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# Solvent effects on the molecular resonance structures and photo-physical properties of a group of oxazine dyes

M.S. Zakerhamidi\*, Sh. Golghasemi Sorkhabi

Research Institute for Applied Physics and Astronomy, University of Tabriz, Tabriz, Iran

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## ABSTRACT

Absorption and fluorescence spectra of two oxazine dyes were recorded in various solvents in the range of 300–800 nm, at room temperature. The solvatochromic behavior of these substances and their solvent–solute interactions, both specific and non-specific, was analyzed using linear solvation energy relationship concept, suggested by Kamlet–Taft. The ground and excited state dipole moments of these substances and molecular resonance structures were also evaluated by a solvatochromic shift method.

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## 1. Introduction

We live in a colorful world, the preparation and use of dyestuffs is one of the oldest human activities. With the advent of the industrial revolution, chemistry began to play a prominent role in the improvement of the existing colorants and their applications [1]. Among the groups of organic dyes, the oxazine family of dyes constitutes a widely used set of fluorescent stains in modern biology and histology. They are commonly used as probe for the investigation of many chemically important systems, and have been studied extensively both experimentally [2] and theoretically [3]. Many experimental and theoretical works demonstrate that spectral and optical properties of oxazine dyes are sensitive to their solvent environment [4].

Aside from substituent change, it is known that the photo-physical behavior of a dissolved substance is strongly influenced by its environment [5,6]. The solvation effects are based on the assumption that solute–solvent interactions are of two kinds: non-specific–dipolarity/polarizability [7] and specific–hydrogen-bond formation [8]. The specific hydrogen bond formation is sub-divided into solute's hydrogen-bond donor (HBD)/solvent's hydrogen-bond acceptor (HBA) and solute's HBA/HBD complex [9,10]. The effects of solvent polarity on spectroscopic behaviors are interpreted by the means of linear solvation energy relationship (LSER). This method of analysis is applied using the Kamlet–Abboud–Taft (KAT) solvatochromic parameters. According to the KAT formalism, the observed shift

of compounds in solvent is given by the following equation [8,11]:

$$v = v_0 + a\alpha + b\beta + s\pi^* \quad (1)$$

The solvent effects' are described by the solvent parameters  $\pi^*$ ,  $\alpha$  and  $\beta$ . The  $\pi^*$  scale is an index of solvent dipolarity/polarizability, which measures the ability of the solvent to stabilize a charge or a dipole due to its dielectric effect [12].  $\alpha$  is the scale of solvent's hydrogen-bond-donor (HBD) acidities, which describes the ability of the solvent to donate a proton in a solvent-to-solute hydrogen bond [13]. The  $\beta$ , scale of hydrogen-bond-acceptor (HBA) basicities, measures the ability of the solvent to accept a proton (i.e., to donate an electron pair) in a solute-to-solvent hydrogen bond [14].  $v_0$  is the regression value of the solute property in the reference solvent. The regression coefficients  $a$ ,  $b$  and  $s$  in these equations measure the relative susceptibilities of the solute property, such as absorption, fluorescence and other spectroscopic parameters.

In this work, the photo-physical properties of a group of oxazine dyes (oxazine 720 and oxazine 750) were investigated in different solvent environments, using Kamlet–Abboud–Taft linear solvation energy relationship, in order to understand the effects of specific and non-specific interactions' effects on the molecular resonance structures of solutes. Also, the spectral features of this group were studied for estimation of ground and excited state dipole moments.

## 2. Experimental

### 2.1. Materials

Oxazine 720 and oxazine 750 were obtained from Exciton and were used without further purification as solutes (Table 1). All the

\* Corresponding author. Tel.: +98 411 3393027; fax: +98 411 3347050.

E-mail address: [Zakerhamidi@tabrizu.ac.ir](mailto:Zakerhamidi@tabrizu.ac.ir) (M.S. Zakerhamidi).

solvents used in the study were of highest available purity from Merck. The selected empirical polarity parameters, polarity functions and physical properties, of the employed solvents, are listed in Table 2.

## 2.2. Absorption and fluorescence spectroscopy

A double beam Shimadzu UV-2450 scan spectrophotometer was used to record the absorption spectra over a wavelength range between 300 and 800 nm, which is combined with a cell temperature controller. Fluorescence of substances' solutions was studied with a JASCO FP-6200. Quartz cuvettes were used for measurements in solution via  $1 \times 1 \text{ cm}^2$ . The solute concentrations were chosen to be  $5 \times 10^{-6} \text{ M}$  for all the samples.

## 2.3. Estimation of dipole moments

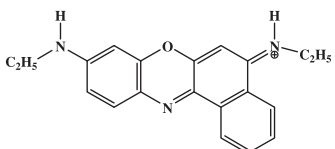
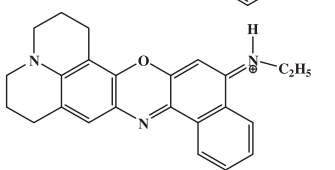
Solvatochromic shift in solvents of different properties provides means to determine the dipole moments of the molecules [15]. Based on a quantum mechanical perturbation theory [16,17] of absorption ( $\nu_a$ ) and fluorescence ( $\nu_f$ ) band shift of a spherical solute in different solvents of varying permittivity ( $\epsilon$ ) and refractive index ( $n$ ), the difference between the dipole moments of the ground and excited singlet state is described by following equations [18,19]:

$$\tilde{\nu}_a - \tilde{\nu}_f = m_1 f(\epsilon, n) + \text{const.} \quad (2)$$

$$\tilde{\nu}_a + \tilde{\nu}_f = -m_2 [f(\epsilon, n) + 2g(n)] + \text{const.} \quad (3)$$

where

**Table 1**  
Molecular structure of oxazine dyes.

Dye	Molecular weight (g/mol)	Molecular structure
Oxazine 720	431.87	
Oxazine 750	469.92	

**Table 2**  
Spectroscopic polarity parameters, physical properties and polarity functions of employed solvents [5].

Solvents	$\epsilon$	$n$	$\alpha$	$\beta$	$\pi^*$	$f_{BK}(\epsilon, n)$	$g_{BK}(n)$
1,4-Dioxane	2.2	1.422	0.00	0.37	0.49	0.044	0.286
Dichloromethane	8.9	1.4242	0.13	0.10	0.73	0.590	0.288
Acetone	21.0	1.359	0.08	0.48	0.62	0.793	0.244
Methanol	33.7	1.329	0.98	0.66	0.6	0.858	0.244
Ethanol	24.3	1.361	0.86	0.75	0.54	0.812	0.246
1-Butanol	17.5	1.399	0.84	0.84	0.47	0.749	0.271
2-Propanol	19.9	1.377	0.76	0.84	0.48	0.779	0.256
1-Hexanol	13	1.418	0.67	0.94	0.40	0.686	0.284
1-Heptanol	11.3	1.424	0.64	0.96	0.39	0.652	0.288
1-Decanol	8.0	1.437	0.7	0.85	0.45	0.553	0.296
DMF	39.2	1.430	0.00	0.69	0.88	0.480	0.292
DMSO	47.2	1.479	0.00	0.76	1.00	0.841	0.324
Water	78.3	1.780	1.17	0.47	1.09	0.771	0.508

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \quad (4)$$

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \quad (5)$$

The solvent polarity parameters  $f(\epsilon, n)$  and  $g(n)$  have the following forms:

$$f(\epsilon, n) = \frac{((\epsilon - 1)/(2\epsilon + 1) - n^2) - ((1/2n^2) + 1)}{(1 - (2\alpha/a^3)(\epsilon - 1/2\epsilon + 1))(1 - (2\alpha/a^3)(n^2 - 1/2n^2 + 1))^2} \quad (6)$$

$$g(n) = \frac{((n^2 - 1)/(2n^2 + 1))(1 - (\alpha/a^2)(n^2 - 1)/(2n^2 + 1))}{1 - (\alpha/a^3)(n^2 - 1/2n^2 + 1)} \quad (7)$$

In the above relations,  $\epsilon$  denotes the dielectric permittivity and  $n$  is the refractive index.  $a$  and  $\alpha$  represent the spherical cavity radius [20] of the solute and average polarizability, respectively. For an isotropic polarizability of the solute, the condition  $2\alpha/a^3 = 1$  is often satisfied and justified [21–23], and functions  $f(\epsilon, n)$  and  $g(n)$  leads to Bakhshiev polarity function:

$$F_{BK}(\epsilon, n) = \frac{2n^2 + 1}{n^2 + 2} \left[ \frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \quad (8)$$

$$g_{BK}(n) = \frac{3}{2} \left[ \frac{n^4 - 1}{(n^2 + 2)^2} \right] \quad (9)$$

Keeping in mind that the symmetry of the investigated solute molecule remains the same, during the electronic transition, and considering the parallelism of ground and excited state dipole moments, based on Eqs. (4) and (5) one obtains [24–26]:

$$\mu_g = \left| \frac{m_2 - m_1}{2} \right| \sqrt{\frac{hca^3}{2m_1}} \quad (10)$$

$$\mu_e = \left| \frac{m_2 + m_1}{2} \right| \sqrt{\frac{hca^3}{2m_1}} \quad (11)$$

$$\mu_e = \frac{m_1 + m_2}{m_1 - m_2} \mu_g \quad (m_1 > m_2) \quad (12)$$

where  $h$  is Planck's constant and  $c$  the velocity of light in vacuum. The parameters  $m_1$  and  $m_2$  can be determined from absorption and fluorescence band shifts, Eqs. (2) and (3).  $\mu_e$  and  $\mu_g$  are the dipole moments in the excited and ground states, respectively. Onsager cavity radii ( $a$ ) for investigated dyes were determined theoretically according to their optimized geometry [27]. The radius of spherical cavity for each solute, used in Onsager solvation model, was calculated from its optimized gas phase geometry. First, the geometry of the molecule was optimized by B3LYP hybrid-GGA functional and 6-31G(2df, 2p) basis set in gas phase. Then, the molecular volume was computed as a volume inside a contour of 0.001 electron/Bohr<sup>3</sup> density and the radius of this spherical's volume was calculated. All calculations were performed by Gaussian 03 program [28].

## 3. Result and discussion

### 3.1. The solvent effect on the absorption and emission spectra

The visible absorption and fluorescence spectra of the oxazine samples ( $5 \times 10^{-6} \text{ M}$ ) were obtained at room temperature (22 °C) in different organic solvents. Spectral data are also summarized in Table 3. The absorption spectra of oxazine samples (Fig. 1) show different active bands. Previously, some researchers reported spectral bands between 400 and 700 nm, in oxazine dyes [29–31]. There is a general agreement that oxazine derivatives show mainly  $S_0$ – $S_1$

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