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Spectrophotometric Investigation of the Role of Organic Solvents in the Ionization of Azo Dyes Derived from Thienopyridine

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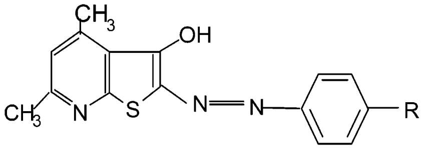
The effects of different organic solvent + water mixtures on the acidity constants of some azothienopyridine derivatives were studied. The organic solvents used are methanol, ethanol, acetone, and dimethylformamide. The results obtained are discussed in terms of the solvent characteristics. The pK_a values of the dyes studied were determined and found to depend largely on both the amount and nature of the organic cosolvent. Hydrogen-bonding interactions of the conjugate base with solvent molecules as well as the solvent basicity contribute the major effect on the ionization process. The effect of the molecular structure of the azo compound on the pK_a value is discussed.

Introduction

The knowledge of pK_a is considered to be of great interest for organic and inorganic compounds, because it has a significant role in many chemical reactions. Therefore, numerous works have been devoted to the determination of pK_a values of different azo compounds.[1−5] From another point of view, in the past decades azo dye chemistry based on heterocyclic systems received a lot of interest. In a broad sense, many of heterocyclic azo dyes show dramatic bathochromic shifts combined with brilliance of shade and high tinctorial strength compared with the cases of conventional anthraquinone dyes and aminobenzene azo dyes.[6] They have also been used as disperse dyes[7] and analytical reagents.[8] Furthermore, azo dyes are the largest group of organic dyes and constitute more than 35% of the global production of all dyes and thus are used widely. However, some azo dyes have toxicological properties and therefore require sensitive and selective methods to determine their physicochemical characteristics.[9] Therefore, the solvent used as a medium for chemical and physical processes plays an important role on the ionization, and the widespread application of azo compounds as dyes; as acid−base, redox, metallochrome indicators; or as histological stains has attracted many studies of their acid−base properties.[6,10] On the other hand, diazo acid dyes containing one sulfonic group have been widely used for dying polyamide fibers.[10] These findings drew our attention to continue our work in this respect, especially determination of pK_a.[11]

In the present article we use some novel azothienopyridine compounds to study the effect of medium on their ionization constants. The heterocyclic azo derivatives under examination are



with R = H (I), CH_3 (II), SO_3H (III), or NO_2 (IV). I = 3-hydroxy-4,6-dimethyl-2-[(phenyl)azo]thieno[2,3-*b*]pyridine (*p*-H); II = 3-hydroxy-4,6-dimethyl-2-[(4-methylphenyl)azo]thieno[2,3-*b*]pyridine (*p*-CH_3); III = 3-hydroxy-4,6-dimethyl-2-[(4-sulfophenyl)azo]thieno[2,3-*b*]pyridine (*p*-SO_3H), and IV = 3-hydroxy-4,6-dimethyl-2-[(4-nitrophenyl)azo]thieno[2,3-*b*]pyridine (*p*-NO_2).

Experimental Section

The preparation of arylazothienopyridine derivatives includes the following: to a solution of 4,6-dimethyl-2-dihydrothieno[2,3-*b*]pyridin-3-one[12] (0.01 mol) in ethanol containing (0.05 mol) sodium acetate, a solution of diazotized amine (0.01 mol) was added dropwise with stirring at 5 °C during 16 min. After addition was finished, the stirring was continued for 1 h, and then the mixture was allowed to stand for 2 h. The solid product was collected and recrystallized from ethanol.[13] Stock solutions (10^{-3} mol 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 then obtained by accurate dilution with the proper solvent. The pH control was achieved by using the modified universal buffer solutions.[14] 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 the procedure described by Douheret[15] (eq 1), where the meter reading $pH_{(R)}$ obtained in each water−organic solvent mixture differs by an amount δ from the corrected reading pH*. where pH* is the corrected value and $pH_{(R)}$ is the pH

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

meter reading obtained in water−organic solvent mixtures. Values of δ for various aqueous−organic solvent mixtures were determined as recommended by Douheret[15,16] at the same ionic strength. The solutions were thermostated at (25 ± 0.05) °C before measuring their spectra. The absorption spectra were recorded on a Shimadzu 2401PC spectrophotometer, containing a thermoelectrically temperature-controlled cell holder, within the

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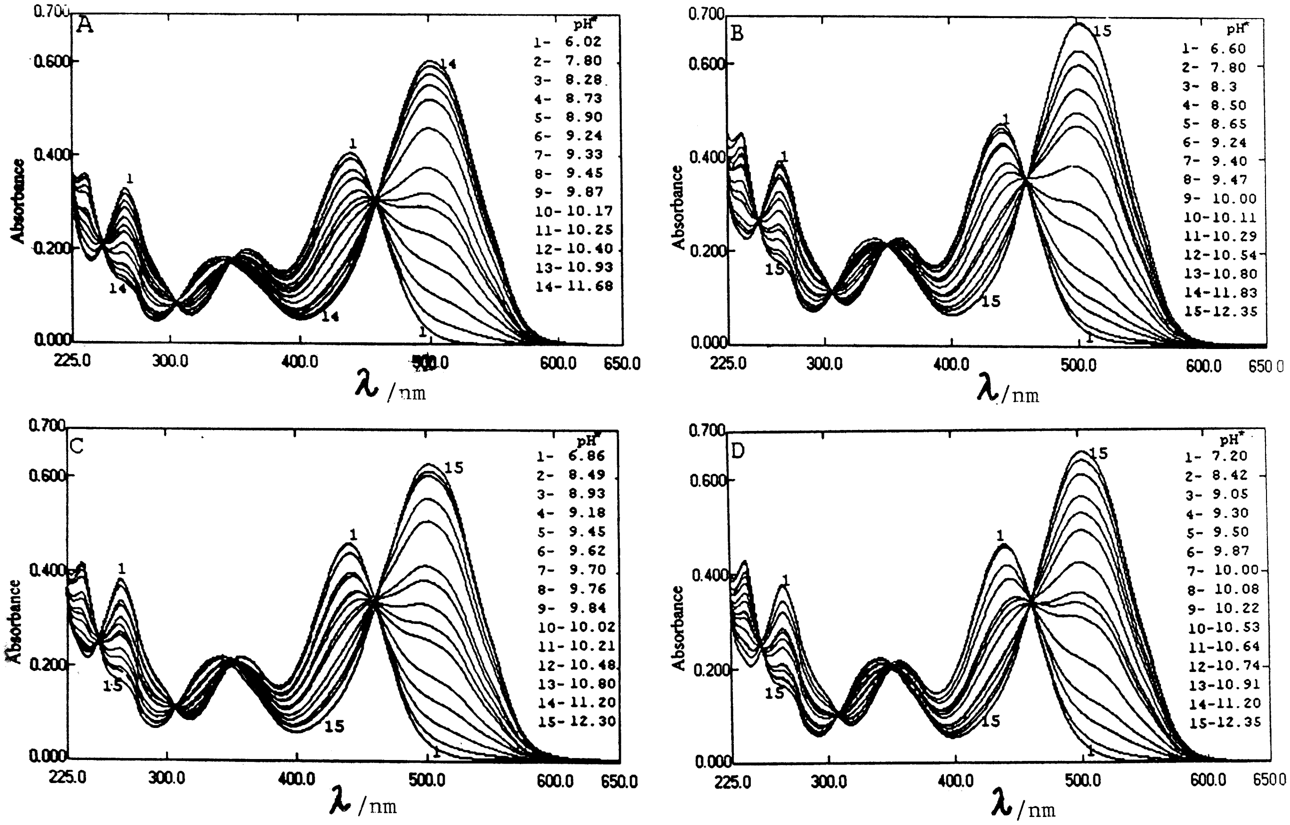


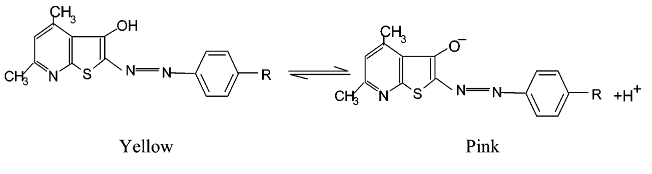
Figure 1. Absorption spectra of 2.0 × 10^{-5} M compound III (p-SO_3H) in water (1) + ethanol (2) at different pH values and $w_2 = 16.59$ (a), 25.42 (b), 34.65 (c), and 44.30 (d).

wavelength range (220 to 650 nm) using 1-cm matched silica cells. The pH measurements were carried out using an Orion 501 digital ionalyzer accurate to ±0.01 pH unit. All measurements were carried out at 25 °C, and temperature control was achieved using an ultrathermostat of accuracy ±0.05 °C.

Results and Discussion

The electronic absorption spectra of the hydroxyazothienopyridines in universal buffer solutions containing different proportions of an organic solvent (methanol, ethanol, acetone, DMF) show mainly two main bands (Figure 1). The shorter wavelength band, appearing at low pH* values (pH* < 8), represents absorption by the nonionized species, whereas the longer wavelength band, observed at higher pH* values (pH* > 10), is due to the absorption by ionized species. On increasing the pH of the medium, the absorbance of the former band decreases while that of the latter band increases, where a fine isosbestic point is achieved, denoting the existence of an equilibrium of the type

$$HA \rightleftharpoons H^+ + A^- \qquad (2)$$



The absorbance−pH* plots obtained in all cases, as shown in Figure 2, are sigmoidal curves, confirming the establishment of an acid−base equilibrium in each case.

The acid dissociation constants, pK_a values, of the compounds were determined from the variation of the absorbance with pH*, making use of three different spectrophotometric methods, namely, the half-curve height, isosbestic point, and limiting absorbance method[17,18] (cf. Figure 3). The results obtained are given in Tables 1−4. Examination of the results cited in Tables 1−4 reveals that the pK_a values of all compounds are largely dependent upon both the nature and the proportion of the organic cosolvent. In general, pK_a values increase with increasing organic cosolvent content in the medium. This can be explained as follows: according to Coetzee and Ritchie,[19] the acid dissociation constant in an aqueous medium (K_{a1}) is related

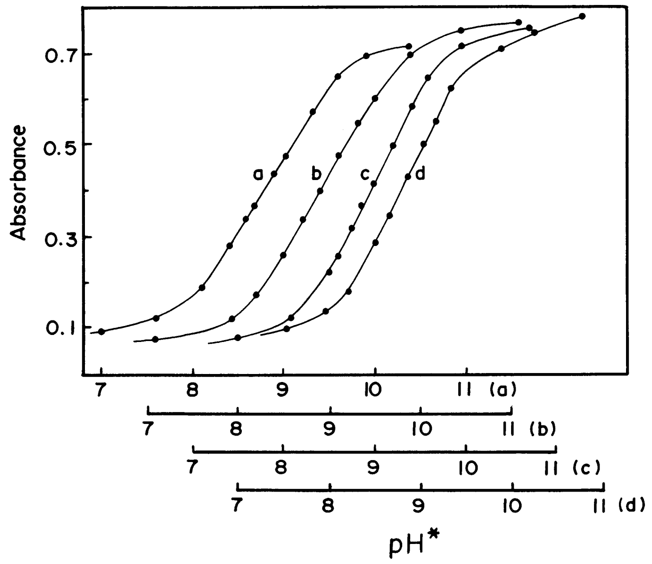


Figure 2. Absorbance−pH* curves of 2.0 × 10^{-5} M compound IV (p-NO_2) in water (1) + DMF (2), in ionized species at 505 nm, with $w_2 = 19.21$ (a), 28.96 (b), 38.81 (c), and 48.75 (d).

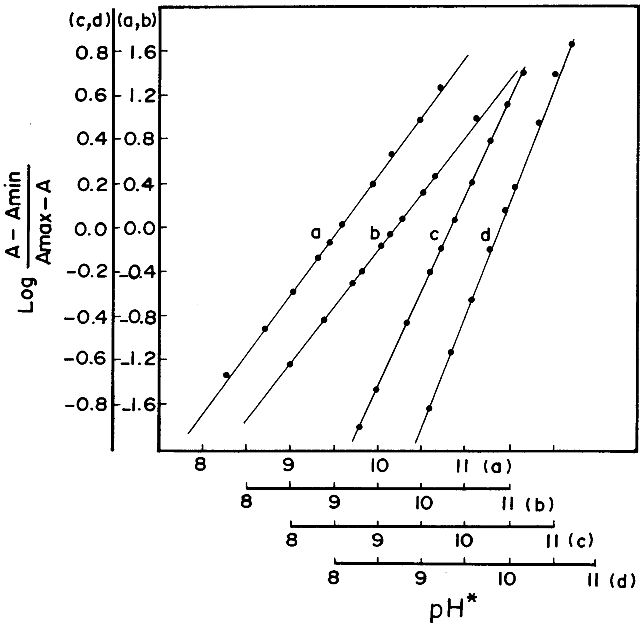


Figure 3. Plot of log[($A - A_{min}$)/($A_{max} - A$)] against pH* of 2.0 × 10^{-5} M compound II (p-CH_3) in water (1) + methanol (2) with w_2 = 16.53 (a), 25.35 (b), 34.56 (c), and 44.21 (d).

Table 1. pK_a Values for 2.0 × 10^{-5} M 3-Hydroxy-4,6-dimethyl-2-[(phenyl)azo]thieno[2,3-*b*]pyridine (*p*-H) in Different Water (1) + Organic Solvent (2) Mixtures at 25 °C

		pK_a				
100w_2[a]	ϵ	method 1	method 2	method 3	mean value	SD
		Water (1) + Methanol (2)				
16.53	73.72	9.60	9.65	9.65	9.63	±0.03
25.35	71.03	9.65	9.70	9.70	9.68	±0.03
34.56	67.88	9.74	9.76	9.75	9.75	±0.01
44.21	64.27	9.87	9.83	9.85	9.85	±0.02
		Water (1) + Ethanol (2)				
16.59	74.46	9.71	9.67	9.73	9.70	±0.03
25.42	72.00	9.75	9.78	9.75	9.76	±0.02
34.65	69.08	9.88	9.90	9.93	9.90	±0.02
44.30	65.54	9.95	10.05	10.10	10.03	±0.06
		Water (1) + Acetone (2)				
16.53	74.92	9.70	9.75	9.70	9.72	±0.03
25.35	72.87	9.88	9.85	9.87	9.87	±0.01
34.56	70.25	10.10	10.05	10.13	10.09	±0.03
44.21	66.99	10.15	10.15	10.13	10.14	±0.01
		Water (1) + DMF (2)				
19.21	76.06	9.35	9.30	9.35	9.33	±0.03
28.96	74.56	9.42	9.40	9.41	9.41	±0.01
38.81	72.73	9.42	9.43	9.42	9.42	±0.01
48.75	70.45	9.42	9.43	9.45	9.43	±0.01

[a] w_2 = mass fraction of component 2.

Table 2. pK_a Values for 2.0 × 10^{-5} M 3-Hydroxy-4,6-dimethyl-2-[(4-methylphenyl)azo]thieno[2,3-*b*]pyridine (*p*-CH_3) in Different Water (1) + Organic Solvent (2) Mixtures at 25 °C

		pK_a				
100w_2[a]	ϵ	method 1	method 2	method 3	mean value	SD
		Water (1) + Methanol (2)				
16.53	73.72	9.65	9.60	9.62	9.62	±0.02
25.35	71.03	9.70	9.75	9.68	9.71	±0.03
34.56	67.88	9.78	9.75	9.78	9.77	±0.02
44.21	64.27	9.80	9.85	9.88	9.84	±0.03
		Water (1) + Ethanol (2)				
16.59	74.46	9.73	9.70	9.75	9.73	±0.02
25.42	72.00	9.75	9.75	9.79	9.76	±0.02
34.65	69.08	9.90	10.00	9.95	9.95	±0.04
44.30	65.54	10.05	10.10	10.05	10.07	±0.03
		Water (1) + Acetone (2)				
16.53	74.92	9.75	9.79	9.80	9.78	±0.02
25.35	72.87	10.00	9.95	10.05	10.00	±0.04
34.56	70.25	10.10	10.06	10.15	10.10	±0.04
44.21	66.99	10.35	10.40	10.44	10.39	±0.04
		Water (1) + DMF (2)				
19.21	76.06	9.25	9.30	9.35	9.30	±0.04
28.96	74.56	9.67	9.62	9.67	9.65	±0.03
38.81	72.73	9.70	9.70	9.66	9.68	±0.02
48.75	70.45	9.82	9.80	9.83	9.82	±0.01

[a] w_2 = mass fraction of component 2.

Table 3. pK_a Values for 2.0 × 10^{-5} M 3-Hydroxy-4,6-dimethyl-2-[(4-sulfophenyl)azo]thieno[2,3-*b*]pyridine (*p*-SO_3H) in Different Water (1) + Organic Solvent (2) Mixtures at 25 °C

		pK_a				
100w_2[a]	ϵ	method 1	method 2	method 3	mean value	SD
		Water (1) + Methanol (2)				
0.00	78.40	9.05	9.10	9.05	9.07	±0.03
16.53	73.72	9.35	9.30	9.35	9.33	±0.03
25.35	71.03	9.45	9.50	9.52	9.49	±0.03
34.56	67.88	9.66	9.70	9.64	9.67	±0.03
44.21	64.27	9.75	9.79	9.77	9.77	±0.02
		Water (1) + Ethanol (2)				
0.00	78.40	9.05	9.10	9.05	9.07	±0.03
16.59	74.46	9.25	9.32	9.35	9.31	±0.04
25.42	72.00	9.55	9.60	9.57	9.57	±0.02
34.65	69.08	9.70	9.75	9.77	9.74	±0.03
44.30	65.54	9.98	9.99	10.05	10.01	±0.03
		Water (1) + Acetone (2)				
0.00	78.40	9.05	9.10	9.05	9.07	±0.03
16.53	74.92	9.84	9.82	9.80	9.82	±0.02
25.35	72.87	9.90	9.95	9.95	9.93	±0.03
34.56	70.25	10.02	10.00	10.05	10.02	±0.02
44.21	66.99	10.15	10.13	10.17	10.15	±0.02
		Water (1) + DMF (2)				
0.00	78.40	9.05	9.10	9.05	9.07	±0.03
19.21	76.06	9.20	9.20	9.15	9.18	±0.03
28.96	74.56	9.33	9.35	9.37	9.35	±0.02
38.81	72.73	9.45	9.45	9.50	9.47	±0.03
48.75	70.45	9.52	9.50	9.55	9.52	±0.02

[a] w_2 = mass fraction of component 2.

to that in a partially aqueous medium (K_{a2}) by the equation

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

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 change in relative permittivity of the medium operates on the activity coefficients of the charged species;[19] one can therefore expect that the increase in the amount of the organic cosolvent in the medium will increase the activity coefficients of both H^+ and A^- ions. According to eq 3, this behavior will result in a decrease in the acid dissociation constant K_a of the compound (i.e., the pK_a value will increase) on increasing the content of the organic solvent. This is consistent with the results reported in Tables 1−4.

However, methanol and DMF have approximately similar relative permittivity constants, (32.6 and 36.7, respec-

Table 4. pK_a Values for 2.0 × 10^{-5} M 3-Hydroxy-4,6-dimethyl-2-[(4-nitrophenyl)azo]thieno[2,3-*b*]pyridine (*p*-NO_2) in Different Water (1) + Organic Solvent (2) Mixtures at 25 °C

		pK_a				
100w_2[a]	ϵ	method 1	method 2	method 3	mean value	SD
		Water (1) + Methanol (2)				
16.53	73.72	9.15	9.20	9.25	9.20	±0.04
25.35	71.03	9.41	9.46	9.47	9.50	±0.03
34.56	67.88	9.53	9.50	9.50	9.51	±0.02
44.21	64.27	9.54	9.55	9.53	9.54	±0.01
		Water (1) + Ethanol (2)				
16.59	74.46	9.25	9.30	9.30	9.28	±0.03
25.42	72.00	9.56	9.60	9.63	9.60	±0.03
34.65	69.08	9.67	9.70	9.66	9.68	±0.02
44.30	65.54	9.72	9.75	9.70	9.72	±0.02
		Water (1) + Acetone (2)				
16.53	74.92	9.20	9.15	9.20	9.18	±0.03
25.35	72.87	9.60	9.60	9.55	9.58	±0.03
34.56	70.25	9.78	9.80	9.83	9.80	±0.04
44.21	66.99	9.90	9.95	9.90	9.92	±0.03
		Water (1) + DMF (2)				
19.21	76.06	8.77	8.75	8.73	8.75	±0.02
28.96	74.56	8.95	8.98	8.95	8.96	±0.02
38.81	72.73	9.05	9.02	9.05	9.04	±0.02
48.75	70.45	9.13	9.08	9.10	9.10	±0.02

[a] w_2 = mass fraction of component 2.

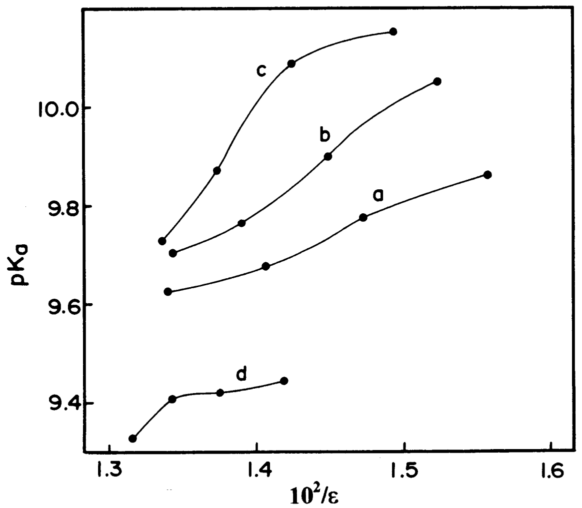


Figure 4. Variation of pK_a of 2.0 × 10^{-5} M compound I (*p*-H) in water (1) + organic solvent (2) with $10^2/\epsilon$ of the medium at 25 °C: (a) methanol; (b) ethanol; (c) acetone; (d) DMF.

tively, at 25 °C), and all the compounds are more acidic in water + DMF than in water + methanol, at the same mole fraction (cf. Tables 1-4 and Figures 2−4). Moreover, although ethanol and acetone have comparable relative permittivity constants also (24.3 and 20.7, respectively, at 25 °C), all the compounds are more acidic in water + ethanol than in water + acetone, at the same mixture mole fraction. In general, pK_a values in all compounds increase with increasing amount 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:

$$\text{DMF} < \text{ethanol} < \text{methanol} < \text{acetone}$$

This behavior 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 pK_a against $1/\epsilon$ of the medium (Figure 4), according to the equation given by Denison and Ramsey[20] and Gilkerson[21] which relates the variation of the pK_a of the acid with the relative permittivity of the medium ϵ. The relative permittivity of water + organc solvent mixtures, ϵ, was obtained using the following equation[11]

$$\epsilon = \epsilon_1 m_{f(w)} + \epsilon_2 m_{f(s)} \tag{4}$$

where ϵ is the relative permittivity of the water + organic solvent mixture, ϵ_1 and ϵ_2 are the relative permittivities of the water and organic solvent, respectively, m_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.[19] 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 to, in addition to the electrostatic effect, the hydrogen-bonding interaction between the conjugate base (A^-) and solvent molecules. Since water molecules have a higher tendency to donate hydrogen bonds than other solvent molecules,[22] the conjugate 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 in the pK_a values as the amount of the organic cosolvent in the medium is increased.

Examination of the results in Tables 1−4 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 dispersive forces, which possibly exist in the media used, between the delocalized charge on the conjugate 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, since the effective density of dispersion centers in each of the organic solvents studied is higher than that of water.[23] Thus, in 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 (cf. Tables 1-4). 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 hydroxyazothienopyridine dyes.

The values of pK_a, reported in Tables 1-4, show that the acidities of the studied azo compounds increase in the following order:

$$p\text{-NO}_2 < p\text{-SO}_3\text{H} < p\text{-H} < p\text{-CH}_3$$

This trend is in accordance with the increase in the electron donor ability of the subsitituent that reflects itself in an increase of the electronic density on the OH group oxygen atom and retards ionization.

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