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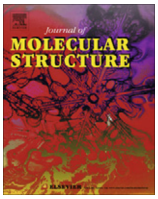

Solvatochromic effects in the absorption spectra of some azobenzene compounds

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ABSTRACT

Solvatochromic behavior of some 4,4′-substituted azoaromatic derivatives has been investigated in solvents of different polarities. The solvent dependent UV/vis spectral shifts, $\nu_{max,}$ were analyzed using some physical parameters such as refractive index, dielectric constant, Kamlet–Taft parameters α (hydrogen bond donating ability) and β (hydrogen bond accepting ability).

The intermolecular interaction types in the azobenzene derivatives solutions were established on the basis of a multiple linear regression analysis. The fitting coefficients obtained from this analysis allowed us to estimate the contribution of each type of interactions to the total spectral shift in the studied solutions.

1. Introduction

Azoaromatic compounds have attracted intensive attention due to their widespread range of applications in dye stuff industry, photoaligning substrates for liquid crystals, photorefractive media, acid–base, redox and metallochrome indicators, optical actuators, optical storage media, etc. [1–5]. The use of these compounds emphasizes the importance of the understanding the solvent effects in the electronic transitions occurring in these molecules.

Universal solvent–solute interactions [6,7] are determined by electronic and nuclear solvent polarization and they can be described by functions of the refractive index n, $f(n) = (n^2 - 1)/(n^2 + 1)$, or $(2n^2 - 1)/(n^2+1)$ and the electric permittivity ε, $(\varepsilon - 1)/(\varepsilon + 2)$, or $\varepsilon - 2)/(2\varepsilon + 1)$. All these functions [6,7] can have different influences on the electronic absorption spectra that manifest in sign and magnitude, giving information on the intermolecular interactions in solutions.

Specific interactions can be present in solutions, the most important ones being hydrogen bondings [6–10]. Their influence on the absorption spectra is very important, depending on whether the solvent molecules can act as donors or acceptors in the formation of hydrogen bondings with the solute molecules.

In this work some azoaromatic derivatives (Fig. 1) were prepared and ultraviolet–visible absorption spectra have been recorded in twenty four solvents in order to study the influence of the solvents on their absorption spectra.

2. Experimental

4-Methylaniline and 4-nitroaniline were obtained from Aldrich Chemical Co. and used as received. The solvents used were of spectrophotometric grade and purchased from Aldrich or Fluka.

The 4,4′-substituted azoaromatic derivatives AZ5–AZ9 were synthesized by conventional diazotization–coupling reactions starting from 4-methylaniline or 4-nitroaniline. The synthetic route toward the target compounds involves the following steps: diazotization of 4-methyl- or 4-nitroaniline, coupling reaction of phenol with diazonium salts and esterification reaction with corresponding acid chloride [10–12].

The procedure described for azoaromatic derivative AZ7 is typical:

(i) Diazotization/coupling

4-Hydroxy-4′-methyl azobenzene: A cold solution of sodium nitrite (6.9 g, 0.1 mol) in 25 ml of water was added dropwise, under stirring at 0 °C to a mixture of 4-methylaniline (10.71 g, 0.1 mol) and 25 ml conc. HCl (0.3 mol) in 150 ml water. The obtained suspension was stirred at 0 °C for 1 h to produce the diazonium salt. The mixture was filtered off and a cold solution of phenol (9.4 g 0.1 mol) and sodium hydroxide (4.0 g, 0.1 mol) in 50 ml water was added dropwise to the filtrate while carefully maintaining the same 0 °C temperature for 5 min. The mixture was neutralized with sodium acetate and then the precipitate produced was collected and washed with excess of water. After the removal of the water, the product was purified by recrystallization from a mixture of DMF and water (1:1).

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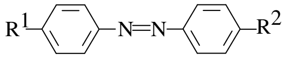

Sample	R^1	R^2
AZ5	CH_3COO	NO_2
AZ6	$CH_3-CH=CHCOO$	NO_2
AZ7	$CH_2=CHCOO$	CH_3
AZ8	$CH_3-CH=CHCOO$	CH_3
AZ9	$Ph-CH=CHCOO$	CH_3

Fig. 1. Structures of investigated azoaromatic compounds.

(ii) Esterification

4-Methyl-4′-oxymethacryloyl azobenzene: A mixture of 4-hydroxy-4′-methyl azobenzene (2.12 g 0.01 mol) and acryloylchloride (3 ml, excess) was dissolved in pyridine at room temperature. Triethylamine (1.9 ml) was added into solution. The resulting mixture was heated at 40 °C and kept stirring for 4 h. Reaction was stopped by addition of acetone in excess. The crude product was precipitated in cold water. The precipitate produced was collected and washed with excess of water. After removal of water, the product was crystallized twice with ether (70% yield).

Ultraviolet–visible (UV–vis) absorption spectra were recorded on Specord M42 spectrophotometer (Carl Zeiss Jena) in 1 cm quartz cells. No concentration dependence of the absorption maxima values of the azoaromatic compounds was observed in the studied concentration range. Dielectric constant, ε refractive index, n and the solvatochromic parameters, α and β were taken from the literature [13–16].

3. Results and discussion

The electronic absorption spectra of the studied azoaromatic derivatives were recorded in different solvents and relevant data were collected in Table 1. The electronic absorption spectra of the studied azobenzene compounds in dioxane are drawn in Fig. 2.

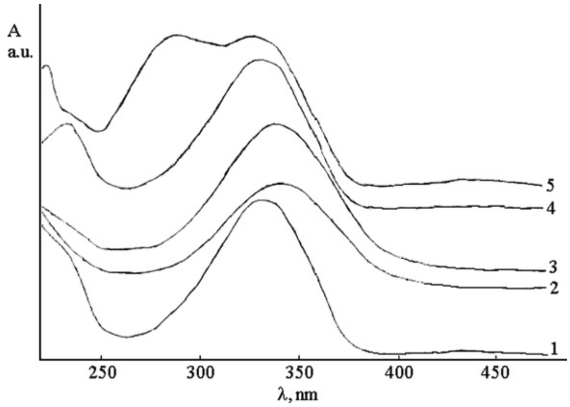

Fig. 2. UV/vis absorption spectra of AZ5–AZ9 in dioxane.

These compounds mainly exhibit a strong absorption band located at about 29850 cm^{-1} (AZ8, dioxane). It is assigned to a π–π^* absorption band due to the conjugation between azo bridge and the aromatic ring system [1,2]. The wave numbers of the π–π^* absorption maxima of azoaromatic compounds AZ5–AZ9 (Table 1) were measured in 24 solvents having a wide variety of parameters including dielectric constant, refractive index and hydrogen bonding abilities (Table 1).

Compared to nonpolar solvents, the maximum of the π–π^* band shows a bathochromic shift in polar solvents (Table 1). The solvent effect for AZ5 (Table 1) reveals that the π–π^* absorption maximum ranges from 29670 cm^{-1} in n-hexane to 29850 cm^{-1} in dimethylformamide corresponding to a difference of $\Delta\nu = 555$ cm^{-1} stabilization energy between these solvents having different polarities. This fact suggests that the azoaromatic derivatives under study are more polar in the excited states than in the ground state.

Plots of the $\pi \rightarrow \pi^*$ absorption band wavenumbers in function of one-parameter proved satisfactory in some cases. In Fig. 3, for example, we have obtained a good correlation between ν_{max} and

Table 1

UV/vis absorption maxima for azoaromatic derivatives and solvent parameters

No.	Solvent	ε	n	β	α	ν_{exp} (cm^{-1})				
						AZ5	AZ6	AZ7	AZ8	AZ9
1	*n*-Hexane	1.89	1.3748	0.00	0.00	29,630	29,240	30,490	30,210	30,490
2	Cyclohexane	2.02	1.4266	0.00	0.00	29,460	29,110	30,300	30,120	30,330
3	1,4-Dioxane	2.22	1.4224	0.37	0.00	29,390	29,070	29,990	29,830	29,940
4	CCl_4	2.24	1.4601	0.00	0.00	29,370	28,990	30,170	29,850	29,940
5	Toluene	2.38	1.4961	0.11	0.00	29,150	28,820	29,810	29,630	29,900
6	Diethyl ether	4.27	1.3526	0.47	0.00	29,500	29,240	30,350	30,030	30,330
7	Chloroform	4.81	1.4459	0.00	0.44	29,330	28,900	29,900	29,760	30,030
8	Ethyl acetate	6.08	1.3723	0.45	0.00	29,440	29,280	30,120	29,940	30,350
9	Dichloromethane	9.08	1.4242	0.00	0.30	29,370	29,070	30,080	29,880	30,300
10	1,2-Dichloroethane	10.42	1.4448	0.00	0.00	29,200	28,940	29,900	29,760	30,120
11	1-Pentanol	15.13	1.4101	0.92	0.70	29,110	28,930	30,080	29,760	30,400
12	1-Butanol	17.84	1.3993	0.88	0.79	29,390	28,570	30,080	29,850	30,400
13	*iso*-Butanol	17.93	1.3955	0.84	0.79	29,590	28,820	30,300	29,940	31,060
14	2-Butanone	18.56	1.3788	0.48	0.06	29,370	29,150	29,850	29,670	29,850
15	2-Propanol	20.18	1.3776	0.95	0.76	29,370	29,280	29,810	29,990	30,490
16	1-Propanol	20.80	1.3855	0.85	0.78	29,500	29,030	30,120	29,880	30,860
17	Acetone	21.01	1.3588	0.48	0.08	29,460	29,280	29,720	29,720	29,760
18	Ethanol	25.30	1.3611	0.77	0.83	29,460	28,860	29,940	29,910	30,490
19	Methanol	33.00	1.3288	0.62	0.93	29,500	29,460	30,210	29,990	30,630
20	DMF	38.25	1.4305	0.69	0.00	28,170	28,820	29,460	29,410	30,030
21	Acetonitrile	37.50	1.3442	0.31	0.19	29,760	29,460	30,350	29,990	30,490
22	Ethylene glycol	41.40	1.4318	0.52	0.90	29,240	27,660	29,630	29,150	30,300
23	Dimethylacetamide	37.78	1.4384	0.76	0.00	29,110	28,940	29,720	29,540	30,030
24	DMSO	47.24	1.4770	0.76	0.00	29,070	28,860	29,590	29,370	29,900

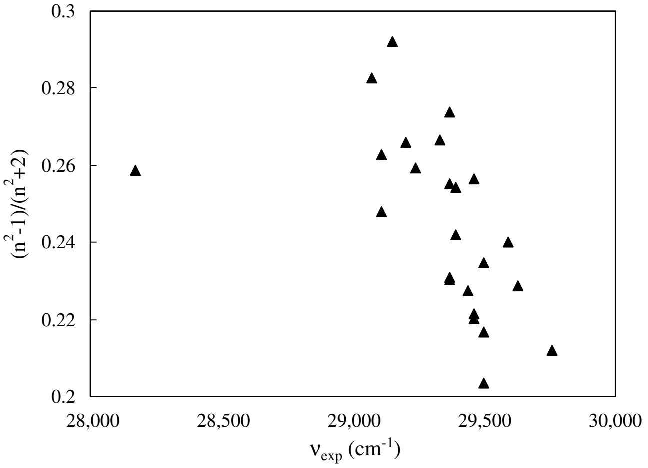

Fig. 3. Wavenumbers in the π–π^* band of AZ5 azobenzene vs dispersion function.

$f(n)$ for AZ5, suggesting the important role of solvent electronic polarizability in determinating the spectral shifts.

From the Fig. 4 it results that the wavenumber in the maximum of the $\pi \rightarrow \pi^*$ absorption band of azobenzene compounds does not depend linearly on the dielectric function $f(\varepsilon)$. Some deviations were observed in the aprotic dipolar solvents. A study of the dependence of the wavenumber in the maximum of the same band on the H-bonding donating ability α of the solvents (Fig. 5) also shows us that the choose of this parameter for linearization is not enough.

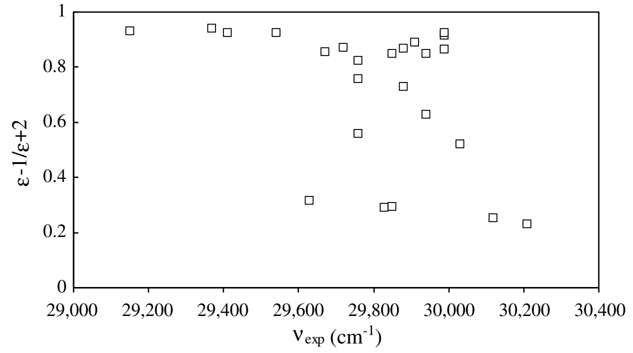

Fig. 4. Wavenumbers in the π–π^* band of AZ8 azobenzene vs orientation function.

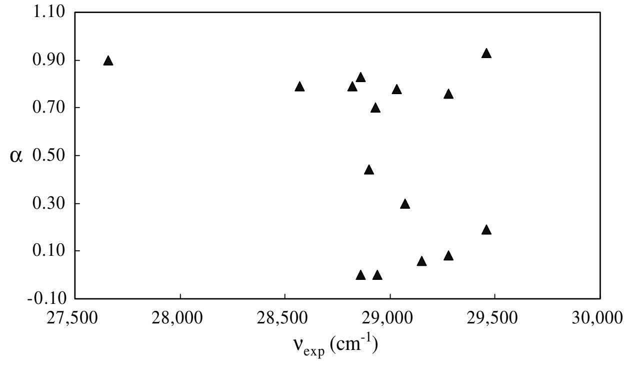

Fig. 5. Wavenumbers in the π–π^* band of AZ6 azobenzene vs α.

Consequently, a multiparametric correlation [17] of spectral data ($\nu_{\max}$) with some independent physically justifiable parameters of the medium could provide information on different interaction in solution.

We tried to establish a correlation between experimental spectral values ($\nu_{\max}$) with the four solvatochromic variables of the polarity function $f(2) = (\varepsilon + 1)/\varepsilon + 2)$, electronic polarizability $f(n) = (n^2 - 1)/(n^2 + 2)$, H-bonding donor ability (α) and H-bonding acceptor ability (β) in order to evaluate the respective contributions to the solute-solvent interactions of the azoaromatic compounds.

In this case, the position of the absorption band, $\nu_{\max}$, in a given solvent has been expressed as a linear function of solvent parameters described above, as follows:

$$\nu_{\max}. = C_0 + C_1 \cdot f(n) + C_2 \cdot f(\varepsilon) + C_3 \cdot \beta + C_4 \cdot \alpha \qquad (1)$$

where C_0 signifies the extrapolated value of the wavenumber in gaseous state and the coefficients C_i $i = 1,2,3,4$ reveals the relative contributions of the considered solvatochromic parameters. The coefficients C_i were determined by multiple linear regression technique [17].

The second term in relation (1) describes the contribution of the orientation induction interactions to the frequency shift and the third term describes the contribution of the dispersion–polarization forces to the total spectral shift.

The results of the multiple correlation analysis are summarized in Table 2. As one can see from the data of this table, the parameters C_i $i = 1,2,3,4$ depend on the structural features of the spectrally active molecules.

The magnitude and size of the coefficients C_i can show the degree of different solute–solvent interactions. The parameters C_1 and C_2 have the highest absolute values which means that the spectral shifts in the π–π^* transition are controlled mainly by both the refractive index and solvent dielectric constant (dispersion and dipolar interactions).

Table 2
Regression parameters in relation (1) for the studied azoaromatic compounds

Compound	C_0 (cm^{-1})	C_1 (cm^{-1})	C_2 (cm^{-1})	C_3 (cm^{-1})	C_4 (cm^{-1})	R	SD	CP
AZ5	30860	−299.1	−5177.8	−100.2	69.0	0.98	32	5
AZ6	30670	6.1	−6196.8	−102.7	−149.2	0.98	34	4.9
AZ7	31830	−771.8	−5121.9	−54.6	238.7	0.99	44	4.9
AZ8	31860	−319.9	−7087.1	−243.5	268.3	0.98	43	5.1
AZ9	31970	285	−6143.9	−59.7	257.9	0.99	36	5.1

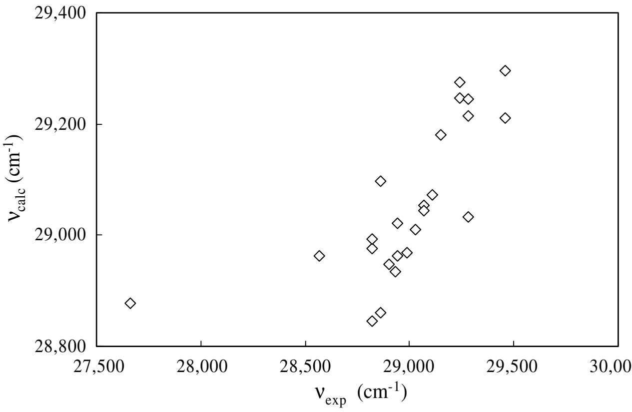

Fig. 6. Relationship between calculated $\nu_{\text{calc.}}$ and experimental $\nu_{\text{exp.}}$ wavenumbers in the maximum of π–π^* absorption band of AZ6 compound.

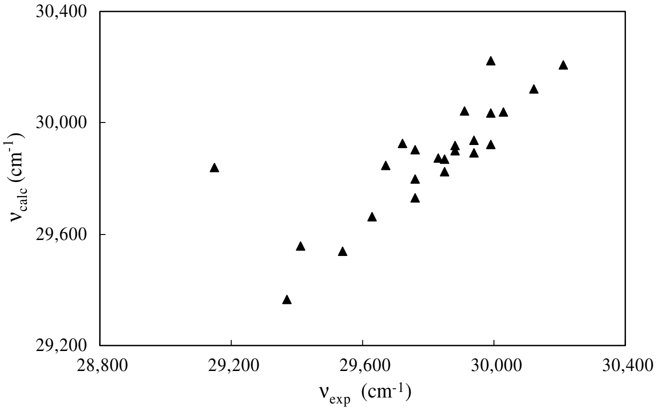

Fig. 7. Relationship between calculated $\nu_{calc.}$ and experimental $\nu_{exp.}$ wavenumbers in the maximum of π–π^* absorption band of AZ8 compound.

Also, it is worth observing that C_3 coefficient is significantly smaller than the C_4 coefficient for AZ6, AZ7 and AZ9. This fact demonstrates the H-bonding donating ability is weaker than the ability to accept the H-bonding.

The negative sign of the C_2 coefficient reflects the mentioned bathochromic spectral shifts in all studied solutions of azoaromatic derivatives [18].

Figs. 6 and 7 display the plots of the calculated absorption maxima using relation (1) as a function of the corresponding experimental values for AZ6 and AZ8 in the selected solvents. As one can see, the calculated values by using relation (1), are in good accordance with the experimental data, excepting the value corresponding to ethylene glycol.

4. Conclusions

Universal and specific interactions determine the shifts of the π–π^* band in azoaromatic derivatives solutions. Coefficients C_1 and C_2 determine the strength of the universal forces, while C_3 and C_4 coefficients characterize the strength of the specific interactions of the analyzed compounds.

The spectral shifts of π–π^* band of azoaromatic compounds in solutions are mainly controlled by the universal interactions.

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