CHAPTER-IV
DISCUSSION

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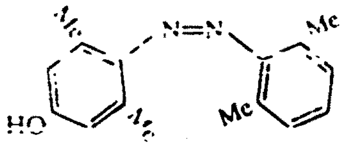
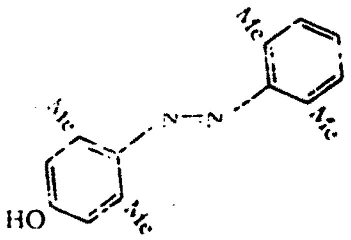
The results described in the previous Chapter can be explained on the basis of structural effects in the dye molecule as well as the solvent molecule. The absorption spectra of malachite green and rose bengal have been amply discussed and explained.

(According to Witts [1] theory dye is a combination of chromophores and auxochromes.) Depending upon the type of dye and nature of chromophoric and auxochromic groups the absorption of electromagnetic radiation in different region like uv/VIS/IR etc. is observed. Hence the absorption spectra of a dye is basically related to structure of dye molecule, however, the additional factors like solvent polarity, viscosity and the planarity and axis of polarizability of dye molecules etc. modify the absorption spectrum. [1,2]. It is well known that substituents and solvent polarity greatly alter the photophysical and photochemical properties of molecules, especially of those which have closely located excited states of different character. The effect can be explained in terms of inversion of low-lying excited states caused by solvent polarity or electron-donating/withdrawing substituents.

It is observed that preventing resonance by deliberate inhibition of co-planarity produces colourless substance, even through the molecule contains a chromophore[1] associated with an aromatic system e.g. mono azo dye, Cis-form is colourless as co-planarity is prevented by ortho-Me groups causing steric hindrance, but the "Trans" form is coloured because it is coplanar and resonance can take place.The structures are shown below :



cis
(colourless)

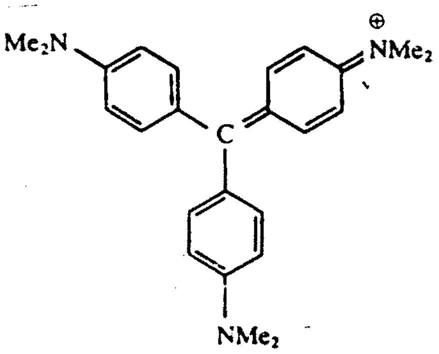


trans
(coloured)

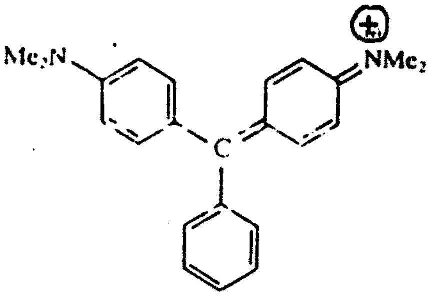
Coplanarity is prevented by o-Me.groups(steric hindrance)

The molecule is coplanar and resonanace can takes place

Similarly, the oscillations of delocalised pi-electrons may occur in more than one directions of the dye molecule. For absorption to occur the direction of oscillation (axis of polarizability) must be at right angles to the direction of propagation of light. Incase of C.I. basic violet, in the cationic form the three benzene rings participate in the resonance via their dimethyl amino groups in all directions in the plane of molecule and hence there is only one principal absorption peak (λmax = 590 nm). But in case of unsymmetrical molecule like malachite green, there are two axes of polarizability differing in degree, lying at right angles and thus two absorption peaks occur, one at λmax = 423 nm and other at λmax = 625 nm. The structures of these compounds are shown below.[1]

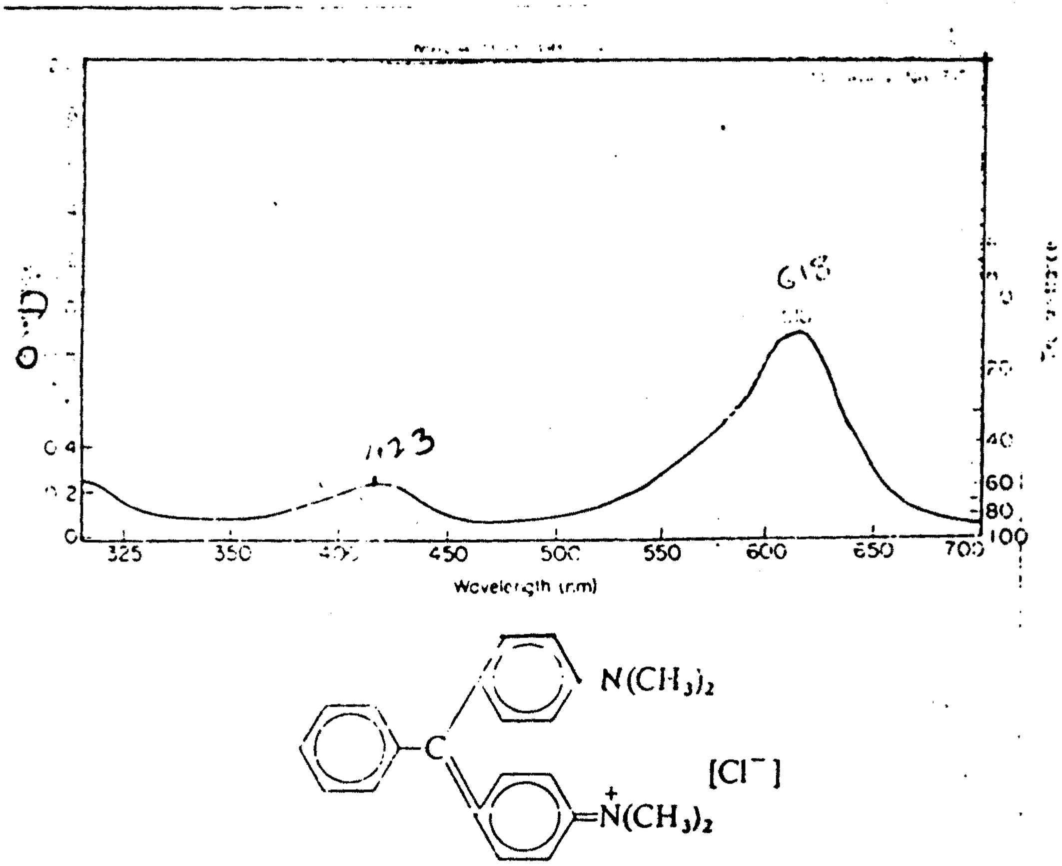


CI BASIC VIOLET



MALACHITE GREEN

Also the factors like association, dissociation, solvolysis etc. modify the absorption spectra of compound. Malik and Verma[3] have carried out spectroscopic studies of malachite green and have reported that, Beer-Lamberts law is obyed in the concentration range 4 x 10^{-6}M to 6x10^{-5}M and no shift in dye spectra is observed by change in concentration but addition of soap (C = 8 x 10^{-5}) causes a shift of λmax from 625 nm to 640 nm. This indicate a definite binding of malachite green with soap, probably in the form of ions. Also for basic

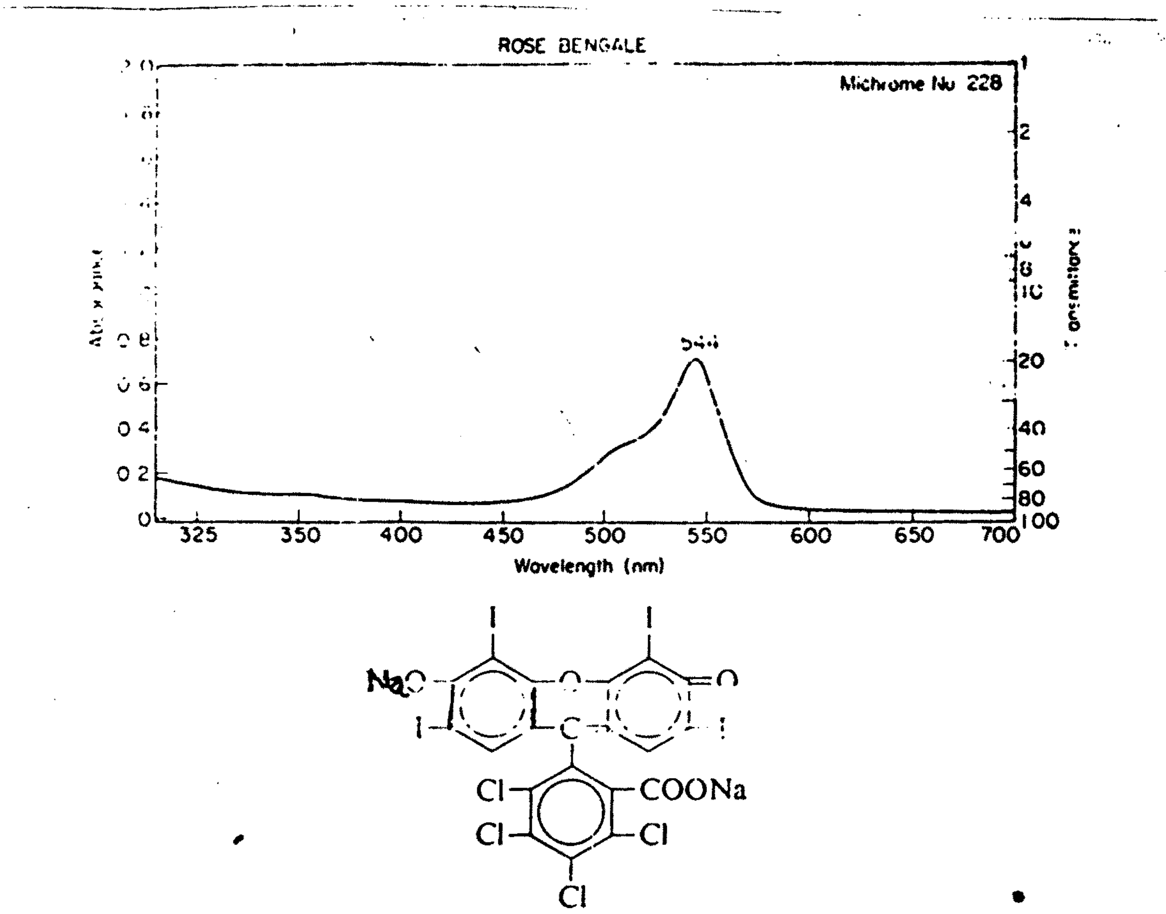


$C_{23}H_{25}N_2Cl$

Molecular weight 365: Cationic weight 330

Fig.10 : ABSORPTION SPECTRA OF MALACHITE GREEN IN AQUEOUS SOLUTION

dyes, no spectral shift was observed with change in pH (2.72, 7 and 9.12) but for acidic dyes it was not true[3] Malachite green is a basic dye belonging to triphenyl methane dye and forms complexes with various other anionic dyes, anions, metals etc. It is reported that formation of MG^+ ion in the solution is responsible for green colour of malachite green solution. The malachite green carbonium ion has a planar central carbon atom with phenyl rings out of the plane in a "Propeller" conformation [4,5] The study of MGCN complex in polar solvents have revealed that only in polar solvents Mg^+ ion released due to photodissociation.[5] The strong exponential rise of MG^+ absorbance cannot be explained by simple excited state ionization mechenism. Cremer and Cremer[5] have suggested that the ionic photodissociation and transient absorption of MG^+ is related to viscosity of solvent.[5-8] and absorption of MG^+ ion shows extinction coefficient $1x10^5$ $M^{-1}cm^{-1}$ at 620 nm and much weak absorbance in 300 nm[5](Fig.10). The rate of ionic photodissociation of complex increases with increase in dielectric constant of solvent when the dissociation occurs from lowest excited state. However, when the ionic photodissociation takes place from high energy excited state, the rate of photodissociation decreases with increase in dielectric constant. It is suggested that the complex (MGCN) has tetrahedral structure and wnen MG^+ ion is formed it is changed to



$C_{20}H_2O_5Na_2Cl_4I_4$

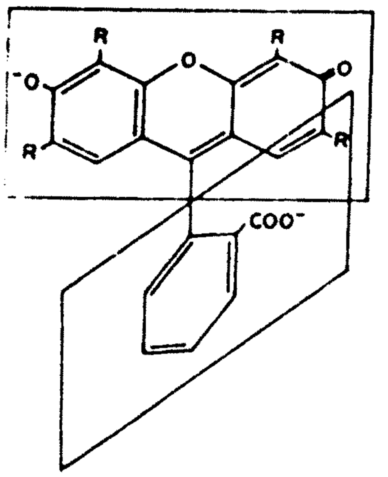
Molecular weight 1018: Anionic weight 972

Fig.11 : ABSORPTION SPECTRA OF ROSE BENGAL IN AQUEOUS SOLUTION

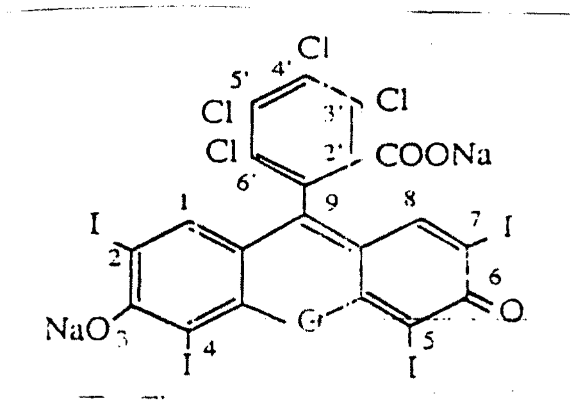
planar structure of carbonium ion. This transition depends upon the dielectric constant and during this transition a charge reorganization by solvent takes place, which modified the absorption spectrum. It has been also shown that malachite green (MG^+) monocation cannot be protonated even by using concentrated H_2SO_4 (4M) as pKa for compound is very high. However, in case of long chain malachite green leuco base (LMGH) in organic solvents absorption spectra is found to be independent of solvent polarity but emission spectra depends upon it.[9]. Reda and Koushi[9] have studied absorption and emission spectra of LMGH in methanol in the concentrange range $4x10^{-6}$ to $1x10^{-3}$ and it is observed that the absorption spectra shows no shift in peak wavelangth and no aggregation malachite green is observed.[9]

Studies on the absorption spectra of rose bengal in different solvents have shown dependence of absorption spectra on nature of solvent, aggregation of rose bengal and structural changes in the rose bengal. the detailed review is given in Chapter-I.

Rose Bengal is a "XANTHENE" type of anionic dye and gives absorption peak at 544 nm in aques solution. The absorption spectra of rose bengal shown in fig.11. The structure of rose bengal can be represented as below

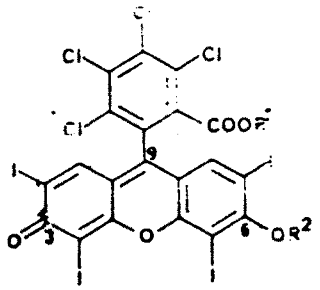


Structure of Xanthene dyes

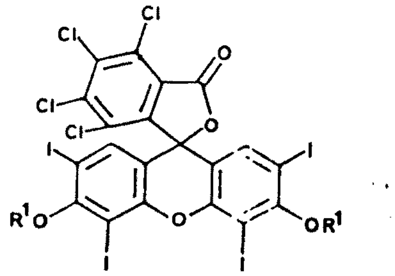


Structure of Rose Bengal

However, rose bengal is found to exist in isomeric forms as quinoid form and lactonic form, as shown below and the change in concentration of various structural isomers in different solvents have different excited states and hence show different absorption spectra.[9].



Quinoid form of RB.



Lactonic form of RB.

Rose bengal differs from fundamental xanthene type of dyes like fluorescein, eosin and erythrosin only in aromatic ring substitution.[11-15] It is reported that the planes of 2'-carboxy phenyl group and xanthene moiety of fluorescein dyes are perperidicular to one another and latter is largely responsible for absorption characteristics of the molecule in the visible region.[10,16-20] Hence the change of solvent induces major changes in the xanthene portion of the dye which modifies the absorption spectra, as there is close relationship between nature of rose bengal and dependence of its structure on the subtle changes of environment.[10] Studies on the spectroscopic properties of xanthene type of dyes have been carried out by many workers.[10,15,21,22] The absorption spectra of "Rhodamine-B" dye in different alcohols like ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl, 1-propanol have been studied by Daniel and Paul[22]. It is reported that in protic solvents there is equilibrium between the mixture of colourless lactone form and coloured Zwetterion form of rhodamine-B dye. The position of equilibrium depends upon both, hydrogen-bonding donating ability and solvent-dielectric polarizability.[22,23] It is suggested that the lactone form is less polar than zwetterian form and hence with increase in temperature, the equilibrium is shifted to less polar form. Similarly at higher concentration of dye cation and dimer appear. The equilibrium constant value decreases from ethanol to 2-propanol and again increases from 2-propanol to 1-butanol to 2-methyl, 1-propanol. This is due to decrease in the percentage of zwetterion form and again increase in the same order.[22]

Dannien and Neckers[15] have reported aggregation of rose bengal molecules in aqueous and alcoholic solution at higher concentration above 10^{-6}M. The formations of aggregates is of two types. The structure of aggregates, which may be layers, is called as `H-Type' aggregate and the other with end-on slipped type is called as "J-Type" aggregate. The formation of H-type aggregate is reported to give blue shift at higher concentration while the J-type aggregation gives a red shift. The study of absorption spectra and emission spectra of rose bengal in methanol have revealed formation of H-type aggregates at concentrations above 2 x 10^{-6}M. Further they have reported formation of dimers, trimers or even multimers of rose bengal at very high concentration and in dilute hydrocarbon solvents rose bengal is found to give even polymers, due to photochemical driving force.[15,23-25] It is observed that the monomer of rose bengal in aques solution gives absorption peak at 545 nm and dimer gives absorption peak near about 515 nm (fig.12). The study of concentration variation of rose bengal solution in methanol, in the range from 5.51 x 10^{-6}M to 2.87 x 1^{-4}M shows no shift in the peak wave lengths.[15] This clearly indicates that solvent effect and concentration effect are more pronounced at higher concentrations. Considering all these aspects about pure malachite green and rose bengal in different solvents, we have selected the higher concentration range for complex MG_2.RB i.e. 4 x 10^{-5}M to 4 x 10^{-4}M for our study. As reported by Kusabayashi et.al. [26] the absorption spectra of complex MG_2.RB four absorption peaks λ_1 λ_2, λ_3 and λ_4 for all the alcohols under study. The two peaks near 420 nm (λ_1) and 620 nm (λ_2) are due to malachite geen (MG) component and the other two peaks near 515 nm (λ_2) and 550 nm (λ_3) are due to dimeric and monomeric form of rose bengal (RB) component.

In our study of absorption spectra of pure MG and RB at equivalent concentration of complex (C=1.6x10^{-4}M), in alcohol, we have observed that absorption intensities of complex at peak wavelengths are higher than those observed for corresponding pure components. This shows that complex MG_2RB is stable in alcoholic solution. (fig.9,Ch.I) and there may be formation of solvent bridge. It is proposed that solvent bridge enhances the transition prohability of absorption for both MG and RB, hence the enhancement in absorption intensities of complex are observed. Further, in all alcohols the absorption spectra shows no appreciable shift in peak wavelengths at λ_1 and λ_4 which are corresponding to malachite green component. This indicates least probability of formation of aggregates by malachite green.

As reported earlier, the green colour of malachite green is due to formation of planar MG^+ carbonium ion from the tetrahedral strtucture of complex. The release of MG^+ ion in solution is due to photo disociation of complex and is reported to be favoured in polar solvents.[5]

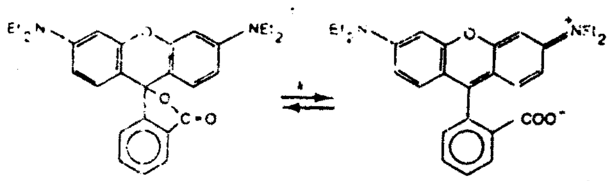
We have observed exceptional high abnormal absorption for complex solution in ethanol at peak wave lengths λ_1 and λ_4. Here we propose that at the polarity of ethyl alcohol, the ionic photodissociation takes place to give MG^+ ion with a planar structure from the tetrahedral complex structure. However, in all other alcohols, the absorption due to malachite green component is weak at low concentration but with increase in concentration of complex the absorption intensity increases. At concentrations above 1.6×10^{-4}M the absorbance at λ_1 and λ_4 is seen to be appreciably high.

The absorbance due to rose bengal component at λ_2 due to dimeric form) and λ_3 (due to monomeric form indicate that within concentration range of conmplex from $4x10^5M$ to $4x10^{-4}$the rose bengal exists in dimeric form. With increase in concentration of the complex, the absorbance at λ_2 and λ_3 are found to increase. This indicate that even in complex solution aggregation of rose bengal may be taking place, as observed in case of pure rose bengal in aqueous and alcoholic solutions. Except in ethyl alcohol, in all other alcohols under study, we have observed that rose bengal is strongly absorbing while malachite green is weakly absorbing. Comparison of absorption spectra of complex in methanol, 1-propanol & 1-butanol shows that with decrease in dielectric constant of alcohol from methanol to 1-butanol the absorbance due to rose bengal both at λ_2 and λ_3 decrease. This shows that increase in dielectric constant favours aggregation of rose bengal. This is further supported by our observation that to have maximum absorbance value of six (arbitrary units), the concentration of complex required increases with decrease in dielectric constant of the solvent.(Refer Table 13, Ch.I) Hence it is very clear that the dielectric constant of the solvent plays an important role in absorption properties of the complex.

In addition to dielectric constant, the structure of solvent molecule also modifies the absorption spectrum. The comparison of absorption spectra of complex in methanol with that in 1-propanol, 1-butanol and 2-butanol, shows that due to decrease in inductive effect of CH_3 group in alcohols with increase in carbon chain length, aggregation is decreased and a red shift is observed. It seems that decrease in inductive effect and the dielectric constant of solvent molecule favours J-type aggregates of rose bengal component of the complex at higher concentration.[15]

Study of dependence of absorption spectra on the complexity of strtucture of alcohol molecule shows that increase in complexity enhances the absorption. The study of absorption spectra of complex in n-butyl alcohol, sec.-butyl alcohol and t-buty alcohols shows a red shift with increase in concentration of complex and by change of solvent from n-butyl to t-butyl alcohol. The absorbance of complex at all peak wavelengths Λ_1 Λ_2, Λ_3 and Λ_4 are nearly same in n-butyl alcohol and t-butyl alcohol. However, in sec.-butyl alcohol the absorbance at peak wavelengths are comparatively higher. This indicates that the secondary alcohols favour aggregations of rose bengal and also formation of MG^+ ion at higher concentration. Similar high absorbance is observed at Λ_2 and Λ_3 for solution of complex in secondary propyl alcohol. However, abnormal high absorption is observed at λ_2 and λ_3 for solution of complex in iso-propyl alcohol and iso-butyl alcohol. And above concentration of complex 1.6 x 10^{-4}M, the absorbance at λ_3 is greater than six. The dielectric constants of iso-propyl alcohol and iso-butyl alcohol are 18.2 and 17.7 respenctively which have slight difference and hence accordingly slight variations in absorption intensities are observed. But the enhancement of absorbance at λ_2 and λ_3 which is due to aggregation of rose bengal, we propose here that more than dimerization further aggregation may be taking place as observed by Danien and Neckers[15] for pure rose bengal in methanol.

In case of xanthene type of dye like 'Rhodamine-B', it has been reported earlier that it exists in two forms as, lactonic (L) form and zwetterion (Z) form as shown below [22].



Lactone (L) Zwitterion (Z)

There exists an equilibrium between these two forms and this equilibrium is affected by dielectric constant of medium. It has been shown that, the 'Z' ion concentration is maximum in ethanol and decreases in case of higher alcohols [22]. Similarly rose bengal is also a xanthene type of dye and exists in two forms as quinoid form and lactonic form. The comparison of absorption spectra of pure components rose bengal and malachite green in given alcohol with that of complex (MG_2.RB) in same alcohol at equivalent concentration shown that the absorption intensities of components in the complex are greatly enhanced than that observed for pure components. (Fig.9,Ch.III). This clearly indicates that rose bengal is associated with malachite green in the form of charge transfer complex and complex is stable in all the alcohols under study.

4.2 ROLE OF SOLVENT MOLECULES

The effect of solvent change on the absorption spectra of the complex studied here seems to be due to two fold action of solvent molecule. The solvent molecules act as medium for the complex and may modify aggregation of the rose bengal component of the complex. As malachite green does not exhibit such aggregation, there should be little effect of solvent molecules. The another effect of solvent seems to be due to formation of solvent bridge betwen the cationic part of malchite green component and the anionic part of rose bengal component. This solvent bridge effect seems to be more predominent in case of ethanol, 2-propanol and 2-methyl, 1-propanol.

4.3 ROLE OF SOLVENT AS A MEDIUM

Rose bengal has been reported to exist as monomer at low concentration and dimer at high concentration and even multimers at very high concentrations.The monomer and dimer spectra of rose begal in aqueous solution are shown in Fig. 12. The concentration range studied here is 4 x 10^{-5}M to 4 x 10^{-4}M and it has been reported that rose bengal mainly exists as dimer in this concentration range[15]15. This is also clear from the absorption spectra of complex, in which the band corresponding to dimer form [λ_2 __515nm] is predominent in all the alcohols studied here. In general as the concentration of complex increase in given alcohol, the absorption band due to dimer increases, but absorption band due to monomer goes on decreasing in intensity. This clearly indicates that as concentration of complex increases the dimer concentration also increases and correspondinngly monomer concentration goes on decreasing. As the dimer is more absorbing than monomer, the intensity of absorption should go on increasing. However, the E values at λ_2 seem to decrease with concentration and the concentration quenching is observed. However, in case of malachite green component E values

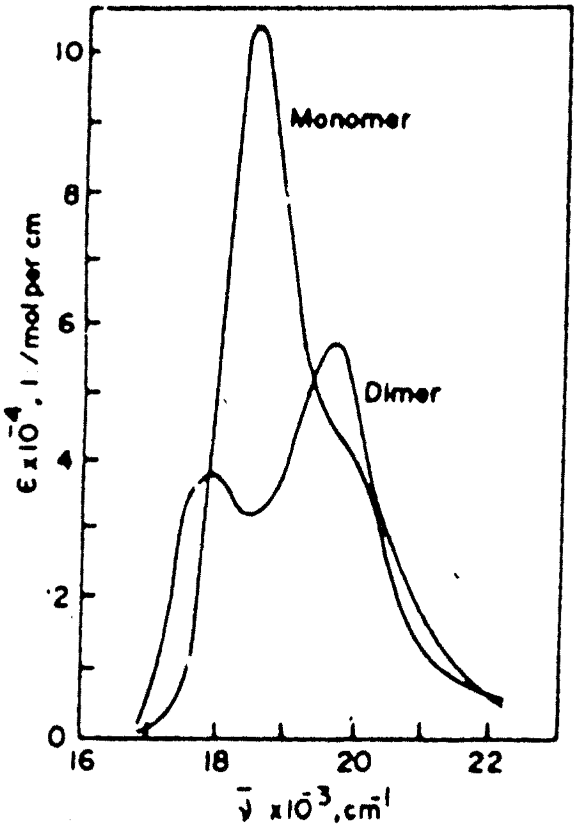


Fig.12 Monomer and dimer spectra of rose bengal ($FlCl_4I_4$).

at λ_4 seem to increase with concentration and hence concentration increase seems to assist absorption.

In case of normal alcohols except ethanol, as dielectric constant decreases, the intensity of absorption also decreases and this is evident by the values of concentration of complex required to have absorbance value of six. (Table 13,Ch.III), in case of rose bengal component. No such effect is observed in case of malachite green component.

However, in case of ethanol, 2-propanol and 2-methyl, 1-propanol abnormal intensities of rose bengal component are observed and they cannot be attributed to only dielectric constant effect.

4.4 ROLE OF SOLVENT AS A BRIDGE BETWEEN MALACHITE GREEN COMPONENT AND ROSE BENGAL COMPONENT.

It has been previously shown in case of MGCN complex[5] that MG^+ ion is responsible for strong absorbance and green colour of the solution. Similarly, it is reported that in case of charge transfer complex of cyanine dyes, the solvent molecule acts as a bridge between cationic and anionic part of the complex[27]. In case of present study the alcohol molecule acts as a solvent bridge between malachite green cation and rose bengal anion, forming, a charge transfer complex. With the normal alcohols malachite green component does not seem to be existing as MG^+ ion and hence weak absorption bands are observed. On the other hand rose bengal exists in quinoid form in presence of these alcohols and since this quinoid form is stable and responsible for absorption, the complex solution in alcohol shows strong absorption bands of rose bengal. At higher concentrations, rose bengal exists as dimer and this dimer is also strongly absorbing thus increasing the absorbance of solution with concentration. It seems that ethanol, 2-propanol and 2-methyl, 1-propanol are more effective in formation of dimers of rose bengal molecules, showing abnormal high absorption intensities of complex in these solvents. However, in case of ethanol as solvent, malachite green bands are greatly enhanced and no such enhancement is observed in other solvents. This is observed especially at higher concentrations. But at higher concentrations rose bengal exists as dimer and it has been suggested by Rohatgi-Mukherjee[21] that these dimers act as effective "Sinks" for exicitational energy, although they may not show energy bands. It seems in case of our complex solution in ethanol, that rose bengal dimers act as energy sinks and this energy is transferred to MG component of the complex via solvent bridge. This energy is responsible for ionic photodissociation of the malachite green component to form MG^+ ion. Thus the concentration of MG^+ ion will be increased and strong absorption band of malachite green will be observed. In case of ethanol solution we have obtained such enhanced bands at higher concentrations only. At lower concentrations of the complex rose bengal mainly exists as a monomer and dimer concentration is very low, the effective transfer of energy from rose bengal component via solvent molecule is not effective. As such MG^+ ion concentration in the solution is greatly reduced and only weak malachite green bands are observed. A slight quenching effect is observed at higher concentrations in case of rose bengal omponent, which clearly indicates that rose bengal component instead of absorbing energy acts as energy sink and these energy sinks are responsible for ionic photodissociation of malachite green component of the complex.

4.5 AGGREGATION OF ROSE BENGAL AND SOLVENT VARIATION

We have studied the concentration range of complex 4 x 10^{-5}M to 4 x 10^{-4}M and for all the solvents studied here a definite red shift was observed in case of rose bengal peaks. It is well known that rose bengal exists in solution form as two types of aggregates as `H'-type and `J'-type. In H-type aggregates the molecules are arranged in the form of layers while the J-type aggregates have end on slipped structure. The H-type aggregates give blue shift while J-type aggregates give red shift at higher concentrations[15]. Dannian and Neckers[15] have observed red shift of emission for rose bengal in methanol, however, no red shift in absorption spectra was recorded by them. They have studied fluorescence and absorption spectra of pure rose bengal in methanol in the concentration range 5.51×10^{-6}M to $2.87\text{x}0^{-4}$M. Probably this concentration range is low to exhibit the red shift in absorption spectra of rose bengal. In our studies we have used higher concentration range of the complex (up to 4×10^{-4}M) and hence the red shift in the absorption spectra of rose bengal component of the complex is observed. This red shift seems to be due to J-type aggregates of the complex molecule in different alcohols. In general it can be said that this observed red shift has inverse relation with dielectric constant of medium, which indicates that low dielectric constant medium is favourable for the formation of J-type aggregates. This is also supported by the fact that rose bengal exists in the form of H-type aggregates in aqueous solution[15].

The explaination for the effect of solvent variation on the absorption spectra of complex is of qualitative nature. These effects cannot be quantitatively accounted for, because molecular energy levels diagrams of the complex as well as the components rose bengal and malachite green are not available. We have studied here only the absorption spectra of complex solutions. More light is likely to be thrown by extendng the studies to the emission and excitation spectra of the complex in all the solvents used here.

HIGHLIGHTS OF THE WORK

1. The complex $MG_2.RB$ has been shown to be stable in solutions for all the alcohols studied here.

2. The rose bengal component has been shown to exist in dimeric form in all the alcohols. These dimers have shown to be J-type aggregates.

3. The red shift observed in various alcohols has been shown to be due to existance of J-type aggregates of rose bengal component and it's inverse relation with dielectric constant is explained

4. The abnormal enhancement of malachite green bands and correspondingly quenching of rose bengal bands is explained on the basis of solvent bridge between rose bengal dimer and the malachite green component. Effective energy transfer of excitation

energy from rose bengal dimer to malachite green component takes place through the solvent bridge. Thus enhancing the malachite green bands and quenching the rose bengal bands.

5. The system deserves extension of work to fluorescence emission spectra and excitation spectra, which is likely to throw more light on the problem. Thus study can be extended to other complexes and other solvents.

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