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Concentration effect on the absorption spectra of oxazine1 and methylene blue in aqueous and alcoholic solutions

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Abstract

The visible absorption spectra of oxazine-1 (OX) in aqueous and alcoholic solutions were studied as a function of the dye concentration. Due to the structural similarity of OX and MB, the optical characterization of methylene blue, MB, was also investigated for comparison. OX in aqueous solutions appears to exist almost in its monomeric form at concentrations below about 1×10^{-4} M, while MB exhibit strong tendency to aggregate even at the low concentrations. The dimerization behavior of OX and MB in water was analyzed in terms of monomer–dimer equilibria. The nature of the interacting pairs in these dyes was discussed using the exciton theory.

Keywords: Oxazine dyes; Methylene blue; Ionic dyes; Aggregation; Dye dimerization; Exciton theory

1. Introduction

The molecular association of ionic dyes in solutions due to the strongly attractive electrostatic forces is a well-known phenomenon [1–9]. The presence of aggregates in the dye solutions may influence considerably in their photo-physical behavior. The strength of the molecular association depends on the several factors including the dye concentration and structure, temperature, pressure, solvent and other factors [10–13]. The structure of the aggregates has been studied by applying exciton theory to the analysis of the absorption spectra [14].

The dye aggregation leads to a strong coupling of the molecular transition dipoles, resulting in excitonic absorption band, which is considerably different from the absorption of the monomeric species. The presence of the aggregates formed by ionic dye molecules can be detected from the observed fluorescence quenching, deviation from the Beer's law in high concentration, and the ratio of the dimer to the monomer absorbance (A_D/A_M).

Oxazine perchlorate, OX, is a cationic oxazine dye with interesting photo-physical and lasing properties [15]. The lasing properties and output power being strongly influenced by the aggregative properties. The molecular associations cause a large decreasing the emission quantum yield and life time of the first singlet excited state of the dye, and therefore, a weaker laser efficiency to be expected. A large amount of investigation has been carried out in recent years on spectroscopic behavior of this group of dyes [16–24]. In aqueous solution, oxazine dyes exhibit aggregations due to the hydrophobic character of the molecular structure.

Thiazine dyes such as methylene blue, MB, containing polar chromophores are an important group of organic compounds which have a variety of industrial and scientific applications [25]. The photo-physical and aggregation properties of this group of dyes have been demonstrated by several authors [26–30]. In spite of substantial reports on the aggregative properties of MB in liquid solutions, based on the authors literature review, aggregation behavior of OX has attracted relatively little attentions.

The choice of OX and MB for this study was motivated by the following considerations. In spite of OX and MB are belong to the two class of molecules (i.e. oxazines and thiazines), they have similar molecular structure. The obvious differences between these two dyes are that the latter has less bulky dimethyl groups and it has a heterocyclic sulfur atom instead of oxygen (Fig. 1). Both OX and MB are cationic symmetric dyes, and their aromatic

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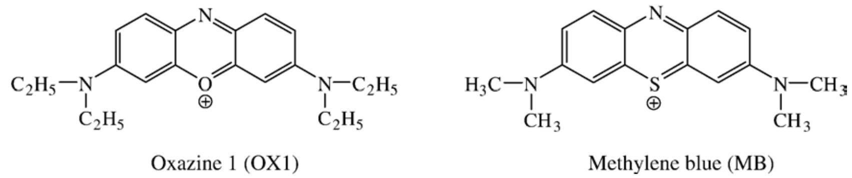

Fig. 1. Molecular structure of the dyes.

skeletons are approximately planar, so that the transition moment vector of them may be considered to be largely parallel to the long molecular axes. In addition, both the dyes are able to accept H-bonds but are very weak H-bond donor; therefore, it is expected to form H-bonds in polar protic solvents. However, the H-bond formation between their monomic units is not well clear.

In this report, we describe the effect of concentrations on visible spectra of OX in aqueous and alcoholic solutions. The aggregative behavior and the monomer–dimer equilibrium of the dye were also investigated. For comparison, the spectral data of MB were investigated.

2. Experimental

2.1. Materials and method

Oxazine 1 perchlorate (oxazine 725 perchlorate) was obtained from Exciton (pro-analysis) and used without further purification as a solute. The oxazine dye appears as green bronzy crystals and is chemically known as 3, 7-bis (diethylamino) phenoxazin-5-ium perchlorate ($C_{20}H_{26}N_3O{\cdot}ClO_4$). Methylene blue was obtained from Merck. The chemical structure of the dye is shown in Fig. 1. All the solvents with high purity (spectroscopic grade) were purchased from Merck.

The absorption spectra of the dyes were recorded on a Cary UV–Vis double-beam spectrophotometer (Model 500) at room temperature. The thermostated sample holder was a series of rectangular cell with 0.5–50 mm path lengths. Precise values of $\lambda_{\max}$ 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. Theoretical considerations

Within the context of the exciton theory developed by Kasha et al. [14], the nature of the interacting pairs in the dimeric systems can be described. The excitonic treatment of the dimer would permit the ground and excited state wave functions of such systems to be defined as follows:

$$\psi_{G,d} = \phi_a \phi_b \tag{1}$$

$$\psi_{E,d} = C_1 \phi_a^* \phi_b + C_2 \phi_a \phi_b^* \tag{2}$$

where ϕ_a and ϕ_b are the wave functions of the interacting monomers. The Hamiltonian operator of the aggregates is normally written in the form

$$H = H_a + H_b + V_{ab} \tag{3}$$

here H_a and H_b are the Hamiltonians of the unperturbed monomers and V_{ab} represent the coulombic potentials approximated by the point dipole–dipole interactions existing between the monomer–monomer components. Replacing the wave function and the Hamiltonian in the Schrödinger equation would results in the standard secular determinant for the dimers as follows:

$$\begin{vmatrix} H_{aa} - E_E & H_{ab} \\ H_{ba} & H_{bb} - E_E \end{vmatrix} \tag{4}$$

$$U = H_{ab}\ H_{ba} = \int\int \phi_a^* \phi_b H \phi_a \phi_b^* d\tau_a d\tau_b$$

where the U is the interaction energy between the two adjacent molecules in the dimer. Each energetic state of the monomer splits into two states of the dimer. The spectral splitting depends on the strength of the interaction between the two adjacent molecules in the dimer.

3. Results and discussion

3.1. Self-association of oxazine 1 and methylene blue in aqueous solution

The absorption spectra of OX in aqueous and ethanolic solutions, at 12 different concentrations ranging from 1×10^{-7} to 1×10^{-3} M, were recorded at room temperature. The spectral data of the dye in 1-butanol, *tert*-butanol and 2-propanol solvents were also obtained in the concentration range 1×10^{-7} to 1×10^{-4} M. The absorption spectra of MB (1×10^{-7}–1×10^{-4} M) in water and alcoholic solutions were also investigated.

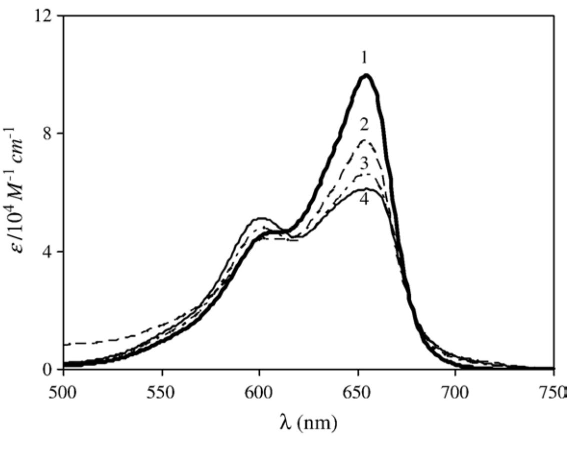

Fig. 2. Absorption spectra of OX in aqueous solution; 1) 50 μM, 2) 100 μM, 3) 500 μM, 4) 800 μM.