Chapter 2

Scope and Object

Scope and Object of the Present Investigation

Considerable interests have been generated recently in studying physico-chemical properties of self assembled surfactant aggregates, especially micelles, reverse micelles and unilamellar vesicles [1-3]. 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 important reasons. Firstly, one can consistently and easily prepare aqueous micellar and vesicular solutions which have 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. 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 [4-7]. Some studies conclude that the changing of the nature of surfactant counter ions affect the properties and structure of the surfactant micelles [8-10]. Another important aspect of the amphiphile that draws the attention is the ability to form aggregate in nonaqueous media. These aggregates in nonaqueous media are of nanometer size and being almost spherical can solubilize large amounts of water, forming water-pool, whose properties have been determined with different techniques [11-13]. The surfactant counter ion is responsible for surface electric interactions at the micellar interface. These interactions can have a strong influence both on the equilibrium shape and size of the micellar aggregates [4,5,8].

Alcohols also affect the micellization process to a large extent [14-16]. They play the role of cosurfactant in the aggregation process. From a practical point of view, alcohols have been used in tertiary oil recovery because they bring about a large decrease of the viscosity of micellar systems used in the process [17]. Moreover they strongly accelerate the rate at which these systems reach equilibrium in the polyphasic range and appear to decrease the adsorption of surfactants in the pores of the rock in the oil field, thereby increasing the efficiency and decreasing the cost of the tertiary oil recovery process. From a fundamental point of view, the approach of microemulsions also led some authors [18] to suggest that the formation and the stability of microemulsions might in part result from their dynamic character enhanced by the presence of alcohol.

Microemulsions differ from micelles by the complex composition and larger sizes of the particles as they contain compartmentalized water (sometimes called water-pool) with surfactants and alcohols having medium hydrocarbon chains (e.g. n-hexanol, n- heptanol, etc.), generally called co-surfactant along with a nonpolar solvent. They are, therefore, characterized by a higher solubilizing capacity of organic molecules and can also be treated as analogical model of biologically functioning systems, which are the basis of living matter. Solubilization of water in microemulsion systems has been found to be dependent on various factors involving the rigidity of the interfacial film, which in turn depends upon the size of the polar head group and the hydrocarbon moiety of surfactant, the type of oils, the presence of electrolyte, the nature and valance of counterion, the temperature, etc. The structure of the interfacial water of microemulsion systems is somehow different from bulk water. In the micro-encapsulated domain, the presence of amphiphilic head groups and the counterion may significantly affect the water mobility. Because of the peculiar chemical and physical properties of the polar interior of reverse micellar aggregates, substantial efforts have been focused on the investigation of the state of water in the pool.

During the last two decades, there has been an increasing awareness of the importance of photochemical and electrochemical effects of dyes due to their interesting role in solar energy conversion and for providing convenient means of probing spectroscopic [19-21] and electrodic process [22-24]. It is commonly believed that the primary process which lead to photo voltage generation in a photogalvanic (PG) cell do not occur at the electrod-electrolyte interfaces, but are results of photochemical reactions in the bulk of the solution; which are followed by diffusion of electrodically active photo products to the electrode surface where electron transfer takes place. Knowledge of the self association properties of the PG solution is important because the aggregates produce grater re-absorption and quenching, decreasing quantum yield and residence time of the first singlet excited state of the dye. The electrochemical rate constant, mass transfer, etc. of PG cell are important because they precisely determine whether the species are likely to react on the electrode or lost by diffusion away or reacting in the bulk of the solution. Self association of dyes (J-and H-aggregates) [25,26] has become more popular recently since the discovery of lyotropic liquid crystalline phases, which are known as chromonics and the spontaneous occurrence of chirality of some cyanine and other dye aggregates although made up by non chiral molecules. Oxazine dyes are also finding increasing applications in the field of electrocatalysis of electrochemical redox processes. Oxazine dye modified electrodes have been shown to be useful in electrocatalytic oxidation of coenzyme, Nicotinamide Adenine Dinucleotide (NADH) in the context of enzyme-based biosensors [27].

The most successful photogalvanic cell [28,29] for solar energy conversion is the ferrous/thionine cell, yet this too is far from ideal conversion efficiency. A better efficiency would be obtained from a PG cell in which each electrode is perfectly selective for a different couple, which could not be achieved so far. In homogenous solution, thermal back reaction of electron transfer also takes place. This dissipation of free energy constitutes a considerable problem in the use of the ferrous/ thionine PG cell for any practical purpose. Various alky substitutions in thionine seem to influence not only the solubilities but also certain physico-chemical properties which in turn must influence the phenomena occurring in the cell.

Keeping the above in view, two anionic surfactants viz. sodium dodecyl sulfate (SDS) and aerosol-OT (AOT) have been selected for the physico-chemical characteristics including thermodynamics of micelle formation as a function of nature and concentration of counter ions (e.g., Li^+, Na^+, K^+, NH_4^+ $(CH_3)_4N^+$, $(C_2H_5)_4N^+$, $(C_3H_7)_4N^+$ and $(C_4H_9)_4N^+$) in aqueous medium. All the surfactants with necessary counterions are prepared by ion exchange technique. To examine the effect of alcohols on micellization on SDS and AOT water- alcohols (ethanol, 1-propanol, 2-propanol) systems have been studied within a temperature range 298-313K.

To investigate the self association and spectroscopic behavior of progressively alkylated thiazines dyes viz. thionine, azure C (monomethyl thionine), azure A (dimethyl thionine), azure B (trimethyl thionine) and methylene blue (tetramethyl thionine) have been studied in aqueous media in presence of two important anionic amphiphile, SDS and AOT within a wide range of surfactant concentrations covering premicellar and postmicellar region. Spectrophotometric investigation is carried out on the above five thiazine dyes in water pool of microemulsion because the physico-chemical environment of the compartmentalized water in microemulsion is different from that of bulk water. The systematic study of the aggregation characteristics of dyes from spectroscopic data is also useful for other important aspects too, e.g., its possible applications in understanding phenomena such as energy transfer in biological systems, metachromasia, hypochromism, conformation of polypeptides and staining properties of dyes for biological specimens. Excitonic interactions between pairs of identical chromophors in a dimer will be considered from spectroscopic measurements and formulated in connection with studies of the concentration dependent properties of dye solutions. Spatial conformations of the dimmer in solution (both in aqueous and microemulsion media) are determined as a function of progressive alkylation of thionine molecule from the consideration of exciton model.

Energy problem has opened new avenues in physical chemistry research ever since electrochemistry has been proved to be the most promising of all modern energy technologies. This is due to its capability in dealing with highest energy densities of all possible alternatives. Two essential features of research activities in this direction are (i) modification of the conventional technologies via incorporating emerging ideas and knowledge in various electrode and electrolytic processes and (ii) development and upgradation of new energy conversion techniques, especially that of solar energy conversion by incorporating new perception of chemistry of electrodics and ionics (specially metal free) at the interfaces and in the bulk. In view of this plan a preliminary study has been drawn.

The area which covers the present investigation is the electrochemical study which includes redox behaviour of all the thiazine dyes at stationary electrode surface in cyclic voltammetry, mechanism of electrode processes and heterogeneous rate constant of electron transfer at the electrodes. Effect of aqueous-organic and micellar media on the electrochemistry of progressively alkylated thiazine dyes at the stationary electrode surface will also be examined. The information will be helpful in further plan of study in electrodics and ionics as mentioned.

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