Chapter II

Scope and Object

The self aggregation of amphiphilic (surfactant) molecules, either in the simplest form of monolayers or in the form of micelles, vesicles, liposomes and microemulsions, provide unique opportunity to bring the embedded molecules closer together, to orient them in specific way and to alter their reactivities. 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 are formed 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 requires 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 [1-3], 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. Over the years a considerable amount of literature on cationic and anionic surfactant-electrolyte systems have been compiled, majority of which involved cetyltrimethylammonium bromide (CTAB) or sodium dodecyl sulfate (SDS) as the surfactants and NaBr or NaCl as the electrolytes. However, in recent years, attention has been focused on the interactions of surfactants with hydrophobic counterions and to this effect symmetrical tetraalkylammonium cations (TAA^+) have been considered in most of the studies. It is also true that SDS is the most well known, and widely used in industry. However, in acidic solutions or at high temperatures, SDS undergoes autocatalytic acid hydrolysis, and dodecanol and sodium hydrogen sulfate are produced. These products are believed to cause skin irritation. In contrast, ammoniumdodecyl sulphate (ADS) is less hydrolyzed in acidic solutions and less skin-irritative than SDS [4]. For these reasons, the use of ADS in the cosmetic and toiletry industry has been expanding. However, little is known on the micellization of this surfactant, and only a few studies can be found in the literature [5,6]. In view of the growing importance and the limited number of studies on ADS, investigations on its aggregation behaviour in aqueous as well as in quaternary tetraalkylammonium bromide salts have been undertaken. The objective behind choosing the ADS/tetraalkylammonium bromide system is obvious; to ensure that the addition of progressively larger TAA^+ ions at high concentrations bring about changes in physicochemical properties of the micellar system on account of the factors related to the size and hydrophobicity of the counterions only and not due to variation of any intrinsic property of added ions with that of the counterions of surfactant.

The stabilities of surfactant systems with respect to temperature prior to their multifold uses need to be known, especially where elevated temperature prevails. Aqueous solutions of most nonionic surfactants become turbid on heating to a temperature known as the cloud point, CP. The CP is a useful property in applications such as detergency, and therefore, it is advisable to operate in the vicinity of the CP for various applications. For the ionic surfactants, no such generalization is available as observance of the clouding phenomenon with these materials has started drawing attention fairly recently [7]. In view of the increasing utilization of the phase behavior of ionic surfactant solutions for a variety of applications, including an alternative approach for extractive preconcentration in chemical analysis, it is timely to have a quantitative generalization with ionic surfactants too. With this viewpoint, an attempt has been made to correlate the tetrabutylammonium bromide salt concentration (other TAA^+ ions did not produce clouding) needed for observing CP in ADS.

Vesicles and micelles represent two of the important classes of self-assembled structures that can be formed by amphiphiles in dilute or semidilute solutions. Vesicles are hollow spheres enclosed by a bilayer of the amphiphiles and are commonly used to encapsulate labile hydrophilic molecules within their interior water. Micelles tend to form 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 [8-10].

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 are 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 with 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 [11]. 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.

Over the past several years, there has been a great deal of interest in the aqueous self-assembly of cationic surfactants into threadlike or wormlike micelles. These micelles are long, flexible, cylindrical chains with contour lengths of the order of a few micrometers as has already been mentioned. The formation of wormlike micelles is linked to the emergence of viscoelasticity in the solution [12,13]. The rheological properties of entangled wormlike micellar solutions are similar to those of semidilute polymer solutions with the difference that the micelles are dynamic in nature (breaking and recombining rapidly) [14,15]. Wormlike micelles can thus be viewed as substitutes for polymers in applications that require thickening or drag reduction [16,17].

Due to their viscoelastic properties, worm like micelles have found applications in many areas, such as home and personal care products and in oil field industry [18]. Frequently they are also used as drag reducing agents for district heating. Fluid that viscosify or gel upon heating are of high interest for biomedical and drug delivery applications, for flow control and separation using micro fluidic devices [19] and as hydrolic fracturing fluids in enhanced oil recovery [20]. The simplicity, low cost and ease of preparation of these systems might make it attractive for some of these applications [21].

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. The presence of an anionic charge on the promoter molecule has been considered to be a deciding factor for microstructural transition because it decreases the average area per surfactant head group, by charge screening, thus allowing the packing parameter to exceed the critical value of ⅓ . However, other important factors including the role of OH group of the promoter molecule have not attracted much attention and the questions regarding its presence and position in the aromatic ring of NaSal remains unanswered till date. 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.

The involvement of weak forces like hydrogen bonding, cation-pi interaction and hydrophobic interactions in morphological transitions from micelles to wormlike micelles and to vesicles in aqueous CTAB is fully explored in the present investigation using uncharged naphthols where the hydrophobic part is very strong and the anionic charge is absent. These dopants, with a strong hydrophobic aromatic ring and a polar hydroxy group, support shape transitions of surfactant micelles very efficiently. The efficiency of hydroxyaromatic compounds in micellar shape transition is very high, and an aqueous mixture of CTAB and 2,3-dihydroxy naphthalene which gives highly viscous rod-like nano aggregates has already been used by some authors as a template for the sol-gel synthesis, providing an aqueous route for tube silicate preparation [22]. Studies on the microstructural modifications by neutral aromatic compounds is rather recent. The work described in this thesis deals with several unusual properties of a surfactant fluid. Firstly, viscoelastic gels under salt free condition is itself rare, in addition the present system displays maximum viscoelasticity at ~26°C and hence may find applications in many personal care products. Secondly, the transition of the wormlike micelles to vesicles as a function of pH is very interesting in respect of the practical applications of the process in drug delivery system.

In view of the above a detail physic-chemical studies will be undertaken on the microstructural transition of cationic micelles. The proposed study would show whether

i) Micellar shape transition (of cationic micelles) is possible in dilute salt free conditions, and

ii) Can the H-bonding effect of the OH group of the hydroxyaromatic and dihydroxyaromatic dopants act as a driving force to bring about microstructural transitions and give rise to significant aggregate growth at low concentrations.

A variety of measurements including shear induced viscosity, spectroscopy (both ^{1}H NMR and UV), and cryogenic transmission electron microscopy (cryo-TEM) will be made to understand the phenomena mentioned above.

Further there is increasing interest in investigating surfactant aggregates that mimic biological membranes, such as phospholipid liposomes or synthetic amphiphile vesicles, because the architecture of these artificial membranes is considerably simpler than that of cell membranes. In addition, surfactant bilayers exhibit some functional characteristics of the natural membrane, such as permeability and chain melting temperature, and they may accommodate compounds that are usually present in the cellular membrane, including small proteins, natural polymers, or even other lipids [23,24]. Since the first preparation of lipid liposomes in the early 1960s [25] and synthetic surfactant vesicles in the late 1970s [26,27], these assembles have been successfully used to understand the complex cell membranes. The gained information on the investigation of synthetic or natural amphiphile vesicles can thus be extended to the understanding of cell membranes. Micelle-forming surfactants have widely been used in the preparation and stabilization of vesicles of synthetic or natural amphiphiles. They affect vesicle properties, such as the fluidity, permeability, curvature, surface potentials, and so on. These characteristics may be relevant for the purpose of vesicle application [28].

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 and secondly, to create microenvironments that promote novel chemistry, which might otherwise not be readily achieved. Dimethyldioctadecylammonium bromide (DODAB) is one typical example of the bilayer forming double-chained cationic surfactants that often behave similarly to biomembrane lipids in an aqueous environment. Its molecular structure can be divided into two parts: the polar head region composed of $N(CH_3)_2^+$ and the apolar tail region composed of two long hydrocarbon chains. A study on the phase behavior of DODAB dispersed in water may add to our understanding of the phase transition properties of biological membranes. Other than being used as a membrane-mimicking model molecule, DODAB has widespread applications such as gene therapy, drug solubilization, surface recognition in nanotemplates, kinetics of chemical reactions, and catalysis [29]. Phase behaviors of DODAB aggregates are believed to have a close relationship to the above applications.

To capture some of the attributes discussed above, the investigations on the solubilisation of the DDOAB vesicle dispersions in presence of micelle forming non-ionic surfactant Tween 20 has been undertaken. In addition, the effect of alkyltrimethylammonium and alkylpyridinium halides on the gel-to-liquid crystalline phase transition temperature of DDOAB vesicle is carried out. The hydroxyaromatic compounds produce marked changes in the rheological and microstructural properties of cationic micelles of CTAB. Therefore, the investigation is further extended to examine the effect on these compounds on the thermal stability of the vesicle.

Detail objectives in this section would, therefore, be

i). To study the solubilisation of the DDOAB vesicle in Tween 20 micelles and to determine the values of the saturation and solubilisation molar ratios for the complete vesicle to micelle transition.

ii). To compare the effects of the alkyltrimethylammonium and alkylpyridinium ions on the phase transition of the DDOAB vesicles.

iii). To study the effect of hydroxyaromatic compounds on the thermal stability of the vesicle.

To investigate on the above mentioned objectives, a variety of measurements including differential scanning calorimetry, turbidity, dynamic light scattering, and fluorescence anisotropy measurements are made.

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