CHAPTER – II

SCOPE AND OBJECT OF PRESENT INVESTIGATION

The visible absorption spectra of organic dyes exhibit a strong dependence on concentration in aqueous solution because of aggregation.[1,2] Aggregation affects colour, solubility and photophysical behaviour of dyes. Self association of fluoroscent dyes leads to self quenching. It plays key role in many technological applications. Important examples include sensitization of silver halide nanocrystals in photographic processes and non-linear optical materials.[3-8] The properties of Oxazine dye aggregate at liquid/solid interfaces have been of interest for long time. It was suggested that solar energy harvesting with wide band gap semiconducting photoconductors may be improved by covering with these dyes to expand the wave length range.[9] The sensitivity of fluorescence detection is often limited by the autofluorescence of biological samples. As the excitation wave length becomes larger, the autofluorescence decreases, and hence detectibility over background increases. The Oxazine dyes display surprisingly long wave length absorption and emission maxima; given their small sizes and as such have been shown to be important fluorescent probe for biological samples.[10,11] They can be excited with simple laser sources such as solid state laser diods. 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.[12] As has already been mentioned in the introduction , an important theoretical tool by which different types of dye aggregates (H, J or intermediate) could conveniently be analysed is the molecular exciton theory of dipole-dipole coupling.[13,14] According to this model, parallel aggregates (H aggregates) absorbs at shorter wave length and head to tail aggregates (J aggregates) show absorption at longer wave lengths compared to the monomer. Intermediate geometries give rise to band splitting where the monomer units are thought to be arranged obliquely with the molecular plane oriented with respect to each other at an angle θ. In the above geometries the excited states of the dimer are described by exciton states in which the exciton is delocalised over both monomer units. A number of researchers have computed and rationalized dimer parameters with the aid of exciton theory. But no systematic study has so far been made on the different Oxazine dyes having different sizes and shapes. Temperature dependence of monomer-dimer equilibrium has also been studied for some other dyes to understand the thermodynamics but surprisingly none of the authors considered temperature dependence of aggregate geometries in solution. In view of the non-rigid structure of molecular aggregates in solution, it is very much likely that the geometry of the aggregates be dependent on temperature of the system. This study is of interest for a number of reasons: it could give a better insight of the nature of interaction in the aggregate system and it may also explain the previously observed temperature dependence spectra of some dyes.[15,16]

On the other hand, the electrostatic interaction between oppositely charged surfactants and dyes are well understood but do not in themselves explain the spectral changes observed. It seems probable that once the electrostatic forces have brought together the oppositely charged molecules, hydrophobic interactions take place, dramatically changing the microenvironment experienced by the chromophore. Knowledge of dye surfactant interaction should be of great value in understanding the chemical equilibria, mechanism and kinetics of surfactant sensitized colour reactions. Study of organic dyes in a micellar medium is important for understanding the thermal and light induce reactions in biomembranes also[17,18] Such reactions go through the involvement of excited and free radical species whose behaviour in a micellar medium can be significantly different from that in a homogenous aqueous medium. Further, organic dyes have vastly been used in photo-electrochemical energy conversion devices, wherein their radox chemistry plays an important role[19,20]. There have been reports in the past that use of these dyes as sensitizers in photo-electrochemical devices for solar energy conversion suffer from very poor power conversion efficiency[21,22]. This drawback has been variously attributed to slow discharge of photo-produced intermediate dye radicals (viz., semi reduced/leuco dyes) at the cell electrode as compared to radical – radical recombination reaction in the bulk of the solution. To make the discharge process favourable, it is necessary to arrest the recombination reaction in the bulk homogeneous pahse. Attempts have been made in the past to slow down the bulk reactions in a suitable micellar medium[23]. Some Oxazine dyes have been considered sensitizers in photogalvanic devices in the past. The dye surfactant interactions have been the subject of interest also because they mimic many biological processes taking place between the large organic molecules and biomembranes and can act as a model redox system[24,25]. Further, such interactions between ionic dyes and charged surfaces is of interest in numerous applications ranging from the design of electronic devices to the characterization of drug-delivery system.

Keeping the above aspects in view the plan of work has been undertaken. Four Oxazine dyes with different shapes and sizes viz., Brilliant cresyl Blue, Cresyl Violet, Cresyl fast violet and Nile Blue A have been selected for the present study. Formation constants (Equilibrium constant) and thermodynamic parameters are determined . 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 conformation of the dimer in solution are determined as a function of temperature from the consideration of exciton model. Electrochemical analysis of the dyes have been made by cyclic voltammetry at solid glassy carbon microelectrode. Kinetics of the quasireversible electrode reactions are studied at appropriate scan rates. Mechanism of electrode processes are also considered. Fundamental detail of the physiochemical aspects of the interaction of dyes with ionic and non-ionic surfactants are examined. Emphasis are given on the thermodynamics of the interaction of the above dye – surfactant system. Attempts have been made to compare the nature of the dye in respect of above interaction in aqueous and micellar phase.

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