



## Spectral Study of Aggregation Behavior of Remazol Brilliant Violet-5r Dye in Cationic Ligand Solutions

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### Authors' contributions

This work was carried out in collaboration between all authors. Author AEH designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors AED and KME managed the analyses of the study. Author AEH managed the literature searches. All authors read and approved the final manuscript.

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### ABSTRACT

An UV-VIS spectrophotometric investigation has been made to study the interaction and aggregation of anionic remazol brilliant violet-5R (RBV-5R) dye in acidic ethanol amine and tallow amine solutions. As a consequence of increasing the concentration of ethanol amine, the maximum absorbance spectra was shifted to higher energy (blue shift) with increasing in the intensity and a new band with a maximum peak at 420 nm (H-band) was appeared, which is as a result of formation of new complex (dye-ethanolamine) or dye-dye aggregation (H-Aggregate). This was an evidence of aggregation by London dispersion and hydrophobic forces attraction. The binding constant,  $K_b$ , was determined using the modified Benesi-Hildebrand Equation and the standard free energy change  $\Delta G^\circ$  was found  $-12.13 \text{ kJmol}^{-1}$ . By addition of acidic tallow amine solution to the dye, the changes in spectral features were recorded above the critical micelle concentrations. Spectra of aggregated dye molecules due to incorporated in micelles are increases with addition of tallow amine surfactants. It is shown that electrostatic interactions play a key role in dye binding to micelles. The surfactant micelle, which has a longer alkyl hydrocarbon chain, enables greater solubilization of dye. Thus, the hydrophobic interaction of the dye with micelles increases.

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## 1. INTRODUCTION

The interactions between dyes and ligands are an important in many industrial applications such as detergency, emulsion polymerization, enhanced oil recovery, drug delivery and textile dyeing [1-3] and subjects of numerous investigations [4-10]. The purpose is to define physical interactions and focusing on the influence of ligand structure on aggregation of dyes rather than other variables, e.g. ionic strength, solvent and temperature. The formation of aggregated dye molecules in aqueous solutions was first suggested to explain deviations of certain highly colored molecules from Beer's law [6]. It is known that dyes are amphiphiles, i.e. they have bulky non-ionic moieties attached to ionic head groups. Aggregation occurs in a stepwise manner, through dimers, then trimers, etc. by the stacking of flat molecules. A number of techniques have been used to study aggregation of dyes, (e.g. light scattering, potentiometry, conductivity, and colorimetry), and more recent analytical measurements [ultraviolet-visible (UV-vis) spectrometry]. Absorption spectroscopy is the technique most widely used and yield most information about aggregation due to observation of spectral shifts, Beer's law deviations. Thus, much attention has been given to spectrophotometric studies of monomer/dimer equilibria - which rely on detection and identification of the individual species at the molecular level [11-15]. The strength of aggregation between two or more dye molecules depends upon a number of factors: structure of dye (dyes contain charge within the chromophore, so they tend to be more sensitive to environmental changes than dyes containing localized groups), solvent, temperature and

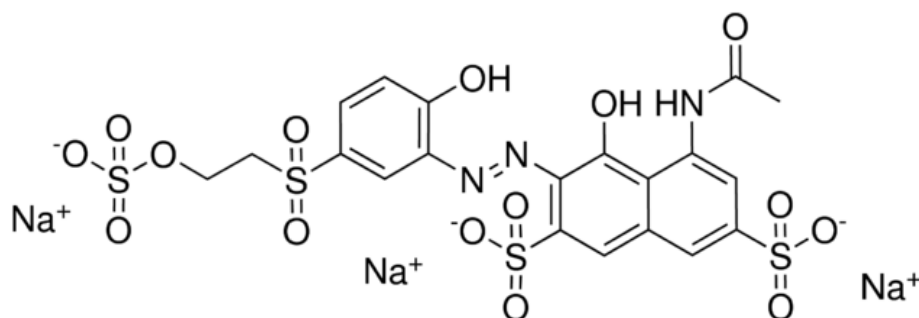
interaction with ligand. However, until more recently, an understanding of the nature of molecular interactions between dyes in solution lacked much clarity. Many experiments were done under different conditions (i.e. solvent, ionic strength, concentration) so that dimerisation or aggregation data could not be directly compared [16-19]. The aggregated surfactants known as micelles are responsible for the solubilization of the hydrophobic substances in water [4]. Therefore, surfactants that start to aggregate into micelles at low concentrations, are good candidates for this purpose.

The main objective of this project was to study the effects of chemical structure and concentration of ligand (surfactant) on the solubilization and aggregation of dyes in aqueous solution. For this reason, the interactions of remazol brilliant violet-5R (RBV-5R) with two ligands (Ethanol amine and Tallow amine) were investigated spectrophotometrically and optimization conditions of aggregations and calculate the binding constant and standard free energy.

## 2. MATERIALS AND METHODS

### 2.1 Materials

All materials were used as received without further purification. Remazol Brilliant Violet - 5R (RB-5R) was obtained from Aytemizler Textile Co. in pure form. The chemical structure of RB - 5R ( $C_{20}H_{16}N_3Na_3O_{15}S_4$ ) (MW 735.5815 g/mol) dye is represented in Fig. 1, which is Solid dark blue to dark violet powder. The purity of ethanol amine ( $C_2H_7ON$ ) and Tallow amine ( $C_{19}H_{34}N$ ) were found 99.5 % and 98.95 % respectively.



**Fig. 1. Structure of dye Remazol Brilliant Violet 5**

## 2.2 Preparation of Dye and Ligand Solutions

The dye solution was prepared by dissolving the powdered dyestuff in Milli-Q water to a final concentration of ( $1 \times 10^{-4}$  M). An appropriate volume of the stock solution was added to the media. The concentration of stock solution of 0.1 M ethanol amine and  $1.9 \times 10^{-4}$  M tallow amine were prepared using Milli-Q water and acidified to about pH = 2. A series of different concentration of acidic aqueous solutions of a specific ligand were prepared and added to the certain amount of dye according to the Table 1.

## 2.3 Spectrophotometric Measurements

The absorption spectra of dye solutions were recorded using single beam Biochrom Ltd, Cambridge CB4 of England (UV-Visible spectrophotometer) with a matched pair of quartz cuvettes (1cm in optical path length).

**Table 1. Different concentration of acidic aqueous solutions of a specific surfactant**

$C_{19}H_{14}N$ [ $10^{-5}$ M]	$C_2H_7ON$ [ $10^{-3}$ M]	Additions [ml]
0.76	4	1
1.52	8	2
2.28	12	3
3.04	16	4
3.80	20	5
4.56	24	6
5.32	28	7
6.08	32	8
6.80	36	9

## 3. RESULTS AND DISCUSSION

### 3.1 UV-visible Spectra of Dye (RBV-5R)

The spectrum of aqueous solution of dye ( $10^{-5}$  M) was exhibited maximum absorbance ( $\lambda_{max}$ ) at 583 nm as shown in Fig. 2. The molar extinction coefficient ( $\epsilon_0$ ) of dye was calculated as  $10673 \text{ mol}^{-1} \text{ L cm}^{-1}$  at wavelength 583 nm, with excellent correlation ( $r^2 > 0.999$ ).

### 3.2 UV-visible Spectra of (RBV-5R) in the Presence of Ethanol Amine

The absorption spectra of a fixed concentration ( $6 \times 10^{-5}$  M) of dye and several different concentration of ethanol amine ranging from  $4 \times 10^{-3}$  to  $36 \times 10^{-3}$  M in acidic aqueous media are

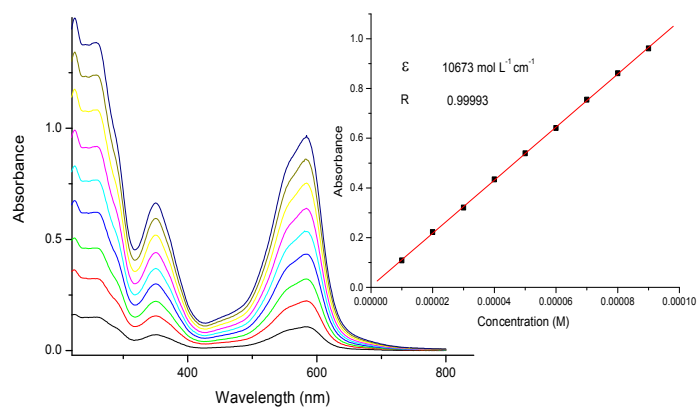
illustrate in Fig. 3. The maximum peak of absorbance of dye at ( $\lambda_{max} = 583 \text{ nm}$ ), initially decreased and a little bit shift to the high energy after first addition of ligand and then increasing again with further addition of the same ligand. The observed  $\lambda_{max}$  shift values of RBV-5R are attributed to the binding with ethanol amine. The hypsochromic shift is a clear indication for the complexation of anionic dye with cationic ligand and increased with increasing hydrophobicity of dyes. Going from aqueous solution to the more hydrophobic environment, the maximum absorbance shifted a lower wavelength in its absorption maxima. The increasing absorbance of shifted peak can be assumed to some sort of association or complex formation between dye and ethanol amine [14-19].

The complex formation of the dye-ligand is a consequence of mutual influences of electrostatic interactions. In the present case, the formation of ion pair (dye-ligand) reduced the electrostatic interaction between anionic dye molecules and thus enhanced dimerization of dyes by London dispersion and hydrophobic forces [20]. An enhancement in the absorbance with hypsochromic spectral shift was observed due to addition of ethanol amine. In Fig. 3, as can be seen, the new peak was formed at 420 nm and increased gradually after addition of ligand concentrations (H-band aggregation), this was an evidence of blue shift [15]. Because of the amphipathic nature of dye and presence of aromatic moiety, it is a tendency to aggregate in aqueous media, especially at higher concentration of polar ligand.

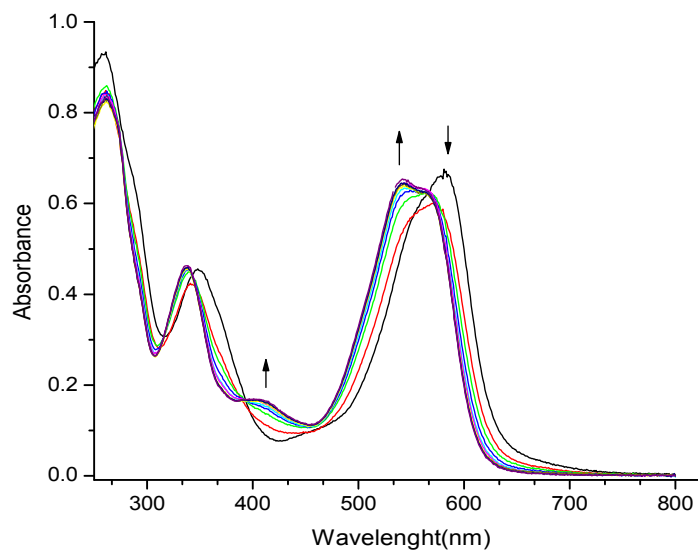
After the aggregates and the H-band became evident, the ligand was added to the dye solution in increments of  $4 \times 10^{-3} \text{ mol/L}$  until no further growth in the spectra. After about  $20 \times 10^{-3} \text{ mol/L}$  of the ethanol amine, no further change in the absorbance intensity of either the monomers or the aggregates occurred, which indicates the reach of the saturation point where every accessible exchanging site on the ligand has been occupied by a dye molecule (Figs. 3 and 4). As more dye molecules are binding with ligands the absorbance values of  $\lambda_{max}$  reaches a limiting value and becomes almost constant [20].

#### 3.2.1 Determination of binding constant

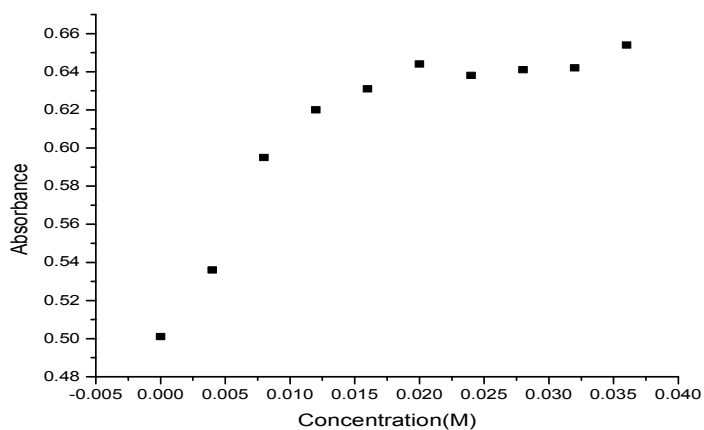
The appearance of isosbestic point in the UV-Vis spectra suggests that when an aqueous solution of dye is treated with ligand solution, the dye monomers are bonded with ligand and converted to aggregation and equilibrium is reached.



**Fig. 2. UV-visible absorption spectra of dye (RBV-5R)**

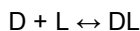


**Fig. 3. Absorption spectra of (RBV-5R)  $6 \times 10^{-5} \text{ M}$  at various addition of ethanol amine Tab.1**



**Fig. 4. Absorbance of dye interacted as a function of ethanol amine added**

The spectrophotometric data were employed to calculate the binding constants of dye–ligand. The equilibrium for the complexation of the dye (D) with ethanolamine (L) can be assumed to follow as:



where D, L, and DL represent the Dye, Ligand, and Dye–Ligand respectively with binding constant ( $K_b$ ). The binding constant,  $K_b$ , and molar extinction coefficient  $\epsilon_m$  can be determined using the Benesi–Hildebrand Equation [21]:

$$D/\Delta A = 1/(\epsilon_m - \epsilon_0) + 1/K_b(\epsilon_m - \epsilon_0)C_m$$

where  $\epsilon_0$  is the molar extinction coefficient of the dye,  $\epsilon_m$  is the molar extinction coefficient of the RBV-5R fully bound to ligand,  $C_m$  is the surfactant concentration,  $K_b$  is the binding constant, D is the total concentration of dye,  $\Delta A = A - A_0$  is the difference between the absorbance of RBV-5R in the presence and absence of ligand.

As shown in Fig. 5, the plot of  $D/\Delta A$  against  $1/C_m$  was found to be linear and the value of  $K_b$  was calculated from the slope and the intercept.

The binding constants  $K_b$  was found 134.13 and the standard free energy change  $\Delta G^\circ$  can be calculated from the values of  $K_b$ , as follows  $\Delta G^\circ = -RT \ln K_b$ . The  $\Delta G^\circ$  was found  $-12 \text{ kJ mol}^{-1}$ , which is an indication of the tendency of the binding of dye (RBV-5R) to ethanol amine ligand.

### 3.3 UV–visible Spectra of (RBV-5R) in the Presence of Tallow Amine

Tallow amine is long-chain molecules and the presence of both hydrophobic and hydrophilic groups within the same molecule which can play as surfactant and form aggregation in certain concentration known as CMC. The surfactant aggregates known as micelles which are responsible for the solubilization of the dyes. Because the concentration of Tallow amine used is higher than CMC concentration [17], the micelles will be formed immediately after first addition. The changes in spectrum of the dye in aqueous solution produced upon addition of tallow amine in acidic media are illustrated in Fig. 6. There is loss in absorbance peak of dye (583 nm) together with the simultaneous appearance of a new absorption peak in the spectrum at (420 nm). The presence of isosbestic point indicates

equilibrium between two different species free dyes in solution and species binding with tallow amine ligand, i.e. there is equilibrium between (ligand- dye) and free dye in bulk solution [1,20].

The hypsochromic shift is a clear indication for the incorporation of dye with cationic micelles and increased with increasing hydrophobicity of surfactants. However, the observed subsequent increase of new absorption (420 nm) is attributed to the presence of aggregated dyes in micelles. Going from aqueous solution to the more hydrophobic micellar environment, the maximum absorbance of RBV-5R shifted a lower wavelength in its absorption maxima.

Furthermore, it is not only shows that the aqueous spectrum becomes successively replaced by a micellar spectrum, but also that a micellar concentration is reached where there are no further spectral changes, i.e. incorporation into the micelle reaches completion.

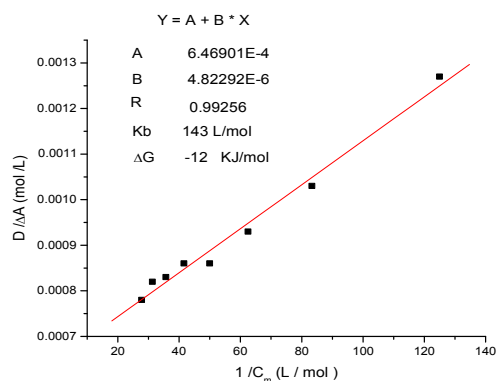
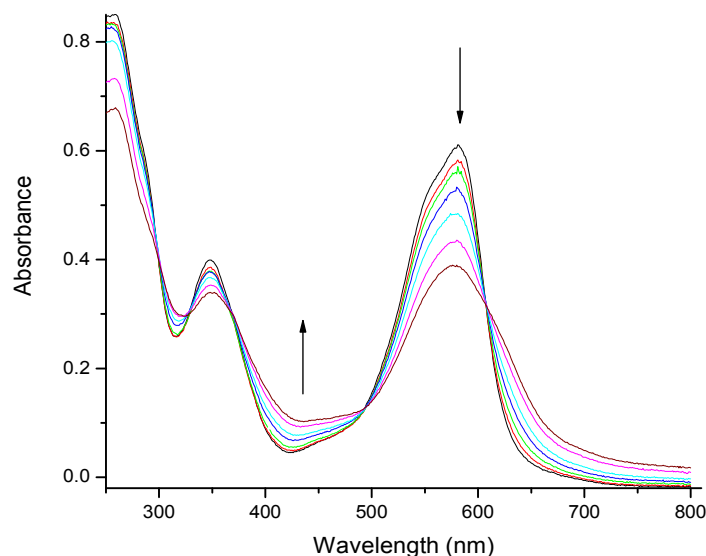
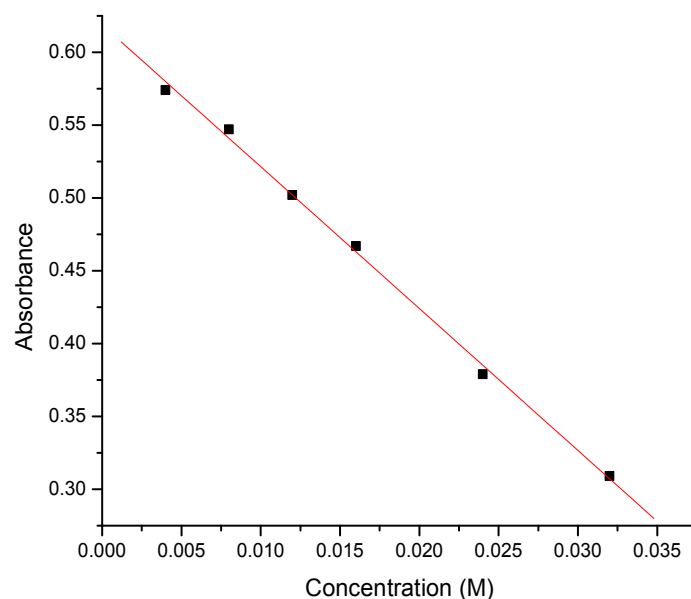


Fig. 5. The plot of  $D/\Delta A$  against  $1/C_m$  for ethanol amine

In Fig. 7, the decreased absorbance of dye at 583 nm is plotted against cationic surfactant concentration added and it is clear that the changes that occur do so above its CMC. Above the CMC, the amount of monomer of dye decreases linearly with the increase in surfactant concentration is regarded to be caused by the incorporation of dye molecules to micelles. Consequently, the changes are attributed to solubilization of free dye in cationic surfactants micelle. It is demonstrated that the location of a dye in a surfactant micelle can be assessed from the absorption spectrum of the dye-containing micellar solution.



**Fig. 6. Absorption spectra of (RBV-5R)  $6 \times 10^{-5}$  M at various concentration of  $C_{19}H_{41}N$  Tab.1**



**Fig. 7. Absorbance of monomer of dye as a function of tallow amine added**

As more dye molecules are incorporated to micelles the absorbance values of  $\lambda_{max} = 583$  nm reaches minimum value.

#### 4. CONCLUSION

Spectrophotometric study of (RBV-5R) dye in the presence of ligand showed that ionic and hydrophobic interaction depends strongly on alkyl hydrocarbon chain length of surfactant.

Ionic interaction indicates a decrease in polarity around the chromophore of dye molecule and the hydrophobic interaction plays an important role in interaction dye-ligand. There is an isosbestic point indicates for an equilibrium between two different species [1]. The magnitude of  $K_b$  is comparable to those of some recently reported [16]. The standard free energy change  $\Delta G^0$  was found  $-12.13 \text{ kJmol}^{-1}$  so the interaction of dye - surfactant was spontaneous. In addition of tallow amine to the dye the changes in

absorption features were recorded above the critical micelle concentrations. It is demonstrated that the location of a dye in a surfactant micelle can be assessed from the absorption spectrum of the dye-containing micellar solution. The affinity of the dye for the surfactant micelles increased when the tail of surfactant increase. The absorbance decreases in the presence of tallow amine is due to solubilization of the dye monomers into micelles. The solubilization power is related to the structure of both the surfactant and the dye [20,22].

### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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