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Spectral and aggregative properties of two oxazine dyes in aqueous solutions containing structure-breaking and multifunctional additives

A. Ghanadzadeh Gilani *, S. Shokri

Department of Chemistry, Faculty of Science, University of Guilan, Rasht, Iran

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ABSTRACT

This study demonstrates the visible spectral data for two oxazine dyes, brilliant cresyl blue (BCB) and Nile blue (NB) in aqueous additive solutions as a function of the dye and additive concentrations at room temperature. The added organic additives were thiourea (TU) and two basic mono and di-amino compounds, i.e. diethanolamine (DEA) and aminoethyl ethanolamine (AEEA). The monomer and dimer spectra as well as dimerization constants (K_d) of the studied dyes in water with or without TU were determined and analyzed using DECOM Program. Due to the multiple properties of the additives (having various functional groups), different absorption characteristics were observed for these dyes in water with or without additives. A reduction of the dimerization parameters for the dyes in aqueous additive solutions was observed. The exciton theory was used to analyze the dimer structure. The nature of deprotonation of the dyes in the basic media (adjusted by addition of additive) was interpreted in terms of direct and indirect mechanisms of proton transfer process.

1. Introduction

Oxazine dyes are an important group of organic compounds with interesting photophysical and photochemical properties [1–3]. The unique properties of this group of organic dyes make them suitable for many technological applications and promising materials for various optical and photonic devices [4–6]. Many efforts have been carried out in recent years on photophysical properties of this class of dyes. It is well reported that the spectral properties of oxazine dyes are sensitive to their local environment, solvent polarity and polarizability, and environment basicity [7–14]. In the past, several authors have reported spectral data of this class of dyes in aqueous solutions containing various additives and surfactants [15–17].

In this study, we focus on the two-oxazine dyes, which are structurally similar to each other (Fig. 1a). Brilliant cresyl blue (BCB) and Nile blue (NB), with planar molecular structure, which have a wide variety of biological and chemical applications [18,19]. The structure of both the dyes, with two amino groups forming the push–pull conjugated system, consists of an electron donor and an electron withdrawing aromatic system. Both the dyes have hydrogen bond donor/acceptor groups; therefore, they are expected to form H-bonds in hydrogen bond donor/acceptor media. Comparing to the BCB, NB is a dye with more hydrophobic nature. The obvious differences between these two dyes are that the NB has a bulky benzyl ring instead of methyl group in BCB and their molecular structures consisting of different counter anions.

It is well reported that due to influence of the counter-anion, the spectral properties of a dye in solution may depend on its anion nature [20,21]. For instance, the negative charge in perchlorate anion is uniformly distributed among the oxygen atoms. Therefore, besides the electrostatic attraction, the perchlorate anion tends to interact with cation through hydrogen bonding or dipole–dipole interaction. Note that, the perchlorate anion can also be solvated by hydrogen bonding to water or the additive, and thus, the cation–anion interaction decreases. However, influence of the counter–anion on the dye spectral characteristics is out of scope of this paper.

It is well reported that chemical additives alter the physical and physicochemical properties of materials. The different kinds of organic additive of various concentrations have many applications in various industries [22]. The organic additives (Fig. 1b) used in the current study were thiourea (TU) and the two basic compounds (2-aminoethyl) ethanolamine (AEEA), and diethanolamine (DEA). The additives, which have different functional groups, may form H-bonds directly with the polar groups of the dye molecules. TU (an organosulfur compound) is a white crystalline solid with a planar molecular structure. Both AEEA and DEA have a basic chemical nature with pK_b values around 4.5 and 5.1, respectively.

AEEA is a diamine (with one secondary and one primary amine groups). It is very hygroscopic and can absorb the carbon dioxide in the air [23]. It is used as a reagent or chemical intermediate for production of surfactants, chelating agents, and curing agents. It is also used as a nonionic surface-active agent in chemical industry. DEA is an aliphatic bifunctional molecule with both amine and alcohol groups. It is a secondary amine and a primary diol and acts as a base in aqueous solution. DEA is used in a wide variety of applications including gas purification,

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* Corresponding author at: Department of Chemistry, University of Guilan, 41335 Rasht, Iran. Tel./fax: +98 131 3233262.
E-mail address: aggilani@guilan.ac.ir (A.G. Gilani).

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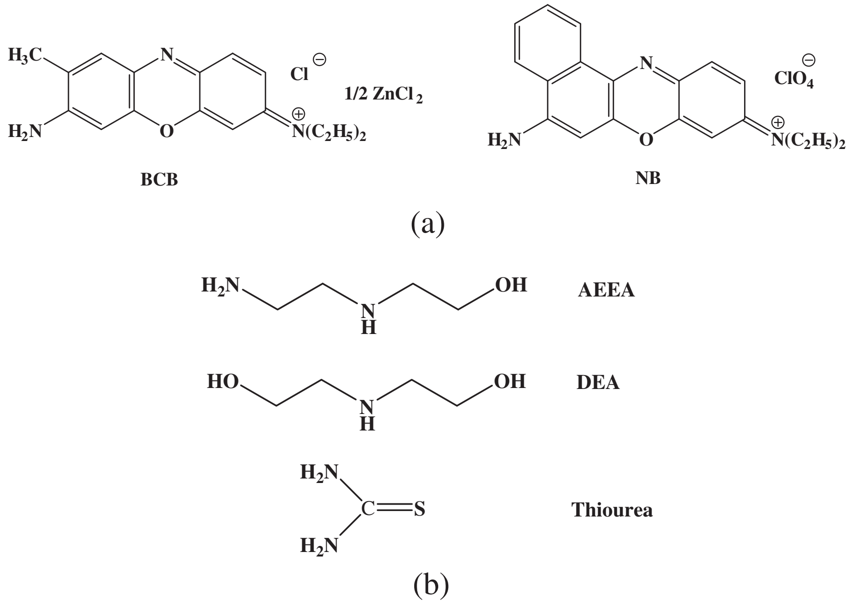

Fig. 1. (a) Structure of the oxazine dyes, (b) structure of the additives used.

surfactants and detergents, textiles, agricultural chemical intermediates, and cosmetics.

In our previous paper [17], the spectral data of NB and BCB in aqueous and aqueous urea solutions as a function of the dye concentration was reported. It was found that the spectral characteristics of the dyes have been strongly altered in the presence of urea. In this report, we describe the spectral characteristics and systematic spectral variations of BCB and NB due to the presence of TU and alkaline additives (AEEA and DEA). Thus, a systematic comparative study on the spectral performance of the dye was carried out in this investigation. In addition, these additives possess polar multifunctional groups and their molecules can interact with themselves and with other polar groups present in the dyes through the hydrogen bonding and dipole–dipole interactions. Thus, the multiple effects, which expected to contribute to the dye spectra, were studied and interpreted.

2. Experimental

2.1. Materials

Brilliant cresyl blue zinc chloride double salt, BCB, was of analytical reagent grade (purity > 0.99) and obtained from Merck. BCB appears as deep green to dark blue crystalline powder. Laser grade Nile blue A (NB) perchlorate was purchased from Exciton (95% purity). NB appears as dark green crystal and is chemically known as 5-amino-9-diethylaminobenz [α] phenoxazonium perchlorate. The molecular structures of the dyes used in this study are shown in Fig. 1a. The investigated dyes were used with no further purification. Deionized and redistilled water with an electrical conductivity less than 5 $\mu S\ cm^{-1}$ at $T = 298.2$ K was used throughout all experiments. Reagent grade thiourea (purity ≥ 0.99) was obtained from Merck. Diethanolamine, DEA, (purity > 0.98) and (2-aminoethyl) ethanolamine, AEEA, (purity > 0.98) were used as additives in this work and were obtained from Merck. AEEA and DEA are viscous and colorless liquids that dissolve easily in water. The chemical structures of the additives used in this study are shown in Fig. 1b.

2.2. Sample preparation

The stock solutions of BCB (1×10^{-3} M) and NB (5×10^{-4} M) were prepared by dissolving accurately weighted dyes in distilled water. The stock solutions were prepared in 100 ml volumetric flask at room temperature. The testing solutions were prepared by diluting the stock solutions to proper concentrations. The aqueous additive solutions were prepared from the stock solutions by appropriate dilutions. The various concentrations of the aqueous additive solutions were prepared by micropipetting and aliquot of the stock solutions. In the case of AEEA and DEA, an aliquot of the dye stock solution was transferred into a 10 ml volumetric flask, and then appropriate amount of the additive was added using a Brand Transferpette micropipette (with an accuracy of ±0.001 ml) and then diluted with distilled water. All sample weighing was carried out with an AND electronic analytical balance (model HR-200) with an accuracy of ±0.0001 g.

2.3. Preparation of buffer solutions and pH measurement

The pH stability was carried out using four different buffer solutions (Table 1). All compounds (analytical grade) used for the preparation of buffer solutions were obtained from Merck and Aldrich chemical companies and used without any further purification. The buffer solutions were prepared as described in the literature [24]. The buffer solutions were prepared with appropriate chemical compounds, such as sodium hydroxide, sodium tetraborate (borax), sodium bicarbonate, sodium hydrogen phosphate, potassium chloride and hydrochloric acid. A digital pH meter Genway model 3505 was used for determination of pH.

2.4. Measurement of absorption spectra

The absorption spectra of the dyes 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 and were mounted in a thermostatted holder. Precise values of λ_{max} and $\lambda_{shoulder}$ were obtained from the first derivative of the

Table 1
Composition of reagents used for the preparation of the buffer solutions and corresponding pH values.

Buffer compounds	pH
50 ml of 0.025 M $Na_2B_4O_7 \cdot 10H_2O$ (borax) + 4.6 ml of 0.1 M HCl	9
50 ml of 0.5 M $NaHCO_3$ + 22.7 ml of 0.1 M NaOH	11
50 ml of 0.5 M Na_2HPO_4 + 26.9 ml of 0.1 M NaOH	12
25 ml of 0.2 M KCl + 66 ml of 0.2 M NaOH	13