

CHAPTER-II

Scope and Object

The self aggregation of amphiphilic molecules, either in the simplest form of monolayers or in the form of micelles, vesicles, liposomes and microemulsions, all provide unique opportunities to bring other molecules closer together, to orient them in specific way and to alter their reactivities. Thus, much of the impetus for the study of reactions in micelles, vesicles or microemulsions is that they model, to some extent, reactions in biological assemblies. Normal micelles that form within aqueous surfactant solutions above a surfactant concentration (or a concentration range), usually called critical micelle concentration (cmc), are a topic of major interest due to their unusual physicochemical properties as a result of surfactant aggregation. A complete understanding of the micellization phenomena, its fundamental aspects, use of related studies for technological developments, and understanding molecular behavior require a comprehensive knowledge of the forces and factors controlling the process. One approach that is widely being practiced for the said knowledge has been the study of effect of additives, especially electrolytes, on the micellization characteristics of ionic surfactants. The alteration or modifications of important physicochemical properties of aqueous surfactant solutions is highly desirable as far as potential applications of such systems are concerned.

The self-assembled structures of surfactant systems have been widely utilized in many industrial and commercial applications including food, cosmetic and pharmaceutical formulations and modern technologies. Certain changes in the solvent quality provide us the opportunity to study the role of solvophobic effect and the increasing use of surfactants in the area of water free or water poor media makes this type of research field more interesting. Most of the investigations carried out focused mainly based on two aspects: the requirement from a solvent for amphiphilic assembly and what are the structural properties of the aggregates formed in these media. The solvents which bring about self-association of conventional amphiphiles have high cohesive energies and dielectric constants and considerable hydrogen bonding ability. Evans et al. suggested that the hydrogen bonding ability is a prerequisite for micellization to happen. Therefore, the presence of organic solvents in aqueous micellar solution

alters the biophysical behaviour, as well as the tendency of the surfactant molecules to keep away the contact from the bulk phase and, as a result of this, it affect the various micellization parameters such as critical micelle concentration (cmc), degree of counterion binding (β), average aggregation number (N_{agg}), etc. So that, knowledge of association of surfactant molecules and of their possible interactions with the solvents is very much essential for the proper understanding of their behavior in solution.

The objective of this work is to understand the physic-chemical changes of surfactant to determine the interaction with the solvent having polarity different from water. Surfactant chosen for this study is Didodecyldimethylammonium bromide (D₁₂DAB). D₁₂DAB is very important cationic surfactant from scientific as well as industrial points of view, since, is a well known double-tailed cationic surfactant, which form spontaneous vesicles and bilayer aggregates in water at low concentration (near critical aggregation concentration, cac) due to its inverted cone molecular geometry. The solubility limit of the surfactant in water within a small concentration regime restricts exploration of its interfacial and bulk characteristics to a great extent in aqueous medium. Due to the presence of geometrical restrictions of D₁₂DAB having inverted cone molecular geometry and negative surface curvature (concave-up) of the aggregates is formed (reverse micelle), but in the presence of highly polar solvents, the morphology is immediately changes into vesicle. To understand polarity tuned self aggregation process of D₁₂DAB water is being replaced by acetonitrile solvent. Acetonitrile is an important solvent with weak hydrogen bonding ability, less polar than water (Dielectric constant (ϵ) = 37.5), in which D₁₂DAB is highly soluble. To precisely understand the self assembly process of D₁₂DAB in pure acetonitrile and mixed solvent medium of water and acetonitrile have been investigated along with their morphological changes, as well as thermodynamic parameters.

Another objective is to understand the microenvironment and dynamics of the confined geometry, the microstructural modification between acetonitrile based non-aqueous RMs with that of aqueous RMs have been investigated. The RMs are formulated and characterized in cyclohexane using cationic surfactant D₁₂DAB and anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT), by solubilizing water and acetonitrile at different binary compositions. The double tailed cationic surfactant D₁₂DAB also can effectively form RMs in nonpolar solvents without a

cosurfactant. This study extended the knowledge on the gradual changes occurring in the microstructure of the RMs on going from aqueous to non-aqueous RMs via several mixed compositions of water and acetonitrile.

To understand the interaction between different types of double tailed cationic surfactant with non-ionic dye in non-aqueous polar solvent have been studied. Spectroscopic fluorescent probe 7 hydroxy coumarin is used to study the dye surfactant interaction with didodecyldimethylammonium bromide, didecyldimethylammonium bromide and ditetradecyldimethylammonium bromide in acetonitrile medium.

The scope of the study open the field in understanding of solvent-tuned self-assembly process, which provide the deeper insight into the supramolecular chemistry and also new technology. This also provides the effect of binary mixtures of acetonitrile and water are widely used as reaction media in diverse fields of physical-organic chemistry, reverse phase liquid chromatography, and electrochemistry, solvent extraction, and atmospheric chemistry.

References are provided in BIBLIOGRAPHY under “References for Chapter II”
(Page 134-135)