J. Chem. Eng. Data **2003,** *48*, 652−656

Effect of Medium on the Acidity Constant of Some New Arylazopyrazolopyrimidine Derivatives

Elham M. Abd-Allah,[†] Nasr M. Rageh,[*,‡] and Hassan M. A. Salman[‡]

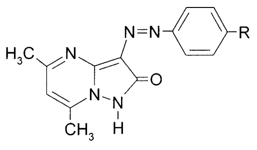
Department of Chemistry, Faculty of Science, El-Minia University, El-Minia, Egypt, and Department of Chemistry, Faculty of Science, South Valley University, Qena 83523, Egypt

---

The acid dissociation constants of some new 8-[(aryl)azo]-2,4-dimethylpyrazolo[1,5-*a*]pyrimidine-7(6H)-one derivatives were determined in aqueous−organic solvent mixtures. The organic solvents are methanol, ethanol, acetone, and dimethylformamide. The results obtained were discussed in terms of the solvent characteristics. The ionization constants of the title dyes depend largely on both the ratio 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. It has been concluded that the pK_a values increase by increasing the amount of organic cosolvent in the medium. The effect of molecular structure of the azo compound on the pK_a value is discussed.

Introduction

The knowledge of the pK_a is considered to be of 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 the different azo compounds.[1−5] The widespread application of the azo compounds as dyes; acid−base, redox, and metallochrome indicators; or histological stains has attracted many studies of their acid−base properties.[6−9] In continuation of our studies on the acid−base properties of azo compounds,[1,6,10] we have investigated the medium effect on the ionization constants of some arylazopyrazolopyrimidine 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 arylazopyrazolopyrimidine derivatives under investigation have the structures given below.



R = H (I); OCH_3 (II); CH_3 (III); Cl (IV); NO_2 (V).

Experimental Section

The preparation of arylazopyrazolopyrimidine derivatives includes the following two steps.

Preparation of Arylazopyrazolinone Derivatives. 3-Amino-4-(arylazo)pyrazolin-5-one derivatives were prepared similarly to the literature method.[11] The appropriate amine (aniline, *p*-toludine, *p*-anisidine, *p*-chloroaniline, and *p*-nitroaniline, 0.02 mol) was dissolved in dilute HCl (20 mL, 3 N), and the resulting solution was cooled in an ice bath to 5 °C. To this solution was added dropwise with stirring a cold solution of sodium nitrite (1.6 g, 0.023 mol in 20 mL of H_2O). The resulting diazonium salt was added slowly with stirring to a cold solution of 3-aminopyrazolin-5-one (1.98 g, 0.02 mol) in 40 mL of (1:1) water/ethanol (the latter compound was prepared[12] by the reaction of ethyl cyanoacetate with hydrazine hydrate and sodium ethoxide). After completion of the addition, stirring was continued for 30 min; then a solution of sodium acetate (20 g in 60 mL of H_2O) was added until complete precipitation of the dye. The precipitated solid was filtered, washed with cold water, and recrystallized from ethanol to give the corresponding arylazopyrazolinone derivative.

Preparation of Arylazopyrazolopyrimidine Derivatives.[13,14] Each of the resulting azo dyes from the above step was refluxed for 4 h with acetylacetone in the (1:1) molar ratio in 30 mL of acetic acid. The reaction mixture was then cooled to room temperature, whereby a solid compound was precipitated. The precipitated solid was filtered, washed with cold ethanol, and recrystallized from ethanol to give the corresponding arylazopyrazolopyrimidine derivative. The purity of the compounds was checked by elemental analyses and IR spectra (cf. Table 1).

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.[15] To account for differences in acidity, basicity, dielectric constant, and ion activities for a water + organic solvent mixture relative to pure water, 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[16] (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*.

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

Values of δ for various aqueous−organic solvent mixtures were determined as recommended by Douheret[16,17] at the same ionic strength. The solutions were thermostated at 25 °C before measuring their spectra. The absorption spectra were recorded on a Shimadzu 2401PC spectropho-

---

[†] El-Minia University.

[‡] South Valley University.

[*] Corresponding author.

10.1021/je020194t CCC: \$25.00

Table 1. Analytical Data, Colors, Melting Points, Yield, and IR Spectral Bands of Compounds

				mp	yield	analyses/% [calcd (found)]				relevant IR bands/cm^{-1}		
compd	emp form.	form. wt	color	°C	%	C	H	N	Cl	ν(NH + CH)	ν(C=O)	ν(N=N)
I	$C_{14}H_{13}N_5O$	267.13	reddish orange	220	88	62.89 (63.20)	4.90 (4.82)	26.22 (26.08)		3150−2920 b	1640 vs	1440 s
II	$C_{15}H_{15}N_5O$	281.15	yellow	215	83	64.02 (64.31)	5.38 (5.58)	24.90 (24.84)		3200−2915 b	1642 vs	1440 s
III	$C_{15}H_{15}N_5O_2$	297.15	yellow	210	83	60.58 (60.84)	5.08 (5.02)	23.57 (23.46)		3140−2900 b	1630 vs	1430 s
IV	$C_{14}H_{12}N_5OCl$	301.63	red	250	77	55.70 (55.92)	4.01 (3.95)	23.22 (23.00)	11.77 (11.62)	3200−2922 b	1642 s	1437 m
V	$C_{14}H_{12}N_6O_3$	312.13	red	260	79	53.82 (54.10)	3.88 (3.73)	26.92 (26.84)		3210−2920 b	1645 s	1435 m

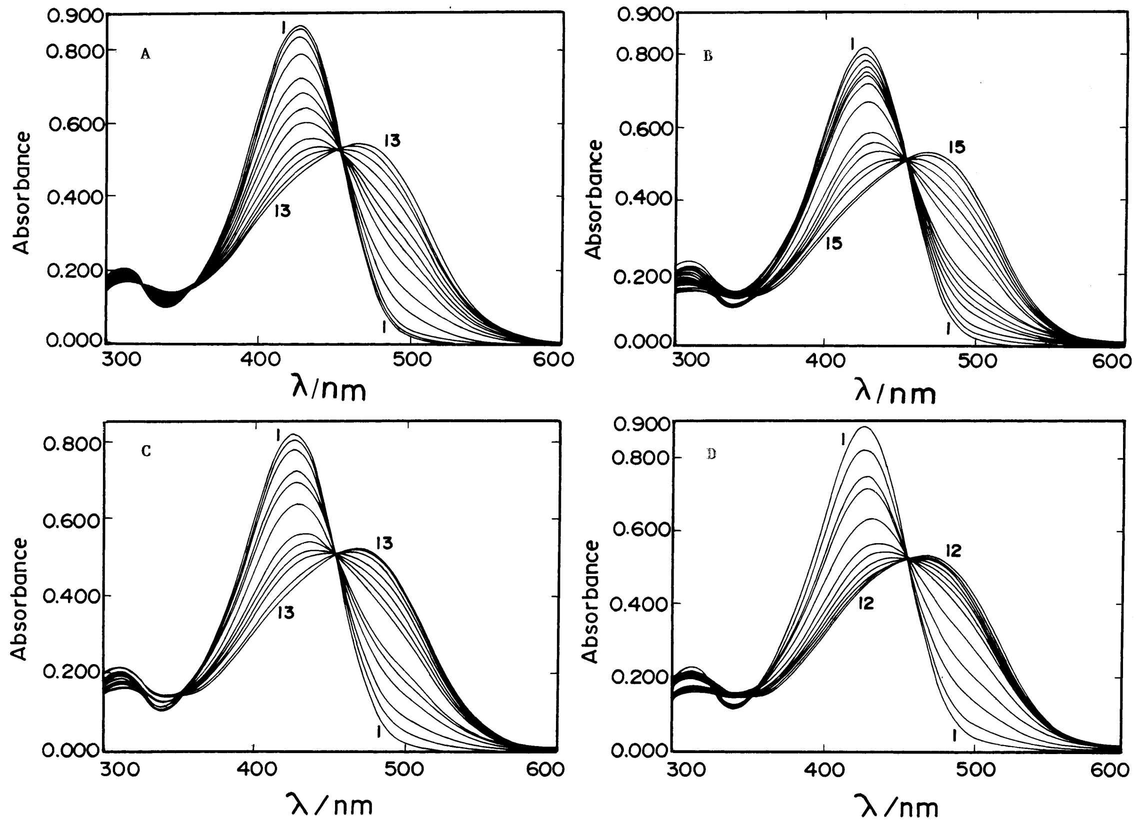
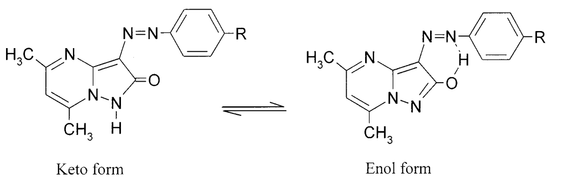


Figure 1. Absorption spectra of 2.0 × 10^{-5} M compound V (p-NO$_2$) in water (1) + methanol (2) at different pH's: (A) W_2 = 8.49 methanol; pH* = (1) 4.17, (2) 5.15, (3) 5.84, (4) 6.53, (5) 6.86, (6) 7.11, (7) 7.30, (8) 7.48, (9) 7.66, (10) 7.90, (11) 8.12, (12) 8.59, and (13) 9.02. (B) W_2 = 16.53 methanol; pH* = (1) 4.36, (2) 5.81, (3) 6.08, (4) 6.39, (5) 6.78, (6) 6.89, (7) 6.93, (8) 7.10, (9) 7.52, (10) 7.68, (11) 7.87, (12) 8.10, (13) 8.32, (14) 9.05, and (15) 10.39. (C) W_2 = 25.35 methanol; pH* = (1) 5.49, (2) 6.33, (3) 6.67, (4) 7.05, (5) 7.21, (6) 7.39, (7) 7.83, (8) 7.99, (9) 8.15, (10) 8.36, (11) 8.89, (12) 9.56, and (13) 10.06. (D) W_2 = 34.56 methanol; pH* = (1) 5.83, (2) 6.57, (3) 7.16, (4) 7.31, (5) 7.68, (6) 8.09, (7) 8.32, (8) 8.56, (9) 8.70, (10) 9.01, (11) 9.41, and (12) 10.03.

tometer, containing a thermoelectrically temperature-controlled cell holder, within the wavelength range of 280 to 600 nm using 1 cm matched quartz 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 compounds can exist in the following tautomeric forms:



It was found that they exist in the keto form in solids state while in solution the enol form predominates.[1,14] The visible absorption spectra of 8-[p-substituted phenylazo]-2,4-dimethylpyrazolo[1,5-a]pyrimidine-7(6H)-one derivatives in universal buffer solutions containing different proportions of an organic solvent (methanol, ethanol, acetone, and DMF) show mainly two bands (Figure 1). The shorter wavelength band, appearing at low pH* values (pH* < 6.0), represents absorption by the nonionized species, whereas the longer wavelength band, observed at higher pH* values (pH* > 8.8), 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

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

The acid dissociation constants, pK_a's, 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,

Table 2. pK_a Values for (2 × 10^{-5} mol dm^{-3}) of 8-[(Phenyl)azo]-2,4-dimethylpyrazolo[1,5-*a*]pyrimidine-7(6H)-one, (p-H), in Water (1) + Organic Solvent (2) Mixtures at 25 °C

	pK_a				
100w_2	method 1	method 2	method 3	mean value	SD
Water (1) + Methanol (2)					
8.49	7.60	7.65	7.65	7.63	±0.03
16.53	7.65	7.70	7.75	7.70	±0.04
25.35	7.75	7.85	7.80	7.80	±0.04
34.56	7.90	7.90	7.85	7.88	±0.03
Water (1) + Ethanol (2)					
8.52	7.55	7.70	7.65	7.63	±0.06
16.59	7.75	7.80	7.80	7.78	±0.03
25.42	7.90	7.95	7.85	7.90	±0.04
34.65	8.05	8.10	8.10	8.08	±0.03
Water (1) + Acetone (2)					
8.49	8.00	7.90	7.80	7.90	±0.08
16.53	8.05	7.95	8.00	8.00	±0.04
25.35	8.25	8.30	8.35	8.30	±0.04
34.56	8.40	8.40	8.45	8.42	±0.03
Water (1) + DMF (2)					
9.67	7.65	7.60	7.55	7.60	±0.04
19.21	7.65	7.65	7.60	7.63	±0.03
28.96	7.70	7.70	7.65	7.68	±0.03
38.81	7.75	7.70	7.80	7.75	±0.04

Table 3. pK_a Values for (2 × 10^{-5} mol dm^{-3}) of 8-[(4-Methoxyphenyl)azo]-2,4-dimethylpyrazolo[1,5-*a*]-pyrimidine-7(6H)-one, (p-OCH_3), in Water (1) + Organic Solvent (2) Mixtures at 25 °C

	pK_a				
100w_2	method 1	method 2	method 3	mean value	SD
Water (1) + Methnol (2)					
8.49	7.75	7.80	7.80	7.78	±0.03
16.53	7.80	7.90	7.80	7.83	±0.05
25.35	7.86	7.96	7.96	7.91	±0.05
34.56	7.94	7.97	7.94	7.95	±0.02
Water (1) + Ethanol (2)					
8.52	7.55	7.60	7.60	7.58	±0.03
16.59	7.60	7.65	7.70	7.65	±0.04
25.42	7.89	7.84	7.94	7.89	±0.04
34.65	7.9	7.95	8.00	7.95	±0.03
Water (1) + Acetone (2)					
8.49	7.77	7.82	7.72	7.77	± 0.03
16.53	7.89	7.84	7.94	7.89	± 0.04
25.35	8.10	8.05	8.15	8.10	± 0.04
34.56	8.30	8.41	8.35	8.35	± 0.05
Water (1) + DMF (2)					
9.67	7.52	7.50	7.48	7.50	±0.02
19.21	7.68	7.63	7.58	7.63	±0.04
28.96	7.68	7.63	7.60	7.64	±0.03
38.81	7.70	7.67	7.70	7.69	±0.02

Table 4. pK_a Values for (2 × 10^{-5} mol dm^{-3}) of 8-[(4-Methylphenyl)azo]-2,4-dimethylpyrazolo[1,5-*a*]-pyrimidine-7(6H)-one, (p-CH_3), in Water (1) + Organic Solvent (2) Mixtures at 25 °C

	pK_a				
100w_2	method 1	method 2	method 3	mean value	SD
Water (1) + Methanol (2)					
8.49	7.40	7.45	7.50	7.45	±0.04
16.53	7.6	7.50	7.55	7.55	±0.04
25.35	7.65	7.65	7.60	7.63	±0.03
34.56	7.57	7.80	7.85	7.80	±0.03
Water (1) + Ethanol (2)					
8.52	7.80	7.85	7.75	7.80	±0.04
16.59	7.93	7.98	7.88	7.93	±0.04
25.42	8.14	8.20	8.14	8.16	±0.03
34.65	8.30	8.40	8.35	8.35	±0.04
Water (1) + Acetone (2)					
8.49	7.90	8.00	7.9	7.93	±0.047
16.53	8.10	7.90	8.10	8.03	±0.057
25.35	8.15	8.22	8.18	8.18	±0.029
34.56	8.38	8.45	8.38	8.40	±0.033
Water (1) + DMF (2)					
9.67	7.72	7.62	7.67	7.67	±0.041
19.21	7.73	7.83	7.78	7.78	±0.041
28.96	7.88	7.83	7.88	7.86	±0.024
38.81	7.92	7.87	7.87	7.89	±0.024

Table 5. pK_a Values for (2 × 10^{-5} mol dm^{-3}) of 8-[(4-Chlorophenyl)azo]-2,4-dimethylpyrazolo[1,5-*a*]-pyrimidine-7(6H)-one, (*p*-Cl), in Water (1) + Organic Solvent (2) Mixtures at 25 °C

	pK_a				
100w_2	method 1	method 2	method 3	mean value	SD
Water (1) + Methanol (2)					
8.49	7.10	7.15	7.20	7.15	±0.04
16.53	7.40	7.35	7.40	7.38	±0.03
25.35	7.50	7.54	7.45	7.50	±0.04
34.56	7.60	7.55	7.55	7.57	±0.03
Water (1) + Ethanol (2)					
8.52	7.40	7.30	7.35	7.35	±0.04
16.59	7.50	7.55	7.50	7.52	±0.03
25.42	7.65	7.60	7.55	7.60	±0.04
34.65	7.74	7.65	7.64	7.68	±0.05
Water (1) + Acetone (2)					
8.49	7.62	7.67	7.72	7.67	±0.04
16.53	7.74	7.65	7.70	7.70	±0.04
25.35	7.85	7.95	7.95	7.92	±0.05
34.56	7.96	8.02	8.02	8.00	±0.03
Water (1) + DMF (2)					
9.67	7.25	7.30	7.35	7.30	±0.04
19.21	7.30	7.35	7.33	7.33	±0.02
28.96	7.38	7.30	7.38	7.35	±0.04
38.81	7.40	7.40	7.37	7.39	±0.02

and limiting absorbance.[18,19] The experimental error in determined pK_a values was checked by using the least-squares method. The results obtained are given in Tables 2−6. Examination of the results shown in Tables 2−6 reveals that 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 an increase of the organic cosolvent content in the medium. This can be explained as follows. According to Coetzee and Ritchie,[20] the acid dissociation constant in aqueous medium (K_{a1}) is related to that in a partially aqueous medium (K_{a2}) by the equation

$$K_{a1} = K_{a2}(\gamma_{H^+}\gamma_{A^-}/\gamma_{HA}) \qquad (3)$$

where γ is the activity coefficient of the subscripted species in a partially aqueous medium relative to that in a pure aqueous one. As the electrostatic effect operates on the activity coefficients of any charged species,[20] 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 (i.e., high pK_a value) on increasing the organic cosolvent content in the medium, which is consistent with the results reported in Tables 2−6.

However, methanol and DMF have approximately similar relative permittivity constants (32.6 and 36.7, respectively, at 25 °C), and all the compounds are more acidic in water + DMF than in water + methanol, despite the fact that the same mole fraction of each is used (cf. Tables 2−6). Moreover, although ethanol and acetone also have comparable relative permittivity constants (24.3 and 20.7, respectively, at 25 °C), all the compounds are more acidic in

Table 6. pK_a Values for (2×10^{-5} mol dm^{-3}) of 8-[(4-Nitrophenyl)azo]-2,4-dimethylpyrazolo[1,5-*a*]-pyrimidine-7(6H)-one, (p-NO_2), in Water (1) + Organic Solvent (2) Mixtures at 25 °C

	pK_a				
100w_2	method 1	method 2	method 3	mean value	SD
		Water (1) + Methanol (2)			
8.49	7.00	7.10	7.05	7.05	±0.04
16.53	7.10	7.13	7.13	7.12	±0.02
25.35	7.18	7.13	7.18	7.16	±0.03
34.56	7.20	7.18	7.22	7.20	±0.02
		Water (1) + Ethanol (2)			
8.52	7.10	7.20	7.15	7.15	±0.04
16.59	7.25	7.15	7.30	7.23	±0.04
25.42	7.36	7.28	7.26	7.30	±0.04
34.65	7.44	7.40	7.40	7.41	±0.02
		Water (1) + Acetone (2)			
8.49	7.12	7.12	7.15	7.13	±0.02
16.53	7.24	7.29	7.24	7.26	±0.03
25.35	7.35	7.30	7.39	7.35	±0.04
34.56	7.46	7.51	7.54	7.50	±0.03
		Water (1) + DMF (2)			
9.67	6.80	6.70	6.80	6.77	±0.05
19.21	6.73	6.88	6.88	6.83	±0.07
28.96	6.88	6.93	6.88	6.90	±0.03
38.81	6.93	6.93	6.87	6.91	±0.03

water + ethanol than in water + acetone, where 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 (Tables 2−6). This behavior indicates that other solvent effects beside the electrostatic one contribute to the ionization process of the investigated compounds.

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.[20] 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,[21] 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. $\gamma_A{}^-$ 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 values as the amount of the organic cosolvent in the medium is increased. Another factor to be considered, in this context, is the higher stabilization of the intramolecular H-bonding within the conjugate base, A^-, as the amount of the organic cosolvent of the medium is increased, which in turn retards the ionization; that is, pK_a increases.

Examination of the results in Tables 2−6 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, 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., $\gamma_A{}^-$ and $\gamma_H{}^+/\gamma A^-$ decrease), since the effective density of dispersion centers in each of the organic solvents used is higher than that of water.[22] 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 2−6). 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 hydroxyazopyrazolopyrimidine dyes.

Effect of Molecular Structure

The values of pK_a, reported in Table 2−6, show that the acidity of the studied azo compounds decreases in the following order: *p*-NO_2 > *p*-Cl > *p*-H > *p*-OCH_3 > *p*-CH_3. This trend is in accordance with the increase in the electron donor ability of the substituent, which reflects itself in an increase of the electronic density on the OH group oxygen atom and consequently increases the intramolecular H-bond strength and retards ionization.

Literature Cited

(1) Ibrahim, S. A.; Rageh, N. M.; Mohamed, A. A.; Ebead, Y. H. Medium effects on theacid dissociation constants of some hetero azo compounds. *J. Chem. Eng. Data* **1999**, *44*, 451−455 and references therein.
(2) Makita, S.; Saito, A.; Hayashi, M.; Yamada, S.; Yoda, K.; Otsuki, J.; Takido, T.; Seno, M. Electronic spectra of push−pull 4-phenylaminoazobenzene derivatives. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1525−1533.
(3) Simoncic, B.; Span, J. A study of dye-surfactant interactions (part 3) Thermodynamic of the association of C.I. acid orange 7 and cetylpyridinum chloride in aqueous solution. *Dyes Pigm.* **2000**, *46*, 1−8.
(4) El-Taher, M. A.; Gaber, A. A. Medium effect on acidity constants of some heterocyclic nitrogen azo methines. *Talanta* **1996**, *43*, 1511−1518.
(5) Boraei, A. A.; Taha, F.; Mohamed, A. H.; Ibrahim, S. A. Medium effect and thermodynamicstudies for the proton-ligand and metal−ligand formation constants of the ternary systems M^{II} + Adenosine-5′-triphosphate (ATP) + Asparagine. *J. Chem. Eng. Data* **2001**, *46*, 267−275.
(6) Rageh, N. M. Acidity constants of some hydroxyazopyrazolopyrimidines in mixed aqueous−organicsolvents. *J. Chem. Eng. Data* **1998**, *43*, 373−377 and references therein
(7) Georgriadou, K. L.; Tsatsaroni, E. G. Synthesis, characterization and application of disperse dyesderived from N-2-hydroxyethyl-1-naphthylamine. *Dyes Pigm.* **2001**, *50*, 93−97.
(8) Pevzner, E.; Ehrenberg, B. Principal component analysis of the absorption and resonance Raman spectra of the metallochromic indicator antipyrazole III. *Spectrochim. Acta* **2000**, *part A 65*, 637−651.
(9) Blus, K. Synthesis and properties of diazo acid dyes. *Dyes Pigm.* **1999**, *43*, 183−188.
(10) Hammam, A. M.; Ibrahim, S. A.; AbouElwafa, M. H.; Mohammed, A. A.; Rageh, N. M. Acidityconstants of some hydroxyazopyrazolopyrimidines in mixed aqueous−organic solvents. *J. Chem. Eng. Data* **1993**, *38*, 63−66.
(11) Nada, A. A.; Mohamed, N. R.; Mahran, A. M.; Ibrahim, Y. A. The photorearrangement of some 4-Arylazopyrazoline-5-one Derivatives. *Heterocycl. Commun.* **1998**, *4* (3), 271−276.
(12) Ishimaru, T. Chemotherapeutics: I. Cyanoacetohydrazide. *Yakugaku Zasshi* **1957**, *77*, 796−798; *Chem. Abstr.* **1957**, *51*, 17892.
(13) Elfahham, H. A.; El-Gemeie, G. H.; Ibrahim, Y. R.; El-Nagdi, M. H. Studies on 3,5-Diaminopyrazoles: New Routes for the Synthesis of New Pyrazoloazines and Pyrazoloazoles. *Leipzig Ann. Chem.* **1988**, 819−822.
(14) Salman, H. M. A.; Mohamed, A. A.; Ibrahim, S. A.; Ahmed, A. A. Co(II), Ni(II), Cu(II) and Cd(II) Complexes of Some New Arylazopyrazolopyrimidine Derivatives. *Synth. React. Inorg. Met.-Org. Chem.*, in press.

(15) Britton, H. T. S. *Hydrogen ions*; Chapman Hall: London, 1952; p 364.

(16) Douheret, G. The Dissociation of Organic Compound in Aqueous Organic Media. I. Determinationof the Liquid Junction Potential and the Effect of the Medium on the Hydrogen Ion in Theses Systems and the Study of the Dissociation of some Acid−Base Couples. *Bull. Soc. Chim. Fr.* **1967**, *4*, 1412−1419.

(17) Douheret, G. Liquid Junction Potential and Medium Effect in Mixed Solvent (Water-DipolarAprotic Solvent). Application to the Standardization of the Glass-Calomel Electrodes System in these Mixtures. Dielectric Properties of these Mixtures. *Bull. Soc. Chim. Fr.* **1968**, *8*, 3122−3131.

(18) Issa, R. M.; Sadek, H.; Izzat, I. I. Spectrophotometric studies on dihydric phenols. *Z. Phys. Chem., Neue Folge* **1971**, *75*, 17−25.

(19) Issa, R. M.; Hammam, A. M.; Etaiw, S. H. Electronic absorption spectra of some 2,3-benzcarbazoloquinones. *Z. Phys. Chem. (Leipzig)* **1972**, *78*, 177−182.

(20) Coetzee, J. F.; Ritchie, C. D. *Solute−Solvent Interactions*; Marcel Dekker: New York, 1969; pp 221−222.

(21) Franks, F.; Ives, D. J. G. Structural properties of alcohol-water mixture. *Q. Rev.* **1966**, *20*, 1−44.

(22) Grunwald, E.; Price, E. Relative Strength of Picric, Acetic and Trichloroacetic Acids in VariousEnvironments. Dispersion Effect in Acid−Base Equilibria. *J. Am. Chem. Soc.* **1964**, *86*, 4517−4525.

Received for review October 16, 2002. Accepted February 27, 2003.

JE020194T