

CHAPTER I

INTRODUCTION

The search for renewable sources of energy has led to an increasing interest in photochemical cells because of their possible role as transducers of solar to electrical energy. It has been observed that photo effects in electrochemical systems are enhanced if the electrodes are coated with dye stuff. It has been reported that pure metal electrodes become sensitive to light when coated with a dye or immersed in a dye solution.¹ Convenient, continuously tunable lasers can now be produced to cover the entire visible spectrum using organic dyes as lasing medium. The visible absorption spectra of organic dyes exhibit strong dependence on concentration in aqueous solution because of self aggregation.^{2,3} Aggregation affects colour, solubility, photophysical and photochemical behaviour of dyes. A systematic study of the aggregation characteristics of dyes from spectrophotometric data has become a useful field of research because of its possible application in understanding such phenomena as energy transfer in biological systems, metachromatism, hypochromism and conformation of polypeptides, and staining properties of dyes for biological specimens etc. The force responsible for holding the component molecules in the dimer or in polymer is not yet well understood. Nevertheless, it is clear that for ionic dyes, aggregation would be possible if there exists some very strong attractive interaction, which first of all overcomes the coulombic repulsion and then brings the component molecules to a reasonable distance to form dimers and subsequently high polymers. The geometry of the dimer in solution viz, the inclination of the component molecules in the dimer as well as their minimum distance of approach are of great significance in order to understand the role of hydrophobic interaction and steric factors in such aggregate formation. There have been different approaches to the problem, the simplest of which is the theory of exciton coupling.⁴ The splitting of the energy levels has been nicely

explained by the theory of exciton interaction. For a perfectly parallel dimer, only the high frequency or the short wave length peak is expected to appear, whereas for the head to tail dimer only the red shifted peak is allowed. But for any intermediate geometry, both peaks may appear.

The electrochemical and photoelectrochemical effect of dyes are attracting attention partly due to the interesting role of the dyes in solar energy conversion and partly because they provide convenient means of probing electrodic process. It is commonly believed that the primary processes which lead to photo voltage generation in a such system do not occur at the electrode-electrolyte interface, but are results of photochemical reactions in the bulk of the solution which are followed by the diffusion of electrodicly active photo-products to the electrode surface where electron transfer taken place.⁵ Mechanism and kinetics of electrode processes precisely determine whether the electroactive species are likely to react on the electrode or lost by diffusing away or reacting in the bulk of the solution.

On the other hand, a surfactant (surface active agent) is a molecule or ion that possess both polar (or ionic) and non-polar moieties, i.e., it is amphiphilic. Large variations in structure are possible, the polar group can have varied charge and nature (e.g. alkyl sulphate, alkyl phosphate or alkyl ammonium) and be attached to alkyl groups of varying lengths (8-18 carbon atoms) or to other hydrophobic moieties.

In very dilute solutions, surfactants dissolve and exist as monomers but when their concentration exceeds a certain minimum, the so called critical micelle concentration (cmc) they associate spontaneously to form aggregates. The term "micelle" is used for an entity of colloidal dimensions, in dynamic equilibrium with the monomer from which it is formed. As the surfactant concentration increases above the cmc, the addition of fresh monomer results in the formation of new micelles, so the monomer concentration remains

essentially constant and approximately equal to the cmc. Micelles formation is a result of the dual nature of the surfactant molecule, the hydrophobic part trying to escape from the bulk water, and the hydrophilic part interacting strongly with the water. Water has an open structure because of three dimensional hydrogen bonding, which permits the existence of clusters of water molecules containing cavities of specific sizes which can accommodate non-polar chains.⁶ For a given surfactant, at a given temperature, only a certain amount of monomer can be accommodated in the cavities and any further addition of surfactant will result in the formation of micelles. In other words, the further addition of surfactant provides a driving force to minimize contact of the monomer hydrocarbon chains with water. Therefore, according to Langmuir's principle of differential solubility, the hydrocarbon chains cluster to form a core (micellar core) while the polar groups interact with the water.⁷

Each micelle consists of a certain number of monomer molecules (aggregation number, N) which determines its general size and shape. The exact size and shape of micelles is still uncertain but it is assumed that an ionic micellar in dilute aqueous solution is roughly spherical. The charged (or polar) hydrophilic groups are directed towards aqueous phase (stern layer), while the hydrocarbon chains are directed away from the water (forming the hydrophobic central core). The region adjacent to the stern layer contains a high density of counter-ions of the polar heads (Gouy Chapman double layer) and separates the hydrophobic interior from the bulk aqueous phase.⁸

It is interesting to note that although it is usually assumed that there is a fairly well-defined water layers around the micellar surface, there is no agreement on the composition of the micellar core, i.e. whether it consists of pure hydrocarbon or of hydrocarbon mixed with water. However, water penetration in micellar core is still a matter of controversy.

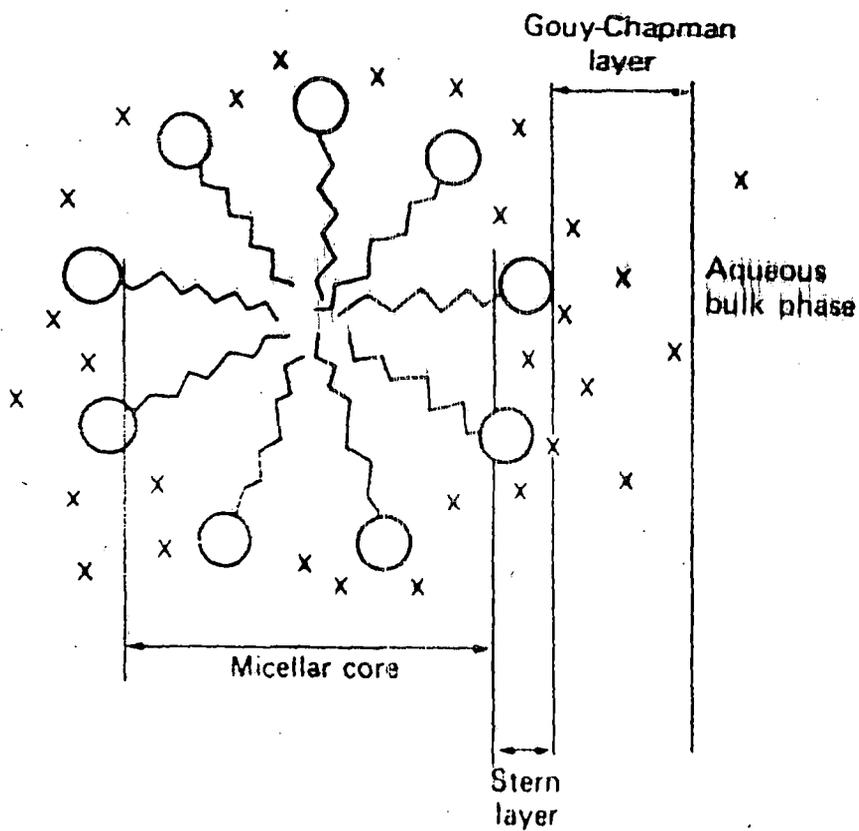


Fig. 1. Two dimensional representation of a model spherical ionic micelle. x: counter-ions, O: ionic head-groups, \sim : hydrocarbon tails.

Current thought on the controversial "water exposure of micelles" is founded mainly on low angle neutron scattering experiments.⁹ This modern concept discusses the main characteristics of the molecular conformation in micelles in terms of the predictions of the "interphase model".¹⁰ Interphase theory predictions are in agreement with experimental data and are particularly consistent with some principal features of micellar structure.

- (i) the micellar core is virtually devoid of water, according to Langmuir's original principle of differential solubility;
- (ii) micellar chains are randomly distributed and steric forces determine the final structure;
- (iii) contact of the hydrophobic sections of the micelle with water results from a disordered structure in which the terminal groups or chain ends are near the micellar surface and thus exposed to bulk water.¹⁰

Although the "water penetration" concept of the hydrophobic sections of micellar is now less acceptable than the "water exposure" concept, this controversial topic still under debate.^{11,12}

In analytical chemistry the main use of surfactants is in spectrophotometry and fluorimetry, particularly in the development of new methods of metal ion determination. Micelles are responsible for many of the practical applications of detergents such as: (i) enhancement of the solubility of organic compounds in water, owing to their incorporation in the micelle, where they experience an altered micro-environment (ii) catalysis of many reactions, usually explained in terms of a "concentration effect" in the micellar pseudophase (iii) alteration of reaction pathways, rates and equilibria.⁸

Typical chromophoric reagents which have been used to determine metal ions by use of surfactants as a third component include derivatives of the triphenylmethane series, azo compounds¹³⁻¹⁵, anthraquinone dyes, phenoxazine, oxine derivatives etc.¹⁶⁻¹⁹ Although considerable attention has been paid to the analytical applications, the nature and mechanism of these types of reaction are still not clearly understood. However, involvement of micelles in practical problems such as detergency has been known for a long time. The fundamental investigations on micelles in the early days were concerned mainly with the structure and properties of micelles as association colloids, the monomer-micelle equilibrium and solubilization by micelles.²⁰ In recent years, the use of micelles as "model" systems²¹ for a variety of problems related to monolayers, colloidal systems in general, proteins, enzymes and membranes as also the monomer-micelle equilibrium system as a "model" system for hydrophobic interactions² which are of central interest in biology have expanded the range of interest in micellar phenomena greatly. An additional impetus has been the recognition of the important role of micelles in physiological systems.²²

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