# Self - aggregation of Rhodamine-6G in aqueous medium and aqueous solution of urea

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**ABSTRACT**

*The self-aggregation of Rhodamine-6G [1 x 10$^{-6}$ to 4 x 10$^{-4}$] in water and in aqueous solution of urea (0.1-0.3M) has been investigated by recording electronic spectra in the wavelength range 460 to 600nm. Analysis of the spectral data yielded the dimer dissociation constant, individual characteristic monomer and dimer spectra. By applying the excitaton 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. Similarly, data have also been obtained for aqueous solution of Rh-6G in urea. The significant observation is the change in dimer geometry from sandwich type to end-on-end type in the presence of urea. 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 interactions are the major factors in the phenomenon of aggregation.*
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## INTRODUCTION

The phenomenon of aggregation of dyes, drugs, surfactants etc. has been extensively studied by spectrophotometry, light scattering, osmometry, polarography etc. [1,2]. The results of these studies have indicated that the dye molecules in-spite of repulsion due to similar charges undergo self-aggregation to form dimer, trimer and higher aggregates [3], the charges being maintained as far as possible in the aggregate [4]. The forces which hold the dye molecules together are believed to be hydrogen bonding, van der Waal's forces, London dispersion forces and other short–range forces [1]. The most predominant force has been recognized to be hydrophobic interaction, which help the system to get rid of the thermodynamically unfavorable state. Thus the water structural features seem to play the role of catalyst in inducing aggregation.

The state of a thiazine, Rh-6G in water has been investigated by several workers [5-8]. The study of Mukerjee et al have shed light on the intermolecular interaction involved in the formation of the dimer and trimer. The inference drawn by them can be examined by application of the exciton model, proposed by Kalsha et al [9], with the help of detailed analysis of the spectral data of Rh-6G in aqueous salt and non-aqueous electrolyte solution. Thus we have carried out systematic spectrophotometric studies of the state of the Rh-6G in aqueous salt solution and aqueous urea solution in the concentration range of the dye, where aggregation does not exceed dimerization.

## 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$^{0}$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 $\lambda$ max value obtained was 525 $\pm$ 1 nm, While molar absorption coefficient was found to be 8.3 x 10$^{4}$ dm$^{3}$ mile$^{-1}$ cm$^{-1}$. The spectrum of Rh-6q in water (1x10$^{-6}$m) has a shape similar to that reported in the literature with $\lambda$ max = 624 $\pm$ nm (5-8). Hence the dye was used without further purification.

The urea procured from Qualigens fine chemicals was stored in an evacuated desicator. All solutions were prepared on a molarity basis. The stock solution of Rh-6G stored in reagent bottle wrapped with black paper, was used within one week of its preparation.

826

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## 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 $27 \pm 1^0$C. The spectra are reproduced in fig. 1 examination of fig 1 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 lsobestic 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[7].
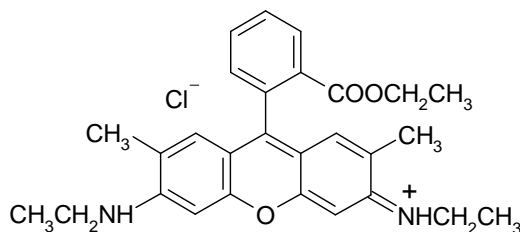


Rhodamine - 6G(FW 479.02)

The dimer dissociation constant K can be expressed as

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

Where, the total dye concentration $C = C_m + 2 C_D$ being the concentrations 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 (E) it Rh-6G can be expressed as function of those the monomer (Em) and dimer (E $_{D/2}$) species, assuming that the Beer - lambert is applicable to both species.

$$\varepsilon = \alpha\varepsilon_m + (1-\alpha)\varepsilon_{D/2}$$

The $E_M$ and E $_{D/2}$ values obtained at different wavelengths allows us to generate the monomer and the dinmer spectra (Frg. 1 (2)

Further, the concentration of the monomer and dimer species were calculated with the help of E and $\alpha$ values. It was observed that the plot of log $C_D$ against log $C_M$ (eqn 1) results in a straight line with a slope of $\cong 2.0$ as compared to expected value of 2.0. This substances our assumption that the monomer dimer equilibrium is only pre dominant equilibrium existing in the solution under investigation further, both 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 $7.0 \times 10^{-4} \pm 0.2$ mole L$^{-1}$ and free energy of dimer is 18.04 kJ. These values are in excellent agreement with those obtained by Selwyn and Seinfeld. They have reported dimer dissociation constant at $22^0$C to be $5.0 \times 10^{-4}$ mole 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 x 10$^{-19}$ A          (3)

Where A = $\int \varepsilon (V) \, d V$

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

| Solvent | $\varepsilon_M X 10^4$ dm$^3$mole$^{-1}$cm$^{-1}$ | $\varepsilon_{D/2 \times 10}^4$ | | $\frac{\varepsilon_N}{\varepsilon_P}$ | $\theta$ | $\frac{f}{}$ | | $\mu X 10^{-30}$ $\frac{\varepsilon_m}{M \quad D}$ | | U/cm$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | P | N | | | M | D | M | D | |
| 0.1 | 11.6 | 6.7 | 1.1 | 0.1634 | 44.0 | 0.35 | 0.21 | 12 | 8.5 | 842 |
| 0.3 | 13.6 | 6.9 | 1.6 | 0.2318 | 51.42 | 0.37 | 0.20 | 8.6 | 12.2 | 791 |

Table 1 The dimer dissociation constant and the spectral data of Rh-6G in aqueous and in aqueous urea solution at $27^0$C Using[10]

$$f = \frac{8\pi^2 mv/u^2}{e^2 3h}$$

827

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where 'm' and 'e' are the mass and charge on the electron, $\mu$ the transition dipole moment, h Planck constant and $\nu$ the frequency at maximum absorbance. These parameter 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, $\Delta$E, depends on the interaction $\left[ U = \dfrac{\Delta E}{2} cm^{-1} \right]$ 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. 2). Since the real systems are non-ideals, we always find some intensity of both bands. The ratio $\varepsilon_N/\varepsilon_P$, the molar absorption coefficients of the dimer species at the $\lambda_{max}$ of the N and P - branches respectively, gives some indication of the dimer geometry[2]. Our results (Table 1) indicate that Rh-6G dimer in water exist further, the angle between the transaction dipoles of the Rh-6G molecules in dimer can be evaluated using[2].

$$\tan^2 \theta/2 = \varepsilon_N/\varepsilon_P \qquad \text{......} \qquad (5)$$

assuming that distance between the dipoles remains unchanged.

The spectral data presented in Fig. 1 clearly indicate that with increase in concentration of Rh-6G the extent of aggregation also in crease. The role played by water structural effects (entropy and enthalpy contribution) in aqueous dye solution has been discussed earlier by Mukerjee et.al[8]. They concluded that dispersion forces are the important contribution to interaction force, in addition tot he driving force provided. by the water structural effect. Application of exciton model[9] has provided sufficient information about the dimer geometry to allow qualitative extension of their interpretations.

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 cm^{-1} which is definitely less than if H-bonding were the dominant factors (~20 kJ mole[-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[13], However, the quadrapole moment of the benzene molecule does influence the orientation of water molecules above and below the molecular plane. The interaction between the Rh-6 molecules in the dimer species should therefore, include interactions such as, ion-dipole, dipole-dipole, dispersion forces and infractions involving higher multi poles 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 $\varepsilon_N/\varepsilon_P$ (=0.1) ration 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 diploes of the Rh-6G molecules in the dimer species are aligned, with respect to each others through an angle $\theta = 44^0$.

Thus the dipole - dipole and ion - dipole infraction 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.

Urea is known to be a water-structure-breaking solute. According to Frank and Frank's model, urea causes increase in the fraction of dense water molecules (non-H-bounded water molecules)[21] It is also known that urea forms channel-like structures around hydrocarbon chains having chain length greater than 5 carbon atoms[22,23]. There are no reports of channel structures of urea around the aromatic moieties. Thus we may conclude that, in addition to water structural effects, there may exist certain specific urea-Rh-6G interactions, however, the exact nature of the interactions is hard to elucidate. We believe that the predominant interactions are mainly of van der Waal's and dispersion types. It is these interactions which switch the dimer geometry from the sandwich-type to the end-on-end-type ($\varepsilon_N/\varepsilon_P$=1.7, Table 1).

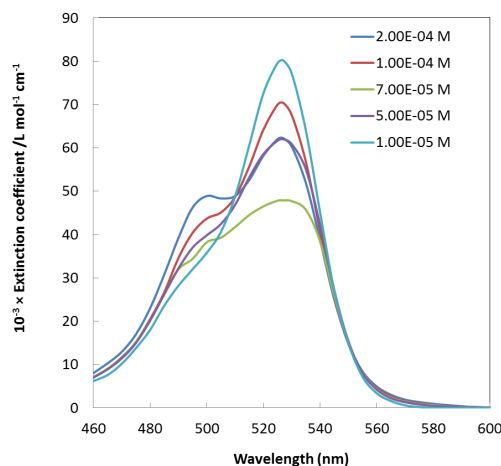*Effect of urea and aggregation of rhodamien - 6 G*



**Fig. 1 Absoroption spectra of Rhodamine-6G in aqueous solutions**
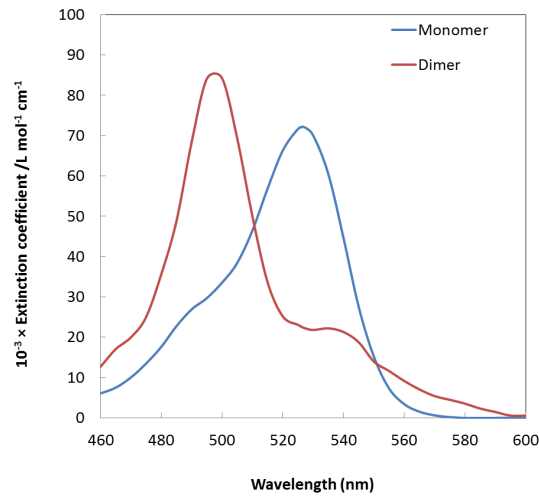
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**Fig. 2 Resolved absoroption spectra of monomer and dimers of Rhodamine-6G in aqueous solutions**
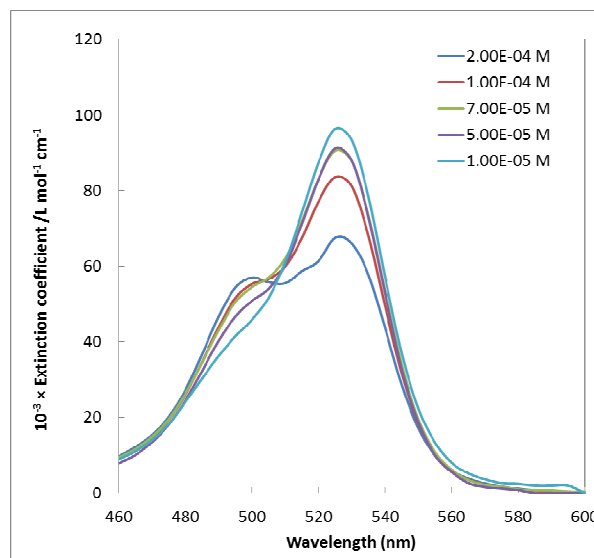
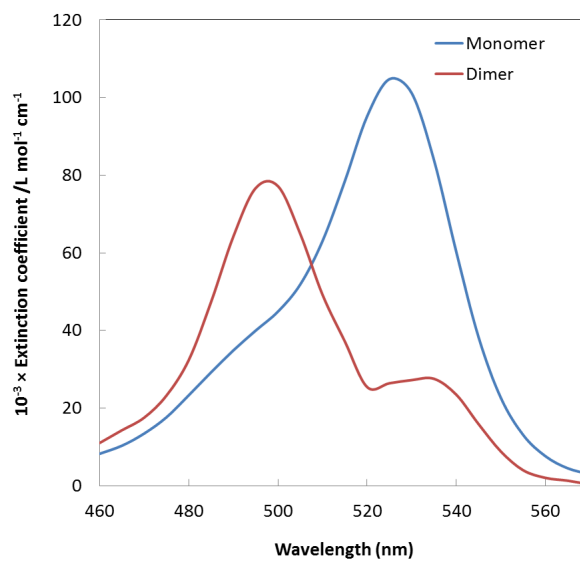**Fig. 3 Absoroption spectra of Rhodamine-6G in 0.1M aqueous urea solutions.**

**Fig. 4 Resolved absoroption spectra of monomer and dimers of Rhodamine-6G in 0.1M aqueous urea solutions.**

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## CONCLUSION

Urea increases the dissociation of rhodamine 6G dimers, but the values of dimer dissociation constants are low as compared to that in pure water. Urea causes reduction in hydrophobic hydration through water structure disruption and some kind of specific interaction with the dye cations. Lower K values are believed to be due to specific interactions of urea with the dye cations.

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