Dimerization of methylene blue in aqueous and mixed aqueous organic solvent: A spectroscopic study

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ABSTRACT

The dimerization of methylene blue (MB) dye in aqueous and mixed aqueous organic solvents has been investigated spectrophotometrically at 303.15 K. The organic solvents chosen for the study include ethylene glycol, 2-methoxy ethanol, 2-ethoxy ethanol, tetrahydrofuran and dioxane. The dimerization constant K_D of MB in aqueous as well as the mixed aqueous media has been computed from their UV–visible spectra. Addition of the organic solvent of low dielectric constant resulted into lowering of the K_D perhaps due to the overall decrease in dielectric constant of mixed media. However, decrease in K_D in the mixed media was not in order of decreasing dielectric constant of the mixed media. In fact, introduction of hydrophobic methyl or ethyl group in ethylene glycol led to an increase in K_D in the order 2-ethoxy ethanol > 2-methoxy ethanol > ethylene glycol even though the dielectric constant of ethylene glycol is higher than that of methyl or ethyl substituted ethylene glycol. The change in the fraction of monomeric dye (α) in the presence of the mixed aqueous organic solvent as a function of the dye concentration has also been computed. The spectra for the monomer and the dimer species of MB have been re-constructed using the K_D values and the results have been analysed in the light of the molecular exciton theory. Both the twist (θ_1) and the tilt (θ_2) angles between the transition dipoles of the MB molecules in the dimer have been computed. It was observed that the presence of the organic solvent led to decreasing not only the twist but also the tilt angle. The results indicated that the dimer essentially has sandwich geometry with a slight deviation from the exact parallel stacking arrangement of the dye molecular planes highlighting the importance of dispersive forces including the hydrophobic effects in the formation of the dye aggregates.

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1. Introduction

Most of the organic dyes undergo self-aggregation in the solution leading to the formation of dimer, trimer and other higher aggregates [1–7]. Dyes and dye-aggregates find increasing applications in the development of the dye sensitized solar cells and non-linear optics materials [8–10]. The aggregation of dyes is most favoured in water which has been ascribed to its high dielectric constant that reduces the electrostatic repulsion between the similarly charged dye molecules and the disruption of the hydrogen bonded water structure by the dye molecules also favour formation of dye aggregates [3,4,11,12]. Aggregation of dye in solution depends on many factors like dye concentration, solvent dielectric, ionic strength, temperature and presence of organic solvents [1,3,12–16]. Based on spectroscopic behaviour, the dye aggregates with intense and very narrow absorption peak that is red shifted from the region of monomer band has been termed as J-band whilst the blue shifted band is known as H-aggregates [1,3,4]. Formation of

dye aggregates has also been reported in heterogeneous media, such as micelles or vesicles [12,17,18]. The recent report which showed that formation of a particular type H- or J-aggregate of a dye may be facilitated in ionic liquid environment has once again underlined the importance of the role of the solvent media in the dye aggregation phenomena [19]. However, in spite of the large number of studies, the aggregation of dyes in mixed aqueous organic solvent has not been adequately studied as to understand the influence of the hydrophobic character of the mixed solvent on the formation of dye aggregates. In continuation to our study on the behaviour of self-aggregating systems especially in mixed aqueous organic solvent [6,20–22], we now report the aggregation behaviour of methylene blue (MB) in aqueous and mixed aqueous–organic solvent media with a view to further highlighting the importance of the solvent hydrophobicity on the aggregation of the dye. The organic solvents chosen for the present study include ethylene glycol (EG), 2 methoxy ethanol (ME), 2-ethoxy ethanol (EE), tetra hydro furan (THF) and dioxane (DIO). Methylene blue is one of the most commonly used thiazine dyes known for its pronounced methachromic behaviour, which readily undergoes aggregation in various solutions [4, 14,18,23]. A schematic structure of MB is shown in Fig. 1.

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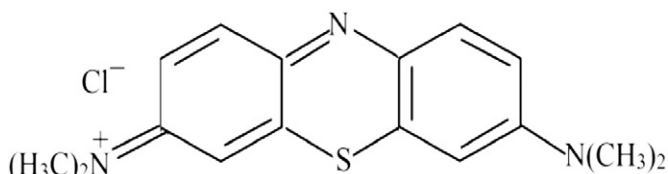 E-mail address: naorem.homendra@gmail.com (H. Naorem).

Fig. 1. Schematic structure of MB.

2. Materials and methods

2.1. Materials

The high purity sample of MB dye obtained from Hi Media Laboratories, India was used as received. The reagent grade sample of EG was obtained from Merck (India) Ltd whilst the samples of ME, EE, THF and DIO were procured from Loba Chemie, India. The organic solvents were purified following established procedures [24] and were fractionally distilled using a long fractionating glass-column prior to their use. Stock solutions of about 5×10^{-4} M MB dye in aqueous or mixed aqueous organic solvent were prepared in 100 mL volumetric flask and the dye solutions (10 mL) of desired concentration were then prepared by diluting the stock solution with appropriate amount of the solvent. Doubled distilled water was used all through the study. Dye solutions were kept in the dark during storage.

2.2. Methods

Visible absorption spectra of the dye solutions were recorded in a CARY-100 Bio UV–visible spectrophotometer (Varian) using a pair of 1 cm quartz cuvettes connected to a Cary-Dual-Cell Peltier Accessory (Varian) for temperature control. The cuvettes were treated with dilute hydrogen peroxide solution prior to measurements to avoid dye deposition on the walls. The absorption spectra of the dye solution were recorded in the wavelength interval between 500 and 750 nm at 303.15 K.

2.3. Determination of dimerization constant

Assuming the equilibrium to be between the monomer (M) and the dimmer (D) species of MB in the solution (M + M = D), the dimerization constant K_D of the dye at a temperature may be expressed in terms of the ratio of the concentration of dimers C_D to monomer C_M according to Eq. (1).

$$K_D = \frac{C_D}{C_M^2} \tag{1}$$

By the law of mass balance, the total dye concentration (C) may be related to C_M and C_D of the dye in equilibrium as

$$C = C_M + 2C_D. \tag{2}$$

The total absorbance, $A(\lambda)$, of the dye in solution per unit of optical length at a given wavelength λ is given by:

$$A(\lambda) = \varepsilon_M(\lambda)C_M + \varepsilon_D(\lambda)C_D \tag{3}$$

where $\varepsilon_M(\lambda)$ and $\varepsilon_D(\lambda)$ represents the molar absorptivity of monomer and dimer species respectively. The total absorbance $A(\lambda)$ may, therefore, be expressed as

$$A(\lambda) = \varepsilon_D(\lambda)\left(\frac{C}{2} - \frac{-1 \pm \sqrt{1 + 8K_D C}}{8K_D}\right) + \varepsilon_M(\lambda)$$
$$\times \left(\frac{-1 \pm \sqrt{1 + 8K_D C}}{4K_D}\right). \tag{4}$$

From Eq. (4), the value of K_D along with $\varepsilon_M(\lambda)$ and $\varepsilon_D(\lambda)$ may be numerically solved by a non-linear regression analysis of $A(\lambda)$ as a function of dye concentration (C) at any wavelength. The value of K_D was such computed that the difference between the observed and the calculated absorbance was always less than or equal to ± 0.005 and the K_D thus obtained was reproducible to within $\pm 1.5\%$ of the reported value. The monomer and the dimer spectra of the dye may then be reconstructed using the computed values of $\varepsilon_M(\lambda)$ and $\varepsilon_D(\lambda)$.

3. Results and discussions

The absorption spectra of MB in pure aqueous media at 303.15 K in the concentration range 10–60 μM along with the spectra in terms of molar absorptivity are shown in Fig. 2. The spectra showed a strong band at 665 nm along with a weaker band at 604 nm, which has been attributed to the monomer and the dimer species of MB [1,4]. With an increasing concentration of MB, the intensity of the dimer band increases at the expense of the monomer band with a clear isobestic point at around 620 nm (Fig. 2b) indicating the presence of an equilibrium between the monomer and the dimer species of MB in the
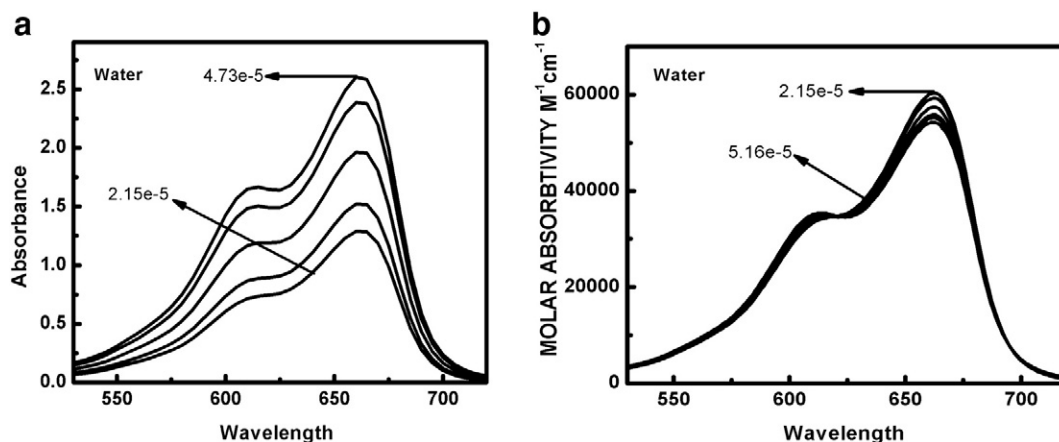

Fig. 2. Spectra of different concentrations of MB in water at 303.15 K (a) in terms of absorbance and (b) in terms of molar absorptivity.