

Interaction of amino acids and glycine peptides with sodium dodecyl sulfate (SDS) and hexadecyltrimethylammonium bromide (HTAB) has been explored by Singh et al. Apparent molar volumes of glycine, alanine, valine, leucine, lysine, diglycine and triglycine were determined in aqueous solutions of SDS and HTAB using density measurements. Contribution of charged end groups (\(-\text{NH}_3^+\), \(-\text{COO}^-\)), CH\(_2\) group and alkyl chains of the amino acids towards partial molar volume has been evaluated for a homologous series of amino acids. Results indicated that ion-ion, ion-polar and hydrophobic-hydrophobic group interactions are responsible for the partial molar volumes of transfer from water to aqueous SDS and HTAB. They have reported that interactions of the amino acids and peptides are stronger with SDS compared to HTAB. Comparison between hydration numbers of different amino acids indicated that hydration numbers are almost same at 1 mol kg\(^{-1}\) level of cosolvent/cosolute. Increasing molality of cosolvent/cosolute beyond 1 mol kg\(^{-1}\) lowers hydration number of amino acids due to increased interaction with solvent. Yan et al. have studied the effect of glycyl dipeptides: glycylglycine, glycyl-L-valine, and glycyl-L-leucine on the micellar properties of gemini surfactant pentamethylene-1,5-bis(dodecyldimethyl ammonium bromide): 12-5-12 by conductivity and fluorescence measurements. Enhancement in micellization of surfactant has been observed in the presence of glycyl dipeptides. Negative free energy and positive entropy of micellization have been evaluated using the mass action model.

Additive effect of ethylene amines (ethylenediamine, diethylenetriamine, triethylenetetramine, and tetraethylenepentamine) on the surface and mixed micellization properties of cationic gemini surfactants butanediyl-1,4-bis(dimethyl cetylammonium bromide): 16-4-16, pentanediyl-1,5-bis(dimethylcetylammonium bromide): 16-5-16 and hexanediyl-1,6-bis(dimethylcetylammonium bromide): 16-6-16 at 303.15 K has been investigated using surface tension. Mixed micellization and
synergistic interactions at all mole fractions for the proposed systems were reported. They observed that increase in concentration of additives decreases the critical micelle concentration (cmc) and minimum surface area values ($A_{\text{min}}$) and increases the surface excess ($\Gamma_{\text{max}}$). Increase in spacer chain length of gemini surfactants exhibited an increase in cmc, and $A_{\text{min}}$ values along with a decrease in surface pressure ($\pi_{\text{cmc}}$) and surface excess ($\Gamma_{\text{max}}$). Evaluation of thermodynamic parameters indicated thermodynamically stability and spontaneity of the proposed mixed system. Attractive interactions were reported to be increasing with spacer chain length of the gemini surfactants in the order: $16-6-16 > 16-5-16 \approx 16-4-16$.

Ahmad et al$^{57}$ have carried out the cloud point study to determine thermodynamic parameters for tetrabutylammonium dodecyl sulfate (TBADS) in the presence of quaternary bromides, alcohols, and amines as additives. They found that clouding of TBADS in presence of quaternary salts and short chain amines was exothermic and solvated water molecules released from the domain of micellar aggregation with increasing temperature made entropy values ($\Delta S^c$) negative. Among investigated additives, higher chain amines and alcohols were reported to be increasing the micelle size and decreasing the randomness of the system thereby exhibiting the positive $T\Delta S^c$ values and negative Gibbs energy change, $\Delta G^c$. Negative value of Gibbs free energy, $\Delta G^c$ for all the systems revealed the spontaneity of clouding phenomenon.

Chavda et al$^{58}$ analysed the partitioning of monohydric alcohol 1-butanol and dihydric alcohol 1,4-butanediol into the micelles of cationic surfactants by employing small angle neutron scattering (SANS), conductance and viscosity techniques. From these studies they concluded that although these alcohols change the micellar properties and contribute to reduction in electrostatic and hydrophobic interactions yet they behave in a different manner. SANS measurements were used to explore the affect of alcohols on the micellization behavior of cationic gemini surfactant (N,N-bis(dimethyldodecyl)-1,4-butanediammonium dibromide: 12-4-12) and conventional cationic surfactant tetradecyltrimethylammonium bromide (TTAB). Viscosity measurements indicated micellar growth as butanol gets partitioned into both surfactant systems, however, micellar growth in the gemini surfactant system was more pronounced due to enhanced micellar properties and solubilization. It has been reported that viscosity and micellar
size of 100 mM TTAB in the presence of butanol at concentration higher than 5% decreases. These results were also supported by SANS results. Partitioning of the alcohols and their locations in the micelles deduced from 2D NMR experiments were consistent with the number and position of hydroxyl groups making a significant contribution to both hydrophobic and electrostatic aspects of self-assembly process.

Using conductometric technique, influence of ionic and nonionic hydrotropes (aniline hydrochloride, 2-methylaniline hydrochloride, 4-methylaniline hydrochloride, hydroxybenzene, 1,3-benzenediol, benzene-1,2,3-triol) on the micellar behavior of cationic gemini surfactant, butanediyl-1,4-bis(dimethylctethylammonium bromide): 16-4-16 has been investigated by Khan et al.\textsuperscript{59} Critical micelle concentrations for different mixing mole fractions at different temperatures were calculated and found to increase with increase in temperature. Synergistic interactions observed in all the binary combinations decrease slightly with increase in temperature due to thermal impedance. Highly negative micellar interaction parameter and lower activity coefficient value confirm the existence of synergistic interactions in these systems.

Soni et al\textsuperscript{60} have studied the effect of 26 non electrolyte additives (including 12 alcohols, 7 glycols and 7 amides) on the association and clouding behavior of silicone surfactants (SS) in aqueous solutions. They reported that addition of the water soluble polar organic liquid additives increases the critical micelle concentrations (\textit{cmc}) and cloud point of SS, whereas the partially water soluble polar organic liquid additives decreases the \textit{cmc} and cloud point of SS. The observed changes of free energy changes for the process in mixed solvent systems and water revealed the negative values of $\Delta G_m$ which indicate that presence of additives facilitate the micelle formation at lower concentrations, ultimately decreasing the \textit{cmc} as well as cloud point.

Effect of different alkanols viz., ethanol, butanol and hexanol on the micellar characteristics of alkyltrimethylammonium bromides (dodecyltrimethylammonium bromide: DTAB, tetradecyltrimethylammonium bromide: TTAB and hexadecyl trimethylammonium bromide: HTAB) in the presence of 0.1 M salts has been investigated using viscosity and dynamic light scattering (DLS) techniques by Kuperkar et al.\textsuperscript{61} Conductometric measurements were carried out to explore the role of counterions in binding phenomenon in the presence of salt and alcohol. Viscosity
results confirmed the general trend of micellar growth and transitions. They observed that long chain alcohols \((n \geq 5)\) act as cosurfactants whereas short chains \((n \leq 3)\) act as additives. For butanol, behavior was intermediate with strong dependence on the concentration of additives. Butanol initially screens the charges resulting into structural transition and eventually penetrates the micelles to form the mixed aggregates of lower size and viscosity. Medium chain alcohols in micellar aggregate induce micellar transition by anchoring at the micellar interface and decreasing the micellar surface charge density, whereas, their hydrophobic tails intercalate between the surfactant tails thus modifying the packing structure which in turn changes the rheological properties.

Graciani et al\(^{52}\) have investigated the influence of butanol, pentanol, and hexanol on the micellization of alkanedyil-\(\alpha,\omega\)-bis(dimethyldecylammonium) bromide type dimeric surfactants \(12\text{-s-}12,2\text{Br}^-\ (s = 3, 4, 6)\). Influence of nature and concentration of alcohol on the \(cmc\), micellar ionization degree, average micellar aggregation number and polarity of the micellar interfacial region was investigated using conductivity and fluorescence measurements. Presence of alcohol decreased the average micellar aggregation number that has been attributed to the decrease in interfacial Gibb’s energy. Decrease in aggregation number was accompanied by an increase in the polarity of interfacial region.

Influence of different aliphatic alcohols (methanol, ethanol, propanol, butanol, iso-butanol, tert-butanol, pentanol, heptanol, decanol and hydrocarbons \((n\)-hexane, cyclohexane, benzene\)) on the cloud point of non-ionic surfactant polyoxyethylene(7.5) nonylphenyl ether (PONPE-7.5) was studied by Fernandez et al.\(^3\) They reported that short-chain alcohols (methanol, ethanol, propanol and butanol) increase the cloud point by promoting the formation of expanded water structures and favoring the micelle hydration. This influence increased with the concentration of the additive and was negligible at low concentrations. Effect of longer-chain alcohols suggests their preferential solubilization in the inner core of the aggregate that increases the volume-to-area ratio for the micelle and the cloud point decreases. Effect of branching and cyclization were also studied by using two series: \(n\)-butanol, iso-butanol and tert-butanol, and \(n\)-hexane, cyclohexane and benzene, respectively. For both the series, addition of compound provoked a marked decrease in the cloud point. These effects can
be explained in view of the site of their solubilization in the micelle. Benzene molecule interacts preferentially with the ethylene groups, leading to strong dehydration, while the aliphatic compounds are solubilized in the inner core.

Yu et al.\(^6\) have studied the effect of inorganic and organic salts on the aggregation behavior of cationic gemini surfactants 12-4-12 and 12-4(OH)\(_2\)-12. They have reported that salt effectively reduces the critical micelle concentration of these gemini surfactants. Ability of salts to promote the surfactant aggregation decreases in the order: \(\text{C}_6\text{H}_5\text{COONa} > p\text{-C}_6\text{H}_4(\text{COONa})_2 > \text{Na}_2\text{SO}_4 > \text{NaCl}\). Only \(\text{C}_6\text{H}_5\text{COONa}\) distinctly reduced the \(\text{cmc}\) and surface tension value at \(\text{cmc}\). For 12-4-12 solution, penetration of \(\text{C}_6\text{H}_5\text{COO}^-\) anions and charge neutralization induced a morphology change from micelles to vesicles, whereas other salts only slightly increased the micellar size. 12-4(OH)\(_2\)-12 solution changed from micelle/vesicle coexistence to vesicles with addition of \(\text{C}_6\text{H}_5\text{COONa}\), whereas, other salts transfer the 12-4(OH)\(_2\)-12 solution from micelle/vesicle coexistence to micelles. As compared with 12-4-12, two hydroxyls in the spacer of 12-4(OH)\(_2\)-12 promote micellization of 12-4(OH)\(_2\)-12 and reduce the amount of \(\text{C}_6\text{H}_5\text{COONa}\) required to induce micelle-to-vesicle transition.

1.2.2 Mixed Systems of Surfactants

Mixing of surfactants has been the subject of intense research in the last decade owing to fundamental, technological and commercial considerations.\(^65\)\(^-\)\(^68\) Practical arena prefers surfactant-surfactant mixed systems in lieu of pure surfactants as these mixed systems usually exhibit superior performance properties. These mixtures are often preferred as solublizers, emulsifiers, flow field regulators, membrane mimetic media, nanoreactors for enzymatic reaction, templates for nanolithography, microelectronics, microfluidic devices, nanosensors and molecular coverings.\(^69\)\(^-\)\(^81\) In addition, the surfactant-surfactant mixtures also carry interest in micellar catalysis.

Micellization in surfactant-surfactant mixtures involves a more complex interplay of intermolecular forces in comparison to the micelle formation by a single surfactant. Interactions between surfactants are generally electrostatic and hydrophobic in nature. Evaluation of different micellar parameters in the mixed state involves the estimation of the nature and strength of interactions between two surfactants.
Surfactant-surfactant mixtures often exhibit nonideal behavior dependent upon surfactant structure in terms of the size of head as well as tail group. Interactions leading to non-ideality in surfactant-surfactant mixed solutions may be either favorable or unfavorable. In case of favorable mixing, these system exhibits enhanced interfacial properties such as lower critical micelle concentration and higher surface activity relative to the individual surfactant. This type of mixing behavior is known as synergism. Favorable or synergistic interactions make the system more attractive and useful as it results in reduction of total amount of surfactant to be used in a particular application thereby reducing its cost and environmental impact. Synergetic effects are important for a wide range of surfactant-based phenomena such as foaming, emulsification, solubilization and detergency. Therefore, investigation of the surfactants with similar and different nature in aqueous mixtures has attracted a great deal of attention in literature.

Based on the type of surfactant, numerous types of mixtures are possible viz. cationic-cationic, cationic-nonionic, anionic-anionic, anionic-nonionic and nonionic-nonionic. In literature, an extensive study on the surfactant mixed systems has been performed in order to explore their micellar and structural behavior.

Das et al. have reported mixed micellization behavior of binary and ternary mixtures containing cationic surfactants: hexadecylpyridinium chloride (HPyCl), tetradeyltrimethylammonium bromide (TTAB), and dodecylpyridinium chloride (DPC) in aqueous medium using tensiometry and conductometry. They have observed that \( cmc \) value increases with decrease in tail length which signifies that self aggregation behavior in these systems is dictated by dominant effect of hydrophobic interaction. The \( cmc \) values obtained by tensiometry and conductometry for pure and binary combinations (HPyCl/TTAB and DPC/TTAB) signify concurrence of interfacial saturation by surfactant monomer and their self aggregation in bulk solution. In HPyCl/DPC mixture, tensiometric \( cmc \) precedes conductometric \( cmc \) at lower mole fraction of HPyCl due to decrease in degree of counterion binding at micellar interface. Negative deviation in experimental \( cmc \) for all the binary combinations infers Van der Waals attractive interaction among similarly charged surfactant head groups.
Ray et al\textsuperscript{91} have studied the interfacial adsorption and micellization behavior of pure and mixed alkyltrimethylammonium bromides, decyl-, dodecyl-, tetradecyl- and hexadecyltrimethylammonium bromide (DeTAB, DTAB, TTAB and HTAB) using tensiometric, conductometric, fluorimetric, viscometric and calorimetric methods. Critical micelle concentration, aggregation number, micellar polarity counterion binding and thermodynamics of adsorption were determined. They have reported that binary components of the mixtures undergo moderate synergistic interactions despite chain length difference. Contribution of terminal methyl, methylene and hydrophilic tetramethylammonium groups towards standard Gibbs free energy, enthalpy and entropy of micellization processes were found to be positive for the systems studied.

Azum et al\textsuperscript{92} have investigated mixed micellization behavior of alkanediyil-R,α,ω-bis(tetradecyldimethylammonium bromide): 14-s-14 (s=4,5,6) with cationic surfactants, hexadecyltrimethylammonium bromide (HTAB) and tetradecyltrimethylammonium bromide (TTAB) using conductance and fluorescence techniques. Evaluation of critical micelle concentration, interaction parameters, micellar mole fractions and activity coefficients for different mole fractions indicate attractive attractions between dimeric and conventional surfactants. Motomura’s theory was used to calculate the micellar mole fractions and contribution of conventional surfactant and was reported to be more in comparison to the ideal mixing state. Fluorescence quenching results were also found to be in concurrence with the results obtained from conductometric study.

Jiang et al\textsuperscript{93} have investigated the exchange dynamics for several mixed surfactant systems comprising gemini and conventional surfactants (12-2-12/TX-100, 14-2-14/TX-100, SDS/TX-100, 14-2-14/Brij-35, 12-2-12/TTAB, and 14-2-14/TTAB) using their \textsuperscript{1}H NMR spectra for comparing the line widths and line shapes of the peaks. They have reported that for SDS/TX-100 mixed system, addition of SDS fastens the exchange rate of TX-100 in solution, while, TX-100 slows down exchange rate of SDS. From the results they have shown that exchange rate of mixed surfactant gets enhanced in the three cationic/nonionic mixed systems, while the exchange rates were lowered by each other for the two cationic/cationic mixed solutions.
Chakraborty et al\textsuperscript{94} have investigated the mixed micellization behavior of hexadecylpyridinium chloride (HPyCl), hexadecyltrimethylammonium bromide (HTAB) and polyoxyethylene(10)cetyl ether (Brij-56) in different combinations in aqueous medium by tensiometric, conductometric, calorimetric, spectrophotometric, and fluorimetric techniques. Different physicochemical properties such as critical micelle concentration, micellar dissociation, thermodynamic parameters, interfacial adsorption and micellar aggregation number determined were favorable for nonspherical micelles in HTAB/Brij-56, HpyCl/Brij-56 and HpyCl/HTAB/Brij-56 mixtures while HPyCl/HTAB system exhibited spherical shape.

Bakshi et al\textsuperscript{95} studied the mixed micellization of nonionic surfactant polyoxyethylene alkyl ether (\(C_{10}EO_8\), \(C_{12}EO_4\) and \(C_{14}EO_8\)) with twin tail alkylammonium bromides (12-0-8, 12-0-10, 12-0-12 and 12-0-16) employing fluorescence, dynamic light scattering and electron spin resonance measurements. Micelle formation in the mixtures of \(C_{10}EO_8\)/\(C_{12}EO_4\)+twin tail surfactants occurred due to the synergistic interactions and increase in hydrophobicity of the cationic component. Variation in micelle mole fraction suggested that mixed micelles are rich in nonionic component. An increase in hydrophobicity of nonionic surfactant from \(C_{10}EO_8\) to \(C_{14}EO_8\) induced antagonistic mixing in the mixtures of \(C_{14}EO_8\) with twin tail surfactants of longer hydrophobic tail.

Zhu et al\textsuperscript{96} carried out surface tension and dilational viscoelastic studies of water in presence of surfactants, Tyloxapol and Triton-X-100 (TX-100) with hexadecyl trimethylammonium bromide (HTAB). Results predicted nonideal mixing and attractive interactions between constituent surfactants in the mixed micelles and monolayer. Using Maeda theory, it was suggested that chain-chain interaction among surfactants were not too high. Interpretation of surface dilational viscoelasticity results illustrated that maximum value of dilational modulus \(|\varepsilon|\) for these surfactant mixtures lies between the values exhibited by the individual surfactant. Higher value of \(|\varepsilon|\) for Tyloxapol/HTAB system in comparison to the TX-100/HTAB system infers that surfactant with high surface activity has higher mole fraction in the mixed monolayer.

Ruiz and Aguiar\textsuperscript{97} have examined the aggregation behavior of binary system of octaoxyethylene monododecyl ether (\(C_{12}EO_8\)) with dodecyltrimethylammonium
bromide (DTAB), tetradecyltrimethylammonium bromide (TTAB) and hexadecyltrimethylammonium bromide (HTAB) by fluorescence. Study established that in addition to electrostatic interactions between head groups, secondary effects of steric character due to varying alkyl chain length in alkyltrimethylammonium bromide accounts for the existence of synergism. Increase in micellar micropolarity on the incorporation of ionic component was consistent with the corresponding change in micellization entropy due to formation of open micelles with more hydrated structure. Study also concluded that micellar hydration is predominant factor in the formation of proposed mixed micelles.

Saian and Asadabadi\textsuperscript{98} used drop-weight method to study the influence of octyl phenol ethoxylate (Triton-X-100) and dodecyltrimethylammonium chloride (DTMAC) surfactants on the interfacial tension of the individual and binary mixed systems. Results indicated that addition of Triton-X-100 with bulk mole fraction less than 0.01 enhances the influence of DTMAC in lowering interfacial tension. For bulk mole fractions up to 0.2, interfacial composition and attractive interactions in binary mixtures calculated from the theory of nonideal interactions exhibited a different trend. Attractive interaction parameter has maximum absolute value at the bulk mole fraction of 0.01 and lower values at bulk mole fraction between 0.05-0.1. Experimental and ideal area per molecule at interface exhibited variation in agreement with the interaction parameter.

Sehgal et al\textsuperscript{99} have studied the properties of mixed monolayers and micelles in the mixture of dodecyltrimethylammonium bromide (DTAB) and dimethyldodecyl ammoniopropane sulfonate (DPS) by interfacial tension, fluorescence, dynamic light scattering (DLS) and viscosity. Authors have explained the deviation from ideality on the basis of Clint theory. Interaction parameter and composition of the mixed micelles and monolayers were obtained with the help of regular solution theory. Microviscosity of the pure and mixed micelles was monitored by fluorescence polarization measurements using rhodamine B as a fluorescence probe. Hydrodynamic radii of the micelles were obtained in mixtures at different mole fractions of surfactant from DLS measurements. Change in viscosity at high concentration of DTAB revealed that minima got shifted to a higher value in the mixed state. This minima suggested structural change in the mixed micelles.
Organization of amphiphilic nonionic surfactants, polyoxyethylated octyl phenols (OP-10, OP-30) in mixtures with ionic surfactants, hexadecyltrimethyl ammonium bromide (HTAB) and sodium dodecyl sulphate (SDS) have been investigated by Dash and Misra.\textsuperscript{100} Employing conductometric method in conjunction with fluorescence, surface tension, zeta potential and DLS measurements, they have observed antagonistic interactions for the systems studied (OP-10/OP-30+HTAB/SDS). Antagonism was found to be more prominent in presence of OP-10 as compared to OP-30. Observed antagonistic effect was attributed to formation of hydrophobic complex and was supported by fluorescence and surface tension measurements. Zeta potential and DLS studies suggested the association of ionic surfactants to nonionic micelles.

Ray et al\textsuperscript{101} studied the micellization of mixed binary surfactant systems of sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (SDBS) by conductometry, tensiometry, fluorimetry and microcalorimetry at different mole fractions. Counter-ion binding, micellar aggregation number, thermodynamics of micellization, interaction of components in mixed micelles and their composition therein alongwith amphiphile packing in micelles indicated antagonistic interaction in mixed micelles. Difference in head groups of SDS and SDBS has manifested interesting solution and interfacial behaviors. Packing parameter of the amphiphiles in the pure and mixed micelles advocated spherical geometry of the assemblies.

Janczuk et al\textsuperscript{102} have carried out surface tension studies on systems comprising sodium dodecyl sulphate and sodium hexadecyl sulphonate. Evaluation of molecular parameters for the mixed micelles and monolayers indicated that these surfactants do not exhibit synergism in the adsorbed monolayers and micelles, however, a small maxima in surface concentration excess at water/air interface and a minima in the surface tension corresponding to \textit{cmc} was observed at $\alpha$ = 0.4 and 0.2.

Mahajan et al\textsuperscript{103} have carried out tensiometric, fluorescence and viscometric measurements on the interfacial and bulk properties of mixtures comprising anionic (Sodium bis(2-ethylhexyl)sulfosuccinate: AOT) and zwitterionic surfactants \{3-(N,N-dimethyldodecylammonio)propane sulfonate: DPS, 3-(N,N-dimethyltetradecyl ammonio)propane sulfonate: TPS, 3-(N,N-dimethylhexadecylammonio)propane sulfonate: HPS\} in aqueous media. These mixtures have been reported to be exhibiting
synergism and synergistic interactions increase with elongation of hydrocarbon chain of the zwitterionic surfactant. Among all the systems reported highest synergism was observed for AOT+HPS mixtures. This study demonstrated that the AOT+DPS/TPS/HPS mixtures behave nonideally, whereas binary mixtures of SDS with same zwitterionic surfactants show nearly ideal behavior. These observations confirmed that twin-tail surfactant (AOT) introduces synergism more efficiently than single chain surfactant (SDS) in the mixture.

Parekh et al.\textsuperscript{104} have studied the mixed surfactant systems of anionic (sodium dodecyltrioxyethylene sulfate: SDES) and gemini surfactants \{N,N’-bis-(dimethyldodecyl)-\(\alpha,\omega\)-dialkanediammonium dibromide: 12-s-12, s = 2, 4, 6\} at different molar ratios by surface tension measurements. Results indicated that synergism and vesicle formation on mixing leads to rich phase behavior, where mixture of vesicles and non-spherical micelles coexists. Negative interaction parameters for the micelles as well as interface indicate strong synergism. Microstructure of mixed surfactant system was reported to vary with mixing ratio and asymmetry of the two surfactants that enlarges phase region. Strong interactions, low \(cmc\) and negative interaction parameter values were reported to be due to the weakening electrostatic head group repulsions which favor the mixed micelle formation.

Surface properties of binary mixed systems of decyl- and dodecylpyridinium chloride or bromide, sodium pentyl- and heptylsulfonate have been investigated by Goralczyk et al.\textsuperscript{105} Analysis of results concerning the composition of mixed monolayers indicated that monolayers are rich in more surface active alkylpyridinium ions (\(R_nPy^+\)). Properties of mixed films depend on both the ionic strength and the nature of inorganic electrolyte added. With increase in electrolyte concentration, content of more surface active ion in the adsorption film gets enhanced and this enhancement was highest in the presence of sodium iodide and smallest for sodium chloride. Mutual interactions in the mixed adsorbed films were attractive, however, strength of these attractive interactions weakened with the increase in ionic strength. These interactions were also found to be dependent upon the nature of inorganic ions with the order: \(\text{Cl}^- > \text{Br}^- > \Gamma\).

Li et al.\textsuperscript{106} have measured the synergistic interactions between sodium dodecyl sulfonate (SDS) and zwitterionic surfactants of varying alkyl chain length (alkyl
dimethylammoniopropane sulfonates: C_{12}DPAS, C_{10}DPAS and C_{8}DPAS) at 40.0°C in aqueous 0.1M NaCl medium. They have reported that synergism in these mixtures exhibits maxima at 7:3 molar ratio. Fluorescence studies on SDS+C_{12}DPAS mixed system showed that addition of a small amount of anionic surfactant reduces the mixed micellar aggregation number to a value lower than pure zwitterionics. However, addition of C_{12}DPAS to sodium dodecyl sulfonate enhances the mixed micellar aggregation number to a value much larger than sodium dodecyl sulfonate. Study reports that mixed micellar aggregation number is highest at the composition point where efficiency of mixed micelle formation is maximum.

Murphy and Taggart\textsuperscript{107} have explored the surface and electrochemical properties of cationic surfactants, octyl-, decyl-, dodecyl-, tetradecyl- and hexadecyl trimethylammonium bromide (OTAB, DeTAB, DTAB, TTAB and HTAB respectively) and sodium octyl-, decyl- dodecyl-, tetradecyl- and hexadecyl sulphates (SOS, SDeS, SDS, STDS, SHDS respectively) in their ternary mixed states employing surface tension, conductivity and fluorimetry. The \textit{cmc} values obtained using molecular-thermodynamic theory were of the same order as the pseudophase separation approximation and experimental \textit{cmc} values. They have demonstrated the suitability of molecular-thermodynamic theory for the prediction of \textit{cmc} values with individual species concentrations and molar ratios.

Gharibi et al\textsuperscript{108} have studied the interaction of cationic surfactants alkyltrimethyl ammonium bromides (octadecyl, dodecyl, tetradecyl, hexadecyltrimethyl ammonium bromide) with nonionic surfactant (Triton-X-100: TX-100) using potentiometric and surface tension techniques. They have reported new methods for the evaluation of physicochemical parameters, concentration of free monomer of ionic and nonionic surfactants, degree of dissociation of ionic surfactants and mole fraction of surfactants in mixed micelles. Comparison of new methods and previous methods indicated noticeable difference between values of calculated synergetic parameters. Comparison between \textit{cmc} values indicates synergistic effect for octadecyltrimethylammonium bromide with Triton: TX-100, whereas, cosurfactant effect has been observed between dodecyl, tetradecyl and hexadecyltrimethylammonium bromides and Triton: TX-100.
Minimum structural effects on the magnitude of interaction parameters were also observed for these systems.

Singh and Ismail\textsuperscript{109} have studied the mixtures of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) and sodium dodecyl sulfate (SDS) in water using surface tension, conductance, emf and fluorescence emission methods. They found that system exhibits synergism at mole fraction of AOT less than 0.7. Molal conductance versus concentration behavior of AOT was found to be different from other ionic surfactants. Values of counter ion binding from emf data show that counterion binding behavior of the mixed micelles is controlled entirely by AOT. Aggregation number determined by fluorescence quenching method indicated that as mole fraction of first component $a_1$ increases, number of AOT molecules remains constant and that of sodium dodecyl sulfate decreases in the mixed micelles.

Hierrezuelo et al\textsuperscript{110} have carried out fluorescence study on the micellization of binary surfactant system formed by $n$-octyl-d-thioglucopyranoside (OTG) and sodium dodecylsulphate (SDS) in 0.1 M NaCl aqueous solution. Data reported by treatment based on Gibbs-Duhem equation exhibited reasonable agreement with regular solution theory suggesting that mixed system behaves as a regular solution. Mixing thermodynamic function values reveal that electrostatic repulsions between sulphate groups of sodium dodecyl sulfate controls the stability of mixed micelles. Variation in micellar aggregation number with solution composition infers that micellar size is determined by delicate balance between two opposing contributions namely the repulsive interactions between headgroups of ionic surfactant and steric interactions favoured by size of headgroup of sodium dodecylsulfate in comparison with that of OTG. Micellar micropolarity show little variation and is in accordance with the trend observed for the aggregation number.

Bakshi and Kaur\textsuperscript{111} have characterized binary mixtures of polyoxyethylene alkyl ethers ($C_{10}EO_8$, $C_{12}EO_4$ and $C_{14}EO_8$) with series of monomeric cationic, zwitterionic and phosphonium cationic surfactants from steady state fluorescence measurements. They have observed that the hydrophobicity of both nonionic as well as cosurfactant components strongly influences the nature of mixed micelles. Study demonstrates that the presence of bulky head groups in phosphonium surfactants significantly contributes
towards unfavorable mixing and increase the polarity of palisade layer of mixed micelles in comparison to ammonium head groups. Such increase in the polarity of stern layer has been reported to be reducing the hydrophobic environment of mixed micelles and decreases the mean micelle aggregation number. This effect further increases with hydrophobicity of the cosurfactant and was attributed to the screening of polar head group repulsions.

Ohta et al\textsuperscript{112} using surface tension measurements have examined the influence of polar head group size on the interaction and miscibility of binary surfactant mixtures in adsorbed films and micelles. Mixtures studied comprised of polyoxyethylene alkyl ether (C\textsubscript{10}EO\textsubscript{5}, C\textsubscript{8}EO\textsubscript{5}, C\textsubscript{10}EO\textsubscript{5} C\textsubscript{8}EO\textsubscript{4}), dodecyltrimethylammonium bromide (DTAB) and dodecylammonium chloride (DAC) surfactants. They have reported that lack of balance in hydrophilic group size makes packing of C\textsubscript{10}EO\textsubscript{5} and C\textsubscript{8}EO\textsubscript{4} molecules less favorable than that of C\textsubscript{10}EO\textsubscript{5} and C\textsubscript{8}EO\textsubscript{5} molecules both in adsorbed film and micelle. However, interactions between cationic surfactants (DTAB or DAC) and C\textsubscript{8}EO\textsubscript{4} is stronger than between same species both in the adsorbed film and the micelle. Results indicated that DAC molecule with smaller head group and higher surface charge density interacts more strongly with C\textsubscript{8}EO\textsubscript{4} molecules than DTAB molecules and these interactions are stronger in micelles than the adsorbed films.

Formation of viscoelastic solution of worm-like micelles and one-dimensional micellar growth on addition of lipophilic polyoxyethylene dodecyl ether (C\textsubscript{12}EO\textsubscript{3}) to hexadecyltrimethylammonium bromide (HTAB) and sucrose monohexadecanoate (P\textsubscript{1695}) in aqueous media has been reported by Engelskirchen et al.\textsuperscript{113} Steady and oscillatory shear rheological measurements show that in the aqueous HTAB system, extent of micellar growth decreases with increasing dispersion of polyethylene oxide (EO) chain in the mixture in order: C\textsubscript{12}EO\textsubscript{3} > C\textsubscript{12}EO\textsubscript{2}+C\textsubscript{12}EO\textsubscript{4} > C\textsubscript{12}EO\textsubscript{0}+C\textsubscript{12}EO\textsubscript{4} > C\textsubscript{12}EO\textsubscript{1}+C\textsubscript{12}EO\textsubscript{5}. In the C\textsubscript{12}EO\textsubscript{0}+C\textsubscript{12}EO\textsubscript{6} mixed system, micellar growth does not occur but phase separation was observed. In P\textsubscript{1695}+C\textsubscript{12}EO\textsubscript{n} system, viscoelastic solution is formed at relatively lower concentration of C\textsubscript{12}EO\textsubscript{n} and micellar growth decreases in the order: C\textsubscript{12}EO\textsubscript{3} ≈ C\textsubscript{12}EO\textsubscript{2}+C\textsubscript{12}EO\textsubscript{4} > C\textsubscript{12}EO\textsubscript{1}+C\textsubscript{12}EO\textsubscript{5} > C\textsubscript{12}EO\textsubscript{0}+C\textsubscript{12}EO\textsubscript{6}.

Hierrezuelo et al\textsuperscript{114} used conductance and fluorescence spectroscopic techniques to describe interactional behavior in mixtures of MEGA-10 with n-alkyltrimethyl
ammonium bromide based cationic surfactants (DTAB, TTAB, HTAB). All the systems exhibited negative deviation from ideal behavior and the combined effect of electrostatic and short range interactions was responsible for nonideality in these systems. By using static quenching method, they observed that in the mixed systems of DTAB and TTAB with MEGA-10, aggregation number gets initially reduced and afterwards becomes almost constant with value closer to the aggregation number of pure ionic micelle. However, in the systems involving HTAB, size of micelles initially increases and then decreases slightly for mixtures with a high content of the ionic component. Fluorescence polarization data suggests that increasing participation of cationic component induces formation of less compact micelles and this effect becomes more pronounced as the alkyl chain length of ionic component decreases. Greater interactions imply enhanced packing of hydrocarbon chains and consequent formation of micelles with more ordered structures.

Synergism in zwitterionic/anionic surfactant systems of N-dodecyl-N,N-dimethyl-3-ammonio-1-propane sulfonate (ZW3-12)/sodium dodecyl sulfate (SDS), N-dodecyl-N,N-(dimethylammonio)butyrate (DDMAB)/SDS, N-octyl-N,N-dimethyl-3-ammonio-1-propane sulfonate (ZW3-08)/sodium octyl sulfate (SOS) and zwitterionic/cationic systems of ZW3-12/dodecyltrimethylammonium bromide (DTAB), DDMAB/DTAB has been witnessed by McLachlan and Marangoni. Conductivity and NMR techniques were employed for cmc determination. ZW3-08+SOS and DDMAB+SDS systems behaved synergistically at all mole fractions studied, while the ZW3-12+SDS system exhibited synergistic behavior above mole fractions 0.30. Greater negative deviations from ideal behavior were demonstrated in DDMAB+SDS system than other zwitterionic/anionic systems. Zwitterionic/cationic systems of ZW3-12+DTAB and ZW3-08+DTAB displayed only slight deviations from ideal behavior, therefore indicating near ideal mixing.

1.2.3 Mixed Systems of Triblock Polymers

Polymeric aggregates of triblock polymers (TBPs) offer good candidature to accomplish the rising demands of emerging fields in nanotechnology and biomedical science research due to associated advantages like low toxicity, high stability and small
Unique solution behavior of these polymeric aggregates is also useful for the emulsion stabilization, viscosity regulation, catalyst support and surface modifications. All these applications make micelles of triblock polymer an interesting and engaging subject of research. Triblock polymers constitute an important class of water soluble surface active EO-PO-EO block copolymer nonionic surfactants which are commercially available under the trade name Pluronics (BASF) with a wide range of molecular compositions. Chemically triblock polymers are fabricated of hydrophobic blocks polypropylene oxide units (PO), and hydrophilic blocks polyethylene oxide units (EO), and are formulated as \( \text{EO}_x\text{PO}_y\text{EO}_x \), where \( x \) and \( y \) represent the number of EO and PO units respectively.

These polymers exhibit unique morphological architecture due to their amphiphilic character. In water or organic solvents, these polymers get self-assembled into wide range of morphologies of micro to nanometer dimensions depending upon their chemical nature. These micellar aggregates possess core-shell morphology with compact core of water insoluble polypropylene oxide (PO) blocks surrounded by highly swollen corona of water soluble polyethylene oxide (EO) blocks. Application of these polymeric micellar aggregates is controlled by the characteristic properties of its core and shell. For property modification and fabrication of novel aggregates with desired structures, two aspects are usually adopted namely the alteration in synthetic parameters or modification in surroundings. Alteration in synthetic parameters is carried out by changing the polymer architecture, block nature or length and molecular weight of the polymer, whereas, modification in surroundings is brought about by changing the environment of block copolymer in terms of temperature, ionic strength, solvent type and presence of cosolutes. As per needs, one or both of these aspects can be used, however, alteration in synthetic parameters is time consuming and tedious to implement in comparison to the modification of surroundings. As a consequence, past decade has witnessed great efforts being devoted to the investigation of physicochemical properties of polyethylene oxide and polypropylene oxide based block copolymers under different solution conditions. Resulting nanosize micellar aggregates of triblock polymers have been efficiently applied in pharmacology, cosmetology and encapsulation technologies. These applications have been based on their tendency to act as nanocontainers for...
solubilization and targeted release of hydrophobic drugs. Rapidly increasing interest in triblock polymers has also been due to their biodegradability and biocompatibility.\textsuperscript{136-149}

Mixing of two or more triblock polymers provides us a means for altering the surroundings and modification of surfactant properties as mixing of structurally and morphologically different polymers exhibits complementary effect on the system during its adjustment to external environmental changes such as temperature and concentration. Mixed micelles from cooperative self assembly of different triblock polymers exhibit significantly improved stability and enhance their application potential.\textsuperscript{150} Mixed micelles thus formed can be feasible candidate for fine tuning the micellar properties and matching up with the constantly rising demands of diverse industrial fields.

Zhuang et al\textsuperscript{151} have investigated self-assembly behavior of AB/AC amphiphilic diblock polymer mixtures in dilute solution by real-space-implemented self-consistent field theory in three dimensions. They have reported that two diblock polymers cooperatively self-assemble into hybrid aggregates and their morphologies were dependent on the mixture ratio and interaction between their hydrophilic blocks.

Bakshi et al\textsuperscript{152} have reported fluorescence and viscometric study on the mixed micellization of binary triblock polymer (TBP) mixtures P103 (EO\textsubscript{17}PO\textsubscript{60}EO\textsubscript{17})+F127 (EO\textsubscript{97}PO\textsubscript{69}EO\textsubscript{97})/P84 (EO\textsubscript{19}PO\textsubscript{43}EO\textsubscript{19})/L64 (EO\textsubscript{13}PO\textsubscript{30}EO\textsubscript{13})/P104 (EO\textsubscript{18}PO\textsubscript{58}EO\textsubscript{18})/ P123 (EO\textsubscript{20}PO\textsubscript{70}EO\textsubscript{20}) in aqueous media at 30 °C. They observed that binary mixtures P103+F127/P84/L64 undergo mixed micelle formation due to synergistic interactions while P103+P104/P123 show antagonistic behavior. Nonideal behavior of the proposed combinations has been found to be significantly dependent upon variation in the PO/EO ratio of unlike TBP components.

Yang et al\textsuperscript{153} have studied the formation of mixed micelles of BO\textsubscript{8}EO\textsubscript{41} and BO\textsubscript{12}EO\textsubscript{76}BO\textsubscript{12} and found that BO\textsubscript{12}EO\textsubscript{76}BO\textsubscript{12} (BO: polybutylene oxide) being highly hydrophobic could not be dissolved in water even at room temperature. Addition of BO\textsubscript{8}EO\textsubscript{41} into the solution induces formation of mixed micelles and thus increases the solubility of BO\textsubscript{12}EO\textsubscript{76}BO\textsubscript{12}. Presence of BO\textsubscript{12}EO\textsubscript{76}BO\textsubscript{12} in the solution decreases the \textit{cmc} value of BO\textsubscript{8}EO\textsubscript{41} to 0.9 mg/mL at 298.1 K. They also reported that aggregation number of the mixed micelles were determined mainly by BO\textsubscript{8}EO\textsubscript{41} (around 60 at 25 °C)
and was not affected by the presence of BO₁₂EO₇₆BO₁₂ even though BO₁₂EO₇₆BO₁₂ was responsible for the very low \textit{cmc} value. This conclusion is a little bit different from the general understanding of micellization process whereby the \textit{cmc} and the aggregation number are intercorrelated and are determined mainly by the more solvent phobic block. More importantly, \textit{cmc} of BO₁₂EO₇₆BO₁₂ was always much smaller than that of BO₈EO₄₁ and was even too small to be measured precisely.

Trong et al\textsuperscript{154} have studied micelle formation of triblock polymer F127 and Pluronic EG56 (branched molecule with three branches of F127) by calorimetric and rheological measurements. Micellization in these systems was reported to be endothermic with enthalpy of formation/melting for both polymers proportional to the total concentration. Rheological analysis before gelation for F127 revealed that initially solubility of monomers exhibit progressive changes like decrease in relative solution viscosity which was followed by micelle formation. Enthalpy measurements revealed the dependence of micelle concentration on temperature as well as volume fractions.

Portnaya et al\textsuperscript{155} have reported the micellization characteristics, structure and morphology for the binary mixture of β-casein and triblock polymer, Lutrol (EO₁₀₁PO₅₆EO₁₀₁). Isothermal titration calorimetry experiments revealed that addition of lutrol to monomeric and assembled β-casein results into mixed micelle formation. Above \textit{cmc} of β-casein, strong perturbations caused by penetration of hydrophobic oxypropylene sections of lutrol into the protein micellar core lead to disintegration of the micelles and reformation of the mixed lutrol/β-casein micelles. Negative enthalpy of micelle formation and cooperativity increases with increasing β-casein concentration in solution. Zeta-potential measurements show that lutrol interacts with protein micelles even below its critical micellization temperature. Lutrol effectively masks the protein charges probably by forming a coating layer of ethylene oxide rich chains. Small-angle X-ray scattering and cryogenic-transmission electron microscopy (cryo-TEM) indicate swelling of β-casein micelles in the presence of lutrol along the small axis that confirms the formation of mixed micelles.

Han and Jiang\textsuperscript{156} have studied self assembly of AB/BC diblock polymer mixture based on hydrogen bonding by Monte Carlo simulation. They observed that micellar structure is a function of intensity of associative interactions, directional dependency of
H-bonding and intrinsic repulsive interaction between A and C blocks. Decreasing directional dependency and increasing H-bonding interaction has an equivalent effect on micelle structure and H-bonding association for AB/BC diblock polymer mixture.

Tian et al\textsuperscript{157} investigated the mixed micellization of diblock polymer polystyrene-blockpoly(methacrylic acid) with triblock polymer poly-\text-(methacrylic acid) -block-polystyrene-block-poly(methacrylic acid), depending upon the system have found single and two-peaked distributions of sedimentation velocity after prolonged equilibration. Honda et al\textsuperscript{158} have used a temperature jump method to initiate the micellization and noted the effect of micellization conditions on the formation of mixed micelles in the mixture of diblock poly(methylstyrene)-block-poly(p-vinylphenethyl) alcohol: KT-326 and KT-327 with slightly different block lengths in benzyl alcohol by means of static and dynamic light scattering techniques.

1.1.4 Surfactant-Polymer Mixed Systems

Surfactant-polymer mixtures belong to a special category of soft materials possessing superior characteristic features (surface activity, viscosity, wetting, foaming, solubilization etc.) in comparison to either of the pure component.\textsuperscript{159,160} As self assemblies of these mixtures range from micro to nanoscale, it consequently opens doors for current and potential applications in diverse fields such as data storage, photonics, biomimetics and catalysis.\textsuperscript{161,162} Other important technical applications based on interfacial and rheological properties of these complex fluids and colloid formulations are in the fields of nanomedicine and nanotemplating. Scientific view behind these mammoth applications is vast variety of intermolecular interactions resulting from multiple probable combinations.\textsuperscript{163-177} Surfactant polymer mixtures also carry importance in research aimed at the basic understanding of biological behavioral motifs as nature too extensively employs the analogous systems (i.e. charged biomacromolecules and phospholipids) to create functional self-assembled nanostructures.\textsuperscript{178-182} Understanding of the core principals of physics involved in the self association of surfactant-polymer mixture may thus be helpful in manipulation of these systems to suit the needs of academia as well as industry.
Several plausible scenarios for exploring the interactions between surfactant and polymer components in surfactant-polymer mixtures have been proposed. According to these, surfactant-polymer interactions are mainly dependant upon tail length and head group of surfactant along with hydrophobicity and flexibility of the polymer component. In the mixed state, surfactant binds noncovalently to the polymer and induces cooperative self association at a given surfactant concentration known as critical micelle concentration. This self association results in formation of “bead-like” structures wherein surfactant micelles are bound to the polymer backbones.\textsuperscript{179} Besides bead like structures, other types of complexes have also been reported wherein surfactant monomers are bound to the polymer in a non-aggregated form. Because, mode of interaction in these complexes is dependant on the type of surfactant and polymer involved therefore ionic surfactants interact strongly with nonionic polymers than non-ionic surfactants. Similarly, interactions between ionic surfactant and oppositely charged polymer are coulombic in nature at lower surfactant concentration and hydrophobic at higher surfactant concentration. However, interaction of non-ionic polymers with surfactants is usually hydrophobic in nature.

Triblock polymers constitute an important class of nonionic amphiphilic block copolymers among numerous commercially available water soluble polymers. Triblock polymers and their mixtures with surfactants are widely employed on account of their adaptive properties to various environmental conditions that arise from their vast possible architectural and chemical compositions.\textsuperscript{183-193} Though carrying inherent importance, yet, interactions in surfactant neutral polymer systems have comparatively been less understood than surfactant-polyelectrolyte interactions.

Barbosa et al\textsuperscript{194} have investigated complex formation between triblock polymer \(\text{EO}_{71}\text{G}_7\text{EO}_{71}\) (G: phenyl glycidyl ether), surfactant sodium dodecyl sulfate (SDS) and various amphiphiles (penicillins/cloxacillin/dicloxacillin) by dynamic light scattering and isothermal titration calorimetry. Different polymer/amphiphilic systems were studied at constant polymer concentration with varying amphiphile concentrations. For all these systems, relaxation time distributions show a well-defined single mode with a shift toward slightly faster times, which indicate that electrostatic interactions between complexes is minimum, so, it is possible to estimate size in terms of the apparent
hydrodynamic radii. Isothermal titration calorimetric data reveals interaction between surfactant, hydrotropes and triblock polymer even at lowest SDS concentration.

Punjabi et al\textsuperscript{195} explored interactions between sodium dodecyl sulfate (SDS), dodecyltrimethylammonium bromide (DTAB), Triton-X-100 (TX-100) with diblock and triblock polymers (EO\textsubscript{18}BO\textsubscript{9}, EO\textsubscript{13}BO\textsubscript{10}EO\textsubscript{13} where BO stands for polybutylene oxide). They observed that addition of ionic surfactant to the polymer solution induces change in shape from spherical to prolate ellipsoids, destabilize them and suppresses micelle formation at high surfactant loading. Resultant polymer-surfactant complexes are hydrophilic in nature and characterized by high turbid and cloud points. It has been observed that triblock polymer micelles are easily destabilized than diblock polymer indicating importance of interaction between hydrophilic chains and surfactants.

Wettig and Verall\textsuperscript{196} have reported interaction between triblock polymers F68 (EO\textsubscript{80}PO\textsubscript{30}EO\textsubscript{80}), F108 (EO\textsubscript{141}PO\textsubscript{44}EO\textsubscript{141}), P123 (EO\textsubscript{13}PO\textsubscript{50}EO\textsubscript{13}) and N,N-bis(dimethyl-\alpha,\omega-alkanediammonium) bromide type dimeric surfactants (12-3-12, 12-6-12) using conductivity, fluorescence and equilibrium dialysis techniques. They have reported that interactions observed in these systems were markedly different from those generally observed in surfactant polymer systems. It has also been observed that increased surfactant concentration in the polymer coil region results in gradual change from clusters of monomer surfactant polymers to the formation of regular micelles.

Li et al\textsuperscript{197} have carried out isothermal titration calorimetry and dynamic light scattering (DLS) studies on the interactions between gemini surfactants of m-s-m type (m = 8, 10, 12, 18 and s = 3, 6, 12) and triblock polymers (P103: EO\textsubscript{17}PO\textsubscript{60}EO\textsubscript{17}, F108: EO\textsubscript{141}PO\textsubscript{44}EO\textsubscript{141}). Study revealed that addition of gemini surfactant to the triblock polymer is accompanied by large endothermic enthalpy changes. One broad peak in the enthalpograms of F108 and two broad peaks for P103 solutions indicated interactions between surfactant and triblock polymer monomers. DLS results revealed that lower concentrations of gemini surfactant can also induce stabilization of loose aggregates of monomers (F108) or triblock polymer micelles (P103). Transitions observed in the hydrodynamic radii were consistent with breakdown of micelle clusters on addition of gemini surfactant followed by mixed micelle formation and de-aggregation into monomer P103.
Ge et al\textsuperscript{198} have studied structural transition during complex formation between triblock polymer F127 (EO\textsubscript{97}PO\textsubscript{69}EO\textsubscript{97}) and nonionic surfactant TX-100 using \textsuperscript{1}H NMR spectroscopy, dynamic light scattering and isothermal titration calorimetry. Three concentration regions of TX-100 were identified wherein TX-100/F127 complex undergoes temperature-induced structure transitions. Between 5-10 °C, F127 monomers were mainly adsorbed on the surface of TX-100 micelles. Between 15-25 °C, TX-100 micelles prompted F127 micelle formation, whereas, within 30-40 °C, TX-100 gets inserted into F127 micelles. At higher concentration of TX-100, it leads to the breakdown of F127 aggregates and thus obtained monomers thread through TX-100 micelles to form complex with TX-100 micelle.

Ortona et al\textsuperscript{199} have studied interactions of triblock polymer PE6200 (EO\textsubscript{11}PO\textsubscript{28}EO\textsubscript{11}), 25R4 (PO\textsubscript{19}EO\textsubscript{33}PO\textsubscript{19}) with sodium decyl sulfate (C\textsubscript{10}OS), decyltrimethylammonium bromide (C\textsubscript{10}TAB) and pentaethylene glycol monodecyl ether (C\textsubscript{10}EO\textsubscript{5}). Investigation of aggregation behavior of these systems by surface tension measurements illustrate that triblock polymers in their non-aggregated state interact more with anionic surfactant (C\textsubscript{10}OS) than cationic (C\textsubscript{10}TAB) and nonionic (C\textsubscript{10}EO\textsubscript{5}) ones. Similar lowering in aggregation number of C\textsubscript{10}OS was shown by fluorescence quenching measurements. Number of polymer chains necessary to bind each C\textsubscript{10}OS aggregate was 6 for PE6200 and 2 for 25R4. Furthermore, this surfactant also induced same increment in the gyration radius of the polymers as revealed by viscosimetry. Calorimetric results were also applied by a simple equilibrium model to the aggregation processes.

Niemiec and Loh\textsuperscript{200} used calorimetric technique to follow the interaction of random copolymers (EO\textsubscript{19}PO\textsubscript{15}, EO\textsubscript{34}PO\textsubscript{25}, EO\textsubscript{116}PO\textsubscript{48}, EO\textsubscript{43}PO\textsubscript{11}, EO\textsubscript{106}PO\textsubscript{27}, EO\textsubscript{204}PO\textsubscript{52}) and triblock polymers (L35: EO\textsubscript{11}PO\textsubscript{16}EO\textsubscript{11}, L64: EO\textsubscript{13}PO\textsubscript{36}EO\textsubscript{13}, F77: EO\textsubscript{52}PO\textsubscript{35}EO\textsubscript{52}, F88: EO\textsubscript{103}PO\textsubscript{39}EO\textsubscript{103} and F127: EO\textsubscript{97}PO\textsubscript{69}EO\textsubscript{97}) with ionic surfactant, sodium dodecyl sulphate. Profile of isothermal titration calorimetry (ITC) curves indicated that interaction increases with increase in the polymer hydrophobicity revealing the intermediate behavior of these triblock polymers. For non-aggregated triblock polymers with large EO blocks, ITC curves revealed that sodium dodecyl sulfate interacts with PO and EO blocks almost independently, being more favorable with PO block, which
controls the critical micelle concentration value. Due to this fact the interaction of surfactant with triblock polymer is more intense (as measured by a smaller \(cmc\) value) than that with a random copolymer of similar composition.

Kelarakis et al\(^{201}\) investigated polymer-surfactant vesicular complex formation in aqueous medium. They have reported that introduction of ionic single-tailed surfactant to aqueous solution of \(\text{EO}_{18}\text{BO}_{10}\) [\(\text{EO}: \text{poly(ethylene oxide)}, \text{BO}: \text{poly(1,2-butylene oxide)}\)] leads to the formation of vesicles with dispersed particles having hydrodynamic radius of few hundred nanometers. Dynamic light scattering showed that at initial stages, dimensions of these aggregates do not depend on the sign of charge on the surfactant head group. Small angle X-ray scattering (SAXS) analysis indicated the coexistence of smaller micelles of different sizes and varying polymer content. In strong contrast to the dramatic increase in size of dispersed particles induced by surfactants in dilute solution, \(d\)-spacing of corresponding mesophases gets reduced monotonically upon increase in surfactant loading. This effect has been attributed to the stabilization of smaller aggregates at the expense of vesicular structures within gel phase.

Ghosh et al\(^{202}\) have explored structural features of mixed micelles comprising hydrophobic triblock polymer \(\text{L121} (\text{EO}_5\text{PO}_{68}\text{EO}_5)\) and anionic surfactant sodium bis(2-ethylhexyl)sulfosuccinate (AOT) in water by small angle neutron scattering measurements. They have observed that L121 or AOT alone form vesicles in water whereas in the mixed state and at appropriate ratio of the two components, a thermodynamically stable isotropic solution containing micelles of prolate ellipsoidal shape is formed. Size and fractional charge of these ellipsoids decrease as AOT/L121 ratio increases that imply an increase in associated charge of aggregates and coulombic repulsions between surfactant molecules.

Effect of surfactants on the self-assembly of triblock polymer \(\text{F108}\) in the aqueous solution by measuring the percolation transition temperature, micellar size, zeta potential and rheological properties has been studied by Nambam and Philip.\(^{203}\) Different kind of surfactants such as anionic sodium dodecyl sulfate (SDS), cationic cetyltrimethylammonium bromide (CTAB) and nonionic nonylphenol ethoxylate (NP9) were employed for the investigations. Addition of SDS to TBP solution resulted in a dramatic reduction of the viscoelastic properties, while no significant reduction was
obtained with CTAB and NP9. The magnitude of decrease in the elastic modulus in the presence of SDS indicated formation of a soft solid-like microstructure due to self-assembled triblock polymer. This observation confirm the fact that strong electrostatic barriers imparted to the micellar interface by SDS molecules at the core-corona interface restrict the self-assembly and growth of micelles. Hydrodynamic diameter of F108+SDS mixed micelles at 313.15 K decreases from 14 to 5 nm as SDS concentration increases from 0.06 to 4 mM. With increasing surfactant concentration, zeta potential of the triblock polymer micelles is found to decrease. These results suggest that microstructure and elastic properties of triblock polymer micelles can be tuned by varying the concentrations of ionic surfactant that enhances their application potential as nanocarrier for drug delivery.

Kelarakis et al.\textsuperscript{204} have studied the interaction of sodium dodecyl sulfate (SDS) with poly(ethylene oxide) and poly(alkylene oxide) block copolymers. They observed that addition of SDS induces fundamentally different effects to the self-assembly behavior of block copolymer solutions with respect to its specific compositional characteristics. For EO\textsubscript{18}BO\textsubscript{10}+SDS system, development of large surfactant-polymer aggregates was observed while for BO\textsubscript{20}EO\textsubscript{610}+SDS, BO\textsubscript{12}EO\textsubscript{227}BO\textsubscript{12}+SDS, EO\textsubscript{40}BO\textsubscript{10}EO\textsubscript{40}+SDS, EO\textsubscript{19}PO\textsubscript{43}EO\textsubscript{19}+SDS systems, formation of smaller particles compared to pure polymeric micelles was observed. It was ascribed to the physical binding between hydrophobic block of unassociated macromolecules and nonpolar tail of the surfactant. Analysis of critical micelle concentrations of polymer-surfactant aqueous solutions revealed negative deviation for EO\textsubscript{40}BO\textsubscript{10}EO\textsubscript{40}+SDS and EO\textsubscript{19}PO\textsubscript{43}EO\textsubscript{19}+SDS systems but positive deviations for EO\textsubscript{18}BO\textsubscript{10}+SDS system. Ultrasonic study on EO\textsubscript{19}PO\textsubscript{43}EO\textsubscript{19}+SDS system enabled identification of three regions corresponding to three main steps of complexation namely SDS absorption to the hydrophobic backbone of polymer, development of the polymer-surfactant complex and gradual breakdown of the mixed aggregates.

Thummar et al.\textsuperscript{205} have studied the effect of sodium dodecyl sulfate (SDS), dodecyltrimethylammonium bromide (DTAB) and octylphenol ethoxylate surfactant (TX-100) as additives on the association characteristics of amphiphilic triblock polymer P105 (EO\textsubscript{36}PO\textsubscript{57}EO\textsubscript{36}). Surface tension, dynamic light scattering and viscosity
measurements were carried out for these systems at 303.15 K in presence of 200 mM sodium chloride solutions. Successive addition of surfactant resulted in the increase of critical micelle concentration of the triblock polymer (TBP) and adsorption tendency of the polymer-surfactant complexes at water/air interface. Proposed mixtures exhibited synergistic interaction behavior and drastic decrease in apparent hydrodynamic radius of the TBP micelles with addition of surfactants. This decrease was attributed to the shift of equilibrium between triblock polymer micelles and monomers in favor of monomers. They have reported that drug release and drug diffusion coefficient of the sparingly water soluble drugs increases upon the surfactant addition.

Bakshi et al\textsuperscript{206} have investigated mixed micelle formation of hexadecyltriphenylphosphonium bromide (HTPB) and tetradecyltriphenylphosphonium bromide (TTPB) with triblock polymers: EO\textsubscript{18}PO\textsubscript{31}EO\textsubscript{18}, EO\textsubscript{2}PO\textsubscript{15}EO\textsubscript{2}, EO\textsubscript{2}PO\textsubscript{31}EO\textsubscript{2}, and F68 (EO\textsubscript{77}PO\textsubscript{29}EO\textsubscript{77}) using fluorescence, relative viscosity and cloud point measurements. They have observed that mixtures of HTPB+EO\textsubscript{18}PO\textsubscript{31}EO\textsubscript{18}/EO\textsubscript{2}PO\textsubscript{15}EO\textsubscript{2} and TTPB+EO\textsubscript{18}PO\textsubscript{31}EO\textsubscript{18}/EO\textsubscript{2}PO\textsubscript{15}EO\textsubscript{2} undergo mixed micellization due to synergistic interactions, whereas mixtures of HTPB/TTPB+EO\textsubscript{2}PO\textsubscript{31}EO\textsubscript{2}/EO\textsubscript{77}PO\textsubscript{29}EO\textsubscript{77} demonstrate antagonistic or ideal mixing. Relative viscosity and cloud point measurements also fully support these results. Results suggest that favorable mixed micellization with triblock polymers can be achieved if the difference in number of PO and EO groups is not very large as in case of mixtures of EO\textsubscript{18}PO\textsubscript{31}EO\textsubscript{18} and EO\textsubscript{2}PO\textsubscript{15}EO\textsubscript{2} in comparison to that of EO\textsubscript{2}PO\textsubscript{31}EO\textsubscript{2} and EO\textsubscript{77}PO\textsubscript{29}EO\textsubscript{77}.

Jansson et al\textsuperscript{207} have studied complex formation of nonionic triblock polymer P123 (EO\textsubscript{20}PO\textsubscript{70}EO\textsubscript{20}) with cationic surfactant hexadecyltrimethylammonium chloride (HTAC) in dilute aqueous solution using small-angle X-ray scattering, static and dynamic light scattering and self diffusion NMR. P123/HTAC system has been investigated between 1 wt\% and 5 wt\% P123 and with varying surfactant concentration up to 170 mM HTAC. On mixing P123 and HTAC, two different types of complexes were observed at various HTAC concentrations. At low molar ratios 0.5, P123 micelle-HTAC complex was obtained as HTAC monomers associate non-cooperatively with P123 micelle forming a spherical complex. Interactions investigated by calculating the structure factor using the generalized indirect fourier transformation (GIFT) method
revealed that between molar ratios 1.9 to 9, two coexisting complexes were found, one P123 micelle-HTAC complex and one “HTAC-P123” complex. As HTAC concentration increases above molar ratio 9, P123 micelles were broken up and only HTAC-P123 complex that is slightly smaller than HTAC micelle exists due to stronger electrostatic repulsion.

Kaur et al\textsuperscript{208} have studied the aggregation behavior of twin tail cationic surfactants, didodecyldimethylammonium bromide, ditetradecyldimethylammonium bromide, and dihexadecyldimethylammonium bromide with triblock polymer L64 (EO\textsubscript{13}PO\textsubscript{30}EO\textsubscript{13}) in aqueous solution by employing small angle neutron scattering (SANS), fluorescence, conductivity and surface tension techniques. SANS data analysis has been revealed the vesicle formation in case of pure twin tail cationic surfactants and spherical micelles of pure TBP: L64. Mixed systems of these surfactants with L64 have been reported to be spherical in shape as shape of mixed micelles is predominantly controlled by triblock polymer L64. Surface tension study indicated that the studied mixed system exhibited nonideal and antagonistic behavior.

Lof et al\textsuperscript{209} carried out the rheological study on mixed micelles of triblock polymer P123 and nonionic surfactant (C\textsubscript{12}EO\textsubscript{6}) in aqueous solutions. Purpose of the study was to investigate the time dependence of shape transition of the mixed micelles and characterizing the shape before and after the transition. Rheology results give clear evidence that the P123-C\textsubscript{12}EO\textsubscript{6} mixed micelles grow and change gradually in shape from spherical to elongated (rod like) geometry with increasing temperature.

Castro et al\textsuperscript{210} have characterized the interactions between triblock polymer EO\textsubscript{67}SO\textsubscript{15}EO\textsubscript{67} (SO: styrene oxide) and surfactant sodium dodecyl sulfate (SDS) by static light scattering, dynamic light scattering (DLS) and isothermal titration calorimetry (ITC). They have observed that addition of surfactant changes the physicochemical properties of the micellized triblock polymer. An abrupt change in the hydrodynamic radius of the triblock polymer micelles at low SDS concentrations was reported to be due to the association of SDS molecules with triblock polymer micelles. Thus formed surfactant-polymer complex becomes more charged as more surfactant is added due to interactions between the surfactant and triblock polymer. DLS data suggested that size of the mixed micelles changes depending on the amount of SDS.
These results were also confirmed by ITC measurements. From the ITC data, dehydration and rehydration of triblock polymer chains following formation of triblock polymer rich-surfactant mixed micelles and their distortion were obtained.

1.3 Objectives of Present Work

Visualizing the tremendous use and unique properties of surfactant mixtures, a detailed study of their physicochemical properties is required so as to meet their constantly rising demand in academic as well as commercial sectors. For this purpose, a systematic and comprehensive investigation on the physicochemical properties of various surfactants in the presence and absence of different types of additives has been carried out in the present study. Selection of different surfactants and additives to be used in this work was carried out keeping in view the following objectives:

- To find new surfactant mixtures with improved properties in comparison to the pure surfactants to meet the ever increasing demand of diverse fields more efficiently.
- To identify the mixing range of surfactants where synergistic interactions attain maxima and the mixture exhibits better properties for surfactant based applications.
- To investigate the shape and size of the mixed micelles of surfactant mixtures to control the morphology of mixed micellar aggregates.
- To study the phase separation behavior of surfactants in pure as well as the mixed state so as to have novel surfactant mixtures with improved shelf life.
- To understand the effect of presence of additives on the physicochemical properties of surfactants in order to have an idea about the working potential of surfactants under different conditions.

To accomplish the aforementioned objectives, mixing behavior of surfactant-additive, triblock polymer-triblock polymer, surfactant-triblock polymer, cationic-nonionic and anionic-nonionic surfactant mixtures was investigated using techniques like cyclic voltammetry (CV), small angle neutron scattering (SANS), dynamic light scattering (DLS), surface tension (ST), fluorescence (Flu), viscometry and cloud point (CP) measurement. Investigation involved study of physicochemical aspects of these mixtures in terms of micellization and diffusion behavior, microstructural parameters,
interfacial properties and phase separation behavior. Thesis work has been divided into seven chapters:

Chapter I deals with introduction of surfactant and their mixtures along with a review of literature. Detailed description of materials and experimental techniques employed for the aforesaid investigations has been described in Chapter II.

Chapter III incorporates cyclic voltammetric and cloud point study on the micellization and phase separation behavior of triblock polymer mixed systems comprising of F127: EO97PO69EO97, F88: EO104PO39EO104, P123: EO20PO70EO20, P85: EO26PO40EO26. For cyclic voltammetric investigations, 2,2,6,6-Tetramethyl-1-piperidinylkoxy (TEMPO) has been employed as an electroactive probe. Presence of probe helps to explore the micellar environment of triblock polymer mixtures (F127/F88+P123/P85). Triblock polymers used in this study have different hydrophobicity due to difference in their PO/EO ratio. Influence of hydrophobocity on the mixed micellization behavior of these mixtures has been thoroughly investigated. To determine the shelf life and working temperature range, phase separation behavior of these triblock polymer mixtures has also been studied and correlated to the micellization behavior.

A systematic investigation on the microstructure and mixing behavior of cationic surfactant (benzalkonium chloride) with nonionic triblock polymers (F127: EO97PO69EO70, P123: EO20PO70EO20, P105: EO36PO57EO36, L64: EO13PO30EO13) has been carried out using surface tension, small angle neutron scattering (SANS), dynamic light scattering (DLS) and viscometric measurements. Surface tension measurements were used to study those micellar parameters which determine surface active and interfacial behavior of these mixed systems. DLS measurements were used for measuring average dimensions of mixed micelles like diffusion coefficient and hydrodynamic diameter. SANS measurements were used to determine the micellar shape and size of mixed micelles. Detail of this study has been given in Chapter IV.

Clouding is an important property of nonionic surfactants which determines their working range for a particular surfactant based application. It is very sensitive to the presence of third component i.e. additive, which affects the interactional behavior of
surfactant. In order to investigate the influence of additives of biological origin on the clouding behavior of triblock polymers: P84 (EO\textsubscript{19}PO\textsubscript{43}EO\textsubscript{19}) and L64 (EO\textsubscript{13}PO\textsubscript{30}EO\textsubscript{13}), a study has been carried out using different biomolecules as additives. Triblock polymers P84 and L64 used for this study were of same hydrophobicity and biomolecules employed belonged to category of amino acids, dipeptides, amino alcohols, sugars, hydroxy acids and dicarboxylic acids. Detail of this study is given in Chapter V.

Anionic-nonionic surfactant mixtures are important constituents of cleaning formulations as anionic component maximizes the solubilization capacity and nonionic surfactant component maximizes the tolerance towards water hardness. In view of this, micellization and phase behavior of anionic surfactants: double alkyl chain surfactant, sodium bis(2-ethylhexyl)sulfosuccinate (AOT) and single alkyl chain surfactant, sodium alkylphenol ether sulphate (APES) in the presence of nonionic polyoxyethylene alkyl ethers (POE: C\textsubscript{10}EO\textsubscript{8}/C\textsubscript{10}EO\textsubscript{10}/C\textsubscript{13}EO\textsubscript{10}) has been investigated using surface tension, fluorescence and cloud point techniques. Detailed description of the surfactant mixtures investigated is given in Chapter VI.

Micellar and interfacial behavior of the mixed systems containing cationic benzalkonium chloride and nonionic polyoxyethylene alkyl ether surfactants (C\textsubscript{10}EO\textsubscript{7}, C\textsubscript{10}EO\textsubscript{8}, C\textsubscript{10}EO\textsubscript{9}, C\textsubscript{10}EO\textsubscript{10}) has been examined by surface tension, fluorescence and dynamic light scattering techniques. Surface tension and fluorescence techniques were used to measure the micellar parameters, while, dynamic light scattering illustrates micellar growth in these mixed systems. Detail of this study is included in Chapter VII.
References


