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Acidity Constants of Some Hydroxy Azo Pyrazolopyrimidines in Mixed Aqueous−Organic Solvents

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The acid dissociation constants of four hydroxy azo pyrazolopyrimidine derivatives were determined in aqueous−organic solvent mixtures. The organic solvents are methanol, ethanol, acetone, and dimethylformamide. The results obtained are discussed in terms of the solvent characteristics. The ionization constants of the dyes in question depend largely on both the proportion and the nature of the organic cosolvent. Hydrogen-bonding interactions of the conjugate base with solvent molecules as well as the solvent basicity contribute the major effects on the ionization process. The effect of molecular structure of the azo compound on the pK_a value is discussed.

Introduction

The widespread application of azo compounds as dyes, acid−base, redox, and metallochrome indicators, or histological stains have attracted the attention of many researchers to study their acid−base properties (Jannakaudakis et al., 1972; El-Haty et al., 1991; Issa et al., 1973; Hammam et al., 1979; Etaiw and El-Morsi, 1980). However, the literature lacks studies on the acid−base properties or medium effects on the acid dissociation constants of azo compounds containing the pyrazolopyrimidines moiety, which are thought to be of special interest owing to their biological and therapeutical importance (Mahmoud et al.,1983; El-Gyar et al., 1993). In continuation of our studies on the acid−base properties of azo compounds (Ibrahim et al., 1993; Hammam et al., 1993), we have investigated the medium effect on the ionization constants of some hydroxy azo pyrazolopyrimidine derivatives by the study of the electronic spectra of the compounds in aqueous buffer solutions containing varying proportions of organic solvents of different polarities, such as methanol, ethanol, acetone, and dimethylformamide (DMF). The pK_a values have been determined and discussed in terms of solvent characteristics. The hydroxy azo pyrazolopyrimidine derivatives under investigation have the structures given in Chart 1.

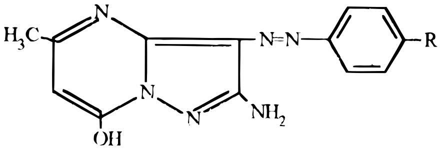
Experimental Section

Hydroxy azo pyrazolopyrimidines were prepared according to the procedure previously described by El-Fahham et al. (1988). 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 the solvent. The pH control was achieved by using the modified universal buffer solution (Britton, 1952). To account for the difference 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 (1967)

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

where pH* is the corrected value and pH(R) is the pH meter reading obtained in water−organic solvent mixtures. Values of δ for various aqueous−organic solvent mixtures were determined as recommended by Douheret (1967, 1968). The solutions were thermostated at 25 °C before measuring their spectra. The absorption spectra were recorded on a Shimadzu 2401PC spectrophotometer, containing a thermoelectrically temperature-controlled cell holder, within the wavelength range of 240−540 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.

Chart 1[a]



R = H, I; Cl, II; CH_3, III; OCH_3, IV

[a] I, 2-amino-3-[(phenyl)azo]-7-hydroxy-5-methylpyrazolo[1,5-*a*]pyrimidine (p-H); II, 2-amino-3-[(4-chlorophenyl)azo]-7-hydroxy-5-methylpyrazolo[1,5-*a*]pyrimidine (p-Cl); III, 2-amino-3-[(4-methylphenyl)azo]-7-hydroxy-5-methylpyrazolo[1,5-*a*]pyrimidine (p-CH_3); IV, 2-amino-3-[(4-methoxyphenyl)azo]-7-hydroxy-5-methylpyrazolo[1,5-*a*]pyrimidine (p-OCH_3).

Results and Discussion

The electronic absorption spectra of the hydroxy azo pyrazolopyrimidines in buffer solutions containing different proportions of an organic solvent (methanol, ethanol, acetone, or DMF) show mainly two bands (Figure 1). The shorter wavelength band, appearing at low pH values (pH < 6.5), represents absorption by the nonionized species, whereas the longer wavelength band, observed at higher pH's (>8.5), 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

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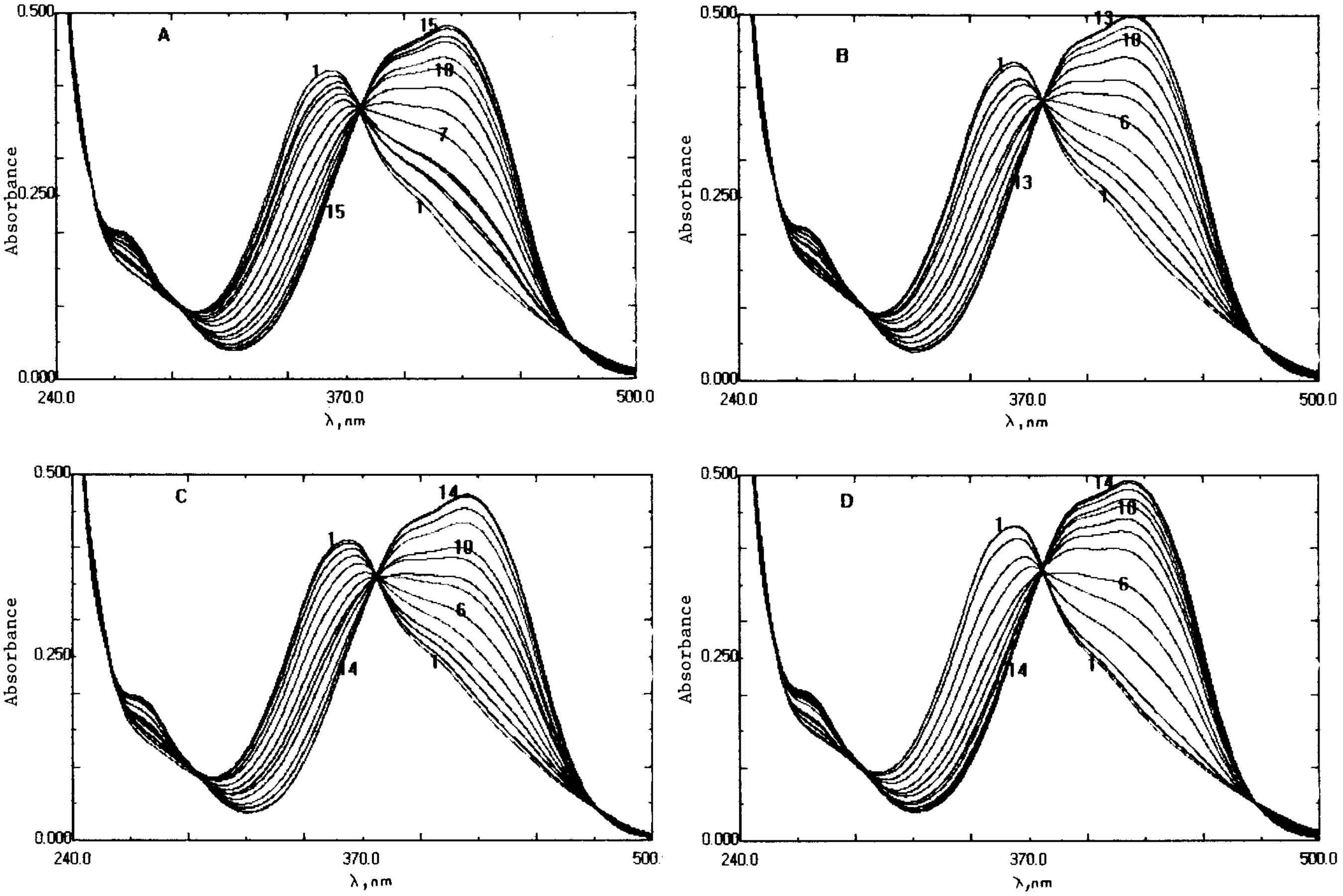

Figure 1. Absorption spectra of 2.0 × 10^{-5} M compound I (p-H) in water (1) + methanol (2) at different pH's: (A) w_2 = 16.53 methanol, pH* (1) 5.00, (2) 5.82, (3) 6.40, (4) 6.49, (5) 6.72, (6) 6.98, (7) 7.01, (8) 7.28, (9) 7.73, (10) 7.80, (11) 7.98, (12) 8.25, (13) 8.54, (14) 9.29, (15) 10.32; (B) w_2 = 25.35 methanol, pH* (1) 4.50, (2) 5.73, (3) 6.46, (4) 6.49, (5) 6.96, (6) 7.17, (7) 7.22, (8) 7.52, (9) 7.78, (10) 8.12, (11) 8.46, (12) 9.27, (13) 10.25; (C) w_2 = 34.56 methanol, pH* (1) 5.00, (2) 5.68, (3) 6.11, (4) 6.47, (5) 6.70, (6) 6.98, (7) 7.25, (8) 7.33, (9) 7.50, (10) 7.70, (11) 8.03, (12) 8.37, (13) 9.18, (14) 10.22; (D) w_2 = 44.21, methanol, pH* (1) 4.56, (2) 5.10, (3) 5.87, (4) 6.53, (5) 6.90, (6) 7.18, (7) 7.44, (8) 7.63, (9) 7.90, (10) 8.00, (11) 8.30, (12) 8.52, (13) 9.32, (14) 10.26.

increases, where a fine isosbestic point is achieved, denoting the existence of an equilibrium of the type

$$\mathrm{HA} \rightleftharpoons \mathrm{H}^+ + \mathrm{A}^- \tag{2}$$

The sigmoidal absorbance−pH* curves are typical dissociation ones confirming the establishment of an acid−base equilibrium in each case. Representative curves are shown in Figure 2.

The acid dissociation constants, pK_a, of the compounds are 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 (Issa et al., 1971, 1972). [In the half-curve height method, Issa et al. (1971) plot the absorbance−pH curve, pK_a = pH at $A_{1/2}$; $A_{1/2} = (A_{\max} - A_{\min})/2 + A_{\min}$, where $A_{\max}$ and $A_{\min}$ are the maximium and minimum absorbance on the absorbance−pH curve. In the isosbestic point method (Issa et al., 1972), the isosbestic point represents the equilibrium between the HA and A−species. By plotting pH against absorbance for ionic and nonionic forms, the pH corresponding to the isosbestic point equals the pK_a value. In the limiting absorbance method (Issa et al., 1971), pH = pK_a + log $(A - A_{\min})/(A_{\max} - A)$; thus, p$K_a$ can be determined from the plot of log $(A - A_{\min})/(A_{\max} - A)$ against the pH, where a straight line is obtained. The pH value where $(A - A_{\min})$ equals $(A_{\max} - A)$ gives the value of pK_a.] The pK_a values were calculated by using a simple program. The experimental error in determined pK_a values was checked by using the least-squares method. The obtained results are given in Tables 1−4.The results listed in these tables show that the pK_a values of all the compounds are dependent upon both the nature and the proportion of the organic cosolvent. In general, increasing the organic cosolvent content in the medium results in an increase in the pK_a value. This can be explained as follows. According to Coetzee and Ritchie (1969), the acid dissociation constant in aqueous medium (K_a) is related to that in partially aqueous medium (K'_a) by the equation

$$K_a = K'_a\,(\gamma_{\mathrm{H}^+}\cdot\gamma_{\mathrm{A}^-}/\gamma_{\mathrm{HA}}) \tag{3}$$

where γ is the activity coefficient of the subscripted species in a partially aqueous medium relative to that in a pure aqueous one. It is known that the electrostatic effect resulting from the change in relative permittivity of the medium operates on the activity coefficients of any charged species (Coetzee and Ritchie, 1969), and one can 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 eq 3, this will result in a decrease in the acid dissociation constant K_a (high pK_a value), which is consistent with the results reported in Tables 1−4.

However, methanol and DMF have similar relative permittivity (32.6 and 36.7, respectively, at 25 °C), and all the compounds are more acidic in water + DMF than in water + methanol, despite that the same mole fraction of each is used (cf. Tables 1−4 and Figure 2). Moreover,

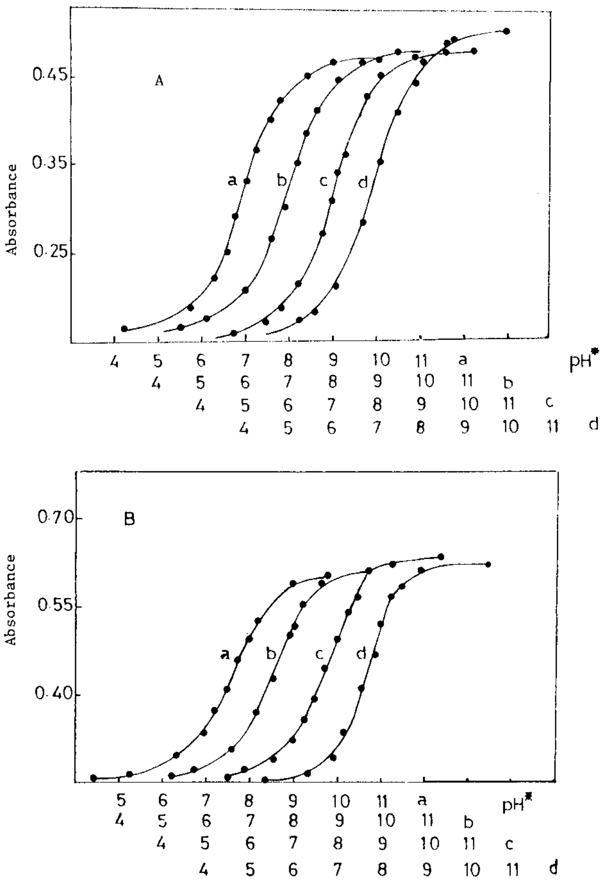

Figure 2. (A) Absorbance−pH* curves of 2.0×10^{-5} M compound I (p-H) in water (1) + DMF (2), $w_2 = 19.21$ (a); 28.96 (b); 38.81 (c); 48.75 (d). (B) Absorbance−pH* curves of 2.0×10^{-5} M compound IV (p-OCH$_3$) in water (1) + acetone (2), $w_2 = 16.54$ (a); 25.35 (b); 34.56(c); 44.21(d).

Table 1. pK_a Values for 2.0×10^{-5} M of 2-Amino-3-[(phenyl)azo]-7-hydroxy-5-methylpyrazolo[1,5-*a*]-pyramidine (p-H) in Water (1) + Organic Solvent (2) Mixtures at 25 °C

mass% 100w_2	ϵ	pK_a method 1	pK_a method 2	pK_a method 3	mean value
		Water (1) + Methanol (2)			
16.53	73.72	7.10	7.12	7.10	7.11 ± 0.01
25.35	71.03	7.15	7.10	7.20	7.15 ± 0.04
34.56	67.88	7.20	7.15	7.20	7.18 ± 0.02
44.21	64.27	7.20	7.20	7.25	7.22 ± 0.02
		Water (1) + Ethanol (2)			
16.59	74.46	7.25	7.18	7.18	7.20 ± 0.03
25.42	72.00	7.30	7.25	7.20	7.25 ± 0.04
34.65	69.08	7.30	7.25	7.25	7.27 ± 0.02
44.30	65.54	7.25	7.30	7.30	7.28 ± 0.02
		Water (1) + Acetone (2)			
16.54	74.92	7.25	7.25	7.28	7.26 ± 0.01
35.35	72.87	7.35	7.45	7.40	7.40 ± 0.04
34.56	70.25	7.48	7.45	7.45	7.46 ± 0.01
44.21	66.99	7.60	7.55	7.55	7.57 ± 0.02
		Water (1) + DMF (2)			
19.21	76.06	6.95	7.00	6.95	6.97 ± 0.02
28.96	74.56	7.00	7.02	6.95	6.99 ± 0.03
38.81	72.73	7.05	7.00	7.00	7.02 ± 0.02
48.75	70.45	7.05	7.04	7.06	7.05 ± 0.01

although ethanol and acetone have comparable relative permittivity also (24.3 and 20.7, respectively, at 25 °C), all the compounds are more acidic in water + ethanol than in water + acetone, where the same mole fraction of each is used. In general, pK_a values in all compounds decrease with increasing relative permittivity of the medium (i.e., the pK_a values of a compound in water + organic solvent are arranged according to the following sequence: DMF < methanol < ethanol < acetone (Tables 1−4, Figure 3)).

Table 2. pK_a Values for 2.0×10^{-5} M of 2-Amino-3-[(4-chlorophenyl)azo]-7-hydroxy-5-methylpyrazolo[1,5-*a*]-pyrimidine (p-Cl) in Water (1) + Organic Solvent (2) Mixtures at 25 °C

mass% 100w_2	ϵ	pK_a method 1	pK_a method 2	pK_a method 3	mean value
		Water (1) + Methanol (2)			
16.53	73.72	7.10	7.15	7.15	7.13 ± 0.02
25.35	71.03	7.20	7.10	7.15	7.15 ± 0.04
34.56	67.88	7.28	7.25	7.28	7.27 ± 0.01
44.21	64.27	7.28	7.30	7.32	7.30 ± 0.02
		Water (1) + Ethanol (2)			
16.59	74.46	7.10	7.15	7.05	7.10 ± 0.04
25.42	72.00	7.14	7.16	7.15	7.15 ± 0.01
34.65	69.08	7.25	7.20	7.30	7.25 ± 0.04
44.30	65.54	7.25	7.30	7.30	7.28 ± 0.02
		Water (1) + Acetone (2)			
16.54	74.92	7.15	7.20	7.20	7.18 ± 0.02
35.35	72.87	7.25	7.30	7.20	7.25 ± 0.04
34.56	70.25	7.31	7.32	7.26	7.33 ± 0.03
44.21	66.99	7.50	7.50	7.45	7.48 ± 0.02
		Water (1) + DMF (2)			
19.21	76.06	6.90	7.00	6.95	6.95 ± 0.04
28.96	74.56	6.93	6.95	7.00	6.96 ± 0.03
38.81	72.73	6.98	7.00	6.95	6.98 ± 0.02
48.75	70.45	7.00	6.95	7.05	7.00 ± 0.04

Table 3. pK_a Values for 2.0×10^{-5} M of 2-Amino-3-[(4-methylphenyl)azo]-7-hydroxy-5-methylpyrazolo[1,5-*a*]-pyrimidine (p-CH$_3$) in Water (1) + Organic Solvent (2) Mixtures at 25 °C

mass% 100w_2	ϵ	pK_a method 1	pK_a method 2	pK_a method 3	mean value
		Water (1) + Methanol (2)			
16.53	73.72	7.23	7.27	7.25	7.25 ± 0.02
25.35	71.03	7.35	7.33	7.37	7.35 ± 0.02
34.56	67.88	7.35	7.45	7.40	7.40 ± 0.04
44.21	64.27	7.50	7.55	7.55	7.53 ± 0.02
		Water (1) + Ethanol (2)			
16.59	74.46	7.33	7.38	7.33	7.35 ± 0.02
25.42	72.00	7.35	7.42	7.40	7.39 ± 0.03
34.65	69.08	7.40	7.45	7.50	7.45 ± 0.04
44.30	65.54	7.50	7.60	7.55	7.55 ± 0.05
		Water (1) + Acetone (2)			
16.54	74.92	7.49	7.44	7.40	7.46 ± 0.04
35.35	72.87	7.54	7.56	7.55	7.55 ± 0.01
34.56	70.25	7.60	7.65	7.63	7.62 ± 0.02
44.21	66.99	7.80	7.75	7.75	7.77 ± 0.02
		Water (1) + DMF (2)			
19.21	76.06	7.15	7.17	7.20	7.17 ± 0.02
28.96	74.56	7.25	7.27	7.29	7.27 ± 0.02
38.81	72.73	7.27	7.30	7.34	7.30 ± 0.03
48.75	70.45	7.32	7.35	7.35	7.34 ± 0.01

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 $1/\epsilon_m$ of the medium (Figure 3) according to the equation given by Denison and Ramsey (1955) and Gilkerson (1956), which relates the variation of the pK_a of the acid with the relative permittivity of the medium (ϵ_m). The relative permittivity of the medium, ϵ_m, is obtained from the relation

$$\epsilon_m = \epsilon_{(w)} m_{f(w)} + \epsilon_{(s)} m_{f(s)} \tag{4}$$

Respectively, ϵ and m_f are the relative permittivity and

Table 4. pK_a Values for 2.0 × 10^{-5} M of 2-Amino-3-[(4-methoxyphenyl)azo]-7-hydroxy-5-methylpyrazolo-[1,5-*a*]pyramidine (p-OCH$_3$) in Water (1) + Organic Solvent (2) Mixtures at 25 °C

mass%		pK_a			
100w_2	ϵ	method 1	method 2	method 3	mean value
		Water (1) + Methanol (2)			
16.53	73.72	7.25	7.30	7.35	7.30 ± 0.04
25.35	71.03	7.40	7.30	7.35	7.35 ± 0.04
34.56	67.88	7.36	7.35	7.40	7.37 ± 0.02
44.21	64.27	7.50	7.40	7.45	7.45 ± 0.04
		Water (1) + Ethanol (2)			
16.59	74.46	7.28	7.33	7.28	7.30 ± 0.02
25.42	72.00	7.40	7.35	7.30	7.35 ± 0.04
34.65	69.08	7.42	7.45	7.47	7.45 ± 0.02
44.30	65.54	7.48	7.50	7.53	7.50 ± 0.02
		Water (1) + Acetone (2)			
16.54	74.92	7.55	7.48	7.50	7.51 ± 0.03
35.35	72.87	7.55	7.60	7.55	7.57 ± 0.02
34.56	70.25	7.75	7.75	7.73	7.74 ± 0.01
44.21	66.99	7.78	7.79	7.83	7.80 ± 0.01
		Water (1) + DMF (2)			
19.21	76.06	7.10	7.15	7.05	7.10 ± 0.04
28.96	74.56	7.15	7.10	7.12	7.12 ± 0.02
38.81	72.73	7.17	7.16	7.18	7.17 ± 0.01
48.75	70.45	7.22	7.27	7.27	7.25 ± 0.02

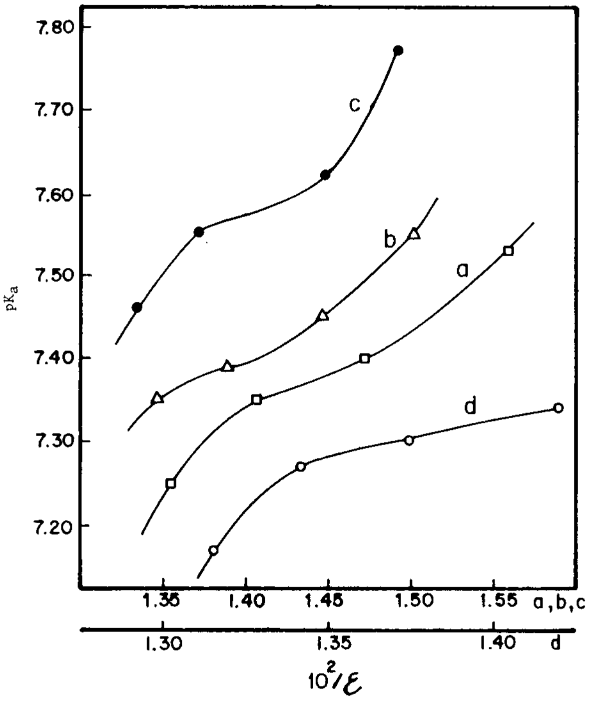

Figure 3. Variation of pK_a of compound III (p-CH$_3$) in water (1) + organic solvent (2) with $10^2/\epsilon$ of the medium at 25 °C: (a) methanol, (b) ethanol, (c) acetone, (d) DMF.

mole fraction and the subscripts w and s refer to water and organic solvent.

In general, effect 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 (Coetzee and Ritchie, 1969). 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 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 (Franks and Ives, 1966), the conjugate base (A$^-$) is expected to be less stabilized by hydrogen-bonding interaction with solvent molecules as the amount of the organic cosolvent in the medium is increased (i.e., γ_{A^-} increases). 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 value 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 (i.e., γ_{A^-} and γ_{H^+} decrease), since the effective density of dispersion centers in each of the organic solvents used is higher than that of water (Grunwald and Price, 1964). 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 hydroxy azo pyrazolopyrimidine dyes.

Effect of molecular structure, the values of pK_a, reported in Tables 1–4, show that the acidity of the studied azo compounds increases in the following order:

$$\text{p-Cl} < \text{p-H} < \text{p-OCH}_3 \le \text{p-CH}_3$$

This trend, hence, 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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