

C A P T E R 6

S U M M A R Y A N D C O N C L U S I O N S :

In chapter 1, a general introduction on photogalvanic effect of thiazine dye is presented. The importance of electrode kinetics, self quenching phenomenon of photogalvanic solution, electrode selectivity, dye incorporated clay (montmorillonite) and zeolite (ZSM-5) modified electrode and quantitative ion-exchange parameters involving such a modified electrode are also mentioned briefly for these are brought to be pertinent with the objectives of the present investigation. Progressively alkylated thiazine dyes viz., thionine, azure C, azure A, azure B and methylene blue are selected not only for their differences in solubilities and other physico-chemical characteristics pertaining to photogalvanic efficiencies but also because they provide an excellent opportunity for studying the effects of molecular size and shapes on various physico-chemical parameters incorporated in the thesis. (Page 1-14)

The scope and object of the present investigation has been incorporated in chapter 2. (Page 15-19)

In chapter 3, results of the investigations on the nature of dye-dye aggregation, the effect of increase of molecular size, temperature and solvent on aggregation, the probable structure of dye aggregates and the thermodynamics of dye aggregation in

aqueous and aqueous-ethanolic media are presented. Self aggregation of the dyes are important not only to understand the selfquenching phenomena occurring in photogalvanic cells, but also for some other important aspects viz. its possible application in understanding such phenomena as energy transfer in biological systems, metachromasia, hypochromasia etc. and the binding processes of dyes by clay minerals which have been incorporated in the present thesis. 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. Section 3.1.4., describes the vibronic exciton model for the interpretation of dimer spectra and includes some more recent development of molecular exciton theory. (page 20-50)

Various characteristics of this dyes, their structures and method of purification are presented in section 3.2. The experimental techniques for the study of dye aggregation is also presented in this section. (page 51-54)

Dimerization constants for the dyes at various temperature and solvents are determined applying an iterative technique by a computer program written in BASIC language and presented in chapter 3.3.1. The dimerization constant decreases with the

increase in temperature and percentage of ethanol in the medium. At a particular temperature and solvent the value of dimerization constant increases upon methylation from thionine to azure B and decreases slightly in the case of methylene blue. At 20⁰C in aqueous medium the values are 2.44×10^3 , 2.95×10^3 , 4.50×10^3 , 8.98×10^3 and 5.01×10^3 lit./mol. for Th, AzC, AzA, AzB and MB respectively. Alkyl substitution effect is found to be significant and it is also evident that hydrophobic and Vander waals forces etc. in dimer formation are important and the steric hindrance caused by bulky substituents also plays an important role.

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Some important thermodynamic functions of dimerization process are determined in order to know the nature of bonding between the monomers in dimer. ΔH , and ΔG values are negative for the five thiazine dyes. ΔH and ΔG values do not differ very much upon progressive methylation. ΔS values, which are also negative, increase to much larger extent due to methylation. It suggests that aggregated dyes are more ordered than free monomer dyes. In general, the high values of ΔH and ΔS can be attributed to the role of hydrogen bonding in aggregate formation apart from hydrophobic and π - π interactions.

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The dimer spectra have been interpreted by using Exciton theory, which predicts a splitting of the electronic transition in the dimer. The model offers a theoretical method for treating the resonance interaction of excited states of weakly coupled composite systems. The vibrational structure in spectra and vibronic interactions are neglected in this treatment. The decomposition of a dimer spectrum into two bands (monomer) show that the monomer visible spectrum corresponds to an electronic transition with two vibronic bands. Transition moments, oscillator strength and resonance interaction energies are determined from the dimer spectra. Using these values twist angle θ and the distances R'_I and R'_{II} (for two different models) between the monomer units in the dimer have been calculated for all the dyes. In view of the results of the previous as well as present study model I seems to be more appropriate.

The interdipole distance (R'_I) varies from 5.59 to 6.76 $\overset{\circ}{\text{A}}$. The lowest value 5.59 $\overset{\circ}{\text{A}}$ is for the AzA. The twist angle θ varies from 28.4 $^\circ$ to 34.8 $^\circ$. The highest value is associated with thionine. No systematic variation of the above parameters is observed on progressive methylation of the dye molecule. It seems apparent that apart from the steric effect hydrophobic as well as the electron donating nature of methyl groups are also involved in the process of dimerization. These are discussed in section 3.3.2. Although the exciton model as described in this section is a simplification of highly complicated problem, it offers

reasonable interpretation for the dimer spectra of present dye systems. (page 87-94)

In section 3.3.3., the dimer spectra of the five dyes are further analysed by vibronic exciton band model and the results of the analysis are given. The additional advantage of the model is that it allows one to analyse the dimer in further detail with respect to the strength of exciton coupling, the frequency and intensity of band origin, band width etc. The monomer spectra were fitted to a five parameter Gaussian equation, assuming that the spectra are due largely to a single harmonic vibronic progression, because some of the monomer fitting parameters are required to fit the dimer spectra. The dimer spectra were calculated and fitted to an adiabatic model using some monomer parameters and the spectra which refer to zero angle between the transition moments (i.e., the minimum series is zero in each spectrum) are shown. Although the monomer spectra fittings are satisfactory, dimer spectra fittings are not always very well. The ν_{00} , which is the position of the (0,0) band of each of the two monomers in dimer, undergoes hypsochromic shift relative to that of the free monomer. The exciton interaction parameters (ϵ) are small ($\epsilon = 0.9$ to 1.15), which provides some supports for the model.

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The electrochemical behaviour of the dyes on clean and modified (montmorillonite and ZSM-5) glassy carbon electrodes as well as the electrochemical processes involved therein in the presence of Fe(III) ions as an oxidant have been discussed in chapter 4. A brief review of the previous work on the redox properties of various dyes on clean and modified electrodes using cyclic voltammetric technique is presented in section 4.1.

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The experimental procedure for electrochemical analysis using cyclic voltammograph is presented in section 4.2. The preparation of colloidal Pt, montmorillonite and ZSM-5 suspensions and the modification of electrode surface are also cited in this section

(page 111-113)

The criteria related to the reversibility and the results thereof on a clean glassy carbon electrode (GCE) in different solvents are discussed in section 4.3.1. The formal potential values (average) for the five dyes are 0.205, 0.175, 0.207, 0.281 and 0.196V for Th, AzC, AzA, AzB and MB respectively in aqueous medium. Voltammetric measurements are consistent with two electron reversible redox couples of dye/leucodye pairs. The value of $0.058/\Delta E$ is rather low ($\ll 2$) even at slow scan rates possibly due to the result of two successive one electron reversible charge transfer, with a fast protonation of the

intermediate to form a species which is more easily reduced than the dye molecule. The current ratio values, $i_{pa}/i_{pc} < 1$, suggest that the electrogenerated leucodyes are involved in reactions which prevent their reoxidation upon scan reversal. Assuming reversibility of electrode reaction, the effective diffusion coefficients of the dyes in different solvents have been calculated at scan rate of 20mVs^{-1} . The values for thionine are 3.05×10^{-6} , 1.80×10^{-6} and $1.10 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ in water, ethanol (50% v/v) and triton X-100 (0.001M) respectively. There is no systematic change in the diffusion coefficient values with the progressive alkylation of dye molecule. But the effect of solvent is very prominent. The nature of the cyclic voltammograms obtained from concentrated dye solution ($1-2 \times 10^{-4} \text{ M}$) in the presence of 0.1M KCl and the effect of pH 's therein have also been discussed specially in view of reactant and/or product adsorption on the electrode surface. The heterogeneous rate constant k for the quasi-reversible processes of the dyes is determined. The kinetic measurements are carried out within the range $300-1000 \text{ mVs}^{-1}$ scan rates. All the values are found to be of the order of $10^{-3} \text{ cm.s}^{-1}$. (page 113-130)

A preliminary study of electrochemistry of dye incorporated montmorillonite and ZSM-5 modified electrode has been discussed in section 4.3.2. The presence of polyvinyl alcohol and Pt in the clay film is found to be critical in attaining better

electrochemical activity of the modified electrode. The modified electrodes exhibit quasi-reversible redox wave of the dyes. At slow scan rates the curves obtained from plotting of I_{pc} vs $v^{1/2}$ deviate from linearity significantly which suggests that the electrode processes are of diffusion type only at high scan rates. However, a rough estimation of apparent diffusion coefficient in montmorillonite film shows that the transport of the charge carriers in montmorillonite modified electrode occurs principally via electron hopping process within the film. Except thionine, the current output for all the dyes are substantially less in clay modified electrode than that in zeolite modified electrode. (page 131-139)

Although Fe(II)/Thionine cell is the most successful PG cell for solar energy conversion, dissipation of free energy due to thermal back reaction of leucodyes with Fe(III) ions constitutes a vital problem. In section 4.3.3., an electrochemical investigation of all the dyes in the presence of Fe(III) ions is reported. The theory of catalytic regeneration mechanism involving an electrode reaction followed by a coupled chemical reaction is applied to derive kinetic parameters of homogeneous reaction. The second order rate constants for the reaction of thiazine leucodyes with Fe(III) ions is found to increase from 0.25×10^4 to 1.6×10^4 lit/mol.s^{-1} upon monomethylation of thionine and to vary from 0.7×10^4 for the dimethyl derivative to 1.4×10^4

lit/mol.s⁻¹ for tetramethyl one. The electron donating nature as well as hydrophobic characteristics of methyl group influence the kinetics of the homogeneous reaction. (page 139-147)

Since the nature of bonding of dyes on montmorillonite and ZSM-5 (zeolite) and the ion exchange characteristics of these substances have a vital role in the electrodic processes of modified electrodes, an investigation on the interaction of montmorillonite and ZSM-5 with the thiazine dyes has been discussed in terms of adsorption and metachromasy in chapter 5. The structure of montmorillonite and ZSM-5 is briefly discussed in the introductory part. A review of the earlier works on adsorption and metachromasy is included in section 5.1.

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The method of preparation of pure Na-montmorillonite along with the experimental techniques of the study of adsorption and metachromasy are presented in section 5.2. (page 164-166)

The adsorption isotherms of the dyes on both the substances (montmorillonite and ZSM-5) are of H-type i.e., of high affinity class indicating a strong adsorbate-adsorbent interaction. From the structures of the thiazine dyes, it is clear that all the dyes can be involved into an ion exchange type of sorption through -S- or ->N- which become positive charge centres by

resonance. These structural considerations assign to the dyes a predominantly flat orientation onto the clay and zeolite surfaces, although other possibilities are not entirely excluded. The probability of distribution among the different orientations is conditioned by various factors such as the basicity of the nitrogen group, the number of resonating structures, the molecular geometry of the dye cations, the nature of the exchange sites, etc. It is, however, to be noted that the flat position is possibly attended with the minimum potential energy.

The adsorption data of all the dyes are found to fit with the Langmuir's equation. The equilibrium constant (Langmuir bonding constant) values in the case of montmorillonite are higher than that of ZSM-5. The variation of adsorption equilibrium constant values due to progressive methylation is found to be similar to that of the variation of dimerization constant values of the dyes. But the maximum adsorption capacity values of both (montmorillonite and ZSM-5) do not vary systematically on methylation of dye molecule. The results suggest that steric hindrance, hydrophobicity, electron donating nature of the methyl group and the specific orientation of the dye molecules on the surfaces are operative simultaneously. All these are discussed in section 5.3.1. (page 166-170)

In section 5.3.2., metachromasy of the dyes in montmorillonite has been described. All the dyes show

bathochromic shift of the α band followed by a hypsochromic shift of the β band as the clay content of suspensions increases. The absorbance intensities of both the bands α and β also changes with clay concentration. The α bands are attributed to monomeric forms of the dye and β band is to dimeric forms. It is assumed that metachromasy in montmorillonite is the consequence of π interaction between the oxygen plane of the aluminosilicate layers and the aromatic dye. (page 170-174)

The metachromasy of the dyes in the presence of ZSM-5 could not be studied precisely due to the excessive scattering of light by the zeolite particles