



Determination of the dimerization constant of pinacyanol dye in mixed aqueous–organic solvent media with different hydrophobic character

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ARTICLE INFO

Article history:

Received 22 March 2012

Received in revised form 31 May 2012

Accepted 27 June 2012

Available online 13 July 2012

Keywords:

Pinacyanol dye

Self-aggregation

Mixed media

Dielectric constant

Solvent hydrophobicity

ABSTRACT

The dimerization constant of pinacyanol (PC) dye in aqueous and mixed aqueous–organic solvent media with different hydrophobic character has been determined spectrophotometrically at 303.15 K. The organic solvents chosen for the study include ethylene glycol, 2-methoxy ethanol, dioxane, tetrahydrofuran, ethylamine, diethylamine, triethylamine, ethanalamine, diethanolamine, and triethanolamine. Though presence of the organic solvents reduced the dye's tendency to form aggregates, presence of equilibrium between the monomer and dimer species of the dye was established in mixed aqueous–organic media containing 5% organic solvent by volume and the dimerization constant, K_D , of the dye in the mixed media has been computed. A comparison of K_D among the mixed media containing 5% organic solvent showed that dimers of the dye are preferentially formed with increasing hydrophobic groups in the ethylene glycol or amines under study despite decreasing dielectric constant of the mixed media. The results would suggest that the dye aggregates are better stabilized in more hydrophobic environment perhaps through enhanced hydrophobic effects.

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1. Introduction

Self-aggregation of dyes in solution is of considerable interest since dye aggregates have emerged as promising nonlinear optical materials besides their usage in light harvesting arrays in artificial photosynthetic systems, in photographic processes, in photodynamic therapy of cancer and in laser technologies [1–6]. Based on the spectroscopic behavior, dye aggregates have been described as J aggregates with sharp red shifted absorption band or H aggregates with a blue shifted band with respect to the monomer band of the dye [7]. Aggregation behavior of a dye in solution is largely dependent on many factors like solvent polarity, ionic strength, and the concentration of the dye [7–13]. For example, aggregation of the dyes is most favored in water owing to its high dielectric constant which impacts a reduction in the electrostatic repulsion between similarly charged dye molecules, and also the disruption of the regular hydrogen-bonded water structure by the dye molecules would favor formation of dye aggregates [9,14,15]. Addition of inorganic salts is reported to generally facilitate the aggregation process while presence of organic solvents like alcohol tends to decrease the formation of aggregates [4,10,11]. Formation of dye aggregates has also been reported in mixed solvents or heterogeneous media, such as micelles or vesicles [8,16]. In spite of a large number of studies, the exact origin of dye aggregation is still not clear [2]. Besides the electrostatic and other short-range forces which hold the dye molecules together, recent studies have shown that water structural effects and the hydrophobic interactions are amongst

the major factors in the process of dye aggregation [1,3,14]. From the aggregation behavior of a large number of synthesized squaraine dyes in solution, Chen et al. [3] reported that the tendency of the dyes to form aggregates increases as the length of the hydrophobic chain of the dye increases while squaraines with quaternary ammonium head groups exhibited less tendency for aggregation. Wurthner et al. [1] from studies on the dimerization of polar merocyanine dyes reported that one of the major driving forces for aggregation is the hydrophobic effects, which is controlled by changes within the microstructure of water around the solute. In spite of the large number of studies, the effect of aqueous–organic mixed solvents has not been adequately studied as to understand the influence of the hydrophobic character of the mixed solvent on the self-aggregation of dyes [2,11,17]. In the present paper, we report the aggregation behavior of pinacyanol chloride (PC) dye (1,1'-diethyl-2,2'-carbocyanine chloride) in mixed aqueous–organic solutions with a view to understanding how changes in the hydrophobicity of the solvent media would affect the self-aggregation of the dye. The organic solvents chosen for the present study are ethylene glycol (EG), 2-methoxy ethanol (ME), dioxane (DIO), tetrahydrofuran (THF), ethylamine (EAM), diethylamine (DAM), triethylamine (TAM), monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA).

2. Materials and methods

2.1. Materials

The sample of PC dye (Sigma-Aldrich) was used as received. Analar grade samples of EG, ME, MEA, DEA, TEA and THF were

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procured from Merck (India) while those of EAM, TAM and DIO were obtained from Glaxo India Ltd. and DAM from SRL, India. All the organic solvents were purified following standard procedures [18]. Aqueous solution of 0.5 mM PC dye was prepared in 100 mL volumetric flask wrapped in aluminum foil and was used as stock solution. Dye solutions (10 mL) of desired concentrations in aqueous or mixed aqueous media were then prepared by diluting the stock solution with appropriate amounts of water and the organic solvent. Double distilled water was used all through the study. All the organic solvents were fractionally distilled prior to their use. Photodecomposition of the dye solutions during storage was minimized by keeping the solutions in the dark.

2.2. Methods

The absorption spectra of the dye solutions were recorded with a Shimadzu UV-2450 UV-visible spectrophotometer using a pair of quartz cuvette of 1 cm optical length kept in a cell holder around which thermostated water from a Haake DC-10 was circulated. All the measurements were carried out at 303.15 ± 0.1 K.

2.3. Determination of the dimerization constant

In very dilute solution where there is an equilibrium between monomer (M) and dimer (D) species of the dye ($2M \rightleftharpoons D$), the dimerization constant K_D of the dye at a temperature may be expressed in terms of the ratio of the concentrations of dimers C_D and monomers C_M according to Eq. (1) [8],

$$K_D = \frac{C_D}{C_M^2} \quad (1)$$

Considering the mass balance of the dye in the volume dispersion, the total analytical concentration of PC dye (C) would be given by Eq. (2),

$$C = C_M + 2C_D \quad (2)$$

The total absorbance, $A(\lambda)$, of PC solution per unity of optical length at a given wavelength may be expressed in the form,

$$A(\lambda) = \epsilon_M(\lambda)C_M + \epsilon_D(\lambda)C_D \quad (3)$$

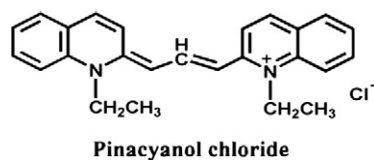
where $\epsilon_M(\lambda)$ and $\epsilon_D(\lambda)$ represent the molar absorptivities of monomer and dimer species respectively. Combining Eqs. (1) and (2), the total absorbance $A(\lambda)$ may be shown to be given by the following expression:

$$A(\lambda) = \epsilon_D(\lambda) \left(\frac{C}{2} - \frac{1 \pm \sqrt{1 + 8K_D C}}{8K_D} \right) + \epsilon_M(\lambda) \left(\frac{-1 \pm \sqrt{1 + 8K_D C}}{4K_D} \right) \quad (4)$$

Nonlinear regression analysis of the total absorbance of the dye solution, $A(\lambda)$ as a function of the dye concentration (C) at any wavelength based on Eq. (4) yields the dimerization constant K_D along with the values of $\epsilon_M(\lambda)$ and $\epsilon_D(\lambda)$, which would allow the calculation of the monomer and dimer spectra.

3. Results and discussion

The absorption spectra of aqueous solution of PC dye show two major peaks, one centered around 600 and the other around 550 nm along with a weak shoulder at around 520 nm. The first two bands have been attributed to the monomer and dimer species of the dye respectively, while the weak shoulder to other higher aggregates [8].



The visible spectra of PC dye in pure aqueous media in the concentration range 1–25 μM is presented in Fig. 1, which shows increasing intensity of the dimer peak at the expense of the monomer peak as the dye concentration increases with significant deviation from Beer–Lambert law owing to formation of dye aggregates in solution. In order to bring out the influence of the added organic solvent, the spectra of a fixed dye concentration (10 μM) were recorded in mixed aqueous media containing different percentage of an organic solvent. Representative spectra of the dye in presence of different percentage of ethylene glycol are shown in Fig. 2. Similar behavior was observed in all the mixed aqueous solutions containing the organic solvents under study. In all such spectra, it was observed that with increasing percentage of the organic solvent, there was a sharp increase in the intensity of the monomer band with small bathochromic shift, which may be due to reduction in the polarity of the mixed media [8]. The relative changes in the intensities of the monomer to that of the dimer band of the dye in the mixed media are shown in Fig. 3 in which the ratio of the monomer to dimer band intensity (A_M/A_D) was plotted against the percentage of the organic solvent. The sharp rise in A_M/A_D in presence of an organic solvent indicates the predominance of the monomer over the dimer species of the dye with increasing percentage of the organic solvent in the mixed media. In the present study we have investigated the aggregation behavior of PC in the mixed aqueous–organic solution by deliberately maintaining the percentage of the organic solvent at 5% by volume

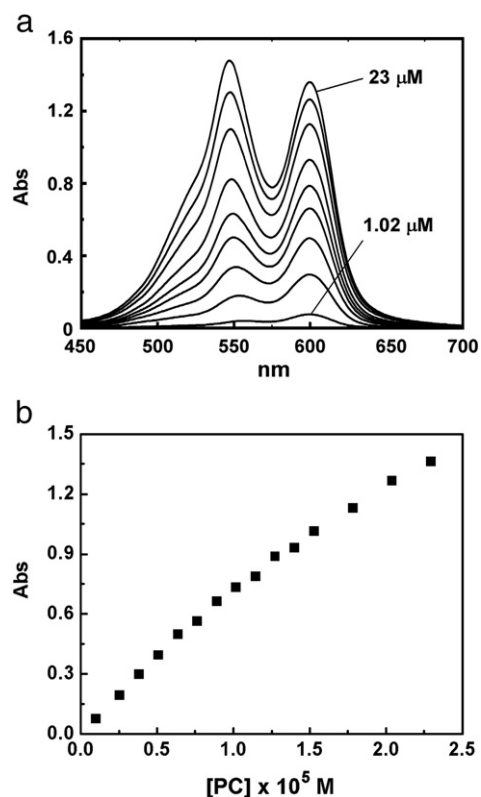


Fig. 1. Absorption spectra of PC dye in water in the concentration range 1–25 μM , (a) absorption vs. wavelength, (b) plot of absorbance at 600 nm as a function of dye concentration.

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