

# **Chapter 2**

## Scope and Object

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Many everyday materials – food, medicines, cleaning agents, paints, plastics – are highly complex at the microscopic levels and consist of several kinds of molecules or tiny particles, which are held together by weak electrostatic forces in a highly organized way. At room temperature, these forces are usually not strong enough to prevent the materials from deforming under stress – which is why they are 'soft'. Generally the materials which consist of very large molecules and are easily deformable are usually referred to as "soft matter". The concept of "soft matter" covers a large class of molecular materials, including e.g. polymers, thermotropic liquid crystals, micellar solutions, microemulsions and colloidal suspensions, and also includes biological materials, e.g. membranes and vesicles.

### Various types of soft matter with their sizes

Polymers	10 nm-1 $\mu$ m
Colloids	10 nm-1 $\mu$ m
Surfactant micelles	5 nm-100 $\mu$ m
Liquid Crystals	5 nm-100 $\mu$ m
Bio Molecules	2 nm-5 $\mu$ m

These substances have a wide range of applications including structural and packaging materials, foams and adhesives, detergents and cosmetics, paints, food additives, lubricants and fuel additives, rubber in tyres etc., and our daily life would be unimaginable without them. In spite of the various forms of these materials, many of their very different properties have common physicochemical origins such as a large number of internal degrees of freedom, weak interactions between the structural elements and a delicate balance between entropic and enthalpic contributions to the free energy. These properties lead to large thermal fluctuations, a wide variety of forms,

sensitivity of the equilibrium structures to external boundary conditions, macroscopic softness and various metastable states.

Vesicles and micelles represent two of the important classes of self-assembled structures that can be formed by amphiphiles in dilute or semidilute solution. Vesicles are hollow spheres enclosed by a bilayer of the amphiphiles and are commonly used to encapsulate labile hydrophilic molecules within their interiors. Micelles tend to occur in a range of morphologies, including spherical, ellipsoidal, and wormlike micelles. Among the most fascinating of these are the 'wormlike micelles', which are flexible cylindrical chains with radii of a few nanometers and contour lengths up to several micrometers. Considerable interests have been generated recently in studying physico-chemical properties of self assembled surfactant aggregates, especially micelles, and unilamellar vesicles . Although many reasons can be cited for the wide spread interest in elucidating the physico-chemical properties of these self organized systems, primarily there are three reasons. Firstly, one can consistently and easily prepare aqueous micellar and vesicular solutions which contain aggregates of colloidal dimensions with characteristic size, shape and surface properties. Hence micellar and vesicular system have been employed as a model system in investigations concerned with understanding colloidal physico-chemical phenomena. Secondly, the similarities between self-assembled surfactant aggregates, such as micelles and vesicles, and biological lipid membranes prompted researchers to employ micelles and vesicles as model biological systems. Quite often they provide microenvironments very similar to the biological environments – thus allowing trial experiments prior to in-vivo study . Thirdly, it has been found that micelles and vesicles can act as unique reaction media. Therefore, investigation on physico-chemical characteristics of micelles and vesicles forms a considerable volume of literature .

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.

Hence, it may be recalled that at low concentrations, the aggregates, especially those of charged surfactant are generally round, globular micelles. In some charged surfactant systems, long worm like micelles are formed at higher concentrations upon addition of salt and acid. However, with anions that associate strongly with surfactant cations, such as salicylate, wormlike micelles grow rapidly at low surfactant and salt concentrations. The rheological behaviour exhibited by these systems is viscoelastic analogous to that observed in solutions of flexible polymers. However, wormlike micelles have a more dynamic structures than that of a polymer since the former break and reform reversibly. The rheological behaviour is, therefore, more complex and fascinating. When sheared below a critical shear rate which depends on temperature and on surfactant and salt concentrations, dilute worm like micellar solution shear thin. In contrast, above a critical shear rate, micellar solutions exhibit time dependent behavior, initially the solutions shear thin, and after an induction period shear thickens.

The shape of the micelles depend strongly upon the actual packing parameters in micellar assembly. The counter ion binding suppresses the micellar charge and decrease the surface area per surfactant head group by reducing the electrostatic repulsion between the head groups, thus promoting the spherical to worm like micelle transition. The addition of different types of molecules leads to large deviation of packing parameters. Many counter ions and cosurfactants are strongly adsorbed at the micellar interface, depending on the amount of separation, this may change the mean distance between polar head groups or increase the volume of the micellar core. However, the theory of spherical to worm like micelle transition and the theory of rheological behaviour of the worm like micellar solutions presently lack strongly predictive powers and therefore, it is important to establish a good descriptive data base of systems undergoing the spherical - to -worm like micelle transition.

Keeping the above in view two major focuses of the present study have been fixed. In section A of the thesis, a detail study will be undertaken on the surfactant aggregation in aqueous solutions in presence of additives. Special emphasis will be given to the spherical to rod/worm like micelle transition at low surfactant concentrations, particularly in presence of neutral additives. Rheological and spectroscopic behaviour of the system will also be examined.

The section B of The thesis constitutes physicochemical characteristic of some biopolymer viz, Sodium alginate and Poly (vinyl alcohol) in solution phase. According to hydrodynamics, the specific viscosity of a Newtonian liquid containing a small amount of dissolved material should depend in the first approximation only upon the volume concentration and the shapes of the suspended particles. The unperturbed dimension (UD) of a given polymer in a solvent does not depend on the nature of the solvent, as long as the solvent has no influence on the rotation of the chain segments. This is true in many cases, especially for nonpolar polymer-solvent pairs, but in the cases of polar polymer - polar solvents systems, the unperturbed dimension vary considerably with the nature of the solvent. Most of the polymeric materials are soluble only in a limited

number of primary solvents, but they could be made soluble in all proportions in mixtures consisting of two or more solvents, which may be individually poor solvent for the polymers. Several mixtures of nonsolvents are also known which produce good solvent systems or at least increase the solvency power of primary solvents. Many present and possible industrial applications of high molecular weight polymer arise from unusual properties they induce to their solutions. The study of their solution property is a prerequisite for the development of this modern domain. The characterization of high molecular weight polymers raises a number of problems. Therefore, systematic studies arising from the coupling of different experimental techniques are required for the elucidation of diverse theoretical and experimental aspects. The most important parameters characterizing macromolecular chains in dilute solution are the molecular weight, the mean square radius of gyration and the intrinsic viscosity. Their determination for very high molecular weight polymers opens a large area for discussing, on the basis of different theoretical approximations. The area of discussion includes such subjects as influence of molecular weight and solvent power on concentration domain, theta condition and unperturbed dimensions, chain flexibility in perturbed and unperturbed state, the type of interaction (short range and long range), the conformational characteristics including the transition phenomena influenced by temperature and solvent.