CHAPTER – 2

SCOPE AND OBJECT

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Perhaps the most important feature of living organisms is the cell membrane. It serves many purposes simultaneously from a simple structural component to a complex element in biochemical process such as ion transport and immunological recognition.

A biological membrane consists of three main layers: glycocalix, protein-lipid bilayer and cytoskeleton. The glycocalix is responsible for, among other things, the surface recognition of cells and consists mainly of the oligosaccharide head groups of the glycoproteins and glycolipids that are incorporated into the membrane. On the inside of the cell, the cytoskeleton is a cross-linked network of protein molecules, which are anchored to bilayer proteins, and this provides some structural rigidity to the membrane. The main central layer is a mixture of lipids and proteins in different ratios depending on the function of the membrane.

The most common membrane lipids are double-chained phospholipids or glycolipids, with 16-18 carbons per chain, one of which is often unsaturated or branched. These properties of lipid molecules are important to the correct functioning of biological membranes because[2] :

1. They can pack readily into bilayer membranes;
2. They have extremely low cmc values so that the membranes remain intact in presence of large amounts of water; and
3. The unsaturation or branching ensures that the membranes are in a fluid state at physiological temperatures.

Much of the interesting physical chemistry of liposomes and vesicles has been established from studies of lipids, either from the natural sources or synthesized as pure lipids. However, the field has been greatly extended by the development of synthetic surfactants capable of mimicking the membrane-forming properties of lipids.

The study of bilayer membranes in the form of liposomes and vesicles has taken a much wider perspective with the development of chemical routes to a greater range of artificial membrane-forming lipids. The incentive of this type of study has been two-fold. Firstly, to build up a better understanding of the functioning of natural membrane lipids but, secondly, to create microenvironments that promote novel chemistry, which might otherwise not be readily achieved. Surfactant aggregates, 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 a limited extent, reactions in biological assemblies.

As has already been mentioned, the importance of interfacial region between aqueous and non-polar part of the self-assembled lipid phase is very well recognized in biological membranes. For the measurement of the electrical potential at the surface of a charged membrane or a similar interface one requires a probe of molecular size which does not disturb the system itself. It has been suggested the use of pH indicators adsorbed to charged micelles and attributed the "apparent" shift of pK_a detectable in the micellar solution, as compared to pure aqueous solutions, to a change of the "local interfacial" proton activity at the surface of charged micelles as compared to that in bulk water. The equilibrium of an indicator, bound to a surface, may be affected not only by an electrostatic potential, but in addition by a different local environment, e.g., by a lower dielectric constant as compared to bulk water and also by specific interactions of the indicator at the surface, if any. Although different types of organic indicator molecules have been applied as spectroscopic probes for studying above properties, surprisingly, two important uv active aromatic amino acids e.g., tyrosine and tryptophan have not been used so far. However, there are certain class of molecules which are biologically quite important but their spectral properties are quite insensitive to the surroundings. It has been found that while the protonation-deprotonation equilibrium of hydroxy group of tyrosine and 5-Hydroxytryptophan influence their electronic spectra to a great extent, the spectral profile of tryptophan is insensitive to acid or base. Thus sometimes, the spectral characteristics, specially fluorescence spectra, are very sensitive to the environments of the systems. Because of this, fluorescence spectroscopy has become one of the fundamental methods for the study of the structure and dynamics of the microheterogeneous systems. The photophysics of probe molecules, therefore, are studied in those systems.

Physical gelation of surfactant micelles and their stimuli responsive behaviour are interesting from biology as well as chemical technology points of view. The most extensively studied system is the cetyltrimethylammonium bromide (CTAB) micelles in presence of a hydrotrope, sodium salicylate. Unlike simple halides, salicylate promotes sphere to worm-like micellar transition at much lower concentration viz., near the cmc of CTAB. The flexible and elongated worm-like micelles under dilute conditions show complex and unusual rheological phenomena, which includes strong viscoelasticity and shear induced structure (SIS) formation. Although it is generally believed that micellar entanglement and transient network formation are responsible for developing shear induced viscoelasticity, precise knowledge regarding the nature of interaction in micellar entanglement and SIS formation is still lacking. It is particularly interesting that while a wide variety of worm-like ionic micellar solution display identical rheological responses, a common element in all of these systems is the presence of salt anions like sodium salicylate. This limitation has perplexed the scenario to some extent and impeded the development of an acceptable theory which may explain micellar shape transition under dilute condition. It has been found in the present work that molecules like 1- and 2-Naphthols with a strong hydrophobic aromatic ring and a polar hydroxy group support shape transitions of surfactant micelles very efficiently.

Keeping the above aspects in view, a number of biologically important organic molecules and their hydroxy derivatives and also 1- and 2-Naphthols are chosen as indicator (probe) molecules for studying the protonation-deprotonation equilibria at the micellar surface of different ionic and non-ionic micelles as well as in aqueous-organic medium. These indicator molecules are, 5-Hydroxyindole, 5-Hydroxy-L-tryptophan, L-Tyrosine, L-Tyrosine-methylester, 1-Naphthol and 2-Naphthol. Fluorescence spectroscopic properties of these molecules have been studied in different solvents to understand the photo-physics of the systems.

Moreover, the role of 1- and 2-Naphthols in developing stimuli sensitive properties of surfactant solutions has been studied. The physicochemical aspects of micellar shape transition, rheological behaviour have been investigated and the microstructure of the system is proposed.