CHAPTER-I
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1.1: INTRODUCTION

Dyes are largely used in textile industry, paint industry, medicine pharmaceuticals etc. As chemists, we are interested in their molecular structure and reactivity.

The molecules behave differently under different experimental conditions and it is well known that depending upon the conditions like pH of medium, temperature, solvolysis....etc., such species show differential behaviour. In addition to these, the processes like ionisation, dimerization and association etc. are also involved due to which a quite large number of species may be produced by a molecule.

Despite the fact that solutions are the preferred medium for any industrial and laboratory chemical processes, our fundamental understanding about this phase of matter remains extremely limited. There has been extensive research interest in liquid phase interactions over past two decades and much of this work has been focussed on neat solvents; because they are widely considered to be simplest starting points for such investigations. Because the interaction between individual molecules in solution occur frequently and have a short persistance time, the most common approach to the solvation and solution phase dynamical relaxation process has been to use a spectroscopically active probe molecule to "read" the information of interest from the solution. Virtually, all our present understanding of solution phase dynamics stems from spectroscopic experiments on dilute probe molecules. Depending upon structural and optical properties of probe molecules, intermolecular interaction can be probed over a distance from $1A^o$ - $10A^o$ [1,2]

Fortunately enough, now a days we have an array of experimental techniques for such diagnostic as well as analytical investigations leading to deep insight in the infrastructure of molecule and its changes in it under different experimental conditions. In general, modern trends in spectroscopic techniques have suppresed the other classes, both in applicability and precision.

Absorption and emission spectroscopy is an important branch of spectroscopy in which high order of sensitivity and extreme selectivity of investigations of molecular properties is possible. Needless to say that the high degree of sensitivity and high order selectivity demands high precision in the techniques and extremely judicious selection of experimental parameters. With the availability of high sensitivity spectrophotometers and spectrofluorimeters, with automatic recording and printing devices of high precision and ease of operation, it is possible to study many aspects of molecule properties under different experimental conditions with very high accuracy.

Though large body of experimental data is available on single solvent systems there is less extensive study on binary solvent systems.[3-11] Moreover, the study on the complex salts formed among the organic dyes is extremely limited. The common conclusion of studies on solutions of these complexes is that, bulk properties of binary solvent systems, such as viscosity or dielectric constant does not reflect the molecular scale interactions responsible for dynamical behaviour of probe molecule. This is not a surprising result because discrete molecular nature of solvent can give rise to a significantly non uniform environment for the solute molecule.

The solvent polarization effect on the intermolecular interaction is complex. The bulk water enlarges the polarity of solute which increases the bimolecular interactions. However, this enhancement of polarity of monomer, promotes a reduction in flexibility of charge distribution of interacting molecule and this leads to cancelleration, at least partly, of energy contributions due to solvent - solute and solute - solvent polarizations.

Any substance which has an ability to impart colour to some other material is called a `Dye'. The basic requirement of good dye is that it should remain strongly fixed on the material and should not fade even after long time or it should not be washed out.

The dyes have a property to absorb light incident upon them and the colour property of a dye is dependent upon the wave-length of light absorbed. Some dyes have a property to absorb all the light incident upon them and hence no light is reflected, due to which such dyes appear to be black. If the incident light is totally reflected, the dye appears white. The absorption spectra of dyes depend upon various factors like structure of dyes, solvent used, pH of medium, temperature etc. and in addition to this, processes like association, dissociation, solvolysis etc. also affect the wavelength of maximum absorption and modify the nature of electronic spectra.

Some dyes have fluorescent properties and variation of fluorescence is observed due to changes in the environment of the dye. Thus the nature of the solvent and the nature of dye play an important role and affect absorption and emission spectra.

Many dyes when mixed in aqueous solution, form a complex salt composed of organic cations and organic anions. The absorption and emission spectra of such dye complex salt is also modified by changes in solvent, pH, temperature etc.

The characteristic absorption and emission spectra of dyes and also the colour properties of dyes are dependent upon chemical constitution of dye molecule. Hence, it is also essential to consider the correlation between colour and chemical constitution of dyes in general.

1.2 :SOLVATOCHROMISM

Nowdays for chemist, the careful selection of an appropriate solvent for study of reaction equilibrium and absorption charateristics is a part of craftman's skill. It is well established that the rates and the equilibrium positions of chemical reactions, as well as the positions and intensity of absorption bands in UV/VIS/Near I.R./I.R./N.M.R. and E.S.R. spectroscopy are solvent dependent.[12-26]

The influence of solvent on reaction was first shown in 1862 by Berthelot and Pean-de-Saint-Gilles[27] in their study on esterification of acetic acid with ethanol, and followed by pioneering work, by Menshutkin [28] in 1890, on alkylation of tertiary amines with haloalkanes. According to Menshutkin " A chemical reaction cannot be separated from the medium in which it is performed" and this statement still remians valid and has been more causually expressed by W.J. Albery [29] recently, as "In searching to understand the reaction in solution, the baby must not be separated from it's bath water".

The influence of solvent on the position of chemical equilibria was discovered in 1 896 by Claisen [30] and Wislicenus [31] independently with simulteneous discovery of keto-enol tautomerism in 1,3-dicarbonyl compounds. Claisen wrote, "It depends on nature of substituents, the temperature and for dissolved compounds also on the nature of solvents, which of the two forms i.e. keto form or enol form, is more stable. In 1903, Stobbe [32] reviewed these results and classified solvents into two groups according to their ability to isomerize tautomeric compounds. His classification reflects the modern division of solvents as hydrogen bond donor [(HBD) protonic] and non-hydrogen bond donor [non HBD, aprotic] solvents

The few recent examples from different areas quoted below demonstrate a powerful influence of solvent on chemical reactions and spectral emission and absorption characteristics. Smithrud D.B. [33,34] and Diedrich F. [35] have shown that the equillibrium constant for 1:1 complex formed between macrocyclic cyclophane receptor and pyrene varies by a factor of ca 10^6 upon changing solvent from carbon disulphide to water, which corresponds to solvent-induced difference in the Gibbs-binding energy $\Delta (\Delta G^o) = 8.1$ Kcal/mol.

The study of comparison of unimolecular heterolysis rate constants of 2-chloro-2-methyl propane in benzene and water has been carried out by Abraham M.H.[36,37,38] and Dvorko et. al. [39] and it is revealed that the rate of reaction is accelerated to an extent of ca 10^{11}, with increasing polarity of solvent.

The effect of solvent on interamolecular charge transfer UV/Vis/Near-I.R. absorption band of solvatochromatic, 2,6-diphenyl (2,4,6-triphynyl- 1 -pyridino) phenolate betaine dye have been studied by Richard[12-16] and it is observed that the absorption band is shifted from λ max 810nm to λ max 453 nm. on changing the solvent from diphenylether to water. This corresponds to solvent induced change in the excitation energy of ca 28 Kcal/mol.

Wohar et. al. [40] have shown that, there is solvent induced I.R. frequency shift for E=0 stretching vibration of tetramethyl urea by DV = 71 cm^{-1} in going from n - hexane (v = 1656 cm^{-1}) to water (v =1585 cm^{-1}) as solvent. Recently Kolling [32] and Fawcett et. al.[33] have reported corresponding solvent effects on the I.R. spectra of ethyl acetate [v(C=o)] and acetonitrile [v(C=N)]

$\Delta\nu$

Scherez et. al.[41] have studied the effect of solvent on the fluorescence spectrum of 1-Phenyl -4-[(4-cyano-1-napthyl}Methylene]-piperidence.The study has revealed that the emission maximum is shifted from λ Max = 407 to λ max = 694 by changing the solvent from n-hexane to acetonitrile.

All these examples lead to a conclusion that change of medium affects the absorption and emission characteristics of substances. The responsible factor for all these effects of medium, is the differential

solvation i) Reactants and products
(-> position of chemical equilibria);
ii) reactants and activated complexes
(-> rate of chemical reactions); or
iii) molecules in the corresponding ground and excited state
(-> physical absorption of electromagnetic radiation.)

The extent of differential solvation depends upon the intermolecular forces between solute and the surrounding molecules. The intermolecular forces include, non-specific forces, such as purely electrostatic forces arising from coulombic forces between charged ions and dipole molecules, (i.e. ion/ion; ion/dipole and dipole/dipole) and polarization forces that arise from dipole moments induced in molecules by nearby ions or polar molecules (i.e. ion/non -polar molecule, dipole/non-dipolar molecule, two non polar molecules), dispersion energy as well as hydrogen bonding between HBD (hydrogen bond donor) and HBA (hydrogen bond accetor) ions or molecules and eletron pair donar (EPD)/electron pair acceptor (EPA) forces [41,42,43]. Obviously intermolecular solute-solvent interactions are of highly complicated nature and very difficult to determine quantitatively.

Chemists have tried to understand solvent effects in terms of so called solvent polarity which is not easy to define and express quantitatively. The definition of solvent polarity given by Richard, C. [12] and Richard, C. [42] in 1965 seems to be becoming more and more accepted by scientific community. [43,44,45,46] Accordingly, solvent polarity is defined simply as solvation capability or solvation power of solvents, which in turn depends upon the action of all possible, specific and non-specific, intermolecular interactions between solute ions or molecules and solvent molecules, excluding, however those interactions belonging to definite chemical alteration of ions or molecules of solute, such as protonation, oxidation, reduction, chemical complex formation ...etc. But even with this concept of solvent polarity it cannot be expressed quantitatively as single physical solvent parameter as dielectric constant, dipole moment... etc. Hence, spectroscopic absorption study may serve suitable model process for recording solvent effects.

The study of spectral absorption of chemical compound by Kundt[47,48] Scheibe et al.[49] and Sheppard [50] have revealed that the absorption of light by chemical compounds is influenced by surrounding medium and solvents and can bring about the change in the position, intensity and shape of absorption bands, Hantzschalter [51] termed this phenomenon as **"SOLVA-**

TOCHROMISM". However, generally accepted meaning of solvatochromism differs from that introduced by Hantzsch [12-16] and it is recommended to replace `Solvatochromism' by the term `Perichromism' (Greek, Peri-around) but the term solvatochromism is well established. A hypsochromic (or blue) shift of the UV/Vis/NIR absorption band with increasing solvent polarity is usually termed as, "Negative solvatochromism". Obviously the solvatochromism is caused by differential solvation of ground and first excited state of the light absorbing molecule or it's chromophore. If with increasing polarity, the ground state molecule is better stabilized by solvation than the molecule in the excited state, the negative solvatochromism will result or vice versa. On the other hand, better stabilization of the molecule in the first excited state relative to ground state, with increasing polarity will lead to positive solvatochromism.

The solvatochromism observed depends upon the chemical structure and physical properties of chromophore and solvent molecules, which for their part determine solute/solvent interaction in ground state and Franck - Condon excited state. The Franck-Condon excited state means first excited state with the solvation pattern in the ground state. The relation between sign of solvatochromism and structure have been studied by various authors [12-16, 52-59] In general, dye molecules with a large change in their permanent dipole moment upon excitation, exhibit a strong solvatochromism. If the solute dipole moment increases, a positive solvatochromism normally results, and if the solute molecule's dipole moment decreases on absorption of energy negative solvatochromism is generally observed. Such solvatochromic behaviour have been observed among the meropolymethine dyes and among the compounds with intermolecular or intramolecular C.T. absorption.[12-16.52,57] In addition to this, ability of solute to donate or accept hydrogen bonds to or from surrounding solvent molecules in the ground state and Franck-Condon excited state, also determines the sign and extent of solvatochromism [60-65] Brooker et. al.[46] and Botrel et. al.[66] and Jacques[67] have studied solvatochromism among some merocyanine dyes and observed that such dyes show even an inverted solvatochromism, i.e. their longer wavelength solvatochromic absorption bands exhibit first bathochromic shift and then hypsochromic band shift, as the solvent polarity increases. This is due to solvent induced change of electronic ground state structure from less polar (in non-polar solvents) to a more dipolar chromophore (in polar solvents) with increasing polarity.[66,67] Thus based on search for quantitative relationships between the solvent influence on UV/Vis/near I.R. spectra and physical solvent parameters, Kundt [47,48] proposed a rule in 1878 which states that, "Increasing dispersion, i.e. refractive index of solvent, results in bathochromic shifts of the solute absorption bands". Various theoretical treatments of solvent effects on the absorption spectra have been discussed by different authors.[53-58, 68-95]

✓ The complexity of solute/solvent interaction has led to corresponding complex, theoretically derived relationships between solvent induced band shifts and physical parameters of solute and solvent.

✓ 1.3: SPECTROSCOPIC STUDY OF DYES :-

✓ Dyes were first used by Windaus and Bruken [96] after the phenomenon of photodynamic action had been discovered by Rabb (96) in 1990. Before this the dyes were used only for imparting colour to an object. After the postulation of Kautsky and-de-Brujin [97], that single oxygen is a reactive intermediate, the work of Foote and Wexler [98] and Corey and Taylor [99] on synthetic application of dye sensitized oxidation process established the postulate. This work opened a new field for study of dyes with respect to their structure, colour property, effect of solvent, pH, pressure and the effect of solute - solvent interaction on the electronic spectra of dyes under various experimental conditions and also on the change in properties of dyes.

✓ The interaction of charged molecules and electrons with the solvent is also important in many chemical reactions. Many dyes depending upon experimental conditions of temperature, pressure, concentration, nature of solvent ...etc. have been found to exist in isomeric forms, due to which absorption and emission spectra show change in shape, intensity and wave length of maximum absorption and emission. The dyes in different solvents and with different concentrations, show dimerization, trimerization .... etc. Such changes can be studied by absorption and emission spectra of dyes under different experimental conditions.[100]

✓ The study of absorption and emission spectra of blue type ion radicals by Hausser and Murrel[101] have shown the formation of dimer at liquid nitrogen temperature; due to charge transfer absorption, while the work of Erickson[102] shows that the antistoke's luminescence of Rhodamine - 6G in ethanol is temperature dependent. The reports of Konig et. al.[103] have shown the anomalous fluorescence behaviour of organic dyes in solution. It is observed that organic dyes like phthalocyanines, porphyrines, cryptocyanines Rhodamine - 6G etc., in solution show anomalous fluorescence i.e. fluorescence at higher energies than those of S_1 - S_o transistion. Such anomalous blue fluorescence of cyanine dyes have also been reported by Teuchner and Dhane.[104] Further study among pseudoisocyanine dyes reveal ed that in addition to intense fluorescence due to aggregation, fluorescence bands at longer wavelengths as well as with U.V. excitation, a blue emission on the shorter wavelength side of S_o - S_1 absorption bands are found. The former is suggested to be due to fluorescence of aggregates of different structures, while latter is shown to be the emission of photo excited `Sx' state of monomeric molecules and quenched by aggregation. [104]

The aggregation of xanthene type of dyes at higher concentrations have been reported by Joshi and Pant [105] and their studies on emission spectra have revealed that these dyes show enhancement of triplet emission. It is suggested that this is due to splitting of singlet-singlet level whereby lower forbidden excitation component comes closer to triplet state. This results in increase of intersystem crossing rate and hence enhancement of triplet emission. The work on eosin and erythrosin dyes shows that aggregation of dyes affects the radiative (T_1 -> S_o) and non radiative [(T_1 -> S_o) and (S_1 -> T_1)] transitions in xanthene dyes.

The effect of intermolecular bonding between solvent and dyes was studied by Simirnova et. al.[106] and it is observed that this intermolecular hydrogen bonding affects the fixation of disperse and reactive dyes.

The study of Mishra and Dogra[107] on absorption and fluorescence spectra on 2 - amino - benzimidazole have revealed that nature of solvent and pH of medium affects the spectral behaviour of the compound. It is observed that the dication of the compound behaved as arylamine and arylammoniumion respectively in ground state, and study of absorption and fluorescence spectra of the compound at different pH values have supported this fact.

The study of the ~~the~~ effect of solvent and pH on the absorption and fluorescence spectra of 7 - aminoindazole was conducted by Phaniraj et. al. [108] and it is shown that the compound acts as proton donor in ‘S_1' state, in all the solvents. However, in ‘S_0' state, it acts as a proton acceptor in H - donor solvents, while in H - acceptor solvents it acts as proton donor. Similarly, the study of the effect of solvent on the absorption and fluorescence spectra of P - (imidazole-Y -1) phenol, carried out by Phaniraj and Krishnamurthy [109] have revealed that, the effect observed is related to co-planarity of imidazole and pH rings of P-(imidazole-Y-l) phenol in `$S_0$' and `S_1' states. Abou Sekknia et. al.[110] have studied the effect of organic solvents of different polarities, using quinoline compounds. It is observed that the band shifts of different quinolines are influenced by solvent polarities. The application of dielectric correlation showed non - linear relationship, which revealed that the dielectric constant of medium is not the only factor influencing the band shift and specific solute - solvent interactions apperantly played active role in this respect.

✓ Chatterjee and Co-workers[111] have reported, that conformation changes occur in a molecule, in polar solvents like MeOH, EtOH etc. and confirmed that the intermolecular H - bonding plays a significant role in spectral characteristics.

Ivan and coworkers[112] have studied effect of solvents and substituents on the absorption spectra of nitrosoaromatic derivatives and explained the influence of substituents on the C-atom and N-Nitrosocompounds. It is shown that, the influence of solvents on the absorption band is characteristics for $\pi-\pi^*$ transition and $n - \pi^*$ transition.

Sinha and Dogra [113] have studied effect of solvent on absorption and fluorescence spectra of 2 - (o-hydroxyphenyl) benzimidazole and shown the presence of different tautomers in the `$S_1$' state which have the same precursor in the `S_0' state. Similar study as a function of $[H^+]$ identified the presence of monocation, dication, Zwitterion, Phototautomers and mono anion species.

Rao Subha and coworkers[114] have studied effect of solvent and pH on the absorption and fluorescence spectra of 2 - amino chrysene. It is observed that the compound acts as proton donor in hydrogen accepting solvents and as proton acceptor in hydrogen donor solvents.

Study of effect of molecular structure and solvent on the stokes shift of cyanine dyes, conducted by Vranchev[115] has revealed that the stokes shift of cyanine dyes increases with increase in n of the solvent and nature of substituent on N - atom of due has no significant effect on stokes shift.

Machedlov-Petrosyan and Lyub chenko[116] have reported the effect of solvent on the ionization of sulphophthalein dyes. Their study have shown that the ionization constant of dyes -OH group in < 90 % acetone solution is linear function of inverse dielectric constant and increased with increase in concentration of acetone. Further it is observed that the effect of substituent on the ionization of -OH group is maximum in dipolar aprotic solvents and their solutions. The ionization of sulphophthalein dyes in alcohol and water was less than that in acetone due to H -bonding between solvent.

Ryzhikov and Gorbunova[117] have studied surfactant induced changes in the spectra of Rhodamine - 6zh dye solutions. It is observed that the addition of surfactants changes the conditions for absorption of dyes and changes in the spectra are limited to intensities and not affecting the shape of the spectra.

Study of Pal et. al.[118] on the electron absorption and emission spectra of some aniline compounds have revealed that the intermolecular bonding is very strong enough and resists the rupture by dioxane, in the excited state only in o-chloroaniline. It is observed that ground and excited electronic states are affected by intermolecular H - bonding.

Study of absorption spectra of dyes by Ivanov and Pavlyuk[119] have introduced a technique to estimate water content in various organic solvents like hydrocarbons, ethers, esters, ketones, amines etc.

Hutchings and Michael[120] have shown unexpected bathochromic shifts in visible absorption spectra of aryl azo dyes, which is related to intermolecular polarization effect and the solvent dipolarity.

1.4 : MALACHITE GREEN (MG.) :

Malachite green is a dye belonging to class of dyes known as triphenylmethane dyes. Rosanaline crystal violet etc. are some other examples of this class of dyes.

Malachite green is largely used in textile industry, Pharmacy, horticulture agriculture etc.

Study on various physiochemical characteristics has introduced the malachite green as a valuable tool for analytical chemist.

Shaburova et. al.[122] have used malachite green for spectroscopic determination of Silicon, While Sato Shigeya and Tenaka Hiroyuki[123] have used it for the spectrophotometric determination of Ge (IV). The spectroscopic characteristics of malachite green have been studied from different angles to know structural changes involved due to different molecular interactions involved.

Iopex[124] has studied the effect of concentration on the visible spectra of xanthene type or dyes like fluorescein, eosine and erythrosine. It is observed that the absorption band of non associated form in dilute solution, can be resolved into three overlapping bands, which represents single electronic transitions with three vibraonic modes.

Berberova et. al.[125] have studied interation of triphenlyl methane dyes, their leucobase and Pseudo bases by polarography and spectroscopy. It is observed that oxidation of leucobases of malachite green and crystal violet to dyes, occurred via the stages of reversible single electron oxidation to form neutral radical and reversible single electron oxidation of carbonium ion. Reaction of these dyes with alkali leads to respective trimethyl radicals. The cation radical intermediates are stable in absence of oxygen.

Mareano and Aranguren[126] have studied the absolute values of non-linear susceptibility of malachite green dye solutions by polarization spectroscopy and introduced a method of measurement of resonant, third order susceptibility of dyes.

Ballard[127] have carried out Helium (I) photo electron studies of surface films of malachite green hydroxide and it is revealed that the film of malachite green is in the covalent form, even though ionic form is more predominant in solution.

The 1% solution of malachite green in deionised water, gives the absorption peaks (λmax) at 422 nm and 618 nm[128]. However the absorption spectrum of MG$^+$ shows maximum absorption λ max = 625 nm.

✓ Philipenko et. al.[129] have studied modifications of ion associates of malachite green cation and alkyl sulphate anions by non ionic surfactants in aqueous solutions. It is observed that addition of cyano Ats, se - 20 (peg - fatty ether) to aqueous solution of malachite green and asociation of malachite green with alklyl sulfate caused a decrease in the light absorption of solution and bathochromic shift of absorption maximum.

✓ The applications of malachite green and malachite green leuco base are due to inherent photochemical nature of the compound. Recently few reports on the photochemistry of leuco base of malachite green (MGH)[130] in different solvents have been appeared. Klevens, [131] Gratzel et. al. [132], Malliaris [133], Miller and Evans, [134] have reported effect of surfactant solutions on the physicochemical properties of many systems. In case of such systems, it is observed that the photochemistry as well as localization of chromophore having alkyl substituent in the micellar solution depend upon the length of alkyl chain. The reports of Teomposon et. al.[135] Colaneri et. al.[136] and Sakaguchi et. al. [137] are also in favour of this statement.

Reda and Kaushi [138] have synthesized long chain malachite green leuco base (LMGH) and studied the spectroscopic properties of the compound in organic solvents and micellar solutions. It is observed that the absorption spectra of MGH in diffrent organic solvents is independent of dielectric constant, but emission spectrum varies with solvent polarity, i.e. dielectric constant. It is well known fact that solvent polarity affects absorption and emission spectra of dyes.

The spectroscopic investigations of Malik and verma [139] on dyes like malachite green, rhodamine-6G, and alizarin red have revealed that there is no spectral shift with change in concentration and Beer's law is obeyed in the concentraction rarge as, for malachite green from $4x10^{-6}$ to $6x10^{-5}$M, for rhodamine 6-G from $4x10^{-6}$ to $4x10^{-5}$ M and for alizarin red from $4x10^{-6}$ to

15×10^{-5} M, in aqueous solution. They have suggested that these dyes exist in monomeric form and there is no possibility of association of molecules in the concentration range stated above. Further, study of effect of addition of soap to dye solution in very small amount, as low as 8×10^{-5} M, have revealed that the absorption maximum of malachite green is shifted from 625 to 640 nm and in case of rhodamine 6-G, it is shifted from 535 to 545nm. Also increase in optical density is observed at 640 nm for malachite green and at 545 nm for rhodamine 6G..

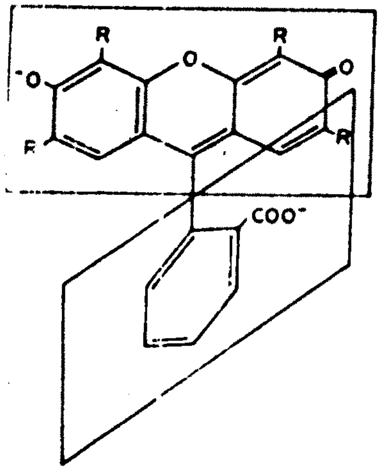
Zhang Yulan [140] have studied the effect of solvent on the absorption spectra of azo dyes and have shown that interaction of dyes and solvent due to disperse force, induced force or dipole force modified the absorption spectra.

Spear Kenneth et.al.[100] have studied photo dissociation dyanamics of malachite green and reported that the malachite green carbonium ion (MG^+) is formed, which is responsible for green colour and the photo dissociation occurs in polar solvents only. However, strong exponential increase in the absorption of MG^+, cannot be accounted on simple excited state ionisation mechanism. The absorption spectra of MG^+ ion shows λ_{max} at 625 nm

1.5 ROSE BENGAL (RB.)

Rose bengal is a dye belonging to xanthene type of dyes. The other examples of this class are : fluorescein, eosine erythrosine etc.

The dyes in general have planar hydrophobic structure with extended system of signle and double bonds and the hydrophilic groups in the peripheral region as shown below.



Molaecular Structure of Xanthene dyes

Neckers and his group[141] have carried out systematic studies on the structural dependence of aggregation characteristics of xanthene dyes Gouterman and other[142] have made extensive studies on covalently linked porphyrins to assess the importance of dimer geometry on the strength of interaction between two flat molecules. It is believed that special electronic transitions within the dimer contribute to its important role in the charge separation process in photosynthetic reaction centre. (Aggregation can bring about drastic changes in the physical and chemical properties of dyes. The dyes having planar hydrophobic skeleton with hydrophilic substituent, tend to aggregate in aqueous solution.) The formation of aggregate modifies absorption spectrum and photophysical properties of dye. The strength of aggregation is strongly dependent on structure of the dye molecules, nature of solvent, nature of added electrolytes, temperature etc.[143]

The extensive conjugation apparent in the dye structure results in small S_1 -> So energy difference and large dipole strength of transition. Hence the spectrum of dye molecules appears in visible region, with high molar absorptivity, imparting colour and depth. All these properties help in aggregation phenomenon. In general, aggregation is normally observed in aqueous solutions but examples of aggregation in ethanol, glycerol and even in benzene have been reported.[143]

Absorption and emission spectroscopy are the techniquies, which are most widely used to study the aggregation phenomenon and the solute - solvent interactions. The true spectrum of the dye solution in water is obtained at very low concentration range 10^{-7} to 10^{-5} M and at higher concentration deviations from Beer's law have been observed.[144 - 147] The simplest prototype of stacking interaction is a dimer and few studies on trimerization also have been reported[143]

Dannian and Neckers[148] have reported formation of aggregates with trimer, tetramer to multimer structure for xanthene type of dyes. In general among these dyes, greater the hydrophilic to hydrophobic ratio in the dye structure, greater is the driving force for aggregation. With increase in concentration spectral changes appear and molar extinction coefficient decreases with blue shift of λmax.

The general features of the absorption spectra of dimers of planer dyes are splitting of monomer band into a strong blue shifted component and variable intensity red shifted band. The type of forces responsible for aggregation of dyes in solution are :

i) London's dispersion force.
ii) Van-der-waals type additive force.
iii) Intermolecular hydrogen bonding.
iv) Coupling by hydrogen bonding solvent bridge.
v) Co-ordination with metal ions to reduce (intermolecular) repulsive force.
vi) Hydrophobic interactions.

A good understanding of splitting parameters can be realised by the theory of excitionic interaction developed by Davydov[143] to explain the interactions among the chromophores in molecular crystals. Application of excition theory to dimers and trimers of dyes have provided most possible explaination for concentration dependent spectral changes for dye aggregates. This theory is applicable to weakly coupled chromophores such as van-der-waals aggregates or H-bonded systems in which intermolecular distances are so large, that electron exchange between moieties is excluded. On absorption of suitable photon, any one of the N-molecules of the aggregate can be excited. The resonance interaction between singly excited zeroeth order states of such loosely coupled oscillators, results in creation of stationary excited states. Each of stationary excited states involve zeroeth order discription. Thus, in excited states, excitation is delocalised. The excitonic interaction between the transition dipoles is purely electrostatic in nature and is strongly dependent on the geometry and interplanar distance in the composite molecule.

Jankiraman[149] have carried out study of crystal structure and molecular structure of rose bengal derivatives and it is observed that rose bengal like other xanthene dyes exists in three or more forms with different structures. These structures were, lactone form, Zwitterionic form and quinoidal form. The spectroscopic study by Zhu and Parker[150] have revealed that rose bengal has stable quinoidal structure.

Study of effect of solvents on absorption and emission characteristics of rose bengal and related dyes have been conducted by various scientists.

De-valle et.al.[151] have carried out comparative photophysical study of rose bengal, eosin-Y and their monoethyl and dimethyl derivatives. It is observed that the fluoresence quantum yields and life times of rose bengal, eosin-Y and their ionised or neutral methyl ethers and methyl esters in 1:1 mixture of dioxane with aqueous buffer of pH = 0.5 or pH = 8.0 are much higher when the phenol group in xanthenic moiety is ionised, than when it is in neutral or methylated form. The infulence of state of COOH group is much lower when it is in Ph moiety. Non-emissive mols, very probably agreegates were observed in 2 x 10-6 M solutions of the neutral forms. Similar association have been reported by Lucia Costantino et. al.[152] and Michaelis[153] for acridine orange dye in aqueous solution. They have also shown that such characteristic behaviour is also shown by all metachromic dyes like methylene blue, crystal violet, cyanine dyes and acridine derivatives.

Study of Danian and Neckers[148] on absorption and emission spectra have revealed that rose bengal forms H-type aggregates in water and protic polar solvents.

Tezak et. al.[154] have carried out study of precipitation of rose bengal in aqueous solutions of lanthanum nitrate. The spectroscopic data have shown that solutions are predominantly ionic.

Amal - Guerri et. al.[155] have carried out spectrophotometric study of ionization and isomerization constants of rose bengal, eosin - Y and some derivatives in 1:1 dioxane and aqueous buffer mixture. It is observed that the quinonoid form is ionised first and carboxylic groups shows much less acidity.

Martinez et. al.[156] haven shown that rose bengal forms four species such as $-H_3R^+$, $-H_2R$, $-HR$ and R_2 at different pH value and Ho.(where Ho is Hammet acidifying function for strongly acidic solutions). They have also shown that polymeric species and excimers are formed in ground state, and in the first excited state respectively at concentrations greater than 10^{-4}M.

Jambers et.al.[157] have carried out study of absorption spectra of rose bengal and its non polar derivatives. It is observed that the dissociation constant of the compound depends upon the nature of solvent.

It is reported by various authors[158-161] that -carboxyphenyl group and xnthene moiety of fluorescein dyes are perpendicular to each other and that the latter is largely responsible for the absorption characteristics of the dye molecule in the visible region. Hence upon charge in solvent from CH_3OH to CH_2Cl_2, the major change takes place in xanthene pattern of dye.[162] The change in structure from quinoid to lactonic form takes place on addition of HCl to aqueous solution of rose bengal.

Sidhu et. al.[163] have carried out, study of role of the dielectric constant of medium in dye sensitized photo oxidations and it is observed that change in dilectric constant of medium does not significantly affect the nature of proportion of reaction products in photooxidation reactions of phenothiazines etc. senstized by rose bengal or eosin-Y.

Sum of all these observations is that rose bengal exists in isomeric forms like quinoid form, lactonic form etc. and the equilibrium of these isomerism is affected by temperature, pH, dielectric constant of medium etc. Also rose bengal shows tendency to form aggregates like dimers, trimers, tetramers etc. in different solvents. Hence study of absorption spectra can reveal the state of dyes in different solvents and under different experimental conditions.

1.6 STUDY OF COMPLEXES

The absorbance measurements for dyes like MG and Rhodamine 6-G at 640 nm and 545 nm respectively have shown that there is large increase in the absorbance of dyes in presence of soap. This indicates a definite binding of soap with dye and it is suggested that probably a complex ion is formed.[139]

This fact developed an interest among the scientists to study complex formation among the dyes, and to study their spectroscopic characteristics under various experimental conditions.

Nelson (1952)[164] in his work on the conducting properties of dyes, has reported that, in case of cationic dyes with triphenyl methane structure, the dark conductivity is changed to appreciable extent by change of anion. Similar study on the conductivity properties of various dyes and their complexes formed between cationic and anionic dyes are studied by Kusabayashi[165] It is observed that, dye complex is formed between cationic dyes like malachite green, crystal violet, methylene blue and the anionic dyes like rose bengal, eosin-Y erythrosine and acid rhodamine etc.[165-167]. The dye complex formed have been found to contain 2 moles of cationic part and 1 mole of anionic part.[165-167] Further study of absorption spectra of dye complexes salt between malachite green and rose bengal have revealed that compound with formula MG_2. RB gives absorpiticn spectra which are different in solid film and in alcoholic solution. The longest wavelength absorption band of the complex is seen to split up into two bands although no such splitting is observed in the absorption spectra of two solid components. However, the study on absorpition spectra of MG_2. RB in ethanol by Kusabayashi et. al. have revealed that the absorption peaks and λ max values of peaks obseerved for complex salt in alcoholic solution are identical with those of individual components.[165,166]

Various reports on absorption and emission spectra of dye complexes are available. Study of Berberova et. al.[168] on oxidative dehydrogenation of malachite green have revealed formation of charge transfer complex of the type D_2A where `D' is donor while `A' is acceptor dye.

Qiu. Xingchu et. al.[169] have reported formation of 1:1 complex of malachite green and tetraphenyl borate and this property is used for testing purity of tetraphenyl borate by study of absorption spectroscopy of complex.

Constantinescu[170] have studied absorption spectra of complex formed between o, m and p-Nitro substituted malachite green and $AuBr_4$ The study of absorption spectra in benzene have revealed that, Beer's law is obeyed upto 0.5-3.2 mug of Au/ml and molar absorptivity is in the range 60,000-100,000 cm-1.

Study of Tamai Naoto et.al.[171] on malachite green (acceptor) and rhodamine-6G (donor) complex, have revealed transfer of excitation energy between dye molecules.

Levshin L.V. et.al.[172] have studied the types of agregation of molecules of rhodamine dyes in the mixture of polar and non-polar solvents, and it is observed that the structure of associated rhodamine dye molecules and composition of solvation shell change non-linearly in relation to ratio of polar and non polar solvents in binary system. Abd-El-Mottaleb et. al.[173] have studied the effect of temperature and nature of solvent on charge transfer complex association constant. It is observed that the complex association constant of cyanine type of dyes increases with increase in temperature and also as the solvent is changed from 3:2 ethyl alcohol-water-mixture to dioxane. Also, the complex association constant increases with increase in temperature in all solvents.

Polwski et.al[11] and Oscar and Neckers[12] have studied uv-visible absorption and fluorescence spectra of complex formed between amylose and rose bengal in aqueous solution. They have suggested two types of mechanism for complex formation, one leading to the structural changes of amylose by rose bengal, and other connected with non-fluorescent complex formation of amylose and rose bengal.

The reports on the spectroscopic study of dyes in different experimental conditions are available but study on the dye complex salt formed between cationic and aninonic dyes seems to be restricted to conductivity properties and very few reports are available on the spectroscopic properties.

1.7 : SCOPE OF PRESENT WORK :-

A vast amount of literature exists today on the effect of solvents on the absorption and emission spectra of chromophores.[175] It is generally observed that the absorption band of any electronic transition of a chromophore is shifted in solvent.[175]

Jambers and Neckers[176] have studied the effect of change of solvent on the absorption spectra of rose bengal and its non-polar derivatives and have shown that rose bengal exists in isomeric forms as quinoid form and lactonic form.

Zhao et. al.[177] have carried out study of absorption spectra of fluorescein dyes (xanthene type) and their ethyl and diethyl derivatives, in various solutions. It is observed that the absorption spectra shows shift in absorption peaks and decrease of absorption strength due to existance of equillibrium between the various isomeric forms of the dyes and their derivatives as Lactonic----> Quinoid-$^{-H}$---> Anion I -$^{-H}$---> Anion II

Spears et. al.[100] have carried out spectroscopic studies, on malachite green leucocyanide (MGCN) and its photodissociation.

It is observed that the ionic photodissociation of MGCN occurs only in polar solvents and the MG^+ ion has excitation coefficient of $1x10^5$ $M^{-1}cm^{-1}$ at 620 nm.

✓ Thus various reports on absorption and emission characteritics of dyes and their derivatives are available, but very little information is available on the absorption and emission properties of dye complex salts formed between cationic and anionic dyes.

Kusakayashi et. al.[165] have reported that cationic and anionic dyes together form complex salts which are composed of organic cations and organic anions. Many such combinations of two dye ions are possible. Different dye complex salts have been prepared by using cationic part of dyes like malachite green (MG), crystal violet (CV) methylene blue (MB) and the anionic part of dyes like eosine (EO), erythrosine (ER), Rose bengal (RB) and acid rhodamine (AR) the complexes formed have been studied by Seyewetz[166] and pelet-Jolivet[167] and it is observed that the complexes are formed by combination of 2 mol portion of cationic part of dye and 1 mol portion of anionic part of dye with the molecular abbrevations quoted above the dye complexes formed are given below with some of their properties.[165]

COMPOSITION	COLOUR	DECOMPOSITION TEMP °C
1) MG_2 - EO	dark purple	160
2) MG_2 - ER	dark brown	240
3) MG_2 - RB	purple	155
4) MG_2 - AR	dark green	220
5) CV_2 - EO	dark green	190
6) CV_2 - ER	dark green	195
7) CV_2 - RB	dark purple	175
8) CV_2 - AR	greenish brown	120
9) MB_2 - EO	dark green	190
10) MB_2 - ER	dark green	185
11) MB_2 - RB	brown	200
12) MB_2 - AR	green	210

For these dye complex salts conductivity properties are studied.[165] The study of absorption spectra of MB_2 RB complex as solid film and in alcoholic solution are found to be different. It is observed that longest wave length absorption band is split into two bands in spite of the fact that no such splitting is observed in solid absorption of these two components. However, the concetration effects and solvent effects on absorption spectra of these complexes have not carried out in detail. Hence in the present work, it is proposed to study the absorption spectra of dye complex salt MG_2 -

RB at different concentrations in the same solvent and the effect of solvent variation also.

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