ABSTRACT

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 are consist of very large molecules and 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. Two major focuses of the present study have been fixed. In Section A of the thesis, a detail study has been undertaken on the surfactant aggregation in aqueous solutions in presence of additives. Special emphasis has been 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 systems are also examined. The section B of the thesis constitutes studies on the physicochemical characteristic of some biopolymer viz, Sodium alginate and Poly (vinyl alcohol) in solution phase.

The unfavorable contact between water and the apolar part of surfactant molecules lead to their congregation into well organized entities, viz., micelles, vesicles, fibers, discs and tubes. Although micelles are usually spherical in shape, under certain conditions, e.g., concentration, salinity or in the presence of hydrophobic counter ions, etc., they may undergo uniaxial growth. This subsequently results in the formation of significantly long yet highly flexible aggregates referred to as "worm-like micelles (WLM)" . The research of WLM has drawn considerable interest because its rheology is very challenging due to the presence of multiple pertinent length scales and stress relaxation mechanisms. This relatively new material has many applications including that of fractured fluids in oil fields, efficient drag reducing agent in hydrodynamic engineering and home care, personal care and cosmetic products . Among the different additives, the hydrotrope, sodium salicylate, is very effective in triggering WLM formation in cationic surfactants even at very low concentrations. However, the use of salicylate as the promoter of WLM formation suffers from some

limitations, especially in the oil fields due to its complex forming tendency with metal ions impurities. In spite of a large number of publications in the field, WLM formation by metal-inert promoters which may work under salt free condition is rather rare and intensive research in this area is warranted. In view of the importance of an efficient WLM promoter, which might be effective for various applications at low surfactant concentrations under salt-free condition, organic π-conjugated molecules with H-bonding functionality, viz., naphthols are highly promising. Moreover, since the dissociation of hydroxyl groups of naphthols is tunable by controlling the pH of the system, a facile route to design pH-responsive morphology transition of WLM can be achieved via customized charge screening as a function of pH. This would find application in drug delivery processes. Stimuli-responsive viscoelastic gels of long wormlike micelles are formed at low surfactant concentrations in the presence of neutral naphthols, where H-bonding plays a key role in micellar shape transition in the absence of any charge screening. Micelle-embedded naphthols also act as novel self-fluorescence probes for monitoring viscoelasticity of the system as a function of applied shear. While UV absorption and Fourier transform infrared studies confirm the presence of intermolecular H-bonds in micelle embedded naphthols, transmission electron micrographs of vacuum-dried samples at room temperature demonstrate the transition in shape from sphere to rodlike micelles.

The viscoelastic gels formed in presence of naphthols are thermoreversible in nature, and the viscosity-temperature profile of each system passes through a maximum. ^{1}H NMR confirms that solubilization sites of naphthols in the micelle are located near the surface. The above study also shows that, on the NMR time scale, the motion of the naphthol molecules is highly restricted in viscoelastic phase, but water molecules rotate freely. While fluorescence quenching via H-bond strengthening is not observed in the micellar phase, UV absorption spectra demonstrate the presence of inter- molecular H bond in micelle-embedded naphthols in their ground electronic states as mentioned above, which was confirmed by FTIR. The ESPT of 2-naphthol is facilitated in presence of CTAB in the submicellar concentration range due to the catalytic effect of surfactant charge where as, ESPT is hindered in postmicellar concentrations due to lack of water accessibility. The micropolarity of OH sites of micelle-embedded naphthols is measured by observing pK_a-shift at the micellar surface relative to bulk water. Based on hydroxyaromatic dopants, a simple and effective route to design pH-responsive viscoelastic worm-like micelles and the vesicles of single tail cationic surfactant (CTAB) is reported. Results are confirmed by observing cryogenic – transmission electron microscopy (cryo-TEM) images. The success of naphthols in effecting microstructural transition of micelles lies in their unique ability to form H-bonding with interfacial water molecules, which have shown unusual H-bond donating property compared to bulk water. The OH groups of micelle-embedded naphthols are protruded toward the Stern layer through ~1 A and the dielectric constant of OH sites has been measured as 45±2 by observing pK_a-shift of acid-base equilibrium of naphthols at the interface relative to that in bulk water. The result of unusual H-bonding may be relevant, not only when considering the H-bonding of the interfacial water molecules in the specific micelle and dopant studied here, but also for the H-bonding interaction of other micelle-dopant systems as well. This offers an interesting route for fluorescence monitoring of unperturbed viscosity as a function of applied shear. In a viscous medium, a fluophore cannot transfer energy efficiently via nonradiative means because of delayed collisions with the surrounding molecules resulting in the increased emission quantum yield.

The results of the investigation on the unperturbed dimension, interaction parameter and related aspects of poly(vinyl alcohol) and sodium alginate in binary solvent mixtures viz. water-acetone, water-ethoxy ethanol for sodium alginate and water-acetone, water-tetrahydrofuran for poly(vinyl alcohol) have been described in Section B of the present thesis. The intrinsic viscosity [η] of three different samples of the polymers (Sodium Alginate; Type-A, Type-B and Type-C) and poly(vinyl alcohol) having different molecular weights were measured in various fractions of solvent composition (Φ_{ace} and Φ_{ee}). Acetone and ethoxy ethanol are the poor solvent for sodium alginate but water-acetone and water- ethoxy ethanol mixtures act as a co-solvent in certain proportions. On the other hand, acetone and tetrahydrofuran are poor solvents for poly(vinyl alcohol) but water-acetone and water- tetrahydrofuran mixtures act as a co-solvent in certain proportions for the poly(vinyl alcohol). From the relation between [η] and [Molecular mass(M)], the unperturbed dimension and molecular expansion factor have been measured. The Huggins constant value in each case was also determined in order to have ideas on the influence of co-solvent system on the aggregation of the polymers. The evaluation of the above interaction parameters and molecular dimensions of sodium alginate, a linear polysaccharide and that of poly(vinyl alcohol) using fundamental laws governing polymer chemistry and physics give new insight regarding the character of such macromolecular chains in binary solvent mixtures. A better understanding of their behavior in solution would help in opening new direction of research with immense application.