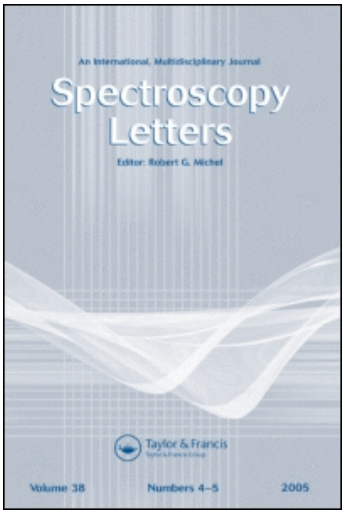

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SOLVENT INFLUENCE ON THE ELECTRONIC ABSORPTION SPECTRA OF SOME AZOAROMATIC COMPOUNDS

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ABSTRACT

Solvent-induced effects on the π–π^* electronic absorption band frequencies of some azobenzene derivatives are described in terms of dipole–dielectric, solute–solvent, and hydrogen bonding interactions. A multiple linear regression equation for ν_{max} was developed based on polarizability–polarity parameters and Kamlet–Taft solvatochromic parameters. Although the polarizability is a major contributor to the interactions in solutions, parameters related to the solvent polarity, hydrogen bond acidity, and hydrogen bond basicity are also statistically significant in determining the spectral shifts.

Key Words: Solvent effects; Electronic absorption spectra; Azoaromatic derivatives

INTRODUCTION

Electronic spectroscopy is one of the few methods that can offer information about the local force fields in condensed state. The frequency modification in electronic absorption spectra, by passing the spectrally active molecules from gaseous phase to liquid solution, measures the difference between the solvation energies of the electronic levels responsible for the absorption band appearance (1–3).

Both theoretical and empirical methods were used to describe the solvent effects on the electronic spectra, the former procedures being based on classical or quantomechanical models. Complete equations that describe the solvent dependence of the electronic absorption band frequency are somewhat complex for practical purpose. Some approximations are generally used in order to express the solvent-induced shifts on physical parameters of the medium such as dielectric constant, refractive index, or functions thereof. However, these methods are often inadequate because they do not take into account the specific solute–solvent interactions (hydrogen bondings, donor–acceptor interactions, etc.).

Thus, in agreement with theoretical results of Bakhshiev (2), the wave number shift of the electronic absorption band ($\Delta\nu = \nu_{sol} - \nu_{vap}$), for a spectrally active molecule, which passes from the vapor state (characterized by ν_{vap}) to the liquid solution (characterized by ν_{sol}), is given by:

$$hc\nu^a = \left[\frac{2\mu_g(\mu_g - \mu_e\cos\varphi)}{a^3}\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{\mu_g^2 - \mu_e^2}{a^3}\frac{n^2 - 1}{n^2 + 2}\right]\frac{2n^2 + 1}{n^2 + 2} + \Delta\nu_{disp,pol} \tag{1}$$

where h is Planck's constant, c is the light velocity in a vacuum, a is the mean radius of the molecular action sphere, μ_g, and μ_e are dipole moments in the ground and excited states, φ is the angle between dipole moments, ε is the dielectric constant, and n is the refractive index of the solvent. The first two terms of Equation (1) describe the orientation-induction component of the frequency shift and $\Delta\nu_{disp,pol}$ expresses the contribution of dispersion and polarization forces, which in Bakhshiev theory depend on the following function:

$$f(n) = \frac{n^2 - 1}{n^2 + 2}$$

Because of the failure of parameters, based on macroscopic properties of solvents, to be in good correlation with the experimental solvent-induced shifts, empirical methods that express the medium influence on the electronic absorption spectra by solvent indexes have been developed and various empirical solvent

polarity scales were proposed (4–8). Of many empirical expressions that have been developed for the evaluation of solvent effects on the processes in solutions, the Kamlet–Taft relation (9) was found to be very successful:

$$\nu_{\max} = \nu_0 + s\pi^* + a\alpha + b\beta \tag{2}$$

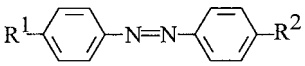
In this equation, $\nu_{\max}$ is the wave number corresponding to the absorption band maximum, ν_0 is a constant; s, a, and b are solvent-independent coefficients measuring the relative susceptibilities of the molecular electron cloud to the solvent properties. Thus, π^* is the polarity/polarizability parameter, which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect (9,10), α describes the solvent ability to donate a proton in a solvent–solute hydrogen bond, and β provides a measure of solvent ability to accept a proton in a solute–solvent hydrogen bond (9,11).

In this way, the interaction between solvent and spectrally active molecule can be separated into nonspecific interactions expressed by so-called polarity and polarizability solvent functions and specific interactions described by means of acidity and basicity solvent parameters (α, β). The coefficients from Equation (2) have no physical meaning, whereas in the Bakhshiev theory they are expressed by the dipole moments involved in electronic transition.

As spectrally active molecules we used azobenzene type compounds. Although, the spectral behavior of some substituted azobenzenes in different solvents can be found in literature, there have been few attempts at a systematic study of solvent-induced effects on the electronic absorption spectra of azobenzene derivatives (12–15).

Herein, we report significant solvent effects on the positions of electronic absorption bands of some substituted azobenzenes (Tab. 1) by a multiparameter equation containing functions of dielectric constant, refractive index, and Kamlet–Taft parameters.

Table 1. Chemical Structures of the Azobenzene Compounds



Sample	R^1	R^2
AZ1	H	NH_2
AZ2	H	$NHCOCH_3$
AZ3	OH	CH_3
AZ4	OH	NO_2

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EXPERIMENTAL

Materials

Commercial 4-aminoazobenzene (Merck) (AZ1) was purified before use. 4-Acetylaminoazobenzene (AZ2) was prepared as described previously (16). 4′-Hydroxy-4-methylazobenzene (AZ3) and 4′-hydroxy-4-nitroazobenzene (AZ4) were synthesized by coupling the corresponding aromatic diazonium salts with phenol and were purified according to literature (17,18). The solvent was spectrograde or purified by known methods.

Measurements

The electronic absorption spectra were carried out with a SPECORD M42 spectrophotometer Carl Zeiss Jena, using quartz cells of 1-cm thickness. No concentration dependence of absorption maxima positions of the azobenzene derivatives was observed in the given concentration range. Dielectric constant (ε^{293}) and refractive index (n^{293}) as well as the solvatochromic parameters α and β were taken from Refs. (9,19,20).

The solvent spectral shifts were statistically analyzed using multiple linear regression by a least-square fitting method in order to determine significant correlations. The obtained values of correlation coefficient, R, were used to test the significance of the correlation.

RESULTS AND DISCUSSION

Azobenzene compounds usually exhibit a low intensity $n-\pi^*$ absorption band in the visible range of the spectrum and a high intensity $\pi-\pi^*$ band in the ultraviolet due to the conjugation between azobenzene and the aromatic ring system (21). For the studied azobenzene derivatives (Tab. 2), in ethanol, these absorption bands are located at about 22,100–23,100 cm^{-1} and 25,800–29,900 cm^{-1}, respectively. The wave numbers of the $\pi-\pi^*$ absorption band maxima of azobenzene compounds AZ1–AZ4 are displayed in Table 2, using 16 aprotic solvents and 8 protic solvents, together with the corresponding solvent parameters.

The values of $\pi-\pi^*$ absorption maxima of AZ1–AZ4 depend on the substituents in the 4 and 4′ positions from the aromatic rings as well as on the solvent nature. Thus, as the electron donor strength of the group in the position 4 increases (compounds AZ2 and AZ1), the $\pi-\pi^*$ band is bathochromically shifted. When the 4 and 4′ positions of aromatic rings are substituted with electron donor and electron acceptor groups, the $\pi-\pi^*$ absorption band is also bathochromically shifted

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Table 2. Electronic Absorption Maxima and Solvent Parameters

		ν_{exp} (cm^{-1})							
No.	Solvent	AZ1	AZ2	AZ3	AZ4	ε	n	β	α
1.	*n*-Hexane	27,660	28,990	29,370	28,010	1.89	1.3748	0.00	0.00
2.	Cyclohexane	27,510	28,900	29,200	27,930	2.02	1.4266	0.00	0.00
3.	1,4-Dioxane	26,140	28,210	28,530	26,700	2.22	1.4224	0.37	0.00
4.	Carbon tetrachloride	27,210	28,610	28,990	27,320	2.24	1.4601	0.00	0.00
5.	Toluene	26,670	28,330	28,740	27,030	2.38	1.4961	0.11	0.00
6.	Diethyl ether	26,040	28,370	28,570	26,630	4.27	1.3526	0.47	0.00
7.	Chloroform	26,880	28,610	28,570	26,420	4.81	1.4459	0.00	0.44
8.	Ethyl acetate	26,040	28,350	28,570	26,630	6.08	1.3723	0.45	0.00
9.	Dichloromethane	26,700	28,600	28,740	26,740	9.08	1.4242	0.00	0.30
10.	1,2-Dichloroethane	26,600	28,450	28,860	26,990	10.42	1.4448	0.00	0.00
11.	1-Pentanol	25,810	28,450	28,250	25,970	15.13	1.4101	0.92	0.70
12.	1-Butanol	25,770	28,560	28,330	25,970	17.84	1.3993	0.88	0.79
13.	iso-Butanol	25,910	28,570	28,410	26,040	17.93	1.3955	0.84	0.79
14.	2-Butanone	25,640	28,170	28,490	26,490	18.56	1.3788	0.48	0.06
15.	2-Propanol	25,840	28,570	28,450	26,010	20.18	1.3776	0.95	0.76
16.	1-Propanol	25,810	28,570	28,450	26,040	20.80	1.3855	0.85	0.78
17.	Acetone	25,810	28,250	28,570	26,600	21.01	1.3588	0.48	0.08
18.	Ethanol	25,840	28,570	28,410	26,250	25.30	1.3611	0.77	0.83
19.	Methanol	25,910	28,860	28,490	26,420	33.00	1.3288	0.62	0.93
20.	Dimethylformamide	25,030	27,860	28,210	25,940	38.25	1.4305	0.69	0.00
21.	Acetonitrile	26,180	28,600	28,690	27,030	37.50	1.3442	0.31	0.19
22.	Ethylene glycol	25,620	28,330	28,250	26,110	41.40	1.4318	0.52	0.90
23.	Dimethylacetamide	24,720	27,890	27,970	25,740	37.78	1.4384	0.76	0.00
24.	Dimethyl sulfoxide	24,750	27,780	27,930	25,670	47.24	1.4770	0.76	0.00

(compound AZ4) due to the increase of the the π orbital energy level and the decrease of the the π^* orbital energy level.

The bathochromic shift of the π–π^* absorption band was observed for all azobenzene derivatives concurrent with increasing solvent polarity, suggesting a stronger stabilization of the excited state related to the ground state. In aprotic solvents, the AZ4 absorption maximum shifts from 28,010 cm^{-1} (hexane) to 25,670 cm^{-1} (dimethyl sulfoxide), resulting in a red shift of about 2300 cm^{-1}. The solvent shift is somewhat less pronounced in protic solvent series.

The solvent-induced spectral shifts are usually attributed to solvent polarizability/polarity effects and hydrogen bonding donating or accepting abilities of the solvents. Correlations of the wavenumbers of absorption band maximum (ν_{max}) of AZ1–AZ4 against single solvent parameter or functions of these parameters proved unsatisfactory. However, for some compounds a high correlation of ν_{max} as a function of $(n^2-1)/(n^2+2)$, $(\varepsilon-1)/(\varepsilon+2)$ or β was obtained (Figs. 1–3). The relationships between ν_{max} and $(n^2-1)/(n^2+2)$ and $(\varepsilon-1)/(\varepsilon+2)$ indicate the presence of orientation-induction and dispersion interactions in solutions of AZ1–AZ4.

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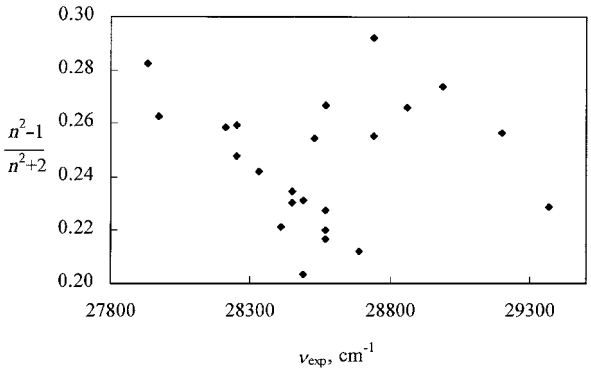

Figure 1. π–π^* Absorption band positions for AZ3 versus $(n^2-1)/(n^2+2)$.

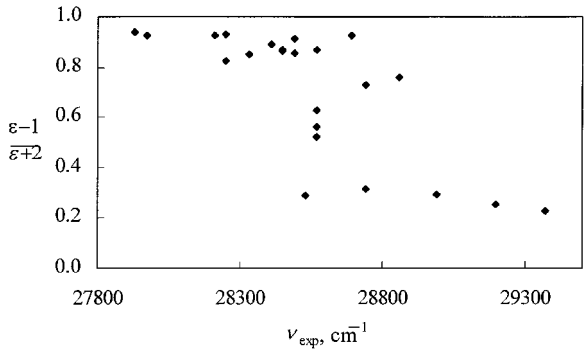

Figure 2. Solvatochromic shifts of ν_{max} related to the π–π^* absorption maxima for AZ3 as a function of solvent polarity.

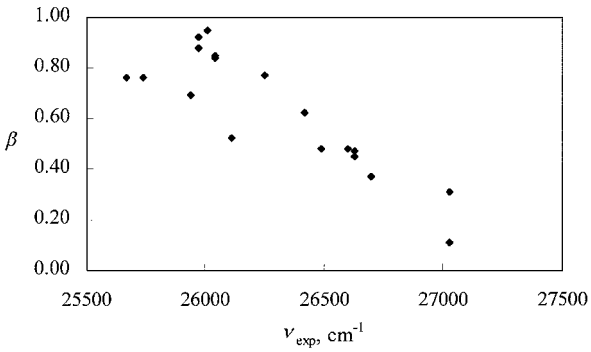

Figure 3. Plot of wave numbers of the absorption maxima for AZ1 against the β values of the solvents.

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The azobenzene compounds under study contain some groups capable of participating in specific interactions with the solvent. Taking into account the H-bond donor solvent tendency to interact with the oxygen from carbonyl or nitro groups, as well as H-bond donating ability of the amino group, these are the likely sites for intermolecular H-bondings in compounds AZ1–AZ4.

In order to characterize the specific interactions, the empirical Kamlet-Taft parameters α and β were used. In the case of azo compounds AZ1–AZ4, the absorption band positions do not correlate well with either α or β. Neither electrostatic solvation nor specific solute–solvent interactions alone cannot explain the observed solvatochromism. Therefore, a combination of medium effects (polarity, polarizability, and hydrogen bondings) were proposed in describing the solvent influence on the electronic absorption spectra of AZ1–AZ4. In these conditions in order to evaluate the solvent effects occurring in AZ1–AZ4 compounds, the following solvent parameters were chosen: $f(n) = (n^2 - 1)/(n^2 + 2)$, $f(\varepsilon) = (\varepsilon - 1)/(\varepsilon + 2)$, α, and β.

Because π^* linearly depends on $f(n)$ and $f(\varepsilon)$[4], Equation (2) can be rewritten as follows:

$$\nu_{\max} = c_0 + c_1 f(\varepsilon) + c_2 f(n) + c_3\beta + c_4\alpha \tag{3}$$

where the coefficients c_i can be regarded as measures of the extent that $\nu_{\max}$ is sensitive to dipolar and hydrogen bonding effects, while c_0 is the extrapolated value of wavenumber in the gaseous state.

The solvatochromic coefficients were obtained using multiple linear regression analysis (MLRA). The magnitude and sign of the coefficients c_i can indicate the degree of the different solute–solvent interactions. Their values are summarized in Table 3. A way of controlling the accuracy of the proposal calculation is to compare the values of the calculated frequencies of the absorption maxima based on Equation (3) with the corresponding experimental values. Figure 4 exhibits a good correlation between the calculated and experimental wavenumbers of AZ4 in the selected solvents.

As seen from Table 3 the values of coefficients c_1 and c_2 are negative suggesting that the solvent effects, due to ε and n produce bathochromic effects in

Table 3. Results of Correlation of $\nu_{\max}$ with Solvatochromic Parameters

Sample	c_0	c_1	c_2	c_3	c_4	R
AZ1	27,949.7	−1469.9	−1517.3	−1607.0	826.6	0.95
AZ2	28,900.0	−789.6	0.0	375.1	692.4	0.90
AZ3	30,537.3	−579.2	−5377.7	−662.3	112.9	0.92
AZ4	29,761.6	−814.4	−8351.1	−1317.1	0.0	0.96

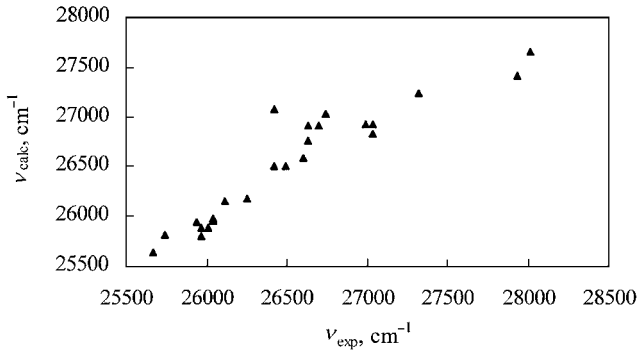

Figure 4. Plot of calculated absorption frequencies versus experimental values for compound AZ4.

the absorption spectra. These bathochromic shifts correspond to a more stabilized excited state as compared to the ground state.

Comparing Equations (1) and (2) one can write:

$$c_1 = \frac{2\mu_g(\mu_g - \mu_e \cos\varphi)}{a^3} \tag{4}$$

Because when $c_1 < 0$, then $\mu_g < \mu_e \cos\varphi$ and the result for these azoaromatic compounds is $\mu_g < \mu_e$. One can say that the projection of the excited state dipole moment on the direction of the ground state dipole moment is higher than the ground state dipole moment. The schematic representation of the dipole moments corresponding to the electronic states involved in the π–π^* transition is shown in Figure 5, where $\Delta\mu_{ge}$ represents the transition dipole moment.

With the exception of AZ2, one can observe (Tab. 3) that the absolute values of coefficients c_2 are much larger than those of c_1, indicating that the effect due to the polarizability of the solvent more strongly affects the frequencies of absorption maxima than that determined by the orientational polarization. The high absolute

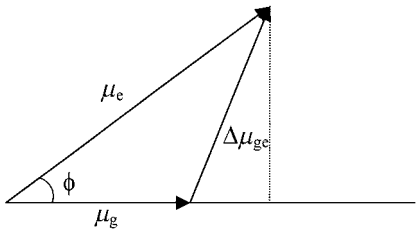

Figure 5. Projection of the excited state dipole moment on the ground state dipole.

values of coefficient c_3 reconfirm the greater bathochromic effect of compounds AZ1 and AZ4. These compounds possess electron donating groups, which can give a stronger interaction between solute and solvent. The decreasing order of $|c_3|$ values for AZ1 and AZ2 follows the electron donating ability of the substituents and thus weaker hydrogen bonds will provide lesser bathochromic shifts for AZ2.

The major finding from the foregoing analysis of the solvent effects is that both polarity and polarizability-based parameters and the solvatochromic parameters α and β are important in defining the solvent induced shifts of the azoaromatic compounds AZ1–AZ4.

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