

CHAPTER 7

Summary and conclusion

7. Summary and Conclusion

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 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.

A chapter wise summary of the study and the conclusions drawn from the experimental work is summarized below. The references have been cited at the end of each chapter.

The First Chapter [**Chapter-1: General Introduction**] describe the general introduction to the various basic concepts and parameters dealt in the present work.

The second Chapter [**Chapter-2: Scope and object**] of the thesis describes the scope and object of the present study.

Chapter Three [**Chapter-3: Studies on Microstructural Transition of Micellar Aggregates in Presence of hydroxyaromatic compounds: Rheology and Spectroscopy**] of the thesis describes the effect of neutral hydroxyaromatic

dopants on the microstructural transition of CTAB micelles, from spherical to wormlike micelles and vesicles. Micellar aggregates that can grow anisotropically under appropriate conditions, changing their shapes from spheres to rods or highly flexible wormlike aggregates, provide some analogies between giant flexible cylindrical micelles and conventional polymeric solutions. The polymerlike micelles (wormlike micelles) which are formed by certain ionic surfactants in solution exhibit very interesting rheological properties. At high concentrations, these solutions show typical viscoelastic behaviour while at very low concentrations more complex and unusual rheological phenomena is observed. Stimuli-responsive properties of viscoelastic gels of long wormlike micelles are fascinating and have created a great deal of interest in recent years.

The most extensively studied system is the cetyltrimethylammonium bromide (CTAB) micelles in presence of a hydrotrope, sodium salicylate. The presence of an anionic charge on the promoter molecule has been considered pivotal in achieving low concentration shape transition of cationic micelles via charge screening because it decreases the average area per surfactant head group allowing the packing parameter to exceed the critical value of $\frac{1}{3}$. However, other important factors including the role of OH group of the promoter molecule have not attracted much attention, and as such, the puzzling question as to why not only its presence but also its position in the aromatic ring of NaSal molecule is so vital remains broadly unanswered. Therefore, to understand the role of the OH group precisely, it was tempting to check what would happen if we use uncharged naphthols where the hydrophobic part is very strong and the anionic charge is absent. In this chapter we have studied effect of neutral 1- and 2-naphthols and also the dihydroxy derivatives, 2,3- dihydroxynaphthalene (2,3-DHN) and 2,7- dihydroxynaphthalene (2,7-DHN), on the shape transition of CTAB micelles and shown that intermolecular H bonding between OH groups of micelle embedded naphthol molecules plays a key role in micellar shape transition in absence of any charge screening of head groups and imparts strong viscoelasticity to the dilute aqueous surfactant solution. The viscosity of the systems comprising of CTAB and the hydroxyaromatic dopants are maximum at the surfactant to dopant mole ratio

of 1:1. Therefore, the shear induced rheological studies were carried out at a mole ratio of 1:1.

To understand the exact role of hydrogen bonding in the above mentioned shape transition, studies with methoxynaphthalenes were also carried out at similar conditions. The methoxynaphthalene-CTAB systems (1-methoxynaphthalene/CTAB and 2-methoxynaphthalene/CTAB), on the other hand, neither display the ability to develop viscoelasticity in the system nor exhibit any viscosity modification with applied shear, and behave completely like a Newtonian liquid. This result is quite surprising in view of the fact that much like 1- and 2-naphthols, both 1- and 2-methoxynaphthalenes are expected to embed into the micelles of CTAB. Though methoxynaphthalenes (MN) possess a similar structure and hydrophobicity to that of the hydroxyl naphthalene (HN) molecules but because the methoxynaphthalenes cannot act as hydrogen bond donors, they fail to assist the micellar shape transition and impart viscoelasticity to the CTAB solution.

The effect of temperature and pH on the shear induced viscoelasticity of the systems showed interesting results. With increasing temperature the viscosity of the system increased upto a critical temperature of $\sim 26^{\circ}\text{C}$ and then decreased. As the temperature was increased, naphthol molecules (uncharged) becomes more soluble and gets partitioned more strongly in the micellar phase. This favors the formation of longer wormlike micelles up to the critical temperature, above this temperature the increased kinetic energy allows the surfactant unimers to hop more frequently between the body and the end cap resulting in the breaking up of the wormlike micelles, thus decreasing the effective viscosity. The motivation behind carrying out the study at different pH stems from the fact that the hydroxyaromatic dopants which, under neutral conditions activate the formation of worm-like micelles at pH ~ 5.0 may on partial ionization of the OH group increase the packing parameter further via charge screening. This in turn could stimulate in designing a route for pH-responsive vesicle formation. As expected the systems showed a transition of morphology from highly viscous wormlike micelles to less viscous globular vesicles. The results were further confirmed by cryo-TEM images.

To understand the kind of interactions which are operative in the micelle-dopant systems, spectroscopic studies were also carried out. The spectral characteristics of naphthols (which contain OH) were compared with those of methoxy naphthalenes (which do not contain OH) under various conditions in order to visualize a consistent molecular picture. The location and orientation of the additive molecules in the micelles were ascertained by ^1H NMR studies. The signals from the aromatic ring protons of the naphthol molecules were shifted upfield when D_2O solutions of CTAB and naphthols were mixed in 1:1 mole ratio. The CH_3 protons of CTAB head group and the adjacent CH_2 protons, which resonate at 3.132 and 3.289, respectively, in D_2O , were shifted upfield and were found to resonate at 2.746 and 2.397, respectively, in the presence of naphthol. However, CH_2 protons adjacent to CTAB head group, were affected the most in presence of naphthols, and unlike pure CTAB, the signal from CH_2 protons emerged on the other side of CH_3 protons of CTAB head groups. From the above observation it was concluded that the solubilized naphthol molecules were penetrated not deep inside the micellar core but were present near the surface probably with a well-defined orientation in which the OH groups are protruded from the micellar surface toward the polar aqueous phase. The degree of upfield shift of the signals from methoxynaphthalenes (in CTAB micelles) were less than those of the naphthols, indicating a stronger partitioning of the naphthols in the micelles.

The possibility of hydrogen bonding and π - π interaction in naphthols were been checked by observing the effect of CTAB micelles on the absorption spectrum of the hydroxyaromatic compounds. UV absorption spectra of the dopants were modified in their ground electronic state showing significant red-shifting and presence of isobestic points. The modifications are explained in terms of the formation of hydrogen bonding network between the micelle embedded naphthol molecules and the interfacial water molecules. The relatively less polar and less mobile water molecules compared to bulk water forms strong H-bond with the OH group of embedded naphthols, which act as H-donors and results in an optimum orientation of aromatic π -electron systems in the micelles to shield the surfactant headgroup charges efficiently; maybe via cation- π interaction; i.e., the cation

charge of surfactant head groups interacts with the quadrupole moment of the aromatic π -system of naphthols. The methoxynaphthalenes on the other hand showed very little shift. Moreover, no isobestic point could be observed. In methoxynaphthalenes the ability of intermolecular H-bond formation disappears and therefore, the small red-shift, with the absence of any isobestic point(s), compared to that in naphthols indicates that a weaker noncovalent interaction takes place. The chapter concludes with the cryo-TEM investigations, which strongly proves the existence of wormlike micelles at ordinary pH and vesicles at high pH value

Chapter Four [**Chapter-4: Interaction of Cationic Micelles with 1 and 2 Naphthols: Self Fluorescence Monitoring of Stimuli-Responsive Viscoelasticity and Location of Surface Activity**] describes a novel technique of fluorescence monitoring of viscoelasticity of the system and the location of the OH groups of micelle-embedded naphthol molecules via measuring the micropolarity of the sites. It is believed that while the aromatic ring of naphthols are embedded in micelles the core of which having dielectric constant around 2-7 only, the OH groups are stood out toward water region. Nmr study also confirms that the aromatic ring of the naphthol resides near the non-polar core in between tetraalkylammonium head groups of the surfactants. Although almost all of the previous studies on the hydrotrope-induced microstructural transitions of micelles argue that the OH groups are protruded out of the micellar surface and remains close to aqueous layer, no experimental verification has so far been reported. To understand the exact nature of the location of the OH group, the micropolarity of the residence sites are determined. Moreover, information regarding the microenvironment of aromatic π -electron system which might have been obtained from the study of spectral characteristics , would not be helpful in determining the location of protruded OH groups of naphthol molecules. Therefore, pK_a shift of the acid-base equilibrium of OH group of naphthols in microheterogeneous medium relative to aqueous solution is considered as the ideal route for getting such information precisely. This shift in pK_a in a cationic micelle like CTAB relative to aqueous solution may be due to the surface potential of the micelle and the polarity variation

at the micellar interface from that of the bulk (in absence of any specific interaction). 1 and 2 naphthols with aromatic π -system in their structures, are fairly surface active and embedded in aqueous CTAB micelles strongly. 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 Å 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. Stimuli-responsive viscoelastic gels of long wormlike CTAB and CPB micelles are formed at low surfactant concentrations in presence of 1- and 2-naphthols. Systems which display shear induced nonlinear rheological changes (such as the present systems) bring about formidable problem in measuring unperturbed solution viscosity because the measuring techniques (e.g., torsional shear rheometry) often apply considerable stress on the system during measurement, and thus the zero-shear viscosity becomes obscure. Both the naphthols are well-known fluophores, and significantly, the quantum yield of emission of the naphthols is found to be very sensitive to the solution viscosity of the present systems. 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.

In the Chapter Five [**Chapter-5: Determination of unperturbed dimension and interaction parameters of sodium alginate in binary solvent mixtures by viscosity measurements**] the results of the investigation on unperturbed dimension, interaction parameter and related aspects of sodium alginate in water-acetone and water-ethoxy ethanol mixtures have been described. The intrinsic viscosities $[\eta]$ of three different samples of the polymer having different molecular weights were measured in various fractions of solvent composition. Acetone and ethoxy ethanol is a poor solvent for PVA but water-acetone and water- ethoxy

ethanol mixtures act as a cosolvent in certain proportions. From the relation between $[\eta]$ and 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 cosolvent system on the aggregation of the polymer. It is observed that there are a maximum in $[\eta]$ vs. Φ_{ACE} and $[\eta]$ vs. $\Phi_{E.E.}$ plots at the solvent composition $\Phi_{ACE} = 0.2$ and $\Phi_{E.E.} = 0.3$ respectively for Sodium alginate. It is observed that K_H values are maximum at the solvent composition $\Phi_{ACE} = 0.3$ and $\Phi_{E.E.} = 0.2$ for all types of alginate polymers respectively indicating that all types of polymers have higher tendency of intermolecular aggregation at this fraction of the solvent. K_H is smallest $\Phi = 0.4$ for both the solvent mixture (Acetone and ethoxy ethanol) under this condition polymer molecules are held closer and make side chains twisted around each other. Unperturbed dimensions under non-theta condition were calculated using various equations in different water-acetone and water- ethoxy ethanol mixtures. The value of K_θ obtained from three different methods of measurements viz., BSF, I-S-K and Berry agree well with each other except in a few compositions of solvents. It is apparent that at $\Phi_{ACE} = 0.4$ and $\Phi_{E.E.} = 0.2$ the polymer has the lowest unperturbed dimensions and at $\Phi_{ACE} = 0.1$ and at $\Phi_{E.E.} = 0.4$ the polymer has the highest unperturbed dimensions. Volume related parameter (α_n) are also computed in this chapter.

In the Chapter Six [**Chapter-6: Studies on solution properties of poly (vinyl alcohol) in water-acetone and water-tetrahydro furan**] unperturbed dimension, Huggins constant (K_H) and volume related parameter (α_n), are determined via the measurement of intrinsic viscosity $[\eta]$ of PVA with two different types of binary solvent mixtures (water- acetone and water- tetrahydrofuran) in the similar way as has been done in the previous chapter for sodium aliginate in water-acetone and water- ethoxyethanol mixtures.

The last chapter of the thesis [**Chapter-7: Summary and conclusion**] summaries the overall work presented in the thesis and describes the conclusions drawn from the experimental section.