

CHAPTER 2

SCOPE AND OBJECT :

During the last few years, 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 electrodic processes. It is commonly believed that the primary processes which lead to photovoltage generation in a photogalvanic (PG) cell 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 electrodically active photoproducts to the electrode surface where electron transfer takes place. Knowledge of the association properties of the photogalvanic solution is thus important because the aggregates produce greater reabsorption 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 diffusing away or reacting in the bulk of the solution. Since thionine is known to be photoreduced reversibly by Fe(II) ions in acidic aqueous solution, many workers have been trying to explore the possibilities of utilizing the system in the construction of PG cell for solar

The efficiency of such a cell is, however, severely influenced by the degree of solubilities of the dye. Various alkyl substitutions in thionine seem to influence not only the solubilities but also certain physicochemical properties which in turn must influence the phenomena occurring in the cell. Since above system is most successful to date for solar energy conversion, almost all the previous workers emphasized that aggregation properties, mass transfer processes, and electrode kinetics must be studied separately in order to understand the factors that limit the performance of the cell. Keeping these in view the object of the present study has been chosen.

Progressively alkylated thiazine dyes, viz., thionine, azure C (monomethyl thionine), azure A (dimethyl thionine), azure B (trimethyl thionine) and methylene blue (tetramethyl thionine) have been selected for the present study. Self aggregation of these dyes have been investigated in aqueous and aqueous-ethanolic solution of various compositions. The systematic study of the aggregation characteristics of dyes from spectroscopic data is also useful for other important aspects too e.g., its possible application in understanding phenomena such as energy transfer in biological systems, metachromasia, hypochromism, conformation of polypeptides and staining properties of dyes for biological specimens. Structural aspects of progressively alkylated thiazine dye aggregates are also studied. The interpretation of the absorption spectra by means of exciton theory allows the determination of the

geometrical disposition of the monomers in all the aggregates. From the changes produced by the dimerization process on some thermodynamic functions, the nature of bonding in the aggregates has also been investigated.

Another aspect covering the present investigation is the electrochemical study which includes redox behaviour of the thiazine dyes at stationary electrode surface in cyclic voltammetry, mechanism of electrode processes and heterogeneous rate constant of electron transfer at the electrodes. Dissipation of free energy due to thermal back reaction of electron transfer in a PG cell constitutes a major problem in the use of Fe(II)/ thionine system for any practical purposes. In view of these an electrochemical technique has been adopted to study thermal back reaction of progressively alkylated thiazine leucodyes with Fe(III) ions. Effect of hydrophobic interaction, if any, in such a reaction will also be examined.

Moreover, electrode surface modified with clay minerals possesses several attractive features: a high concentration of the photoactive dye species can be achieved at the electrode surface and due to the small thickness of the film, the incident light is efficiently absorbed by the dye molecule, present near the electrode. Pores, channels and interlayer spacing of molecular dimensions in clay minerals and zeolites can form molecular gateways which impart a selective screen so that differentiation results on the basis of molecular sizes and

shapes of the solutes. Differential electrode kinetics at two electrodes is another way of differentiation among various species in PG cell. Such discrimination is crucial because otherwise reverse electron transfer often takes place causing dissipation of energy as already mentioned. A preliminary work has been undertaken on the electrochemical characteristics of the five thiazine dyes at the smectite (montmorillonite) and zeolite (ZSM-5) modified electrode using cyclic voltammetric technique.

If the electrochemical experiment is carried out at a modified layer, the same relationships as those of a clean bare electrode hold, except that the area of the conductive channel can now play an important role in defining the type of diffusion behaviour observed. Experiment in the situation can be considered to be a normal electrochemical experiment with a new medium. All parameters accessible to the electrochemist would depend precisely upon the competitive exchange reaction of dye and counter ion. Selectivity coefficients of various ions toward clay minerals explain the above phenomena quantitatively and also influence the extent of dye loading process from an equilibrium solution. Therefore, a chapter of the present thesis contains the study of physicochemical aspects of ion exchange equilibria of the five thiazine dyes onto the montmorillonite and zeolite exchanger in fundamental detail not only because of their involvement in the electrochemistry of clay and zeolite modified electrode but also with a view of deriving some insight into the factors that govern and influence the ion

exchange process, in general. Moreover, adsorption of dyes by clay minerals often results in significant spectral changes, specially in the electronic spectrum. Little is known, however, about the adsorption interactions which cause these alterations. There is much controversy about the origin of this metachromasy as to whether this is due to the aggregation of the dye in layered space or due to π electron interaction between the oxygen planes of montmorillonite and the aromatic ring of the dye. To understand the nature of interaction of the dye molecules with montmorillonite and zeolite (ZSM-5) in further detail the present study has been extended to the investigation of metachromasy of the five thiazine dyes by clay minerals. It may be mentioned that being structurally similar with like charge delocalization and chemical properties, present dyes differ from each other only in molecular weight and alkyl substitution. This fact provides an excellent opportunity for studying the effect of molecular size on the adsorption of the dye and metachromasy phenomena.