Chapter–2 : Scope and Object Of Present Investigation

CHAPTER - 2

SCOPE AND OBJECT OF PRESENT INVESTIGATION

Electrochemical and photochemical effects of dyes are attracting increasing attention partly due to the interesting role of the dyes in solar energy conversion and partly because they provide convenient means of probing electrodic processes. It is commonly believed that the primary processes which lead to photo-voltage 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 photo-products 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 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 photoreduced reversibly by Fe(II) ions in acidic aqueous solution, many workers have been trying to explore the possibilities of utilising the system in the construction of PG cell for solar energy conversion. The efficiency of such a cell is, however, severely influenced by the degree of solubilities of the dye. Various alkyl substitution 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 (although far from having an ideal efficiency or at least efficiency comparable favourably with that of semiconductor solar cells) for solar energy conversion, almost all the previous workers emphasised 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 investigation 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 solution. The systematic study of the aggregation characteristics of dyes from spectroscopic data is also useful for some other important aspects e.g., its possible application in understanding such phenomena as energy transfer in biological systems, metachromasia, hypochromism and 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 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 is also 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.

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 some other inorganic substances (e.g. 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 for, otherwise reverse electron transfer often takes place causing disipitation of energy. A preliminary work has been undertaken on the electrochemical characteristics of five thazine dyes at the montmorillonite 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. As such, a considerable part of the present investigation also includes the study of physicochemical aspects of ion exchange equilibria of the five thiazine dyes onto the montmorillonite exhanger in fundamental detail not only because of their involvement in the electrochemistry of clay-modified electrode but also with a view of deriving some insight into the factors that govern and influence the ion exchange process, in general. However, measurements of dye sorption were used by earlier workers mainly to estimate the surface areas and cation exchange capacities of the adsorbent. Although large amount of work is recorded in the literature on this aspect, studies on the desorption characteristics of the dyes with different inorganic and organic ions are lacking. Therefore, desorption of thionine and four of its derivatives from their respective montmorillonite complexes have also been studied with inorganic and organic ions with different charges and sizes to acquire a better knowledge of the nature of adsorbate-adsorbent interaction, relative strength of binding of adsorbents, cation specificity etc. Such studies also reveal the extent of extractibility of the dye cation from the adsorbent surface from which we can have an idea of the affinity of the ions for the mineral vis-a-vis the relative desorbing efficiency of the ions with size, shape and charge of the ions. It may be mentioned that being structurally similar with like charge delocalization and chemical properties, present dyes differ from each other only in molecular weights and alkyl substitution. This fact provides an excellent opportunity for studying the effect of molecular size of the adsorbate on sorption-desorption phenomena.