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Spectrophotometric investigations of the role of the organic solvent on the acid dissociation constants of some azo dyes derived from 2-aminobenzothiazole

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ABSTRACT

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1. Introduction

During the last decades, tremendous numbers of papers have been devoted to the determination of pK_a values and tautomeric structure of the ionisable molecules [1-9]. This is due to the knowledge of pK_a values provide a basis for understanding the chemical reactions between the compound of interest and its pharmacological target. In addition, they play a major role in the acid-base titration, complex formation and many other analytical procedures. Furthermore, the ionization constants are often used to help discover the structure of a newly isolated substance [10]. In one hand, it is well known that benzothiazole and its derivatives show a broad spectrum of biological activities [11-13] and were investigated in azo push-pull systems [14]. On the other hand, azo compounds surely constitute an important group of compounds from cognitive and applicative points of view. Consequently, they have significantly attracted the interest of chemists and biologists globalwise [15-25]. Also, such compounds have long been well known in the analytical chemistry as chromogenic agents and acid-base indicators [26,27]. Other important applications of these substances include production of drugs in chemotherapy [28,29]. Considering their significant biological activity, pharmacological and physicochemical properties, azo dyes are extremely important.

Owing to the high number of positive applications of benzothiazole and azo compounds in different fields, the present work is focused on the determination of pK_a values of compounds **1–3** in

Proton dissociation constants (pK_a) of a set of hydroxyl azo dyes in various organic solvent + water mixtures have been determined. The results obtained were discussed in terms of the solvent characteristic. Effects of hydrogen-bonding interactions and solvent basicity on the ionization process have been also discussed. In a nutshell, the pK_a values of the investigated compounds were found to be largely depending on both the ratio and the nature of organic cosolvent. In addition, it was very important to know with which structures we are dealing in liquid solutions and how these structures influence physicochemical properties of individual tautomers and their acidity constants. Thus, theoretical calculations have been done in order to obtain an insight into structure features and physicochemical properties of the compounds under study.

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aqueous buffer solutions containing varying proportions of organic solvents of different polarities. Furthermore, we invoked semiempirical PM6 and PM6 (COSMO) levels to predict the structures and properties of all possible tautomers.

2. Experimental

2.1. Synthesis of the azo compounds 1-3

The azo compounds under investigation were synthesized according to the well known standard diazotization procedure described in literature [30]. To an ice cooled stirred solution of 2-aminebenzothiazol (0.01 mol) dissolved in H₃PO₄, a cold solution of NaNO₂ (0.01 mol) was added gradually with stirring for 20 min. To a solution of phenol, resorcinol or β -naphtol (0.01 mol) in ethanol in the presence of sodium acetate, a solution of diazotized amine was added dropwise with vigorous stirring (0–5 °C) during 35 min. After the addition was finished, stirring was continued for 1 hour and the obtained precipitate was isolated by filtration and washed with water and cold ethanol. The solid products were recrystallized from ethanol and air-dried under reduced pressure over silica gel. The purity of the prepared compounds was checked by elemental analysis and FT-IR spectra (Scheme 1).

2.2. Measurements

Stock solutions $(1 \times 10^{-3} \text{ mol } \text{dm}^{-3})$ of the compounds were prepared by dissolving a known mass of the solid in the required volume of each solvent; more dilute solutions were obtained by accurate dilution with the solvent. The pH control was achieved by

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Scheme 1. The compounds investigated with the number of atoms indicated: R = H (1), OH (2) and 3.

using modified universal buffer solutions [31]. To account for differences in acidity, basicity, dielectric constant, and ion activities in partially aqueous media relative to pure aqueous solutions, where the pH meter is standardized using aqueous buffers at 25 °C. The pH values in the former media were corrected by using procedure described by Douheret [32] (Eq. (1)), where the meter reading pH_(R) obtained in each water + organic solvent mixture differs by amount δ from the corrected reading pH^{*}.

$$pH^* = pH_{(R)} - \delta \tag{1}$$

Values of δ for various aqueous + organic solvent mixtures were determined as recommended by Douheret at the same ionic strength [32,33]. The solutions were thermostated at 25 °C before measuring their spectra. The electronic absorption spectra were recorded on a Shimadzu 2401 PC spectrophotometer using 1 cm matched quartz cells within the wavelength range of 340–650 nm. The pH measurements were carried out using an Orion 501 digital ionalyzer accurate to \pm 0.01 pH unit. The FT-IR spectra of the compounds were recorded on Nicolet FT-IR 560 spectrophotometer as KBr discs. All measurements were carried out at 25 °C and temperature control was achieved using an ultrathermostat of accuracy \pm 0.05 °C.

2.3. Quantum chemical calculations

The fully geometry optimization of the isolated molecules **1–3** (Scheme 1) in gaseous phase and in different media were optimized using the semiempirical PM6 and PM6 (COSMO) methods, respectively [34]. From which some physicochemical and structural parameter for each tautomer were estimated. The geometry results were obtained from MOPAC 2007-free license on internet [35]. Heats of formation, dipole moments and other parameters were extracted directly from the data files following the geometry optimizations. All calculations were done on a Pentium IV PC computer.

3. Results and discussion

3.1. Structure and physicochemical properties

The compounds under investigation can coexist in azo and hydrazone tautomeric forms (Fig. 1). It is, therefore, important to know with which structures we are dealing and how these structures influence the features of individual tautomers. However, theoretical calculations have been done in order to throw some light onto the structure features and physicochemical properties of the compounds under study. According to the results of our calculations given in Table 1, the equilibrium constants $(\ln_{298} K^{\circ})$ for compounds 2 and 3 were found to be so high that they should exist mainly as hydrazone tautomers either in the gaseous phase or in solution. Contrary, PM6 method yields negative values of equilibrium constants of compound 1 indicating, without any doubt, that the azo tautomer should be predominant. Inspection of the optimized molecular geometries reveals that the azo and hydrazone tautomers are essentially planar in compound **1**. On the other hand, the main feature of the geometry of compounds **2** and **3** is the planarity of the hydrazone and azo forms, respectively (Fig. 1 and Table 1).

The dipole moments listed in Table 1 apparently differ for the tautomeric forms. Without going in details, calculations clearly indicate that the hydrazone tautomer has the largest dipole moment in the case of **1** and **2**. However, the azo tautomer of compound **3** is more polar than the hydrazone one. Moreover, the dipole moments are increased with increasing the polarity of the medium.

3.2. Electronic absorption spectra in universal buffer solution

The visible absorption spectra of compounds 1-3 in universal buffer solutions containing different proportions of an organic solvent (methanol, ethanol, acetone and DMF) show mainly two bands (Fig. 2). The shorter wavelength band, appearing at 410–430 nm,



Fig. 1. The PM6-optimized structures of the tautomers of compounds 1-3 in ethanol (Scheme 1).

Table 1	
Structural and physicochemical features of tautomers of the investigate	ed azo dyes (Scheme 1).

Comp.	Computational level	Dihedral angle ^a		Dipole moment (D)		ln ₂₉₈ K ^{ob}
		Azo	Hydrazone	Azo	Hydrazone	
1	PM6	179.99	- 179.97	3.23	5.91	- 13.00
	PM6 (COSMO $-C_2H_5OH$)	179.95	179.55	4.63	8.74	-4.97
	PM6 (COSMO $-CH_3OH$)	-179.04	179.84	2.67	8.83	-6.37
	PM6 (COSMO–Acetone)	- 179.05	179.82	2.65	8.69	-6.71
	PM6 (COSMO–DMF)	- 179.05	179.85	2.68	8.86	-6.31
2	PM6	180.00	180.00	3.76	5.50	11.26
	PM6 (COSMO $-C_2H_5OH$)	-178.62	179.70	4.70	7.97	5.98
	PM6 (COSMO $-CH_3OH$)	- 178.61	179.40	4.76	8.04	5.92
	PM6 (COSMO–Acetone)	-178.64	179.67	4.67	7.92	6.01
	PM6 (COSMO–DMF)	-178.60	179.32	4.77	8.06	5.94
3	PM6	- 179.98	179.78	3.67	1.06	16.28
	PM6 (COSMO $-C_2H_5OH$)	179.72	178.52	5.78	2.08	9.22
	PM6 (COSMO $-CH_3OH$)	179.82	178.34	5.85	2.05	9.00
	PM6 (COSMO-Acetone)	179.73	178.48	5.74	2.03	9.30
	PM6 (COSMO–DMF)	179.84	178.34	5.88	2.09	8.92

^a Between $C_2N_9N_{10}C_{11}$.

^b $\ln_{298} K^o = -\delta \Delta H/RT$ ($\delta \Delta H$ denotes the difference in standard enthalpies of hydrazone and azo tautomers).

represents absorption by the neutral form, whereas the longer band observed at 510–550 nm is attributed to the absorption by the ionized species. On increasing the pH of the medium, the absorbance of the former band decreases while the latter band increases. At high pH values the shorter wavelength visible band disappears completely and the longer one attains a more or less constant absorbance value. As a consequence, a fine isosbestic point is achieved, indicating that two species are in equilibrium of the type (Scheme 2).

$$HA \longrightarrow H^+ + A^-$$
(2)

Fig. 3 which represents the plots of the absorbance against pH^{*} values shows a typical dissociation curves, confirming the establishment of an acid–base equilibrium. The acid dissociation constants of the compounds under study were determined using three different spectrophotometric methods namely, the half-curve height, isosbestic point and limiting absorbance methods [36,37]. Tables 2–4 report the pK_a values of the compounds investigated in different media. It is widely clear from the data gathered in Tables 2–4 that the pK_a values of all compounds are largely dependent on both the nature and the proportion of the organic cosolvent. In a broad sense, pK_a values



Fig. 2. Electronic absorption spectra of 4.0×10^{-5} M solution of compound **1**.(R=H) in water (1) + acetone (2) at different pH's: (A) $w_2 = 16.53$; pH^{*} (1) 7.00, (2) 7.20, (3) 7.30, (4) 7.40, (5) 7.50, (6) 7.70, (7) 8.00, (8) 8.20, (9) 8.50, (10) 9.50. (B) $w_2 = 25.35$; pH^{*} (1) 7.10, (2) 7.25, (3) 7.40, (4) 7.55, (5) 7.70, (6) 8.10, (7) 8.50, (8) 9.60, (9) 10.00. (C) $w_2 = 34.56$; pH^{*} (1) 7.10, (2) 7.20, (3) 7.30, (4) 7.40, (5) 7.50, (6) 7.60, (7) 8.00, (8) 8.50, (9) 9.50. (D) $w_2 = 44.21$; pH^{*} (1) 7.10, (2) 7.25, (3) 7.35, (4) 7.40, (5) 7.50, (6) 7.65, (7) 8.15, (8) 8.50, (9) 9.55.



Scheme 2.

increase with an increase of the organic cosolvent content in the medium. This behavior can be interpreted on the basis as follows: according to Coetzee and Ritchie [38], the acid dissociation constant in aqueous medium (K_{a1}) is related to that in a partially aqueous medium (K_{a2}) by the equation

$$K_{a1} = K_{a2} \frac{\gamma_{H-(1)} \gamma_{A(1)}}{\gamma_{H-(2)} \gamma_{A(2)}} \frac{\gamma_{HA(2)}}{\gamma_{HA(1)}}$$
(3)



Fig. 3. Absorbance–pH* curves of 4.0×10^{-5} M solution of compound **2** (R=OH) in water (1) + DMF (2), in ionized species at 518 nm, with w_2 =9.21 (A), 28.96 (B), 38.81 (C), 48.75 (D).

Table 2

 pK_a values for 4.0×10^{-5} M of compound 1 in different water (1) + organic solvent (2) mixtures at 25 °C.

100w ₂ ^a	3	pK _a				SD		
		Method 1	Method 2	Method 3	Mean value			
Water (1) + methanol (2)								
16.53	73.72	7.60	7.65	7.50	7.58	± 0.08		
25.35	71.03	7.60	7.70	7.60	7.63	± 0.06		
34.56	67.88	7.65	7.70	7.60	7.65	± 0.05		
44.21	64.27	7.70	7.70	7.60	7.66	± 0.06		
Water (1) + ethai	10l (2)						
16.59	74.46	7.50	7.60	7.40	7.50	± 0.10		
25.42	72.00	7.50	7.65	7.45	7.53	± 0.10		
34.65	69.08	7.65	7.70	7.60	7.65	± 0.05		
44.30	65.54	7.70	7.60	7.80	7.70	± 0.10		
Water (1) + aceto	one (2)						
16.53	74.92	7.50	7.50	7.45	7.48	± 0.03		
25.35	72.87	7.50	7.70	7.60	7.60	± 0.10		
34.56	70.25	7.50	7.90	7.50	7.63	± 0.23		
44.21	66.99	7.60	7.80	7.60	7.67	± 0.11		
Water $(1) + DMF(2)$								
19.21	76.06	7.40	7.45	7.40	7.42	± 0.03		
28.96	74.56	7.40	7.55	7.40	7.45	± 0.09		
38.81	72.73	7.50	7.50	7.60	7.53	± 0.06		
48.75	70.45	7.60	7.60	7.50	7.57	± 0.06		

 $w_2^a = mass$ fraction of component 2.

where γ is the activity coefficient of the subscripted species in a partially aqueous medium relative to that in a pure aqueous one, and 1 is pure water and 2 is water + solvent. It is known that the electrostatic effect resulting from the charge in relative permittivity of the medium operates on the activity coefficients of the charged species [38], one can, therefore, expect that the increase in the amount of the organic cosolvent in the medium will increase the activity coefficient of both H⁺ and A⁻ ions. According to the above Eq. (3), this behavior will result in a decrease in the acid dissociation constant K_a of the compound (i.e., high pK_a value) on increasing the content of the organic solvent. This finding concurs with the results cited in Tables 2–4.

Interestingly, despite methanol and DMF have approximately similar relative permittivity constants (32.6 and 36.7, respectively, at 25 °C), all the compounds are more acidic in water + DMF than water + methanol at the same mole fraction (Tables 2–4). Moreover, although ethanol and acetone have a comparable relative permittivity constants also (24.3 and 20.7, respectively, at 25 °C), compounds **1** and **2** are more acidic in water + acetone than water + ethanol at the same mole fraction of each is used. In general, pK_a values for all compounds increase with increasing ratio of organic cosolvent in the medium; that is, the pK_a values of a compound in water + organic solvent are arranged according to the following sequence:

DMF < ethanol < methanol < acetone

This finding indicates that other solvent effects beside the electrostatic one have a contribution to the ionization process of the investigated compounds. This fact is further substantiated by the nonlinear relations obtained by plotting of pK_a against $1/\varepsilon$ of the

Table 3

 pK_a values for 4.0×10^{-5} M of compound **2** in different water (1) + organic solvent (2) mixtures at 25 °C.

Method 1 Method 2 Method 3 Mean value Water (1) + methanol (2) 16.53 73.72 10.60 10.40 10.50 10.50 ± 0.06 34.56 67.88 10.60 10.60 10.60 10.60 ± 0.06 34.56 67.88 10.60 10.60 10.60 ± 0.06 44.21 64.27 10.70 10.60 10.60 10.63 ± 0.06 Water (1) + ethanol (2) 16.59 74.46 10.50 10.50 10.60 10.53 ± 0.06 25.42 72.00 10.55 10.60 10.63 ± 0.06 25.42 72.00 10.55 10.60 10.58 ± 0.03 34.65 69.08 10.60 10.70 10.63 ± 0.06 44.30 65.54 10.60 10.70 10.66 ± 0.06 25.35 72.87 10.60 10.40 10.50 10.50 ± 0.10 34.56 70.25 10.50 10.50 10.70 </th <th>100w₂^a</th> <th>3</th> <th colspan="4">p<i>K</i>_a</th> <th>SD</th>	100w ₂ ^a	3	p <i>K</i> _a				SD	
Water (1) + methanol (2) 16.53 73.72 10.60 10.40 10.50 10.50 \pm 0.10 25.35 71.03 10.50 10.50 10.60 10.53 \pm 0.06 34.56 67.88 10.60 10.60 10.60 10.60 \pm 0.00 44.21 64.27 10.70 10.60 10.60 10.63 \pm 0.06 Water (1) + ethanol (2) 16.59 74.46 10.50 10.50 10.60 10.53 \pm 0.06 25.42 72.00 10.55 10.60 10.63 \pm 0.03 \pm 0.66 25.42 72.00 10.55 10.60 10.63 \pm 0.06 25.42 72.00 10.55 10.60 10.70 10.63 \pm 0.06 44.30 65.54 10.60 10.70 10.66 \pm 0.06 Water (1) + acetone (2) 16.53 74.92 10.40 10.50 10.47 \pm 0.06 25.35 72.87 10.60 10.40 10.50 10.50			Method 1	Method 2	Method 3	Mean value		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Water (1	1) + meth	nanol (2)					
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	16.53	73.72	10.60	10.40	10.50	10.50	± 0.10	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	25.35	71.03	10.50	10.50	10.60	10.53	± 0.06	
44.21 64.27 10.70 10.60 10.60 10.63 ± 0.06 Water (1) + ethanol (2) 10.59 74.46 10.50 10.50 10.60 10.53 ± 0.06 25.42 72.00 10.55 10.60 10.63 ± 0.03 34.65 69.08 10.60 10.70 10.63 ± 0.06 44.30 65.54 10.60 10.70 10.63 ± 0.06 Water (1) + acetone (2) 16.53 74.92 10.40 10.50 10.47 ± 0.06 25.35 72.87 10.60 10.70 10.60 ± 0.10 34.56 70.25 10.50 10.70 10.60 ± 0.10 34.56 70.25 10.50 10.70 10.60 ± 0.10 34.56 70.25 10.50 10.70 10.60 ± 0.06 Water (1) + DMF (2) 19.21 76.06 10.40 10.45 10.60 10.49 ± 0.10	34.56	67.88	10.60	10.60	10.60	10.60	± 0.00	
Water $(1) + ethanol (2)$ 16.59 74.46 10.50 10.50 10.60 10.53 ± 0.06 25.42 72.00 10.55 10.60 10.60 10.58 ± 0.03 34.65 69.08 10.60 10.70 10.63 ± 0.06 44.30 65.54 10.60 10.70 10.66 ± 0.06 Water (1) + acetone (2) 16.53 74.92 10.40 10.50 10.50 10.47 ± 0.06 25.35 72.87 10.60 10.40 10.50 10.50 ± 0.10 34.56 70.25 10.50 10.70 10.60 ± 0.10 34.56 70.25 10.50 10.70 10.60 ± 0.11 44.21 66.99 10.60 10.70 1063 ± 0.06 Water (1) + DMF (2) 19.21 76.06 10.40 10.45 10.60 10.49 ± 0.10	44.21	64.27	10.70	10.60	10.60	10.63	± 0.06	
Water (1) + ethanol (2) 16.59 74.46 10.50 10.50 10.60 10.53 \pm 0.06 25.42 72.00 10.55 10.60 10.60 10.58 \pm 0.03 34.65 69.08 10.60 10.60 10.70 10.63 \pm 0.06 44.30 65.54 10.60 10.70 10.70 10.66 \pm 0.06 Water (1) + acetone (2) 16.53 74.92 10.40 10.50 10.50 \pm 0.10 34.56 70.25 10.50 10.70 10.60 \pm 0.10 34.56 70.25 10.50 10.70 10.60 \pm 0.11 44.21 66.99 10.60 10.70 1063 \pm 0.06 Water (1) + DMF (2) 19.21 76.06 10.40 10.45 10.60 10.49 \pm 0.10								
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Water (1	1) + etha	nol (2)					
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	16.59	74.46	10.50	10.50	10.60	10.53	± 0.06	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	25.42	72.00	10.55	10.60	10.60	10.58	± 0.03	
44.30 65.54 10.60 10.70 10.70 10.66 \pm 0.06 Water (1) + acetone (2) 10.53 74.92 10.40 10.50 10.50 10.47 \pm 0.06 25.35 72.87 10.60 10.40 10.50 10.50 \pm 0.10 34.56 70.25 10.50 10.60 10.70 10.60 \pm 0.11 44.21 66.99 10.60 10.60 10.70 1063 \pm 0.06 Water (1) + DMF (2) 19.21 76.06 10.40 10.45 10.60 10.49 \pm 0.10	34.65	69.08	10.60	10.60	10.70	10.63	± 0.06	
Water (1) + acetone (2) 16.53 74.92 10.40 10.50 10.50 10.47 \pm 0.06 25.35 72.87 10.60 10.40 10.50 10.50 \pm 0.10 34.56 70.25 10.50 10.60 10.70 10.60 \pm 0.11 44.21 66.99 10.60 10.60 10.70 1063 \pm 0.06 Water (1) + DMF (2) 19.21 76.06 10.40 10.45 10.60 10.49 \pm 0.10	44.30	65.54	10.60	10.70	10.70	10.66	± 0.06	
Water (1) + acetone (2) 16.53 74.92 10.40 10.50 10.50 10.47 \pm 0.06 25.35 72.87 10.60 10.40 10.50 10.50 \pm 0.10 34.56 70.25 10.50 10.60 \pm 0.11 44.21 66.99 10.60 10.60 \pm 0.06 Water (1) + DMF (2) 19.21 76.06 10.40 10.45 10.60 10.49 \pm 0.10								
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Water (1	1) + aceto	one (2)					
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	16.53	74.92	10.40	10.50	10.50	10.47	± 0.06	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	25.35	72.87	10.60	10.40	10.50	10.50	± 0.10	
44.21 66.99 10.60 10.70 1063 \pm 0.06 Water (1) + DMF (2) 19.21 76.06 10.40 10.45 10.60 10.49 \pm 0.10	34.56	70.25	10.50	10.50	10.70	10.60	± 0.11	
Water (1) + DMF (2) 19.21 76.06 10.40 10.45 10.60 10.49 ±0.10	44.21	66.99	10.60	10.60	10.70	1063	± 0.06	
Water (1) + DMF (2) 19.21 76.06 10.40 10.45 10.60 10.49 \pm 0.10								
19.21 76.06 10.40 10.45 10.60 10.49 ± 0.10	Water $(1) + DMF(2)$							
	19.21	76.06	10.40	10.45	10.60	10.49	± 0.10	
$28.96 74.56 10.35 10.55 10.50 10.47 \pm 0.10$	28.96	74.56	10.35	10.55	10.50	10.47	± 0.10	
$38.81 72.73 10.30 10.60 10.60 10.50 \pm 0.17$	38.81	72.73	10.30	10.60	10.60	10.50	± 0.17	
48.75 70.45 10.50 10.60 10.50 10.53 ±0.06	48.75	70.45	10.50	10.60	10.50	10.53	± 0.06	

 $w_2^a = mass$ fraction of component 2.

56 Table 4

 pK_a values for 4.0×10^{-5} M of compound **3** in different water (1) + organic solvent (2) mixtures at 25 °C

100w ₂ ^a	З	p <i>K</i> _a				SD		
		Method 1	Method 2	Method 3	Mean value			
Water (1) + methanol (2)								
16.53	73.72	9.50	9.45	-	9.48	± 0.04		
25.35	71.03	9.55	9.50	-	9.53	± 0.04		
34.56	67.88	9.60	9.60	-	9.60	± 0.00		
44.21	64.27	9.65	9.60	-	9.60	± 0.04		
Water (1) + etha	nol (2)						
16.59	74.46	9.60	9.60	-	9.60	± 0.00		
25.42	72.00	9.63	9.65	-	9.64	± 0.01		
34.65	69.08	9.65	9.70	-	9.68	± 0.04		
44.30	65.54	9.70	9.70	-	9.70	± 0.00		
Water (1) + acet	one (2)						
16.53	74.92	9.65	9.70	-	9.68	± 0.04		
25.35	72.87	9.70	9.70	-	9.70	± 0.00		
34.56	70.25	9.75	9.80	-	9.79	± 0.04		
44.21	66.99	9.80	9.80	-	9.80	± 0.00		
Water $(1) + DMF(2)$								
19.21	76.06	9.30	9.30	-	9.30	± 0.00		
28.96	74.56	9.35	9.30	-	9.33	± 0.04		
38.81	72.73	9.45	9.40	-	9.43	± 0.04		
48.75	70.45	9.50	9.45	-	9.43	± 0.04		
-								

 $w_2^a = mass$ fraction of component 2.

medium (Fig. 4), according to the equation given by Denison and Ramesy [39] and Gilkerson [40] which relates the variation of the pK_a of the acid with the relative permittivity of the medium ε . The relative permittivity of water + organic solvent mixtures, ε , was obtained using the following equation [41]

$$\varepsilon = \varepsilon_1 m_{f(\mathbf{w})} + \varepsilon_2 m_{f(\mathbf{s})} \tag{4}$$

where ε is the relative of water + organic solvent mixtures, ε_1 and ε_2 are the relative permittivity of the water and organic solvent, respectively, $m_{\rm f}$ is the mole fraction, and the subscripts w and s refer to water and organic solvent, respectively.

In general, effects such as hydrogen bonding, solvent basicity, dispersive forces, and proton-solvent interactions play vital roles in the ionization process of acids in the presence of organic solvents [38]. Thus, the observed increase in the pK_a of the compounds as the proportion of the organic cosolvent in the medium is increased can be ascribed, in addition to the electrostatic effect, to the hydrogenbonding interaction between the conjugated base (A⁻) and solvent



Fig. 4. Variation of pKa of 4.0×10^{-5} M solution of compound **3** in water (1) + organic solvent (2) with $10^2/\varepsilon$ of the medium at 25 °C: (A) methanol, (B) ethanol, (C) acetone, (D) DMF.

molecules. Since water molecules have a higher tendency to donate hydrogen-bonds than other solvent molecules [42], the conjugated base (A⁻) is expected to be less stabilized by the hydrogen-bonding interaction with solvent molecules as the amount of the organic cosolvent in the medium is increased. This will tend to increase the pK_a value of the compound, as Eq. (3) implies. It indicates also that the difference in the stabilization of the ionic form by hydrogen-bond donor solvent molecules plays an important role in the increase of the pK_a values as the amount of the organic cosolvent in the medium is increased.

Examination of the results depicted in Tables 2-4 reveals that the pK_a values in the presence of the poorer hydrogen-bond donor DMF are less than those obtained in the presence of corresponding amounts of the other solvents. This behavior can be ascribed to the high basic character of DMF, which reflects itself in the construction of a strong hydrogen-bond acceptor from the OH group of the nonionized dye molecule and consequently promotes the ionization process (i.e., low pK_a).

If the dispersive forces, which possibly exist in the media used, between the delocalized charge on the conjugated base of the dye (A) and the localized dispersion centers in near solvent molecules as well as the proton-solvent interactions have important effects on the ionization process of the compounds studied, one should expect that by increasing the amount of the organic cosolvent both A^- and H^+ will be highly stabilized by DMF molecules (i.e., γ_A^- and $\gamma_H^+/\gamma_A^$ decreases), since the effective density of dispersion centers in each of the organic solvents used is higher than that of water [43]. Thus, in the light of Eq. (3), the acid dissociation constant of the dyes studied would increase (pK_a decreases) with the increase in the amount of the organic cosolvent in the medium. This is not the case obtained from the results (Tables 2–4). Therefore, one can conclude that neither the dispersive forces nor the proton-solvent interaction effects have an effective contribution to the ionization process of the dyes investigated. The values of pK_a cited in Tables 2–4 show that the acidity of the studied azo compounds decreases in the following order: 2<3<1.

4. Conclusion

The comprehensive spectrophotometric investigations of the effect of both the nature and the proportion of the solvent on the acidity constant have revealed that:

- The pK_a values of all compounds are largely dependent on both the nature and the proportion of the organic cosolvent.
- In general, the pK_a values in the presence of a poorer hydrogen-bond donor DMF are less than those obtained in the presence of corresponding amounts of the other solvents.
- · Both hydrogen-bonding, solvent basicity, dispersive forces, and proton-solvent interactions beside the electrostatic play vital roles in the ionization process.

Furthermore, PM6 calculations demonstrate that compounds 2 and **3** occur mainly as hydrazone forms in the gas phase and in solution, whereas compound **1** in the same media exhibits an ability to exist as azo form.

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