



A comparative study on the aggregate formation of two oxazine dyes in aqueous and aqueous urea solutions

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ARTICLE INFO

Article history:

Received 15 May 2011

Received in revised form 23 July 2011

Accepted 26 July 2011

Keywords:

Brilliant cresyl blue

Nile blue

Oxazine dye

Dye aggregation

Additive effect

ABSTRACT

The visible absorption spectra of two oxazine dyes, brilliant cresyl blue and Nile blue, in aqueous and aqueous urea solutions (0.01–1 M) were studied as a function of the dye concentration. Due to structural similarity of the investigated dyes, their spectral features were compared. The dimerization behavior of the dyes in water with or without urea was analyzed in terms of monomer–dimer equilibrium. The nature and structure of the interacting pairs for these dyes were discussed using the exciton theory. The dimerization constant values of the dyes in aqueous and aqueous urea solutions were calculated. For both the dyes in aqueous urea solutions, a reduction in dimer formation was observed. The excitonic parameters were compared with those of oxazine-1, which is structurally similar to the investigated dyes.

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1. Introduction

It is well reported that photo-physical behavior of a dissolved dye depends on its concentration and the nature of its environment [1–5]. The environment effect is closely related to the nature and degree of dye–solvent interactions. The environment may also influence considerably the aggregative properties of ionic dyes. The molecular association of dyes due to strong attractive electrostatic forces is a well-known phenomenon in solutions. The strength of the molecular association depends on several factors including the dye concentration and structure, temperature, solvent and other factors [6–10]. Presence of the aggregates formed by ionic dye molecules can be detected from the observed fluorescence quenching, deviation from the Beer's law at high concentration, the ratio of the dimer absorbance to monomer absorbance (A_D/A_M), and from the shape of absorption spectra in the visible region.

Brilliant cresyl blue (BCB) and Nile blue (NB) are cationic oxazine dyes with planar molecular structure, which have a variety of medical and scientific applications [11–13]. The dyes are able to accept and donate hydrogen bonds in polar solvents. However, the H-bond formation between their monomeric units is not well clear. The photochemical and photophysical properties of these dyes have been explored by several authors [14,15]. However,

further studies in this area are still important and interesting for practical and scientific purposes.

In our previous paper [16], aggregate formation of oxazine 1, whose molecular structure is relatively similar to those of BCB and NB, in aqueous solutions was reported. In this report, we describe the effect of concentration on the spectral features and aggregative properties of BCB and NB in aqueous and aqueous urea solutions. Therefore, a comparative study on the aggregative behavior of the dyes, with similar molecular structures, was carried out in this investigation.

As far as the authors are aware, a detailed study about the aggregative behavior of the investigated dyes, in particular for BCB in aqueous and aqueous urea solutions, is not available in the literature. This work presents useful spectral data for the investigated dyes.

Nevertheless, detailed analyses of the spectral data and aggregate formation of NB in aqueous solution have been carried out by Antonov et al. [6], and Niazi and Kubista et al. [17].

2. Experimental

2.1. Materials and method

Fig. 1 shows the molecular structures of the oxazine dyes used in this study. Brilliant cresyl blue (BCB) zinc chloride double salt was of analytical grade and obtained from Merck. Nile blue (NB) perchlorate was obtained from Aldrich (95% purity). The investigated dyes with high purity were used with no further purification. Deionized water was used through all experiments. Urea (CON_2H_4)

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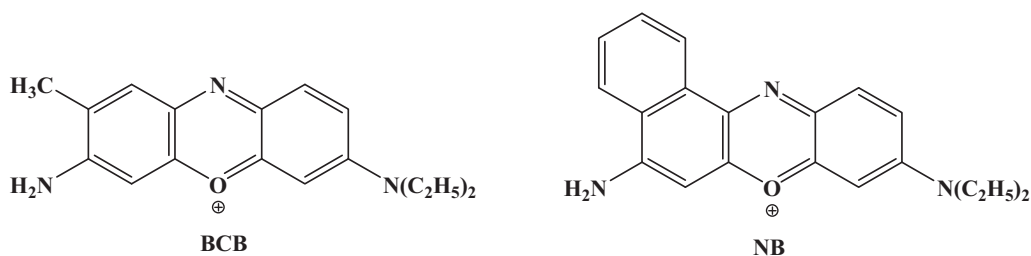


Fig. 1. Molecular structure of the dyes.

was used as additive in this work and was obtained from Merck. The chosen additive is white powder consisting of colorless crystals that dissolve easily in water.

The absorption spectra of the samples were recorded on a Cary UV–vis double-beam spectrophotometer (Model 100) at room temperature. The sample holders were a series of rectangular cell with 1–10 mm optical path lengths. Precise values of λ_{\max} and $\lambda_{\text{shoulder}}$ were obtained from the first derivative of the absorption spectra. Samples used in these experiments were made fresh and changed daily.

2.2. Determination of the dimerization constant

Since the range of concentrations used in this work was below the concentrations at which noticeably higher order aggregates occur, it was assumed that mainly single monomer–dimer equilibrium existed. Therefore, the higher degree of association was not considered. Presuming that monomer + monomer = dimer, the dimer association constant (K_d) can be expressed as [6]:

$$K_d = \frac{[D]}{[M]^2} \quad (1)$$

$$\text{Total analytical concentration} \equiv [C] = [M] + 2[D] \quad (2)$$

moreover:

$$\begin{aligned} \text{Abs}_{\text{total}}(\lambda) &= \text{Abs}_{\text{monomer}}(\lambda) + \text{Abs}_{\text{dimer}}(\lambda) \\ &= \varepsilon_m(\lambda)[M]l + \varepsilon_d(\lambda)[D]l \end{aligned} \quad (3)$$

Here $\varepsilon_m(\lambda)$ and $\varepsilon_d(\lambda)$ correspond to molar absorptivities of monomer and dimer at a given wavelength, and “ l ” is the optical path length. Since this equilibrium exists even at very low concentrations, pure molar absorptivities of monomer and dimer species at a particular wavelength and their concentrations cannot be directly determined.

The linear and/or nonlinear least squares fitting methods were used for calculation of the dimerization constants, K_d , of the dye. These methods mainly consist of two major parts including determination of the dimerization constant and spectra decomposition. A detailed description of these methods and their implementation as an add-in has recently been reported [18]. A brief description about these methods is as follows.

2.2.1. Linear least squares fitting approach

Dividing Eq. (3) by $[C] \times l$ and defining α as fraction of dye molecules present as monomers gives:

$$\alpha = \frac{[M]}{[C]} \quad (4)$$

Combining Eqs. (4) and (1) gives:

$$K_d = \frac{(1 - \alpha)[C]}{2\alpha^2[C]^2} \quad (5)$$

$$\begin{aligned} \varepsilon_{\text{total}}(\lambda) &= \varepsilon_m(\lambda)\alpha + \varepsilon_d(\lambda)\left(\frac{1 - \alpha}{2}\right) \\ &= \left(\varepsilon_m(\lambda) - \frac{\varepsilon_d(\lambda)}{2}\right)\alpha + \frac{\varepsilon_d(\lambda)}{2} \end{aligned} \quad (6)$$

Variation of $\varepsilon_{\text{total}}(\lambda)$ vs. α should yield a straight line with intercepts at $\varepsilon_m(\lambda)$ for $\alpha = 1$ and $\varepsilon_d(\lambda)/2$ for $\alpha = 0$. By systematic variation of K_d and analyzing the straight-line fitness in a series of wavelengths, one obtains optimum dimerization constant as well as monomer and dimer spectra.

2.2.2. Nonlinear least squares fitting method

Introducing Eqs. (1) and (2) into Eq. (3) produces:

$$\begin{aligned} \text{Abs}_{\text{total}}(\lambda) &= \varepsilon_m(\lambda) \left(\frac{-1 + (1 + 8K_d[C])^{1/2}}{8K_d} \right) l \\ &+ \varepsilon_d(\lambda) \left(\frac{[C]}{2} - \frac{-1 + (1 + 8K_d[C])^{1/2}}{8K_d} \right) l \end{aligned} \quad (7)$$

Fitting the experimental data to Eq. (7), using nonlinear curve fitting method in a series of wavelengths, one obtains monomer and dimer spectra as well as optimum dimerization constant, simultaneously.

3. Results and discussion

3.1. Self-association of BCB and NB in aqueous solution

The investigated oxazine dyes typically possess a doublet band, i.e. a maximum (λ_{\max}) and a shoulder ($\lambda_{\text{shoulder}}$), in their absorption spectra. BCB and NB appear to exist almost in their monomeric form at concentrations below 5×10^{-5} M and 3×10^{-5} M, respectively. As the dye concentration increases, the intensity of the shoulder at shorter wavelength increases. The spectral variation indicates formation of dye aggregates. The absorption spectra of BCB in aqueous solutions and aqueous urea solutions at 12 different concentrations, ranging from 1×10^{-6} to 1×10^{-3} M, were recorded at room temperature. The absorption spectra of NB (1×10^{-6} to 5×10^{-4} M) in water and aqueous solutions of urea were also investigated.

Fig. 2 shows the molar absorption spectra of BCB and NB in aqueous solutions as a function of the dye concentration. As it can be seen, the absorption spectrum of BCB in water shows an intense band at 622 nm which is neighbored by a shoulder at nearly 572 nm (Fig. 2(I)). In aqueous solution, the absorption spectrum of NB

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