



A study on solvatochromism of some monoazo dye derivatives

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ABSTRACT

The UV–vis and fluorescence spectra of four monoazo dye derivatives were investigated in the solvents with different polarities. Characterization of UV–vis electronic bands is specified by calculating charge transfer energy (E_{CT}) and ionization potential (I_p). The solvent effects on the absorption and fluorescence band maxima (ν_{max}) were discussed using the solvent parameters. The magnitude and characteristics of the solute–solvent interactions were determined with multiple linear regression analysis. The π – π^* transitions of monoazo derivatives are mainly controlled by global interaction, which is induction–dispersive and orientation interactions.

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1. Introduction

Azoaromatic compounds have attracted much attention in recent times due to their emerging applications in the dye stuff industry, for being excellent photo-aligning substrates for liquid crystals, highly efficient photorefractive media, acid–base, redox, metallochromic indicators and non-linear optical devices such as optical switches, optical data storage and liquid crystalline displays (LCDs). Azo derivatives have also been used in photo-catalytic reactions as a catalyzer when exposed to ultraviolet light [1–11]. Some important food colorants (e.g. sunset yellow and allure red) also belong to the class of azo dyes [12]. Some azo dyes are also used in biological systems where some can be used as inhibitors of tumor-growth [13,14].

The optical properties and solvatochromic behavior of the azo dyes depend on several factors, such as the nature of electron donor/acceptor substituents, the *cis-trans* photoisomerization in azo chromophores, charge transfer (CT) mechanism and the interaction of solute–solvent. Azo dyes, especially containing hydroxyl group in *ortho*-position of the hydrazo group, can exist in three tautomeric forms (enol-azo, keto-azo and hydrazone) with conjugated donor– π –acceptor system, which already make them promising candidates for such applications as mentioned above. This tautomerism is generally observed in the solution phase and a ratio between these forms depends on the solvent used as well as on temperature [15,16]. It is assumed that the tautomers in solution are stabilized by a strong intramolecular *resonance assisted*

hydrogen bond (RAHB) and the tautomeric balance plays an important role for many applications involving electronic transitions [17–21].

The main structural characteristics are mainly due to the presence of azo group ($-N=N-$) connecting to phenyl rings ($Ph-N=N-Ph$) along with the donor/acceptor substituents located at *ortho-meta-para* positions on phenyl ring. Electron-donating substituents can increase the absorption coefficients while electron-withdrawing groups can shift the absorption maxima to longer wavelength. Azo dyes cover the full color spectrum owing to the wide range of donor/acceptor systems. These dyes often exhibit solvatochromism with increasing solvent polarity normally producing a bathochromic shift in λ_{max} . However, if the ground state of the dye is more polar than the excited state, the interaction of polar solvents with the ground state will be stronger than with the excited state, resulting in a hypsochromic shift [22]. Their UV–vis absorption spectra can be influenced by non-specific interactions such as ion–dipole, dipole–dipole, and induced dipole–permanent dipole interactions or by a specific interaction such as hydrogen bonding with solvents. Thus, solvents play an important role in physical and chemical processes and can determine the change in the position, intensity, and shape of absorption bands [23–28]. Solvatochromism is a powerful tool to investigate the physical–chemical properties of molecules [29].

It is well known that the effects of solvents on physical–chemical phenomena and spectroscopic data are better analyzed in terms of a linear combination of solvent properties, including solvent dielectric constant – ϵ , refractive index – n , hydrogen bond donation ability (solvent “acidity”) – α and hydrogen bond acceptance ability (solvent “basicity”) – β . The solvatochromism of several classes of azo compounds has been investigated previously [4,24,30–34]. Azo dyes are known to

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show a positive solvatochromism [24,25,30–41]. The first examples of negative solvatochromism in neutral azo dyes containing both strongly electron-donating and withdrawing moieties were reported [42].

Despite various studies on the spectral properties and solvation behavior of azo disperse dyes in different solvents, there are only few systematic investigations on the azo dyes containing –OH moieties which give rise to –O–H···N intramolecular and intermolecular interactions in order to explain the nature of solvent–solute and solute–solute interactions, and more detailed studies are still needed. The aim of this work is to investigate the solvent influence on the UV–vis absorption and fluorescence spectra of some azo dyes and to evaluate the intermolecular interactions occurring in solutions. The spectral characteristics of the studied azo dye molecules in different solvents at room temperature were analyzed in this paper. A linear correlation between experimental spectral values (ν_{\max}) and the solvent parameters: refractive index functions $f(n) = \frac{n^2-1}{n^2+1}$, or $f(n) = \frac{2n^2-1}{n^2+1}$ and electric permittivity functions $f(\epsilon) = \frac{\epsilon-1}{\epsilon+2}$, or $f(\epsilon) = \frac{\epsilon-2}{2\epsilon+1}$ along with the solvatochromic empiric variables n , ϵ , α and β have been used to discuss the solvatochromic behavior of the analyzed dyes and to evaluate their contributions to the solvent–solute interactions. The chemical structures of the investigated azo dyes are presented in Fig. 1.

2. Materials and methods

The investigated azo dyes in Fig. 1 were synthesized and purified using a previously reported method given in references [43,44].

Both polar and non-polar solvents are spectroscopic grade reagents and are used without further purification. These solvents include water, dimethyl sulfoxide, glycerol, *N,N*-dimethyl formamide, methanol, ethanol, acetone, 2-propanol, iso-butanol, 1-butanol, tetrahydrofuran, butyl acetate, ethyl acetate, chloroform, toluene, benzene, carbon tetrachloride, 1,4-dioxan, cyclohexane, *n*-hexane and *n*-pentane and they are general purpose reagents obtained from Sigma-Aldrich. H₂O was used as double distilled. Each solution was prepared as about 5×10^{-4} M. All UV–vis spectra were acquired using a Shimadzu UV-2550 double beam spectrophotometer in standard 1 cm path length quartz cell at room temperature for spectral analysis. Fluorescence spectra are recorded on a Perkin Elmer LS-55 fluorescence spectrometer. Samples are illuminated with a 50 Hz pulsed xenon source. Excitation wavelengths are 337 nm, 385 nm, 385 nm and 370 nm for AZO1, AZO2, AZO3 and AZO4, respectively. The positions of the absorption and

fluorescence bands are determined by Gaussian curve fit analyses using OriginPro 7.5. Linear correlation and data fit are also performed by using OriginPro 7.5. In each recording, the instrument was zeroed with the solvent before the spectra of the dyes were acquired. Sample recording was done from 200 to 900 nm. Dielectric constant, ϵ , refractive index, n , hydrogen bond donating ability (α) and hydrogen bond accepting ability (β) were taken from the literature [29,45].

The solvent dependent maximum band shifts, ν_{\max} , were analyzed using a wide range of parameters such as refractive index (n), dielectric constant (ϵ) and Kamlet–Taft parameters (hydrogen bond donating ability (α) and hydrogen bond accepting ability (β)). The electronic transitions are assigned and the solvent-induced spectral shifts have been analyzed in relation to the different solute solvent interaction mechanisms. The intermolecular interaction types in the azo derivative solutions have been established on the basis of a multiple linear regression analysis. The multiple linear regression coefficients that correspond to peak maximum regression values have been described using the SPSS 15.0 statistical package program. The fitting coefficients obtained from this analysis allowed us to estimate the contribution of each type of interactions to the total spectral shifts in the studied solutions. We have made an attempt to establish a correlation between the experimental spectral values (ν_{\max}) with the four solvatochromic variables of dielectric function $f(\epsilon) = (\epsilon - 1) / (\epsilon + 2)$, electronic polarizability function $f(n) = (n^2 - 1) / (n^2 + 1)$, H-bond donating ability (α) and H-bond accepting ability (β) in order to evaluate the respective contributions to the solute–solvent interactions of azoaromatic compounds. In this case, the position of the absorption band, ν_{\max} which has been expressed as a linear function of the solvent parameters described above is as follows:

$$\nu_{\max} = C_0 + C_1 f(n) + C_2 f(\epsilon) + C_3 (\beta) + C_4 (\alpha) \quad (1)$$

where C_0 signifies the extrapolated value of the wavenumber in the gaseous state and coefficients C_i ; $i = 0, 1, 2, 3, 4$ reveal the relative contributions of the considered solvatochromic parameters [46]. The coefficients C_i were determined by multiple linear regression techniques. The second term (C_1) describes the contribution of the orientation induction interactions to the frequency shift. The third term (C_2) defines the contribution of dispersion polarization forces to the total spectral shift. The solvatochromic coefficients were obtained using multiple linear regression analysis (MLRA).

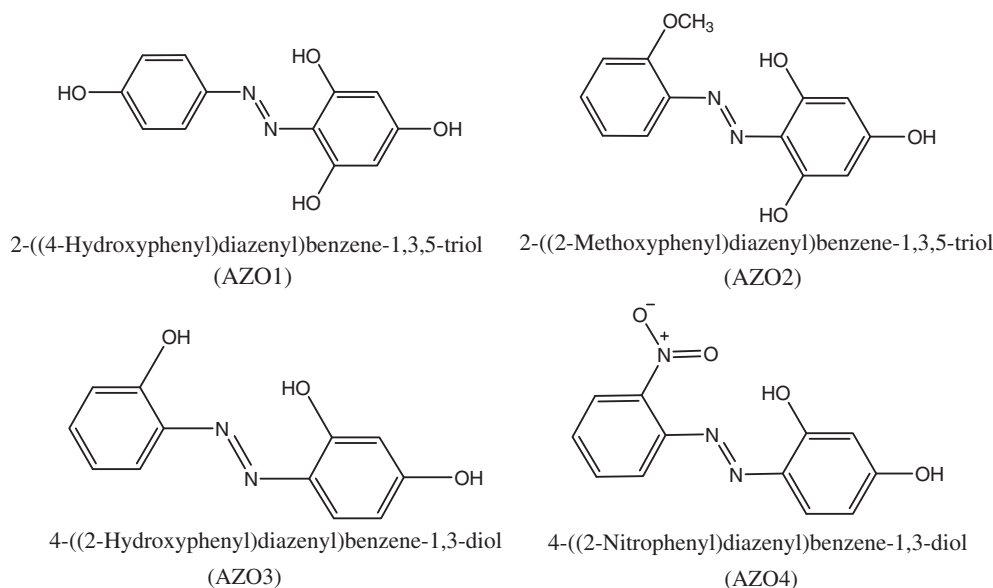


Fig. 1. Structures of studied azo dye molecules.

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