Research Article

Theme- *New horizons in chemical sciences.*
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Absorption Spectra of rhodamine -6G in aqueous electrolyte solution.

P. D. Talap

Department of Chemistry, Govt. College of Arts and Science, Aurangabad, Maharashtra, India.

*Corresponding author E-mail address: *rppawar@yahoo.com*

ABSTRACT
The self-aggregation of rhodamine - 6G [1×10^{-6} to 4×10^{-4}] in water and in aqueous solution of LiCl, [0.1 M, 0.3 M, 0.5 M and 0.7 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.

KEYWORDS
Rhodamine - 6G, electrolyte solution.

1. INTRODUCTION

The phenomenon of aggregation of dyes, surfactants drugs, etc. has been studied extensively, polarography etc. [1,2] The results of these studies have been indicated that the dyes molecules, in spite of repulsion due to similar charges of undergo self-aggregation to form dimer, trimer and higher aggregates [3] the charges being mentioned of far as possible in the aggregates [4]. The forces which hold the dye molecules together are believed to be hydrogen bond, Vander Waals forces, London dispersion forces has been recognized to be hydrophobic interactions, which help the system to get mole of the thermodynamically unfavorable state. (of negative ΔS due to hydrophobic hydration). Thus the water structural features seem to play the role of catalyst in including aggregation.

The state of a thiazine dye, Rh-6G in water has been investigated by several works5-8. The students of Mukerjee et.al have shed light on the intermolecular interaction involved in the formation of the dimer and trimer of Rh-6G. The in inference drawn by them can be explained by application of the exciton model. Proposed by Kasha. et.al [9] with the help of detailed analysis of spectral data of Rh-6G in aq. salt and aqueous. nonelectrolyte solution.

Thus, we have carried out systematic spectrophotometric studies of the state of Rh-6G in aqueous salt solution and aqueous LiCl solution in the concentration range of the dye where aggregation does not exceed dimerization.

2. MATERIAL 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 length 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 curettes was found to match within $\pm$ 0.0001 cm. All the measurements reported in the present work were carried out at 27 ± 1^0C

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

3. RESULTS AND DISCUSSION

The visible spectra of Rh-6G in water, in the concentration range 7×10^{-4} to 1×10^{-6} were recorded at 27 ± 1^0 C. The spectra are reproduced in Fig. 2 examination of fig. 2 revels 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 isobetic point was observed at 510 nm.

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. [7]
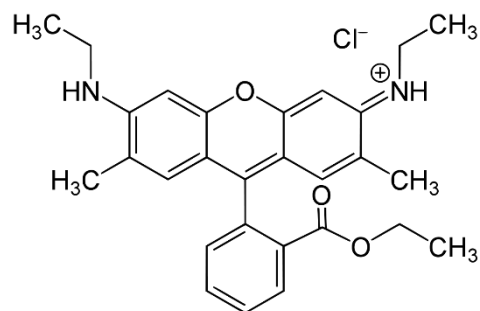
Fig. 1. Rhodomine - 6G (FW 479.02)

The dimer dissociation constant K can be expressed as,

$$K = \frac{C^2 M}{C_D} = \frac{2\alpha^2 C}{(1-\alpha)} \qquad \text{---\textbf{Formula 1}}$$

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

$$\epsilon = \alpha\epsilon_m + (1-\alpha)\epsilon_{D/2} \qquad \text{---\textbf{Formula 2}}$$

The $\in_m$ and $\in_{D/2}$ values obtained at different wavelength allows 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 $\in$ and α values. It was observed that the plot of log C_D against by C_M (Formula 1) results in a straight line with a slope of $\cong 2.0$ as compared to expected value of 2.0. It's 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 formula 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 x $10^{-4} \pm 0.2$ 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 22^0C to be 5 x 10^{-4} mol L^{-1} and ($\Delta G = 4.3$ Kcal)

The oscillator strengths (f) of the monomer and the dimer species were evaluated using [10]

$$F = 1.44 \times 10^{-19} \text{ A} \qquad \text{---\textbf{Formula 3}}$$

where A $\int \epsilon (v) dv$ ---**Formula 4**

i.e. the area under curves while the corresponding dipole moments μ were calculated.

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Table1. The dimer dissociation constant and the spectral data of Rh-6G in aqueous and in aqueous LiCl solution at 27^0C.

Conc. of salt, M	$\in_m$ x 10^{-4} L mol^{-1} cm^{-1}	$\in_n/2$ x 10^4 L mol^{-1} cm^{-1}		$(\in_n/2)_N$ --------- $(\in_n/2)_P$	θ	Oscillator strength		μ x 10^{30} C$_m$		U= ΔE/2 cm^{-1}
		P	N			M	D	M	D	
0.1	9.4	6.63	0.76	0.1146	37.4	0.29	0.170	10.9	8.1	766.4
0.3	9.2	6.67	0.81	0.1214	38.4	0.32	0.16	11.4	7.8	884.4
0.5	9.5	7.93	0.94	0.1185	37.9	0.33	0.19	11.5	8.4	825.7
0.7	10.2	6.47	0.59	0.0912	33.6	0.34	0.16	11.7	7.8	909.1

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

Application of the exciton model to the dimer [9] species reveals that the ground state of the dimer remains doubly degenerate, while the excited state splits into two different energy levels, ΔE, depends on the interaction (U $= \frac{\Delta\epsilon}{2}$ cm^1) between the dye molecules in the dimer species [2, 11] for a perfect sandwich type dimer the transaction 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.3). Since the real system are non-ideal, we always find some intensity of both bands. The ratio $\in_N/\in_P$ the molar absorption coefficient of the dimer species at the λ_{max} of the N and P branches respectively, give some indication of the dimer geometry[2], 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[2] 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 [8]. The concluded that dispersion forces are the important contribution to interaction force in addition to the driving force provided, by the water structure effect. Application of exciton model has provided sufficient information about the dimer geometry to allow qualitative extension of their interactions.

The interaction between the Rh-6G molecules in the dimer species should, therefore, include interactions such as, ion-dipole, dipole-dipole, dispersion forces and infractions 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 $\in_N/\in_P$ (=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 $\theta=44.69^0$. Thus, the dipole-dipole and ion-dipole in fraction will be of smaller magnitude than if the value of θ 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 π electron.

3.1. Effect of added electrolytes

Ex. of fig. (3) indicate that as the concentration of salt is increased the monomer band reduces intensity while the dimer band gains intensity. It can be inferred that all the electrolytes added cause increase in dimerization, but to definite extent. The effect of different salts can be distinguished from each other from the variation of dimer dissociation constants at the studied concentration of electrolytes. With increase in conc. of salt, the dimer dissociation constants decrease in magnitude.

Electrolytes dissolve in water by dissociating into cation and anion, each of which is solvated differently. Water molecules in the first layer being immobilized i.e. electrostricted. The greater the charge density, stronger is the electrostriction, thus Li^+ is the most hydrated ion and is known to be structure making ion.

The ratio $\in_N/\in_P$ for different conc. of the salts are included in (Table 1) along with twist angles between the transition dipoles of the dye cations in the dimer species.

The ratio $\in_N/\in_P$ and twist angle decrease with increase in conc. of LiCl. These values indicate 'P'- branch to be prominent band in dimer spectrum and are in fact observed in G.9 (54-57)

The rhodamine-6G in presence of the salts shows deviation from exact card pack arrangement. As compared to rh-6G dimer in pure water, that in aqueous salts solution show gain in intensity of the N-branch (long wavelengths)
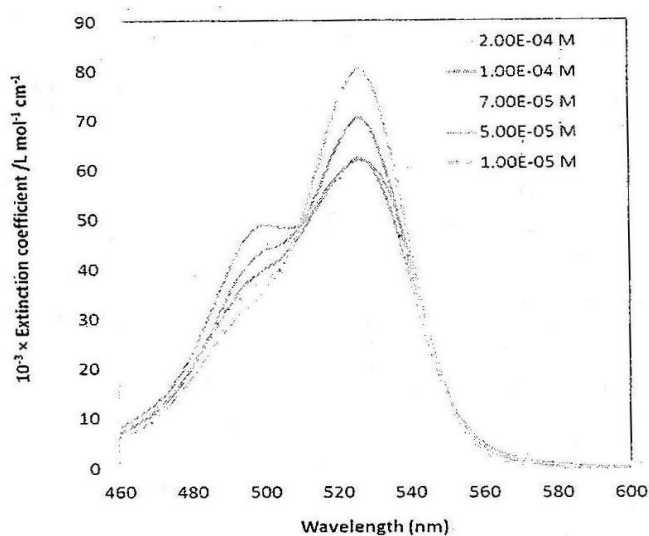

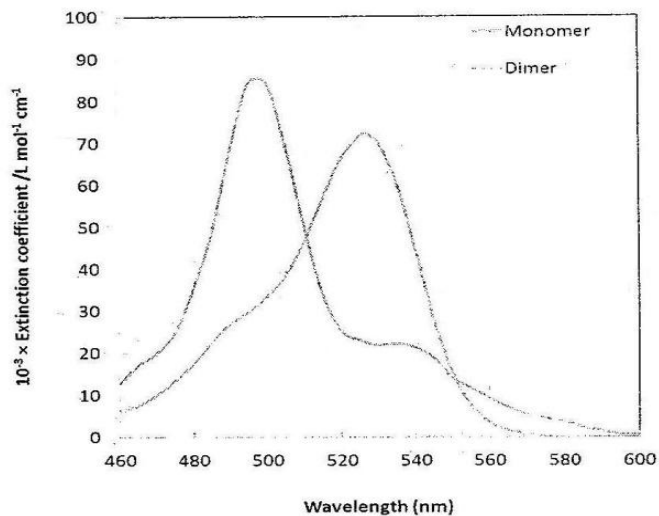**Fig. 2.** Absorption spectra of Rhodamine 6G in aqueous solutions.

Fig. 3. Resolved absorption spectra of monomer andRhodamine-6G in aqueous solutions
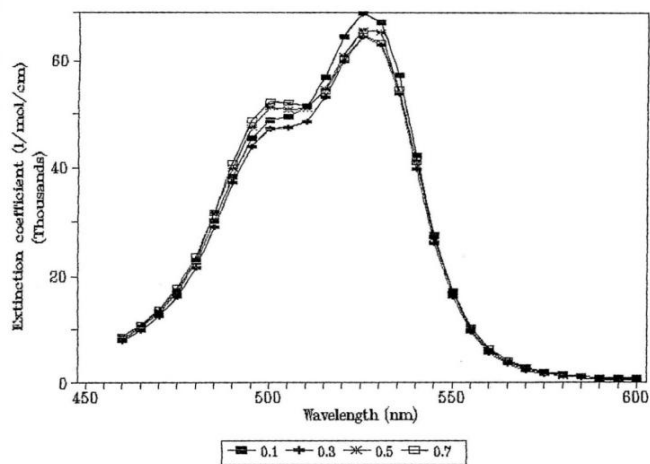

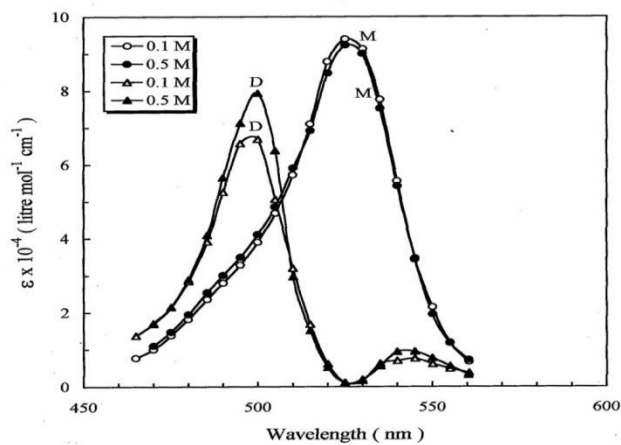**Fig.3.** 1 x 10-4 M Rhodamine-6G + LiCl + H_2O

Fig. 4. Resolved monomer and dimer spectra of rhodamine-6G in presence of 0.1M and 0.5 M LiCl in water.

4. CONCLUSION

The dimer dissociation constant (K) values decrease with increase in concentration of salt LiCl. Thus, the structure breaking electrolyte makes water unavailable for monomeric dye cations. The resulting bare dye cations interaction with each other leading to dimerization. The ratio of $\in_N/\in_P$ are small indicating that transition dipoles in dimer through not exactly parallel, deviate slightly from card pack or sandwich type arrangement.

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