CHAPTER VI

SUMMARY AND CONCLUSION

The visible absorption spectra of organic dyes exhibit strong dependence on concentration in aqueous solution because of aggregation. Aggregation affects colour, solubility and photophysical behaviour of dyes. It also plays key roles in many technological applications including solar energy harvesting, photography and laser technology . Study of the monomer – dimer equilibria is important because it gives more insight on the phenomena and throw light on the origin of forces involved in such processes. The structure of the aggregates in solution may also be determined by studying spectroscopic behaviour of the dyes in solution. A theoretical tool by which different types of dye aggregates (H, J and intermediate) could conveniently be analysed is the molecular exciton theory of dipole-dipole coupling. It explains the modification of spectral features due to aggregation and determines the geometrical disposition of the dimer, which is also a function of temperature.

Oxazine dyes are an important class of organic dyes, which have shown promises in many scientific and technological applications. These includes their applications as fluorescence probes in biological samples, as media to expand wavelength range of a semiconductor for solar energy harvesting and as mediators in chemically modified electrodes in electrocatalysis. Moreover, the monomer and dimer forms of each of these dyes have distinct absorption bands with widely separated maxima. Four oxazine dyes of different shapes and sizes, which are selected for the present study are Brilliant Cresyl Blue (BCB), Cresyl Violet (CVA), Cresyl Fast Violet (CFV) and Nile Blue A (NBA).

A major part of the present study includes interaction of oxazine dyes with anionic and non-ionic surfactants. Significance of this study is many fold. Apart from its great value in understanding chemical equilibria , mechanism and

kinetics in organized microenvironment, there is much current interest in the solubilisation of macromolecular species, such as polymers or enzymes in micelles and compartmentalised water present in microemulsion. The use of dyes as probes in studies of macromolecular conformation and dynamics in such systems is possible but it is first necessary to establish the physico-chemical nature of interaction of dye molecules with surfactants.

In Chapter I, a brief introduction on the molecular interaction in dye solution, electrochemistry of dyes and surfactant micellisation and their significances are presented. (page 1-7).

The scope and object of the present investigation has been incorporated in chapter II (page 8-13)

In chapter III, results of the investigations on the nature of dye-dye aggregation, the effect of increase of molecular size and temperature on aggregation, the probable structure of the dye aggregates in aqueous solution and the thermodynamics of dye aggregation are presented. Self aggregation of the dyes are important to understand the self quenching phenomena occurring in the photogalvanic cells and also the phenomena of energy transfer in biological systems. Analysis of monomer spectra of the Oxazine dyes in terms of Vibronic Exciton Model and also the effect of temperature on monomer spectra have been studied in aqueous solution . The binding force between the monomer units in a dimer and the temperature dependence of aggregate geometrics in aqueous solution have been presented in this chapter. In section 3.1.1, a brief review of previous studies on the general monomer – dimer equilibrium of dyes in the light of classical model is presented. Section 3.1.2 depicts the theoretical aspects of molecular exciton model, section 3.1.3, contains a review on spectral properties of dimer in terms of exciton theory and also includes some more recent development of the exciton theory which can be used to relate the distance and relative orientation of monomeric dye molecules in the dimer. Possibility of

higher aggregate formation is avoided by choosing appropriate concentration range of dye in solution. (page 14-30)

Various characteristics of the four Oxazine dyes; their structures and method of purification are presented in section 3.2. The experimental techniques for the study of dye aggregation are also presented in this section. (page 33)

Dimerisation constants for the dyes at various temperatures are determined applying an iterative technique by a computer program written for the purpose (Section 3.3.1). The dimerisation constant decreases with the increase in temperature in the aqueous media. At a particular temperature the dimerisation constant increases upon methyl and ethyl substitution and also with the size of the molecules. At 20°C in aqueous medium the dimerisation constant values are 2.000 x10^3, 2.507x10^3, 2.857 x 10^3 and 5.002x10^3lit/mol for BCB, CVA, CFV, and NBA respectively. Effect of alkyl substitution and also the bulkyness of the molecules are found to be significant. It is evident that the involvement of hydrophobic and vander Waals' forces etc. in dimer formation are important. Some important thermodynamic functions of dimerisation process are determined in order to know the nature of bonding between the monomers in the dimer. ΔH^o, ΔG^o and ΔS^o values are negative for the four Oxazine dyes. ΔG^o values are -18.48 kJM^{-1}, -18.91 kJM^{-1}, -19.48 kJM^{-1} and -20.96 kJM^{-1} for BCB, CVA, CFV and NBA respectively. The negative values of ΔS^o suggested that aggregated dyes are more ordered than free monomeric dyes in solution. In general, the high values of ΔH^o and ΔS^o can be attributed to the involvement of hydrogen bonding in aggregate formation apart from hydrophobic and $\pi-\pi$ interactions. (page 35-48)

In section 3.3.2, the effect of temperature on the spectra of monomers which are present in equilibrium with dimers in aqueous medium have been analysed. The absorptivity values of the monomer which increases with temperature and also λ_{max} which changes with temperatures are considered. The

thermochromic behaviour of the Oxazine monomer spectra are analysed in terms of Vibronic Exciton Model :

$$I(\bar{v}) = I_{oo} \sum_{m} X^m / m \ ! \ (1 + mV/ \ \bar{v}_{oo}) exp \ \{- 4 ln \ 2/b_g{}^2 \cdot (\bar{v} - \bar{v}_{oo} - mV)^2\}$$

where I_{oo} is the intensity, $\bar{v}_{oo}$ is the position of the (0,0) band, b_g is the Gausian band width, X is the ration of (1,0) to (0,0) band intensities and V is the separation between the bands. The experimental monomer spectra were fitted to the above 5-parameters Gaussion equation. This has been done on computer by means of a general non-linear curve fitting program (KINFIT). Results of fitting indicates that the present physical model describing a vibronic progression of a displaced harmonic oscillator with Gaussian bands of constant band width is well applicable in the present systems under investigation. It is observed that the intensity I_{oo}, and the X i.e., the the ratio of (1,0) to (0,0) band intensities are influenced very much by temperature variation. The parameter X is related to the equilibrium nuclear confirmation in the two electronic states. It is apparent, therefore, that temperature dependence of X may be correlated with the temperature dependence of dimer geometry in solution. This point has further been considered during discussion on dimer spectra. (page 49-56)

In the section 3.3.3, the dimer spectra of the Oxazine dyes (viz. BCB, CVA, CFV and NBA) are analysed in terms of Molecular Exciton Theory of dipole-dipole coupling. There are three types of dye aggregates: H-type, J-type or intermediate type. According to this model the 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 parallely (Model I) or obliquely (Model II) (both models are discussed). The splitting of dimer spectra for the intermediate geometries leads to compute the angle θ between monomer units and intermolecular

separation of the monomer molecules in the dimer. The dimer spectra are decomposed into two bands, which shows that the monomer visible spectrum corresponds to an electronic transition with two vibronic bands. A systematic variation of oscillator strengths for both symmetric and anti-symmetric delocalised exciton states are observed as a function of temperature. This may be due to the variation of geometrical disposition of the dimer in solution with temperature. The oscillator strength values of monomer at 20°C are 0.1815, 0.2703, 0.2654 and 0.7375 of BCB, CVA, CFV and NBA respectively. The oscillator strengths of the low frequency band and high frequency band of the dimer at 20°C are (0.0117 and 0.1222), (0.0343 and 0.1620), (0.0234 and 0.1694) and (0.0654 and 0.4959) for BCB, CVA, CFV and NBA respectively. The angle between the two monomer units in a dimer is found to be a function of temperature. Exciton theory allows to determine θ values which varies from 34.34° to 36.28°, 49.42° to 53.74°, 40.74° to 47.50° and 39.92° to 38.19° respectively for BCB, CVA CFV and NBA for the temperature rise from 20°C to 60°C in each case. Clearly it is evident that rise in temperature results in the partial unfolding of the dimer structure.

From the space filling CPK models, the molecular lengths of the four Oxazine dyes have been calculated as 13.50Å, 11.99 Å, 12.40 Å, 13.54Å for BCB, CVA, CFV and NBA respectively. The intermolecular distances of the monomer pairs in the dimers according to model II at 20°C are found to be 4.30 Å, 5.09 Å, 4.80 Å and 7.40 Å for BCB, CVA, CFV and NBA respectively. The intermolecular distances are also increased with temperatures, which supports unfolding of dimer at high temperature. As the length of the molecule and hydrophobicity increases, the angle θ of the dimer decreases, indicating an enhanced tendency of the dimer to be folded further. However, BCB molecule with less complex structure align most effectively yielding lowest θ values. In most of the cases the intermolecular distance (R) between the monomer pair in the dimer in solution as obtained according to Exciton theory agrees excellently

well with the calculated value taking into account the theoretical lengths of the molecules. (page 56-66)

In chapter IV , interactions of the cationic Oxazine dyes with anionic and non ionic surfactants have been reported. For these interactions, the same series of Oxazine dyes are used viz. BCB, CVA, CFV and NBA and surfactants used for these studies are SDS (anionic), Triton-X 100 and Tween 80 (both are non ionic). To understand the nature of complex formation of the cationic dyes with surfactants at sub and super micellar concentrations, the effect of temperature variations on the binding constant values are determined. The thermodynamic parameters are evaluated from the equilibrium constants of the process at different temperatures. The electron donating nature of the surfactant micelles towards the electron acceptor dyes are also observed in charge transfer type of complex between dyes and non ionic micelles.

In section 4.1, a brief review of the earlier works on the dye surfactant interactions in sub and super micellar concentration of surfactants is presented.(page 73-90)

The experimental procedure for the Oxazine dye-surfactant interaction in the aqueous media is presented in section 4.2. Purification of surfactants, spectrophotometer used and the preparation of solution for these studies are also mentioned in this chapter (page 90-91)

The results of interaction of the Nile Blue A, in aqueous solution with SDS, Triton X-100, and Tween-80 are discussed in section 4.3.1. The electronic absorption spectra of NBA $(1 \times 10^{-5}$ M) with varying concentrations of SDS below cmc are presented. The effect of increasing concentrations of SDS and temperatures are investigated. By using Ketelaar's equation the equilibrium constants and thermodynamic parameters are obtained at three different temperatures (303K, 313K and 323K). The equilibrium constants are 1.43 x 10^9 dm^3M^{-2}, 0.95 x 10^9 dm^3M^{-2} and 0.763 x 10^9 dm^3M^{-2} at three different

temperatures. ΔG^o, ΔH^o, and ΔS^o values are measured as -54.02 kJM^{-2}, -22.67 kJM^{-1}, and $+100$ JM^{-1}K^{-1} respectively for the protonated dye-surfactant complex.

Interaction of NBA-SDS system (above cmc) are also studied at different temperatures (303K, 313K, 323K). The equilibrium constants and thermodynamic parameters are evaluated. The equilibrium constants at three temperature are 363 dm^{3}M^{-1}, 198 dm^{3}M^{-1}, 118.8 dm^{3}M^{-1} and the values of ΔG^o, ΔH^o and ΔS^o are -13.80 kJM^{-1}, -43.38 kJM^{-1}, -94.47 JM^{-1}K^{-1} respectively are measured for the dye micelle complex.

NBA forms (1:1) charge transfer (CT) complex with non ionic surfactant Triton X-100 (TX – 100) above its cmc. The temperature dependence of the interaction shows that with the increase of temperature the intensity of the CT spectra decreases indicating breaking of the complex at high temperature. The equilibrium constants are found to be 2160 dm^{3}M^{-1}, 1160 dm^{3}M^{-1}, and 638 dm^{3}M^{-1} at above three different temperatures. ΔG^o, ΔH^o, and ΔS^o values are -18.50 kJM^{-1}, -55.42 kJM^{-1} and -117.89 JM^{-1}K^{-1} respectively.

NBA, a cationic Oxazine dye forms CT complex with non ionic surfactant Tween 80 above its cmc also. Spectral change with temperatures is observed. The equilibrium constants and also thermodynamic parameters are evaluated by using Ketelaar's equation. The equilibrium constants are found to be 2000 dm^{3}M^{-1}, 1080 dm^{3}M^{-1}, 533 dm^{3}M^{-1} at 303K, 313K and 323K respectively. The thermodynamic parameters, ΔG^o, ΔH^o and ΔS^o are -17.48 kJM^{-1}, -33.27 kJM^{-1} and -65.27 JM^{-1}K^{-1} respectively (page 91-100).

The results of interaction of the Cresyl Violet Acetate (CVA) in aqueous medium with SDS, Triton X-100 and Tween 80 are discussed in section 4.3.2. The electronic absorption spectra of CVA (2 x 10^{-5}M) with different concentrations of SDS (below cmc) are presented. The effect of increasing concentration of SDS and temperatures are investigated. CVA gives well defined

peak at 650 nm in presence of SDS due to protonation. The presence of an isobestic point is indicative of the presence of an equilibrium between the free CVA, SDS and the "CVA-SDS complex". Using Ketelaar's equation, the equilibrium constant values are determined. The equilibrium constants are found to be 3.76×10^9 dm^3 M^{-2}, 2.16×10^9 $dm^3 M^{-2}$, 1.15×10^9 $dm^3 M^{-2}$ at 303K, 313K and 323K respectively for the protonated dye-surfactant complex. The ΔG^o, ΔH^o and ΔS^o values are $-55.84 kJM^{-1}$, -46.19 kJM^{-1} and 30.83 $JM^{-1}K^{-1}$ respectively. Interactions of CVA with SDS (above it's cmc), at different temperatures are also studied. The equilibrium constants are found to be 616 $lit.M^{-1}$, 308 $lit.M^{-1}$, 196 lit. M^{-1} at 303K, 313K and 323K respectively. The thermodynamic parameter values (ΔG^o, ΔH^o and ΔS^o) are found to be $-15.09 kJM^{-1}$, -41.57 kJM^{-1} and -84.6 $JM^{-1}K^{-1}$ respectively. CVA forms charge transfer complex with non ionic surfactant Triton X-100 above its cmc. The spectra of CVA in presence of Triton X-100 micelles passes through a isobestic point (at 575 nm) which indicates the formation of 1:1 dye-surfactant complex. The equilibrium constants at temperatures 303K, 313K, 323K are found to be 940 $lit.M^{-1}$, 611 lit. M^{-1} 427.27 lit. M^{-1} respectively. The thermodynamic parameters ΔG^o, ΔH^o and ΔS^o are also evaluated and are found to be -16.74 kJM^{-1}, -35.63 kJM^{-1} and -60.37 $JM^{-1}K^{-1}$ respectively. The thermodynamic and spectroscopic properties of CVA-Triton X-100 complexes suggest that CVA forms a strong charge transfer (CT) or electron donor – accepter (EDA) complex with Triton X-100. CVA also forms 1:1 molecular complex with non ionic surfactant Tween – 80 above its cmc in aqueous medium. The equilibrium constants at 293K, 303K, and 313K are found to be 900 $lit.M^{-1}$, 561 lit. M^{-1} and 330 $lit.M^{-1}$ respectively. The ΔG^o, ΔH^o and ΔS^o values are evaluated and are found to be -15.87 kJM^{-1}, -45.35 kJ M^{-1}, -96.66 $JM^{-1}K^{-1}$, respectively. (page 101-109)

In section 4.3.3 the interaction of Cresyl Fast Violet(CFV) with SDS, Triton X-100, and Tween 80 are studied in aqueous medium at different

temperatures. CFV forms protonated complex with SDS below its cmc value. The presence of isobestic point (at 622 nm) supports the formation of molecular complex. The equilibrium constants at 303K, 313K, 323K are found to be 7.9 x 10^9 lit .M^{-2} 4.38 x 10^9 lit. M^{-2} and 2.96 x 10^9 lit. M^{-2} respectively at pH 5.25. The values of the thermodynamic parameters ΔG^o, ΔH^o and ΔS^o are found to be -57.94 kJM^{-1}, -38.60 kJM^{-1} and $+ 61.80$ J$M^{-1}K^{-1}$ respectively . CFV also forms strong 1:1 molecular complex with SDS above its cmc. The equilibrium constants and thermodynamic parameters are evaluated at 303K, 313K and 323K. The equilibrium constants are found to be 462 lit. M^{-1}, 324 lit. M^{-1}, 190 lit .M^{-1} respectively at mentioned temperatures.

CFV forms strong CT or EDA complex with non ionic surfactant Triton X-100 above its cmc value. The equilibrium constants are evaluated and are found to be 685 lit. M^{-1}, 432 lit. M^{-1}, 240 lit. M^{-1} at temperatures 303K, 313K and 323K respectively. The thermodynamic parameters are also evaluated. Non ionic surfactant Tween 80 also forms charge transfer complex with CFV dye. The equilibrium constants and thermodynamic parameters are evaluated at three temperatures 293K, 303K and 313K. (page 110-117)

In section 4.3.4, results of the interaction of Brilliant Cresyl Blue (BCB) with SDS, Triton X-100, and Tween – 80 are studied in aqueous medium are reported at different temperatures. BCB forms protonoted molecular complex with SDS, below its cmc. Using Ketelaar's equation, the equilibrium constants of the complex are determined as 6.95 x 10^9 lit M^{-2}, 3.82 x 10^9 lit M^{-2} and 1.79 x 10^9 lit M^{-2} at 297K, 303K and 313K respectively. The thermodynamic quantities are evaluated as -55.66 kJM^{-1}, -51.96 kJM^{-1} and +12.18 JM^{-1} for ΔG^o, ΔH^o and ΔS^o respectively. BCB also forms strong complexes with SDS above its cmc value. From the spectral data, equilibrium constant values at different temperature and the thermodynamic parameters are evaluated. BCB form strong charge transfer (CT) complex with non ionic surfactants, Triton X-100 and

Tween-80 also. The spectral change due to the presence of either Triton X-100, or Tween – 80 are considered and used to determine the formation constant (equilibrium constant) values of the complex.

The equilibrium constants for BCB-Triton X-100 at three temperatures are found to be   720 lit. M^{-1}, 432 lit. M^{-1}, 226 lit. M^{-1} respectively. The equilibrium constants for BCB and Tween 80 at 293K, 303K and 313K are found to be 821 lit.M^{-1}, 425 lit.M^{-1} 231.82 lit.M^{-1} respectively. The thermo-dynamic quantities of the BCB Triton X-100 and BCB Tween 80 interactions are also evaluated (page 118-133).

As mentioned earlier, the Oxazine dyes are finding increasing applications in the field of electrocatalysis of electrochemical redox process. In chapter V, results of cyclic voltammetric experiments with progressively alkylated Oxazine dyes, CVA, CFV and NBA and also BCB, the lightest member of the four Oxazine dyes, have been reported.

A brief review of the previous works on the redox properties of various dyes on clean electrode using cyclic voltammetric technique is presented in section 5.1 (page 142-147)

The experimental procedure for electrochemical analysis using cyclic voltammograph is presented in section 5.2. Cyclic voltammetric experiments with phenoxazine dyes are carried out in water, Triton X-100, a non-ionic surfactant and SDS, an ionic surfactant, at 25°C ± 1°C to understand   their electrochemical behaviour on glassy carbon electrode (GCE). (page 148)

The criteria related to the reversibility and the results thereof on a clean glassy carbon electrode (GCE) in different media are discussed in section 5.3. Dyes are reduced to the colourless leucodyes an forward scan and oxidized back to the corresponding coloured dyes in the reverse scan. Both the processes are two electron transfer processes, for all the dyes studies. The values of 0.058/ΔE is less than 2 in all cases except NBA in aqueous medium which is >

2   at slow scan rates. This is probably due to the result of two successive one electron reversible charge transfer with fast protonation of the intermediate to form a species which is more easily reduced than the dye molecule. The current ratio values, $ip_a/ip_c < 1$, suggest that the electrogenerated leucodyes are involved in reaction which prevent their reoxidation upon scan reversal.

Assuming reversibility of electrode reactions, the diffusion coefficient values of the dyes in different media have been determined at scan rate of 20 mVs^{-1}. The nature of the cyclic voltammograms obtained from concentrated dye solution ($1 \times 10^{-4}M$) in the presence of 0.1M KCl and the effect of pH's have also been discussed. The heterogeneous rate constant k for the quasi-reversible processes of the dyes is determined at slow scan rate in different pH and are found to be of the order of 10^{-4} cm sec^{-1}. (page 149-172)