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About intermolecular interactions in binary and ternary solutions of some azo-benzene derivatives ☆

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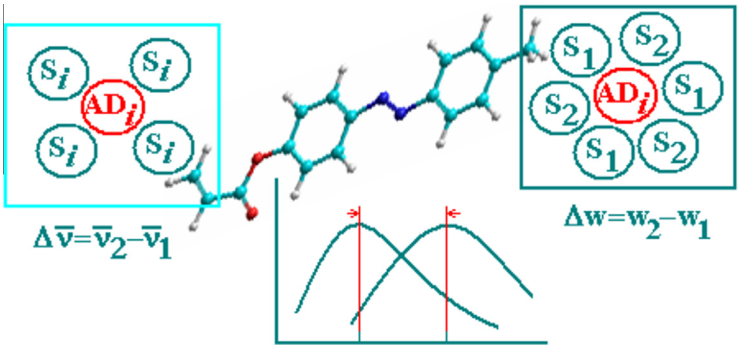
HIGHLIGHTS

- Solvatochromic study of $\pi \rightarrow \pi^*$ absorption band of azo-benzene derivatives.
- Spectral data correlated with energetic characteristics obtained by HyperChem.
- Excited state dipole moments and polarizabilities of the studied molecules.
- Comparison between the interaction energy in solute–solvent molecular pairs.

GRAPHICAL ABSTRACT



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ABSTRACT

The nature and strength of the intermolecular interactions in the solutions of three azo-benzene derivatives (AD*i*, *i* = 1, 2, 3) were established by solvatochromic effects in solvents with different electric permittivities, refractive indices and Kamlet–Taft constants. A quantum mechanical analysis corroborated with spectral data offered information about the excited state dipole moments and polarizabilities of the studied compounds. The separation of the supply of universal and specific interactions to the total spectral shift was made based on the regression coefficients from the equations describing the solvatochromic effect. Supplementary information about the composition of the first solvation shell and the energy in the solute–solvent molecular pairs were obtained analyzing the ternary solutions of AD*i*, *i* = 1, 2, 3 compounds in solvent mixture Methanol (M) + *n*-Hexane (H).

Introduction

Azo-benzene compounds are characterized by relatively simple procedures for obtaining [1–3] and they have a widespread range of applications. They are used in the dye stuff industry, as photo aligning substrates for liquid crystals, as acid-basic redox indicators, as optical storage media, as photorefractive media or as non-linear optical materials [4–9].

In recent years the utilization of azo compounds as food colorants, as sensitizers in photodynamic therapy or as inhibitors for tumor growth has attracted much attention [10–12]. The vast area of their applications emphasizes the importance of understanding the interactions between the azo-benzene compounds and solvent molecules since in most cases dye molecules are utilized as solutions and thus their optical characteristics will be determined by the solvent nature.

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The optical properties of azo-benzene compounds can significantly vary with the nature of electron donor or acceptor substituents in the p-positions of the aromatic rings. These substituents can increase the molar absorptivity or can shift the absorption maxima to longer or shorter wavelengths.

The presence of donor and/or acceptor groups in the conjugated system of an azo-benzene derivative will determine different interactions with the solvent molecules which can modify the azo-benzene derivative spectral behavior in solutions. Although there are studies regarding the solvent action on the electronic transitions occurring in these molecules [13,14], some correlations between the results obtained by quantum mechanical calculations and the solvatochromic effects are also interested.

The aim of this study was to correlate the results obtained by quantum mechanical calculations using the HyperChem Programs with those obtained from the solvatochromic analysis. The spectral studies of some binary and ternary solutions of the studied 4,4′-substituted azo-benzene compounds (AD*i*, $i = 1, 2, 3$) offer information about the nature and the strength of the intermolecular interactions in their liquid phase.

Experimental

Materials

The azo-benzene derivatives (AD*i*, $i = 1, 2, 3$) were obtained by esterification between acryloyl chlorides (namely acryloyl, methacryloyl and phenylacryloyl) and azo chromophore, 4-hydroxy-4-methylazobenzene in the presence of pyridine.

Previously, the azo-chromophore was synthesized by typical preparation procedure via diazotization and coupling reaction between hydroxybenzene and 4-amino-1-methylbenzene.

All solvents (Sigma Aldrich) were spectrally grade and used as received.

Dielectric constant – ε, refractive index – n, H-bonding donor ability – β and H-bonding acceptor ability – α of the solvents were taken from literature [15–18].

Electronic absorption data

The electronic absorption spectra were recorded at Specord UV VIS Carl Zeiss Jena spectrophotometer with data acquisition system, in 1 cm quartz cells. No concentration dependence of the wavenumber in the absorption maxima was observed in the studied concentration ranges.

Theoretical background

Quantum mechanical characterization of the studied molecules

The energetic and electro-optical parameters of the studied 4,4′-substituted azo-benzene compounds were established by quantum-chemical software [19,20]. HyperChem 8.0.6 [21] with the Polak Ribiere algorithm and RMS 0.001 kcal/mol was used for optimizing the structure of the studied molecules by AM1 semi-empirical methods. The results obtained by semi empirical methods are discussed and compared with those determined from solvatochromic analysis.

The E_{HOMO} and E_{LUMO} with changed signs give [19] the molecular ionization potential and electronegativity, respectively. The difference $\Delta E = E_{LUMO} - E_{HOMO}$ [20] characterizes the molecular reactivity of the analyzed compounds.

Log*P* (octanol/water partition coefficient) and the refractivity are considered as descriptors for a given chemical structure. By its sign, log*P* gives hydrophilic/hydrophobic character of a chemical structure; when $\log P < 0$, the chemical structure has hydrophilic character, while when $\log P > 0$, the chemical structure has hydrophobic nature. The liophylicity of chemical compounds is an important factor in its adsorption and distribution in organism. So, log*P* plays an important role in biochemical interactions [22,23].

Hydration energy [19,20] characterizes solution process. The changes in enthalpy involved in solution process are related to breaking quasi-chemical bonds by water molecules, separation of the solvent molecules to accommodate the solute and formation of new attractive interactions between the solute and solvent molecules. The total energy involved in these transformations is named hydration energy [20,23].

The electric dipole moment, polarizability, the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) were estimated by HyperChem 8.0.6., in the limits of AM1 method, considered as being the best for collecting quantitative information [19,20].

The chemical hardness, the electronegativity, the electrophilicity index and the ionization potential can be also estimated [24] from the data of Table 1.

Intermolecular interactions in binary solutions

The theories based on the homogeneous solutions considered as infinite, continuous dielectric media [25,26] express the spectral shifts $\Delta\bar{v}(\mathrm{cm}^{-1})$ of the electronic bands as functions both of the microscopic parameters (such as dipole moment (μ); electric polarizability (α); molecular radius (a); ionization potential (I)) and of the macroscopic parameters (such as refractive index (n) and electric permittivity (ε)) and neglect the influence of the specific interactions on the wavenumber in the maximum of the electronic bands [25–31].

Statistical methods must be applied to express the frequency shifts from the electronic absorption spectra Due to the characteristics of liquid phase [25]. In order to obtain good results in statistical analysis, the aberrant points must be eliminated [32,33] from the experimental data. In these theories, the spectral shift is supposed to be due to the universal interactions (orientation, dispersive, inductive and polarization interactions) and the specific interactions are neglected.

$$\Delta\bar{v} = \Delta\bar{v}_{or.} + \Delta\bar{v}_{disp} + \Delta\bar{v}_{ind.} + \Delta\bar{v}_{ind.-res} \tag{1}$$

Table 1

Computed by HyperChem 8.0.6 energetic parameters, surface, volume, molecular mass, hydration energy, log*P*, dipole moment, polarizability and refractivity of the studied compounds.

Nr.		AD1	AD2	AD3
1	Total energy (kcal/mol)	−69655.81	−73109.84	−87461.66
2	Formation energy (kcal/mol)	29.348	18.444	53.610
3	Bonding energy (kcal/mol)	−3779.44	−4065.44	−4988.92
4	E_{HOMO} (eV)	−8.962	−8.94	−9.127
5	E_{LUMO} (eV)	−0.824	−0.795	−0.891
6	$\Delta E = \lvert E_{HOMO} - E_{LUMO}\rvert$ (eV)	8.138	8.145	8.236
7	Surface (Å^2)	518.34	560.27	623.47
8	Volume (Å^3)	838.41	896.84	1042.01
9	Molecular radius (Å)	4.852	4.802	5.014
10	Molecular mass (u.a.m)	266.30	280.33	342.40
11	Hydration energy (kcal/mol)	−9.23	−7.97	−10.07
12	Log*P*	1.63	1.98	2.44
13	Dipole moment (D)	2.102	2.452	1.541
14	Polarizability (Å^3)	30.02	31.86	39.69
15	Refractivity (Å^2)	89.97	95.64	119.88

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The contribution of each type of interactions [34–36] can be expressed as it follows:

$$\Delta\bar{\nu}_{or.} = \frac{\mu_g(\mu_g - \mu_e\cos\varphi)}{a^3hc} f(\varepsilon, n) \tag{2}$$

$$\Delta\bar{\nu}_{ind.} = \frac{\mu_g^2 - \mu_e^2}{a^3hc} f(n) + 3kT\frac{\alpha_g - \alpha_e}{a^3} f(\varepsilon, n) \tag{3}$$

$$\Delta\bar{\nu}_{disp} = \frac{\alpha_g - \alpha_e}{a^3}\frac{I_uI_v}{I_u + I_v} f(n) \tag{4}$$

$$\Delta\bar{\nu}_{ind.-res} = -\frac{he^2f}{4\pi^2m\bar{\nu}a^3}\frac{n^2 - 1}{2n^2 + 1} \tag{5}$$

Let us neglect the term due to resonant – induction (ind.-res.) interactions from relation (5) [36], because it is very small compared to the terms describing the spectral shifts due to orientation (or.), induction (ind.) and dispersion (disp.) intermolecular interactions.

$\Delta\bar{\nu} = \bar{\nu} - \bar{\nu}_0$ is the total spectral shift (in electronic absorption spectra) caused by universal interactions, expressed in cm^{-1}. In relation (2), I_u, a, α and μ are the ionization potential, the molecular radius, the electric polarizability and the electric dipole moment of the spectrally active (solute) molecule; φ denotes the angle between the dipole moments of the molecule in the two electronic states participating to the electronic transition; $\bar{\nu}_0$ and f are the wavenumber and the oscillator strength of the electronic band for the gaseous phase of the solute; I_v is the ionization potential of the solvent molecules; n and ε are the refractive index and the electric permittivity of the solvent.

When (2)–(4) are replaced in (1) and the functions of n and ε are separated, one obtains:

$$\Delta\bar{\nu} = C_1 f(\varepsilon) + C_2 f(n) \tag{6}$$

$$\frac{\mu_g(\mu_g - \mu_e\cos\varphi)}{a^3hc} + 3kT\frac{\alpha_g - \alpha_e}{a^3} = C_1 \tag{7}$$

$$-3kT\frac{\alpha_g - \alpha_e}{a^3} - \frac{\mu_e(\mu_e - \mu_g\cos\varphi)}{a^3hc} + \frac{\alpha_g - \alpha_e}{a^3}\frac{I_uI_v}{I_u + I_v} = C_2 \tag{8}$$

The relation (6) is obtained in the limits of a theory in which the specific interactions are neglected. In order to obtain information about the strength of the specific interactions in the studied azobenzenes solutions, the Kamlet–Taft solvent parameters were introduced in the final formula describing the solvent influence on the electronic spectra of the studied azo-derivatives [14].

$$\bar{\nu}_{calc.} = \bar{\nu}_0 + C_1 f(\varepsilon) + C_2 f(n) + C_3\beta + C_4\alpha \tag{9}$$

In relation (9), $\bar{\nu}_0$ and C_i $i = 1, 2, 3, 4$ are coefficients (named regression coefficients) which can be determined using statistical methods [14,32,33] when the four solvent characteristics are known (polarity function $f(\varepsilon) = \frac{\varepsilon-1}{\varepsilon+2}$, electron polarizability $f(n) = \frac{n^2-1}{n^2+2}$, H-bonding donor ability β and H-bonding acceptor ability α, respectively.

The free term $\bar{\nu}_0$ signifies the extrapolated value of the wavenumber in the maximum of the studied $\pi \to \pi^*$ absorption band for the gaseous phase of the azo-derivatives; C_i $i = 1, 2, 3, 4$ reveal the relative contributions of the considered solvatochromic terms from (6) [30,37,38]. The term $C_1f(\varepsilon)$ gives the contribution of the orientation-induction universal interactions, the term $C_2f(n)$ estimates the contribution of the dispersion–polarization interactions to the total spectral shift measured in the electronic spectrum of each compound. The last two terms measure the contribution of the specific interactions between the solvent and the spectrally active molecules.

About cell model of ternary solutions

Ternary solutions allow to modify the macroscopic parameters of the liquid by the concentrations of the two solvents and to stimulate the competition between the active (from the intermolecular interactions point of view) solvent to occupy the energetically favored places near the spectrally active molecule [39,40].

Ternary solutions contain homogeneous mixtures of two solvents; one active (with molecules noted by v_1) and one inactive (with molecules noted by v_2) from the intermolecular interactions point of view and a spectrally active molecule (noted by u) and having the role of sensor in estimating the energy w_1 and w_2 of the molecular pairs of the types $u - v_1$ or $u - v_2$ [42–44].

The advantage of the ternary solutions is to have the possibility to obtain solvents with appropriate values of macroscopic parameters (n and ε) in which the universal forces have appropriate values. The specific interactions can be also evidenced in the ternary solutions.

The average relative number p_1 (p_2) of the solvent molecules of types 1 (2) in the first solvation shell of the solute molecule (AD*i*, $i = 1, 2, 3$ in our case) is expressed by:

$$p_1 = \frac{\overline{N}_1}{N} = \frac{x_1\exp\left(-\frac{w_1}{kT}\right)}{x_1\exp\left(-\frac{w_1}{kT}\right) + x_2\exp\left(-\frac{w_2}{kT}\right)}; \quad \left(p_2 = \frac{\overline{N}_2}{N} = 1 - p_1\right) \tag{10}$$

In relation (10) p_1 and p_2 signify the average statistic weights of the molecules of the types 1 and 2 in the first solvation shell of the spectrally active molecule, $\overline{N}_1$ and $\overline{N}_2$ are the average numbers of the corresponding types of molecules in the first solvation shell, N [41–43] is a constant number of solvent molecules in the first solvation shell of the solute molecule, x_1 and x_2 are the molar fractions of the two solvents in the ternary solution, w_1 and w_2 are the interaction energies in molecular pairs of the types: $u - v_1$ and $u - v_2$, respectively, k is the Boltzmann constant and T is the absolute room temperature. Generally, the molecular pair energies are due to the attractive forces, so, they are negative entities.

The average statistic weights of the solvent molecules in the first solvation shell of the spectrally active molecule generally differ from their molar fractions in the binary solvent [42–44].

One can define the excess function (or index of preferential solvation) [45], $\delta_{(1)}$ as being a measure of the extent of preferential solvation of the solute molecule in the active (1) solvent.

$$\delta_{(1)} = p_1 - x_1 \tag{11}$$

When $\delta_{(1)} < 0$, the solvent molecules of the type (2) prevail in the first solvation shell of the spectrally active molecule, while $\delta_{(1)} > 0$ shows a first solvation shell enriched in the active solvent (1). A relation of the type (12) has been established in the cell model of ternary solutions.

$$\ln\frac{p_1}{1 - p_1} = \ln\frac{x_1}{1 - x_1} + \frac{w_2 - w_1}{kT} \tag{12}$$

The dependence of the type (12) with a slope near the unity shows the applicability of the cell model of the ternary solutions in a concrete case. If it is applicable, relation (12) allows us to estimate the difference $w_2 - w_1$ from the value of the cut at origin of the obtained line written as [41,44]:

$$\ln\frac{p_1}{1 - p_1} = m\ln\frac{x_1}{1 - x_1} + n \tag{12'}$$

$$w_2 - w_1 = nkT \tag{13}$$

The difference $w_2 - w_1$ can be estimated by a few methods. In the limits of the cell model, one can approximate this difference and also can compare the energies w_1 and w_2 in pairs of the types $u - v_1$ and $u - v_2$, respectively. So, when $n > 0$, it results $|w_1| > |w_2|$ while $n < 0$ indicates that $|w_1| < |w_2|$.

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Results and discussions

Quantum mechanical characterization of ADi, i-1, 2, 3

Three compounds were studied from the point of view of correlations between the structural and spectral characteristics:

AD1 4-Methyl-4′-oxyacryloyl azo-benzene
AD2 4-Methyl-4′-oxymethacryloyl azo-benzene
AD3 4-Methyl-4′-oxyphenylacryloyl azo-benzene

The optimized with Polak Ribiere algorithm structures of the studied compounds are given in Figs. 1a–c.

Some energetic characteristics, molecular surface and volume, molecular radius, hydration energy, log*P*, dipole moment and polarizability in the ground state of the studied azo-benzene derivatives obtained by HyperChem are listed in Table 1.

As it results from Table 1 and Figs. 1a–c, the studied azo-benzene derivatives (AD*i*, *i* = 1, 2, 3) are characterized by comparable structures with appropriate values of ΔE, molecular radius, hydration energy and log*P* (see Table 1).

The information about the spatial extension and the molecular surface, from which one can estimate the molecular radius, are also listed in Table 1. The compound AD3 having as substitute a benzene ring has the highest values of the surface; volume and molecular radius (see Table 1). Compound AD2 has the highest electric dipole moment; while compound AD3 is characterized by the highest values of polarizability and ionization potential (see Table 1).

Solvatochromic effects in binary solutions

The studied azo-benzene derivatives show individualized $\pi \rightarrow \pi^*$ bands in the UV range of the electronic absorption spectrum [14]. The aspect of these bands is illustrated in Fig. 2a and b for binary solutions of AD1 *i* = 1, 2, 3 achieved in *n*-Hexane and Methanol, respectively.

The electronic absorption spectrum of the compound AD3 is more complicated due to the presence of a benzene ring in the substituent structure. The measurements were made for the band with the higher wavelength. The wavenumber in the binary solutions of the azo-benzene derivatives are listed in Table 2 in which the solvent parameters are also given. The results of the multilinear regression applied to the spectral data [9,27] are listed in Table 3. The minus sign of the regression coefficients indicates a decrease of the wavenumber **(bathochromic effect)**, while the plus sign indicates an increase **(hypsochromic effect)** of the wavenumber in the maximum of the studied $\pi \rightarrow \pi^*$ band.

The electronic absorption spectra of azo-benzene derivatives were recorded in some solvents (Table 2) and the wavenumbers in the maximum of the $\pi \rightarrow \pi^*$ band were similar with those listed in Table 1 from [14]. So, the values of the regression coefficients of Eq. (9) are those from [14] and are listed in Table 3. They are used in the following assertions.

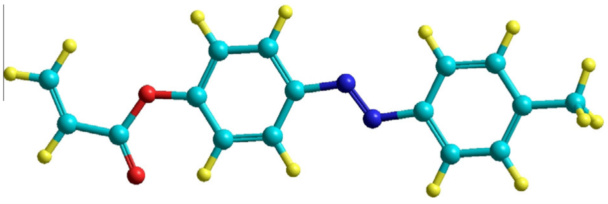

Fig. 1a. AD1 optimized structure by HyperChem 8.0.6 (red – Oxygen; blue – Nitrogen; green – Carbon; white Hydrogen). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

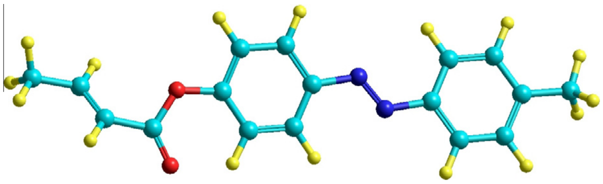

Fig. 1b. AD2 optimized structure by HyperChem 8.0.6 (red – Oxygen; blue – Nitrogen; green – Carbon; white Hydrogen). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

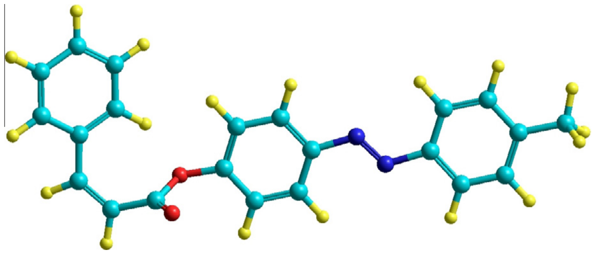

Fig. 1c. AD3 optimized structure by HyperChem 8 0 6 (red – Oxygen; blue – Nitrogen; green – Carbon; white Hydrogen). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

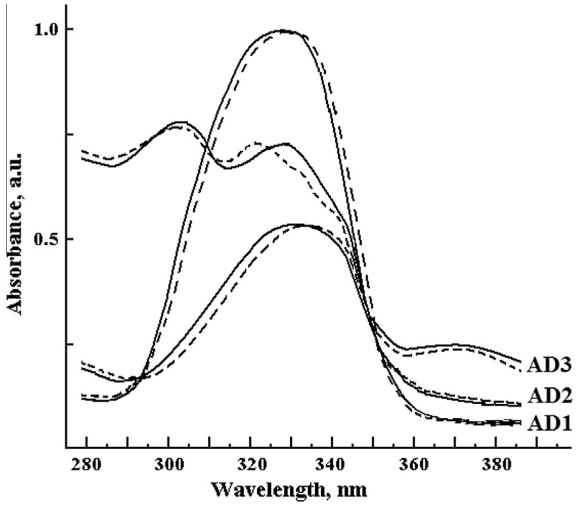

Fig. 2. $\pi \rightarrow \pi^*$ band of the studied azo-benzene derivatives in *n*-Hexane (continuous line) and Methanol (doted line).

The regression parameters C_i $i = 1, 2, 3, 4$ are dependent on the chemical structure of the spectrally active compounds. The negative sign of these coefficients shows the bathochromic contribution of the corresponding terms to the spectral shift. Only the $C_4(\text{cm}^{-1})$ regression coefficient is positive for all studied compounds, showing that when spectrally active molecules donate hydrogen bonds, their electronic band shifts to higher wavelengths.

The regression coefficient $C_2(\text{cm}^{-1})$ characterizes the dispersive forces in AD*i*, *i* = 1, 2, 3 solutions and the product $C_2 f(n)$ is proportional with the strength of the dispersive forces.

The regression coefficient $C_4(\text{cm}^{-1})$ is proportional with the energy implied in the hydrogen bond realized by an acceptor solvent. The higher the spectral shifts caused by the dispersive forces, the higher are the energies of the specific interactions of AD*i*, *i* = 1, 2, 3 compounds with the solvent molecules. The specific interactions realized by the proton transfer from the AD*i*, *i* = 1, 2, 3 towards the solvent molecules cause a hypsochromic effect in electronic absorption spectra.

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Table 2
Solvent parameters and the wavenumbers $\bar{\nu}(\mathrm{cm}^{-1})$ in the maximum of the $\pi \rightarrow \pi^*$ absorption band of the studied azo-benzene compounds.

Nr.	Solvent	ε	αn	α	β	AD1	AD2	AD3
1	*n*-Hexane	1.89	1.3748	0.00	0.00	30490	30,210	30,410
2	Cyclohexane	2.02	1.4266	0.00	0.00	30,300	31,120	30,330
3	1.4 Dioxane	2.22	1.4224	0.37	0.00	29,990	29,830	30,940
4	CCl_4	2.24	1.4601	0.00	0.00	30,170	29,850	30,940
5	Toluene	2.38	1.4961	0.11	0.00	29,810	29,630	30,900
6	Dichloromethane	9.08	1.4242	0.00	0.30	30,080	29,880	30,300
7	Dichloroethane	10.42	1.4448	0.00	0.00	29,900	29,760	30,120
8	1-Pentanol	15.13	1.4101	0.92	0.70	30,080	29,760	30,400
9	1-Butanol	17.84	1.3993	0.88	0.79	30,080	29,850	30,400
10	iso-Butanol	17.93	1.3955	0.84	0.79	30,300	29,940	31,060
11	2-Butanone	18.56	1.3788	0.48	0.06	29,850	29,670	29,850
12	2-Propanol	20.18	1.3776	0.95	0.76	29,810	29,990	30,490
13	1-Propanol	20.80	1.3855	0.85	0.78	30,120	29,880	30,860
14	Ethanol	25.30	1.3611	0.77	0.83	29,940	29,910	30,490
15	Methanol	33	1.3288	0.62	0.93	30,210	29,990	30,630
16	Ethylene glycol	41.40	1.4318	0.52	0.90	29,630	29,150	30,300

Table 3
Regression parameters in relation (9) for AD*i*, *i* = 1, 2, 3.

	$\bar{\nu}_0(\mathrm{cm}^{-1})$	C_1 (cm^{-1})	C_2 (cm^{-1})	C_3 (cm^{-1})	C_4 (cm^{-1})	*R*	SD	CP
AD1	31,830	−771.8	−5121.9	−54.6	238.7	0.99	44	4.9
AD2	31,860	−319.9	−7087.1	−243.5	268.3	0.98	43	5.1
AD3	31,970	285.0	−6143.9	−59.7	257.9	0.99	36	5.1

HyperChem calculations indicate positive values for log *P* and so, a hydrophobic nature of the studied compounds. The dispersive interactions are dominant in binary solutions of AD*i*, *i* = 1, 2, 3, due to their hydrophobic nature and to the small values of the electric dipole moment (see Table 1).

Let us utilise the values of the regression coefficients from Table 3 and the Eqs. (7) and (8) which express these coefficients versus the solvent macroscopic and solute microscopic parameters. One obtains:

$$-92.576\,\mu_e \cos\varphi + 5.311\Delta\alpha + 965.578 = 0 \qquad (1_{AD1})$$

$$-44.042\,\mu_e^2 + 92.576\,\mu_e \cos\varphi - 5.311\Delta\alpha + 333.687\,\Delta\alpha + 5121.89 = 0 \qquad (2_{AD1})$$

For cos φ = 1, the solutions of the system (1_{AD1})–(2_{AD1}) are:

$$\mu_e = 121.891\,D \quad \text{and} \quad \mu_e = 10.166\,D \qquad (3_{AD1})$$

$$\alpha_e = 34.2410^{-24}\ \mathrm{cm}^3 \qquad (4_{AD1})$$

$$-111.490\,\mu_e \cos\varphi + 5.499\Delta\alpha + 593.496 = 0 \qquad (1_{AD2})$$

$$-45.432\,\mu_e^2 + 111.490\,\mu_e \cos\varphi - 5.499\Delta\alpha + 515.721\,\Delta\alpha + 7087.1 = 0 \qquad (2_{AD2})$$

For cos φ = 1, the solutions of the system (1_{AD2})–(2_{AD2}) are:

$$\mu_e = 225.457\,D \quad \text{and} \quad \mu_e = 4.684\,D \qquad (3_{AD2})$$

$$\alpha_e = 44.82110^{-24}\ \mathrm{cm}^3 \qquad (4_{AD2})$$

$$-61.500\mu_e \cos\varphi + 4.831\Delta\alpha - 190.229 = 0 \qquad (1_{AD3})$$

$$-39.909\,\mu_e^2 + 61.500\,\mu_e \cos\varphi - 4.831\Delta\alpha + 458.063\,\Delta\alpha + 6143.9 = 0 \qquad (2_{AD3})$$

Let us consider cos φ = −1. The solutions of the system (1_{AD2})–(2_{AD2}) are:

$$\mu_e = -150.119\,D \quad \text{and} \quad \mu_e = 4.005\,D \qquad (3_{AD3})$$

$$\alpha_e = 51.6010^{-24}\ \mathrm{cm}^3 \qquad (4_{AD3})$$

The solutions of these equations are listed in Table 4. The data in Table 4 were obtained from systems of equations written above and by using HyperChem Programs (I, a, μ_g, α_g) and solvatochromic effects (C_1, C_2). The system of two equations obtained in the solvatochromic study does not allow estimating the three unknown molecular parameters μ_e, α_e, φ: excited states dipole moment and polarizability and the angle between the dipole moments in the electronic states participating to the $\pi \rightarrow \pi^*$ transition. In absence of supplementary information for the third equation, the system was solved in the approximation φ = 0 for AD1 and AD2 and φ = 180° for AD3. Our results indicate that the excitation increases the electric dipole moment and the polarizability of the azo-derivatives under the study.

Electronic absorption spectra of azo-benzenes derivatives in ternary solutions

The electronic absorption spectra of the studied compounds in binary solvent: Methanol (M) + *n*-Hexane (H) was studied in order to obtain more information regarding the intermolecular forces in azo-benzene solutions we studied.

By using the values of the regression coefficients from Table 3 and the solvent macroscopic parameters of *n*-Hexane and Methanol (Table 5), the supply of each type of interactions to the total spectral shift measured in each component of the binary solvent has been evaluated and the results are given in Table 6.

The pair of solvents contains liquids with appropriate values of refractive indices (n_M = 1.331 and n_H = 1.375) and different electric permittivities (ε_M = 1.89 and n_H = 31.0), as it results from Table 5.

Table 4
Data regarding the studied azo-benzene molecules.

Compound	I_u (eV)	μ_g (D)	α_g (A^3)	a (A)	μ_e (D)	α_e (A^3)
AD1	8.96	2.102	30.02	4.852	10.167	34.24
AD2	8.94	2.454	31.86	4.802	4.684	44.82
AD3	9.13	1.541	39.69	5.014	4.005	51.60

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Table 5
Solvent parameters for ternary solutions.

Solvent	n	ε	ρ (g/cm^3)	M (g/mol)	ρ/M	μ (D)
Methanol (M)	1.3314	31.0	0.7918	32.04	24.713	1.69
n-Hexane (H)	1.375	1.89	0.6548	86.18	7.598	0

Table 6
Supply of each type of intermolecular interactions in n-Hexane and Methanol.

ADi	cm^{-1}				%			
	$C_1f(\varepsilon)$	$C_2f(n)$	$C_3\beta$	$C_4\alpha$	$C_1f(\varepsilon)$	$C_2f(n)$	$C_3\beta$	$C_4\alpha$
	n-Hexane							
AD1	−180	−1172	0	0	13	87	0	0
AD2	−73	−1621	0	0	4	96	0	0
AD3	+65	−1406	0	0	4	96	0	0
	Methanol							
AD1	−706	−1041	−51	148	36	53	3	8
AD2	−294	−1441	−226	166	14	68	10	8
AD3	+261	−1249	−56	160	15	72	72	9

Table 7
Volumetric ratio C_1 (%) of active solvent (1), electric permittivity ε of binary solvent, wavenumbers $\bar{\nu}$(cm^{-1}) in the maximum of $\pi \rightarrow \pi^*$ band of azobenzenes, molar fraction x_1 of active solvent and average statistic weight p_1 of the solvent (1) in the first solvation shell of azo-benzenes for ternary solution ADi + M + H (i = 1, 2, 3).

C_1 (%)	ε	$\bar{\nu}$(cm^{-1})			x_1	p_1		
		AD1	AD2	AD3		AD1	AD2	AD3
0	2.00	30,490	30,210	30,490	0.000	0.000	0.000	0.000
5	6.00	30,475	30,205	30,500	0.145	0.054	0.023	0.071
10	10.00	30,470	30,200	30,510	0.264	0.071	0.045	0.143
25	17.8	30,450	30,190	30,540	0.518	0.143	0.091	0.357
50	23.0	30,400	30,180	30,580	0.763	0.321	0.136	0.643
75	25.2	30,330	30,100	30,610	0.906	0.571	0.500	0.857
100	31.0	30,210	29,990	30,630	1.000	1.000	1.000	1.000

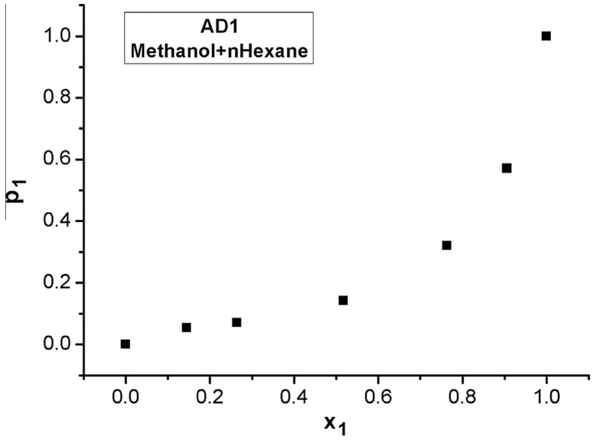

Fig. 3. p_1 vs. x_1 for AD1 in binary solvent Methanol + n-Hexane.

Table 8
$\ln\frac{x_1}{1-x_1}$, $\delta_{(1)}$ and $\ln\frac{p_1}{1-p_1}$ for ternary solution ADi + M + H (i = 1, 2, 3).

$\ln\frac{x_1}{1-x_1}$	AD1		AD2		AD3	
	$\delta_{(1)}$	$\ln\frac{p_1}{1-p_1}$	$\delta_{(1)}$	$\ln\frac{p_1}{1-p_1}$	$\delta_{(1)}$	$\ln\frac{p_1}{1-p_1}$
–	0	–	0	–	0	–
−1.774	−0.091	−2.863	−0.122	−3.749	−0.074	−2.566
−1.025	−0.193	−2.571	−0.219	−3.055	−0.121	−1.791
0.072	−0.375	−1.791	−0.427	−2.254	−0.161	−0.588
1.169	−0.442	−0.749	−0.627	−1.849	−0.640	0.588
2.266	−0.335	0.286	−0.406	0.000	−0.049	1.791
–	0	–	0	–	0	–

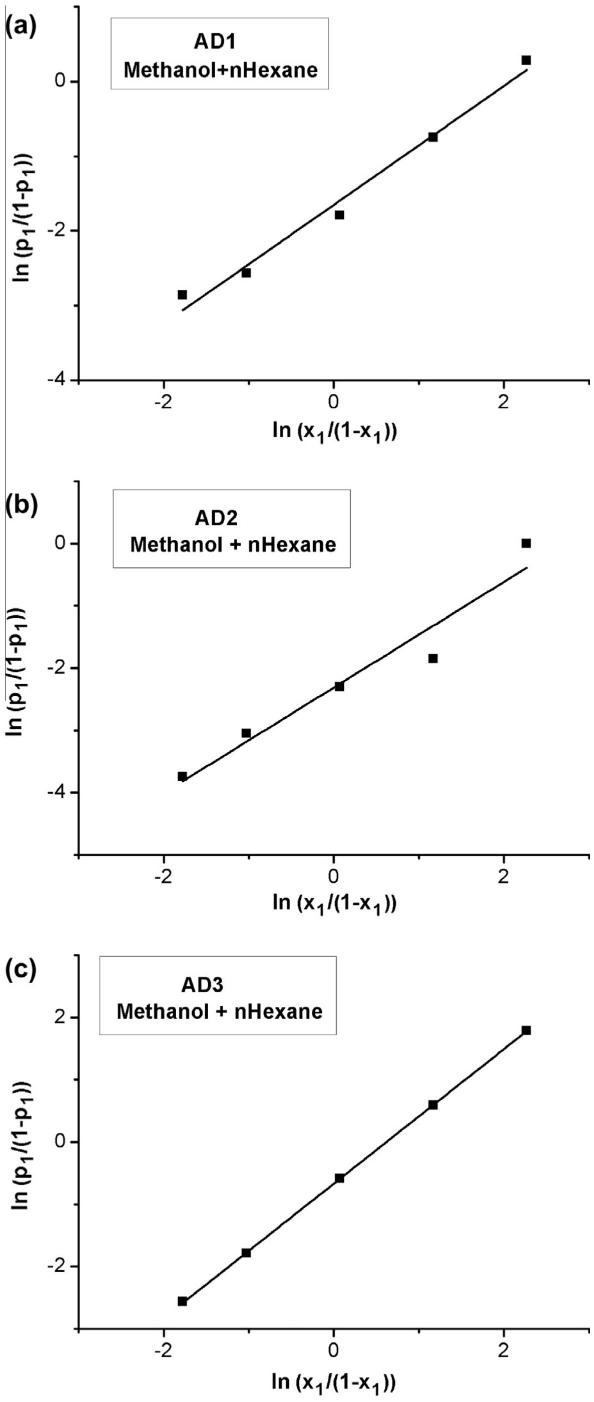

Fig. 4. (a–c) $\ln\frac{p_1}{1-p_1}$ vs. $\ln\frac{x_1}{1-x_1}$ for ADi, i = 1, 2, 3.

In these conditions, one can suppose that the dispersive–inductive interactions are of the same strength in ternary solutions when the active solvent concentration is varied. Only orientation-induction or possible specific interactions will contribute to the spectral shifts measured in ternary solutions with the active solvent in variable volumetric ratios.

The data regarding the ternary solution Azo-benzene derivative + Methanol + n-Hexane are listed in Tables 5 and 7. From these tables it results an exponential increase of the average statistic weight of Methanol in the first solvation shell of azo-benzene

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Table 9
Regression coefficients in equation $\ln\frac{p_1}{1-p_1} = m\ln\frac{x_1}{1-x_1} + n$ for ADi, $i = 1, 2, 3$.

Solvent	Molecule	$m \pm \Delta m$	$n \pm \Delta n$	R	SD	$w_2 - w_1$ $(10^{-20}$ J)
Methanol + n-Hexane	AD1	0.80 ± 0.06	−1.65 ± 0.09	0.97	0.19	− 0.67 ± 0.03
	AD2	0.85 ± 0.12	−2.31 ± 0.18	0.92	0.39	− 0.94 ± 0.07
	AD3	1.08 ± 0.01	−0.67 ± 0.01	0.99	0.01	−0.27 ± 0.00

derivatives (see Fig. 3) when its molar fraction in the binary solvent increases (see Table 8)

In binary solvent M + H, the excess function $\delta_{(1)}$ is negative, showing a prevalence of non-polar solvent n-Hexane in the first solvation shell of the studied azo-benzene derivatives. This result is in accordance with the positive value of the computed by HyperChem parameter $\log P$ which is positive, showing the hydrophobic nature of ADi, $i = 1, 2, 3$.

The linear dependencies of the quantities $\ln\frac{p_1}{1-p_1}$ and $\ln\frac{x_1}{1-x_1}$, shown in Fig. 4a–c, demonstrate the applicability of the ternary solutions model to the spectral data obtained for ADi + M + H ($i = 1, 2, 3$).

In Table 9 are listed the regression coefficients of the lines $\ln\frac{p_1}{1-p_1} = m\ln\frac{x_1}{1-x_1} + n$ illustrated in Fig. 4a–c.

As it results from Table 9, the slope m is near the unity for AD3 and smaller the unity for AD1 and AD2 in ternary solutions ADi ($i = 1, 2, 3$) + M + H.

The cut at origin are negative for all ADi ($i = 1, 2, 3$) in M + H. The negative values of n show that $w_2 - w_1 < 0$. The interaction energies in the solute–solvent molecular pair have negative values being caused by attraction forces, so for negative values of the cut at origin, one can suppose that the binary energies w_1 and w_2 are in the correlation $|w_1| < |w_2|$ for the molecular pairs realized between the compounds ADi ($i = 1, 2, 3$) and the solvent molecules.

Conclusions

The $\pi \rightarrow \pi^*$ band of azo-benzene derivatives generally shifts bathochromically under the influence of the universal interactions, while the specific interactions with the solvents having H-bonding acceptor ability contribute to its hypsochromic shift.

By using a semi-empirical formula of the type (9), the contribution of the universal and of the specific interactions can be separated from the total spectral shift measured in the electronic absorption spectra of azobenzene.

The difference between the interaction energies in solute–solvent molecular pairs of the types $u - v_1$ and $u - v_2$ azo-benzene derivative-active solvent and azo-benzene derivative-inactive solvent was estimated on the basis of the cell theory of ternary solutions. The negative values of the difference $w_2 - w_1$ show that $|w_2| > |w_1|$ and are in accordance with hydrophobic nature of the studied compounds.

The slope of Eq. (10) linearly depends on the correlation coefficient $C_1(\text{cm}^{-1})$.

References

[1] F. Qiu, C. Ge, X. Gu, D. Yang, Int. J. Polym. Anal. Charact. 16 (2011) 36–48.
[2] H. Rau, in: J.F. Rabek (Ed.), Photochemistry and Photophysics, vol. 2, CRC Press, Boca Raton, 1990.
[3] F. Serra, E.M. Terentjev, Macromolecules 41 (2008) 981–986.
[4] G.S. Kumar, Azo-Functional Polymers, Technomic Publ. Lancaster, 1992.
[5] S. Yasuda, T. Nakamura, M. Matsumoto, H. Shigekawa, J. Am. Chem. Soc. 125 (2003) 16430–16433.
[6] J.F. Morin, Y. Shirai, J.M. Tour, Org. Lett. 8 (2006) 1713–1716.
[7] M.S. Masoud, A.E. Ali, M.A. Shaker, M.A. Ghani, Spectrochim. Acta 60A (2004) 3155–3159.
[8] S.K. Yesodha, C.K.S. Pillai, N. Tsutsumi, Progr. Polym. Sci. 29 (2004) 45–74.
[9] M.M.M. Raposo, M.C.R. Castro, M. Belsley, A.M.C. Fonseca, Dyes Pigm. 91 (2011) 454–465.
[10] M.A. Rauf, S. Hisaindee, J. Mol. Struct. 1042 (2013) 45–56.
[11] K. Alizadeh, S. Seyyedi, M. Shamsipur, S. Rouhani, K. Haghbeen, Spectrochim. Acta A; Mol. Biomol. Spectrosc. 74 (2009) 691–694.
[12] H. Faustino, C.R. Brannigan, L.V. Reis, P.F. Santos, P. Almeida, Dyes Pigm. 83 (2009) 88–94.
[13] A. Airinei, E. Rusu, D.O. Dorohoi, Spectrosc. Lett. 34 (2001) 65–74.
[14] E. Rusu, D.O. Dorohoi, A. Airinei, J. Mol. Struct. 887 (2008) 216–219.
[15] C. Reichardt, Solvents and Solvent Effect in Organic Chemistry, Wiley-VCH, Weinheim, 2003.
[16] D.R. Lide (Ed.), Handbook of Chemistry and Physics, 76th ed., CRC Press, Boca Raton, Florida, 1995.
[17] Y. Marcus, Chem. Soc. Rev. 22 (1993) 409–416.
[18] M.J. Kamlet, J.L. Abboud, M.H. Abraham, R.W. Taft, J. Org. Chem. 48 (17) (1983) 2877–2887.
[19] T. Schlick, Molecular Modeling and Simulation, An Interdisciplinary Guide, Springer Verlag, New York, 2002.
[20] H.D. Holtje, W. Sippl, D. Rognan, G. Folkers, Molecular Modeling, Dussedorf-Zuric, John Wiley-VCH Gmbh and Co, New York, 2003.
[21] HyperChem 8.0.6. Molecular Visualization and Simulation Programm Package, Hypecube Inc., Gainesville, 2007.
[22] R.G. Pearson, Proc. Nati. Acad. Sci. (USA) 83 (1986) 8440–8443.
[23] A.S. El-Shahawy, S.M. Ahmed, N. Kr, Sayed, Spectrochim. Acta A 66 (2007) 143–146.
[24] I. Hurjui, L.M. Ivan, D.O. Dorohoi, Spectrochim. Acta A 102 (2013) 219–225.
[25] E.G.Mc. Rae, J. Phys. Chem. 61 (1957) 562–572.
[26] H.G. Bakhshiev, Spectroscopia Mejmoleculiarnix Vzaimodeisrviax, Izd. Nauka, Leningrad, 1972.
[27] D.O. Dorohoi, M. Dimitriu, Rev. Chim. (Buch.) 58 (1) (2007) 1060–1063.
[28] C. Gheorghies, L.V. Gheorghies, D.O. Dorohoi, J. Mol. Struct. 887 (2008) 122–127.
[29] D.O. Dorohoi, C.F. Dascalu, T. Teslaru, L.V. Gheorghies, Spectrosc. Lett. 45 (6) (2012) 383–391.
[30] D.O. Dorohoi, A. Airinei, M. Dimitriu, Spectrochim. Acta A 73 (2) (2009) 257–262.
[31] L.V. Gheorghies, M. Dimitriu, E. Filip, D.O. Dorohoi, Rom. J. Phys. 55 (1–2) (2010) 103–109.
[32] D.O. Dorohoi, Spectrochim. Acta A 75 (2010) 1030e1–1030e5.
[33] G. Henrion, A. Henrion, R. Henrion, Beispiele zur Datenanalyse mit BASIC Programmen VEB D.V.W., Berlin, 1988.
[34] N.G. Bakhshiev, Opt. Spectrosc. 101 (3) (2006) 388–394. Pleiades Publishing Inc. 2006.
[35] N.G. Bakhshiev, S.K. Gularyan, G.E. Dobretsov, A.Yu. Kirillova, V.Yu. Svetlichnyi, Opt. Spectrosc. 101 (5) (2006) 700–708. Pleiades Publishing Inc. 2006.
[36] N.G. Bakhshiev, S.K. Gularyan, G.E. Dobretsov, A.Yu. Kirillova, V.Yu. Svetlichnyi, Optics and Spectroscopy 103 (5) (2007) 741–744. Pleiades Publishing Inc. 2007.
[37] M. Homocianu, A. Airinei, D.O. Dorohoi, Spectrochim. Acta A 82 (1) (2011) 355–359.
[38] C. Nadejde, D.E. Creanga, I. Humelnicu, D.O. Dorohoi, J. Mol. Liquids 150 (1–3) (2009) 51–55.
[39] Iu. Mazurenko, Optika i Spektroscopia T.XXXIII (1972) 1060–1065.
[40] V. Pop, M. Delibas, D.O. Dorohoi, An.Stiint. Univ. Al.I.Cuza Iasi, sIb, Fizica T.XXXII (1987) 79–84.
[41] D.O. Dorohoi, J. Mol. Struct. 700 (2004) 31–43;
D.O. Dorohoi, J. Mol. Struct. 792–793 (2006) 86–92.
[42] D.O. Dorohoi, M. Avadanei, M. Postolache, OAM-Rapid Commun. 2 (8) (2008) 511–515.
[43] M. Avadanei, D.O. Dorohoi, N. Puica Melniciuc, International Conf. of Optics and Photonics, Braga, Portugal, 3–5 May 2011; Proceedings of SPIE, vol. 8001, Art.nr. 80012D, DOI: 10.1117/12.891518.
[44] D.O. Dorohoi, D.Gh. Dimitriu, M. Dimitriu, V. Closca, J. Mol. Struct. 1044 (SI) (2013) 79–86.
[45] V. Sasirekha, P. Vanelle, T. Terme, V. Ramakrishnan, Spectrochim. Acta A 71 (3) (2008) 766–777.

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