
CHAPTER-V
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It is well known that some of the cationic dyes form stable complexes with ionic dyes. These complexes are stable in solution form and exhibit optical properties like absorption, fluorescence etc. Rose bengal, an anionic dye forms a complex with cation of the malachite green having molecular formula $MG_2 \cdot RB$. In the present study, absorption spectra of solutions of this complex in indifferent alcohols has been reported and attempt is made to present a plausible explanation for the observations made.

An extensive review on the spectroscopic studies of dyes in general and malachite green, rose bengal and the complex ($MG_2 \cdot RB$) has been taken in Chapter-I

The complex was prepared by mixing equal volumes of 2M, aqueous solution of malachite green and 1M, aqueous solution of rose bengal with constant stirring for 30 minutes. The complex was precipitated as purple violet flocky mass which was then filtered, washed with distilled water and dried. It was then recrystallized twice from pure ethyl alcohol solution. The alcohols used were methyl alcohol, ethyl alcohol, propyl alcohol

(n- and iso-butyl alcohol, n-, sec., ter. - and iso). The solvents were doubly distilled by using complete glass distillation assembly. The solvents were purified by standard methods prior to distillation. All these details are given in chapter II. The details of preparation of solutions and recording the absorption spectra of these solutions have also been given. The instruments used for recording the spectra were "Shimadzu-160" and "Hitachi-300" UV/VIS spectrophotometers. The preliminary work was carried out with the help of "Shimadzu-160" spectrophotometer however, the final results were recorded on "Hitachi -300" spectrophotometer, for high sensitivity. (Chapter II,)

The absorption spectra of complex consists of four peaks around wavelengths 420 nm, and 620 nm corresponding to malachite green component and 520 nm and 550 nm corresponding to rose bengal Component. The absorption spectra of complex showed higher intensities of absorption for the four bands as compared to the absorption intensities of the pure components at equivalent concentrations. For normal alcohols except ethanol, rose bengal was strongly absorbing while malachite green component was weak absorber of light. In case of ethyl alcohol however, malachite green was observed to be a strong absorber. Solutions of the complex in iso-propyl alcohol and iso-butyl alcohol showed abnormal enhance-

ment of bands corresponding to rose bengal component. Solutions of complex in alcohols studied here invariably showed red shift in the position of the peaks at higher concentrations. The effect of concentration variation of the complex on the absorption spectra for the same alcohol and the effect of solvent variation at the same concentration of complex was also studied. The absorption spectra in different solvents are represented in figures 1-8 and the results are included in tables 1-13. (Chapter-III,)

The relation between colour and chemical constitution of dyes has been brought out and reports on the study of absorption spectra of the pure components have also been discussed. These observations have been used to explain the results of present study. It has been established that rose bengal exists as dimers and multimers at higher concentrations of the dye while the green colour of the malachite green solution is due to formation of cation MG^+ of the dye. The absorption spectra of the complex indicate that rose bengal exists as "J"-type aggregate in these solutions at higher concentrations of the complex. The "J"-type aggregates are shown to be responsible for the observed red shifts in the peak wavelengths. The observed red shift has inverse relation with dielectric constant, which indicates that low dielectric constant of medium is favour-

able for formation of J-type aggregates. The abnormal enhancement effects observed in ethyl alcohol have been attributed to the formation of solvent bridge between cation of malachite green and anion of rose bengal in the complex. It has been established that rose bengal in dimeric form acts as an effective sink for excitational energy, although they may not show energy bands. This excitational energy is transferred to MG^+ ion through the solvent bridge and causing ionic photodissociation of complex to give high concentration of MG^+ ion and this enhances greatly the absorption bands corresponding to malachite green component in the complex. The rose bengal bands are seen to be correspondingly quenched. (Chpater-IV)