Journal of Molecular Liquids 177 (2013) 273–282

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Additive effect on the dimer formation of thiazine dyes

A. Ghanadzadeh Gilani *, T. Ghorbanpour, M. Salmanpour

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

ARTICLE INFO

Article history:
Received 9 July 2012
Received in revised form 8 September 2012
Accepted 12 September 2012
Available online 27 September 2012

Keywords:
Thiazine dyes
Thionine
Azure A
Methylene blue
Dimerization
Additive effect

ABSTRACT

Visible absorption spectra of thionine (Th), azure A (AA), and methylene blue (MB) in aqueous and aqueous additive solutions (0.1–3 M) were studied as a function of the dye concentration. The added additives were urea and aminoethyl ethanolamine (AEEA). Due to the strong structural similarity of the investigated dyes, their spectral parameters were compared at room temperature. The spectral data for each dye were analyzed using DECOM Program. The dimerization behavior of the investigated dyes in water with or without urea was analyzed in terms of monomer–dimer equilibria. The dimerization constant, K_d, values of Th, AA, and MB in aqueous solutions were calculated to be $(5.6 \pm 0.4) \times 10^2\ M^{-1}$, $(2.5 \pm 0.1) \times 10^3\ M^{-1}$, and $(6.5 \pm 0.3) \times 10^3\ M^{-1}$, respectively. However, a reduction of the dimerization constant for the dyes in aqueous urea solutions was observed. The dimer structure and the nature of the interacting pairs in these dyes were discussed using the exciton theory. Finally, due to the unique properties of AEEA, different absorption characteristics were observed for these dyes in pure AEEA and its aqueous solutions.

1. Introduction

Thionine (Th), azure A (AA), and methylene blue (MB), belong to the thiazine group of dyes (Fig. 1a), and have a variety of industrial and scientific applications [1]. They are mainly used for coloring substrates in biological and medical studies and are promising material for photosensitizing applications [2]. Moreover to their traditional uses, the importance of some thiazine dyes is quickly increasing in many other fields [3–5]. In the last few decades, many efforts were focused on the photochemical and photophysical properties of this class of dyes [6–10].

Self-association of thiazine dyes in solutions is a well-known phenomenon [11]. The presence of the dye aggregates plays an important role in chemical and biological processes. Many investigators have suggested that higher aggregates than dimers for thiazines are possible [12]. However, the strength of the molecular association depends on several factors including the dye concentration and structure, temperature, solvent and other factors [13–15]. Therefore, the spectral properties of thiazine dyes are known to be sensitive to their environment and concentration. In aqueous solution, thiazine dyes exhibit aggregations mainly due to the hydrophobic character of the molecular structure. It is well reported that the optical properties of the dyes are strongly influenced by the aggregation phenomena. Significant spectral data of thiazine dyes in particular MB in aqueous solution have been reported by many investigators [16–21].

In the past, several authors have reported spectral data of this class of dyes in aqueous solutions containing various additives and surfactants [22–25]. Thiazine dyes are widely investigated in micellar media as they can be used in photosensitized reactions. Interaction between thiazine dyes and inorganic materials such as clays using visible spectroscopy have been studied by several investigators [26,27]. In addition, the influence of salt type and concentration on the spectral behavior and molecular association of this group of dyes in aqueous solutions have been investigated.

It is well-known that chemical additives alter the properties of materials. The different kinds of organic additive of various concentrations have many industrial applications [28]. They are extensively used in various industries such as chemical, petrochemical, agricultural, and pharmaceutical industries [29–31]. Organic additives are widely used in food and beverage industries [32]. They are used in production of semiconductors and ceramics. Organic additives have an important role in cement and plating industries. Various kinds of organic additives have been used in plant tissue culture and water treatment. They have been shown to induce changes in catanionic vesicle (formed from mixtures of cationic and anionic surfactants) morphology [33].

The organic additives used in the current study were urea and (2-aminoethyl) ethanolamine (AEEA), which has many uses in different industries. Urea (Fig. 1b) is usually a white powder consisting of colorless crystals that dissolve easily in water. Urea as a biologically important additive is used in a broad range of applications. It is well-known as a strong protein denaturant [34–36]. Having different polar groups (i.e. carbonyl and amines groups), urea molecules are able to form hydrogen bonds with water molecules [37] and also with themselves [38]. However, each urea molecule is also able to make bonds with a dye molecule. It weakens hydrophobic interactions in aqueous solution. Addition of urea may increase the solubilities of dyes in water. Urea is known to be a water-structure-breaking additive

* 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. Ghanadzadeh Gilani).

0167-7322/$ – see front matter
http://dx.doi.org/10.1016/j.molliq.2012.09.005

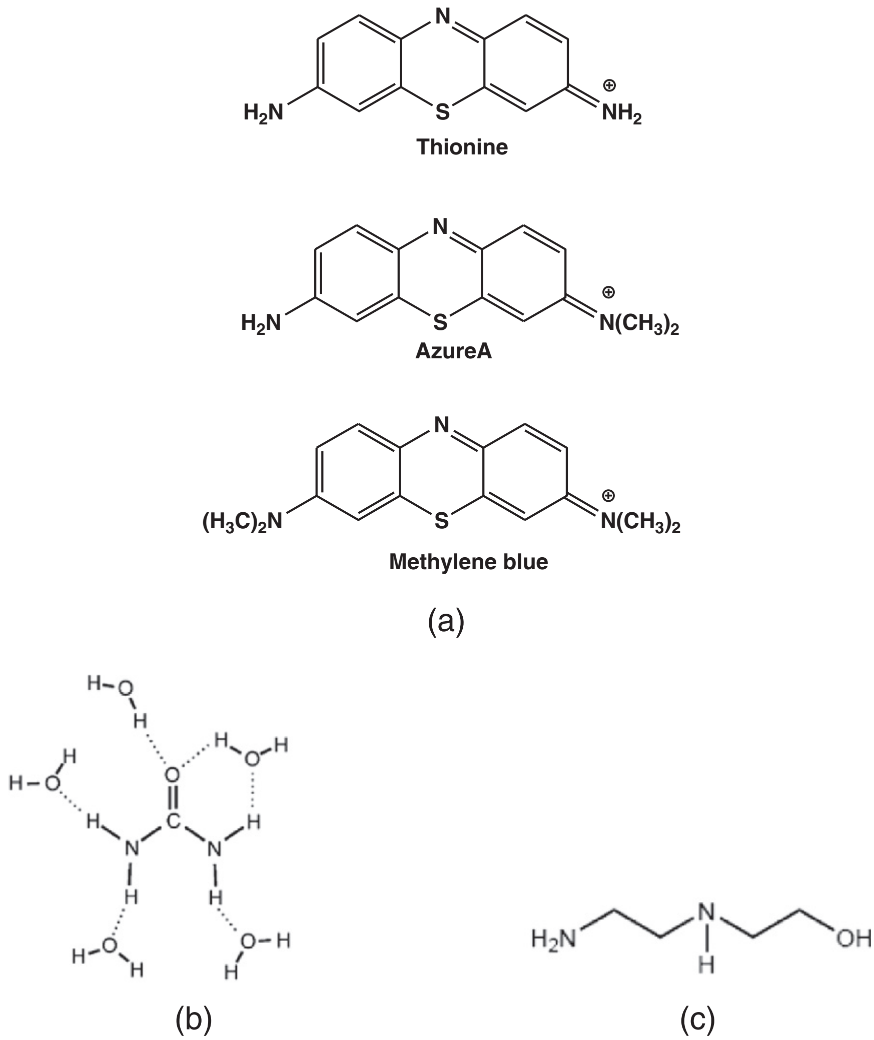

Fig. 1. (a) Structure of thiazine dyes, (b) solvation structure of the urea molecule, (c) structure of AEEA.

[39]. An explanation of the effect of urea on the structure of water, from different point of view, has been the subject of continuing interest in recent years and is given in several papers [40–42].

AEEA (Fig. 1c) is a viscose and a colorless to pale yellow liquid with a mild ammonia-like odor. It is soluble in water and alcohol, but only slightly soluble in ether. AEEA is a diamine (with one secondary and one primary amine groups) which has a basic chemical nature with unique properties (strongly alkaline). It is very hygroscopic and can absorb the carbon dioxide in the air [43]. The pH of AEEA (pH of 1 wt.% solution) is 11.8 and is denser than water. AEEA 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. AEEA, which has amine groups and hydroxyl group, may form H-bonds directly with the polar groups of the dye molecules.

In this report, we describe the effect of concentration on the spectral data and aggregative properties of the thiazine dyes in aqueous and aqueous urea solutions. The monomer–dimer equilibrium of the dyes in aqueous and aqueous urea solutions was investigated. In addition, the spectral behavior of the dyes in amino ethyl ethanolamine (AEEA) and also in aqueous solution of AEEA was investigated. Consequently, a comparative study on the aggregative behavior of the dyes, with a strong similar molecular structure, was carried out in this investigation. The choice of urea and AEEA as additives in this research was motivated by the following considerations. They have strong polar groups and their molecules can interact with themselves and also with other polar groups present in the dyes (solute–solvent interactions) through the hydrogen bonding and dipole–dipole interactions. Therefore, they can potentially alter the driving force for the dye aggregation.

2. Experimental

2.1. Materials and method

Methylene blue chloride and thionine acetate were obtained from Merck. Azure A chloride was purchased from Sigma-Aldrich. The investigated thiazine dyes were of analytical reagent grade and were used with no further purification. Fig. 1a shows the chemical structures of the dyes used in this study. Deionized water was used throughout this experiment. Urea (purity > 0.995) and (2-aminoethyl) ethanolamine, AEEA, (purity > 0.98) were used as additives in this work and were obtained from Merck. The chemical structures of the additives used in this study are shown in Fig. 1b and c.

2.2. Measurement of absorption spectra

The absorption spectra of the dyes were recorded on a Cary UV–Vis double-beam spectrophotometer (Model 100) over a wavelength