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## Self-aggregation of Rhodamine - 6G in aqueous medium and aqueous solution of Bu<sub>4</sub>NBr

Pandurang D. Talap

Department of Chemistry, Rajaram College, Kolhapur, India

### ABSTRACT

The self-aggregation of Rhodamine - 6G [ $1 \times 10^{-6}$  to  $4 \times 10^{-4}$ ] in water and in aqueous solution of Bu<sub>4</sub>NBr (0.1 - 0.3 M) has been investigated by recording electronic spectra in the wavelength range 460 to 600 nm. Analysis of the spectral data yielded the dimer dissociation constant, individual characteristic monomer and dimer spectra. By applying the excitation model for the first time, the interaction energy between the Rhodamine - 6G molecules in dimer species has been evaluated. Further information about the dimer geometry and twist angle between the dipoles of the Rh-6G molecules has been obtained.

### INTRODUCTION

The self-aggregation of Rhodamine - 6G [ $1 \times 10^{-6}$  to  $4 \times 10^{-4}$ ] in water and in aqueous solution of Bu<sub>4</sub>NBr (0.1 - 0.3 M) has been investigated by recording electronic spectra in the wavelength range 460 to 600 nm. Analysis of the spectral data yielded the dimer dissociation constant, individual characteristic monomer and dimer spectra. By applying the excitation model for the first time, the interaction energy between the dipoles of the Rh-6G molecules has been obtained. Similar, data have also been obtained for aqueous solution of Rh-6G in Bu<sub>4</sub>NBr. The significant observation is the change in dimer geometry from sandwich type to end-on-end type in the presence of Bu<sub>4</sub>NBr. It is observed that the contribution to the interaction energy is mainly from Van-der waal's type and dispersion forces in addition to short range forces involving multi poles. However, the contribution from hydrogen bonding interaction between Rh-6G and water molecules is found to be significantly low. It is proposed that water structural effects and hydrophobic interaction are the major factors in the phenomenon of aggregation.

### MATERIALS AND METHODS

The spectra were recorded using an Elico SL 159 UV-VIS spectro photometer in the wavelength range 460 to 600 nm. The matched quartz cuvettes of path lengths, 1, 0.5 and 0.1 cm were used for the purpose of recording the spectra such that the absorbance the values do not exceed 1.5. The path length of the cuvettes was found to match within  $\pm 0.0001$  cm. All the measurements reported in the present work were carried out at  $27 \pm 1^\circ\text{C}$

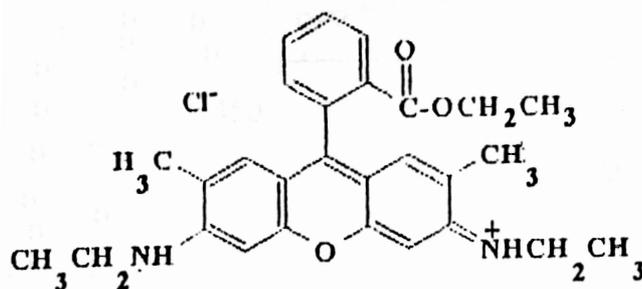
The purity of Rh-6G procured from Qualigens fine chemicals was assessed by recording the spectrum of its solution in absolute alcohol. [GR,E,Merck]. The  $\lambda_{\text{max}}$  value obtained was  $525 \pm 1$ nm, while molar absorption coefficient was found to be  $8.3 \times 10^4 \text{ dm}^3 \text{ mole}^{-1} \text{ cm}^{-1}$ . The spectrum of Rh-6G in water ( $1 \times 10^{-6}$  M) has a shape similar to that reported in the literature with  $\lambda_{\text{max}} = 624 \pm \text{nm}$  <sup>(5,6,7,8)</sup>. Hence the dye was used without further purification.

Tetra-butyl ammonium bromide [John Baker Inc, colored, USA] was dried at  $50-60^\circ\text{C}$  in a vacuum oven.

### RESULTS AND DISCUSSION

The visible spectra of Rh-6G in water, in the concentration range  $7 \times 10^{-4}$  to  $1 \times 10^{-6}$  were recorded at  $27 \pm 1^\circ\text{C}$ . The spectra are reproduced in Fig.1 examination of fig.1 reveals that with increasing concentration the peak at 505 nm, due to the dimer, increases in intensity at the expense of the intensity of that at 525 nm, attributed to the monomer. An approximate isobestic point was observed at 510 nm. The data obtained were analyzed using the following methodology.

Since the concentration of Rh-6G was maintained below the concentration at which appreciable trimerization begins, the only equilibrium believed to be existing in the solution is the monomer dimer equilibrium <sup>(7)</sup>



Rhodamine - 6G (FW 479.02)

The dimer dissociation constant  $K$  can be expressed as

$$K = \frac{C^2 M}{C_D} = \frac{2\alpha^2 C}{(1-\alpha)} \quad \dots \dots (1)$$

Where, the total dye concentration  $C = C_m + 2C_D$  being the concentration of Rh-6G in the monomeric and dimeric forms respectively and  $\alpha$  the fraction of the dye molecule existing in monomeric form. Further, the molar absorption coefficient ( $\epsilon$ ) of Rh-6G can be expressed as function of those the monomer ( $\epsilon_m$ ) and dimer ( $\epsilon_{D/2}$ ) species, assuming that the Beer-Lambert is applicable to both species.

$$\epsilon = \alpha\epsilon_m + (1-\alpha)\epsilon_{D/2} \quad \dots \dots (2)$$

The  $\epsilon_m$  and  $\epsilon_{D/2}$  values obtained at difference wavelength allows us to generate the monomer and the dimer spectra (Fig.2)

Further, the concentration of the monomer and dimer species were calculated with the help of  $\epsilon$  and  $\alpha$  values. It was observed that the plot of  $\log C_D$  against by  $C_M$  (eqn.1) results in a straight line with a slope of  $\cong 2.0$  as compared to expected value of 2.0. This substantiates our assumption that the monomer dimer equilibrium is only predominant equilibrium existing in the solution under investigation further, the monomer and the dimer species were found to follow the Beer Lambert law individually at the respective wavelength the giving credence to the use of eqn.2 Thus the value of the  $K$  so obtained can be accepted with confidence.

The most suitable value for the dimer dissociation constant was found to be  $7 \times 10^{-4} \pm 0.2 \text{ mol L}^{-1}$  and free energy of dimer is 18.04 kJ. These values are excellent agreement with those obtained by Selwyn and Seinfeld. They have reported dimer dissociation constant at 22° to be  $5 \times 10^{-4} \text{ mol L}^{-1}$  and ( $\Delta G = 4.3 \text{ Kcal}$ )

The oscillator strengths ( $f$ ) of the monomer and the dimer species were evaluated using<sup>(10)</sup>

$$f = 1.44 \times 10^{-19} A \quad \dots \dots (3)$$

$$\text{where } A = \int \epsilon(\nu) d\nu \quad \dots \dots (4)$$

i.e. the area under curves while the corresponding dipole moments  $\mu$  were calculated.

Table No.1 : The dimer dissociation constant and the spectral data of Rh-6G in aqueous and in aqueous Bu<sub>4</sub>NBr solution at 27°C.

Conc. of salt, M	$\epsilon_m^1 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$	$\epsilon_{n/2} \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$		$(\epsilon_{n/2})_n$ ----- $(\epsilon_{n/2})_p$	$\theta$	Oscillator strength		$\mu \times 10^{30} \text{ C m}$		$U = \Delta E/2 \text{ cm}^{-1}$
		P	N			M	D	M	D	
0.1	10.57	7.1	1.2	0.1690	44.69	0.33	0.19	11.6	8.1	741
0.2	11.0	6.1	1.7	0.2786	55.65	0.34	0.21	11.8	8.3	1010
0.3	11.8	5.4	1.9	0.3518	61.3	0.34	0.20	12	7.5	909

Where 'm' and 'e' are the mass and charge on the electron,  $\mu$  the transition dipole moment,  $h$  plank constant and  $\nu$  the frequency at maximum absorption. These parameter of Rh-6G in water are collected in table 1.

Application of the exciton model to the dimer<sup>(9)</sup> species reveals that the ground state of the dimer remains doubly degenerate, while the excited state splits into two different energy levels,  $\Delta E$ , depends on the interaction ( $U = \frac{\Delta \epsilon}{2} \text{ cm}^{-1}$ ) between the dye molecules in the dimer species<sup>(2, 11)</sup> for a perfect sandwich type dimer the transition from the ground state to the higher excited state is allowed, resulting in the p-branch, which appears on the shorter wavelength side of the monomer band. In case of end-on-end type of dimer is the only allowed transition,

resulting in band on the longer wavelength side of the monomer band, called the N-branch (fig.2). Since the real system are non-ideal, we always find some intensity of both bands. The ratio  $\epsilon_N/\epsilon_P$  the molar absorption coefficient of the dimer species at the  $\lambda_{max}$  of the N and P branches respectively, give some indication of the dimer geometry<sup>2</sup>, our results (Table1) indicate that Rh-6G dimer in water exist further, the angle between the transaction dipole of the Rh-6G molecules in dimer can be evaluated using<sup>2</sup> assuming that distance between the dipoles remains uncharged.

The spectral data presented in Fig.1 clearly indicate that with increase in concentration of Rh-6G the extent of aggregation also increase. The role played by water structural effects (entropy and enthalpy contribution) in aqueous dye solution has been discussed earlier by Mukerjee et.al.<sup>(8)</sup>. The concluded that dispersion forces are the important contribution to interaction force in addition to the driving force provided, by the water structural effect. Application of exciton model has provided sufficient information about the dimer geometry to allow qualitative extension of their interactions.

The interaction in the dimer can be evaluated by application of exciton model, as discussed earlier. In case of the dimer of Rh-6 in water. We obtained a value of  $654.2 \text{ cm}^{-1}$  which is definitely less than if H-bonding were the dominant factors ( $\sim 20 \text{ kJ mol}^{-1}$ ) This is in accordance with simulation studies of the hydration of benzene in dilute aqueous solutions, which indicate that the hydrogen bonding interaction between water molecules and  $\pi$  electron system of benzene is not appreciable<sup>(13)</sup>. However, the quadrupole moment of the benzene molecule does influence the orientation of water molecules above and below the molecular plane.

The interaction between the Rh-6G molecules in the dimer species should, therefore, include interactions such as, ion-dipole, dipole-dipole, dispersion forces and in fractions involving higher multipoles of course repulsive interactions between similarly charges dye molecules would exist but, they seem to the dominated by the attractive cation-cation interactions.

The observed  $\epsilon_N/\epsilon_P$  ( $=0.1$ ) ratio in water is very small indicating, according to the exciton model, that the dimer geometry is of sandwich type with a slight deviation from an exact parallel stacking arrangement of the dye molecular planes. Further, the transaction dipole of the Rh-6G molecules in the dimer species are aligned, with respect to each other through an angle  $\theta = 44.69^\circ$ . Thus, the dipole-dipole and ion-dipole in fraction will be of smaller magnitude than if the value of  $\theta$  were equal to zero. It is thus clear that the dispersion forces are contributing largely to the interaction energy due to greater mobility of the  $\pi$  electron.

Tetrabutyl ammonium bromide is a water structure making salt, containing the hydrophobic group. In presence of  $\text{Bu}_4\text{NBr}$ , proteins and nucleic acids are transformed from helical 'native' conformation into coiled form<sup>24</sup>. Hence dimerization of Rhodamine-6G is hindered in presence of  $\text{Bu}_4\text{NBr}$ . The dimer dissociation are lower in magnitude as compare to that in water which may be attributed to interaction amongst  $\text{Bu}_4\text{N}^+\text{Br}^-$  and the dye ions.

The interaction energy for dimer in table (1) shows no particular trend about dependence on concentration of  $\text{Bu}_4\text{NBr}$  but the values are larger than that in pure water.

The ratio of extinction coefficient of N-branch to P-branch and the twist angle between the transition dipoles of dye ions in dimer increases with increase in concentration of  $\text{Bu}_4\text{NBr}$ .

## CONCLUSION

$\text{Bu}_4\text{NBr}$  is a water structure making salt, but the values of dimer dissociation constants are low as compared to that in pure water Lower K values are believed to be due to specific interactions of  $\text{Bu}_4\text{N}^+\text{Br}^-$  with the dye cations. Thus it makes available the low entropy structured water for the monomers formed on dissociation of the dimers.

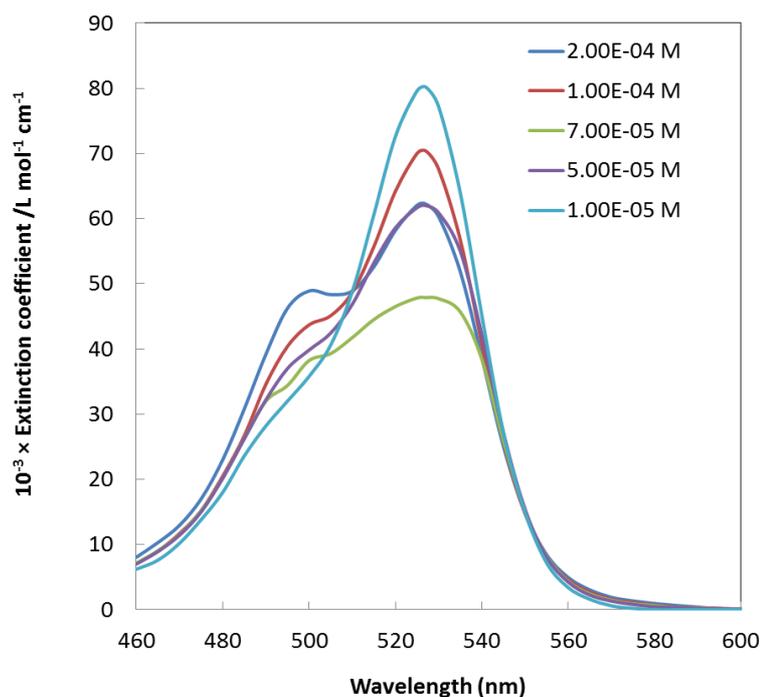


Fig. 1 Absorption spectra of Rhodamine-6G in aqueous solutions

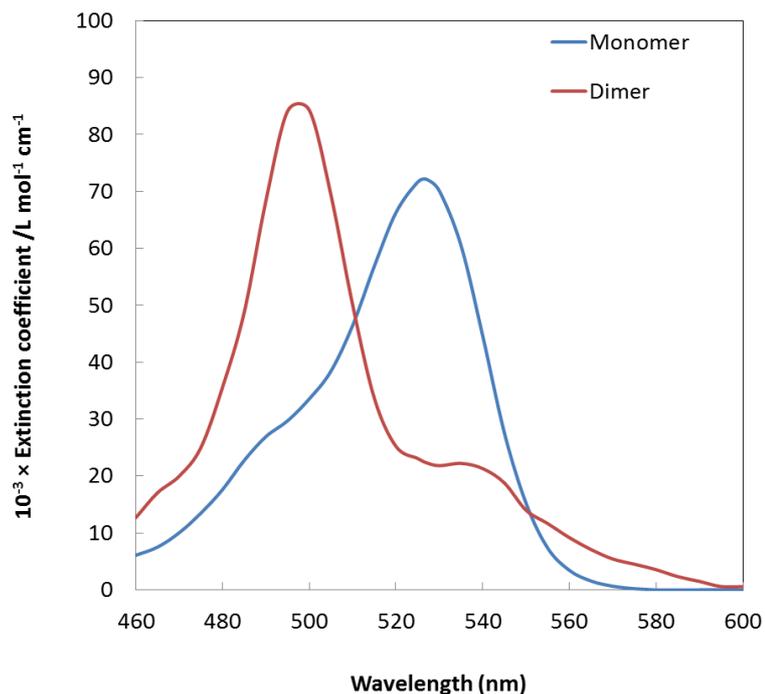


Fig. 2 Resolved absorption spectra of monomer and dimers of Rhodamine-6G in aqueous solutions

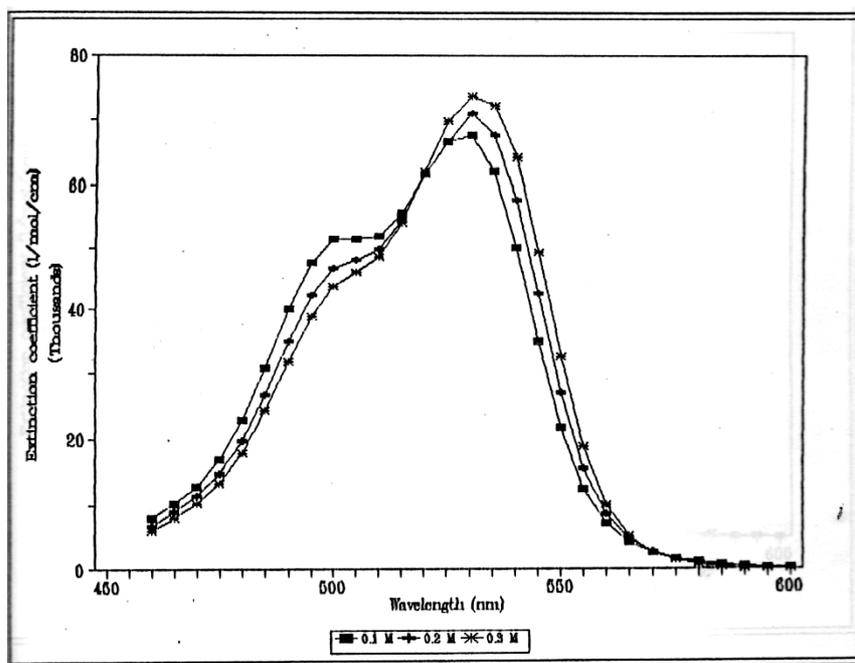


Fig. 3 Absorption Spectra Rhodamine-6G and Bu<sub>4</sub>NBr in aqueous solutions.

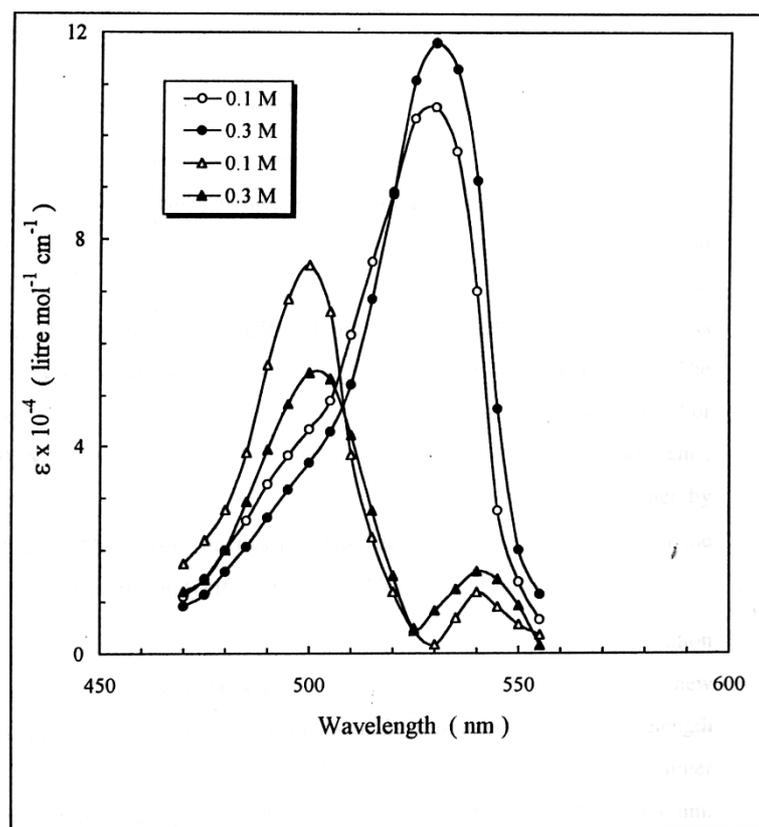


Fig. 4 Resolved monomer and dimer spectra of rhodamine-6G in presence of Bu<sub>4</sub>NBr in water.

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