

Ionization Constants of some 4-arylhydrazo-2-phenyl-2-oxazoline-5-one Derivatives in Different Organic Solvents

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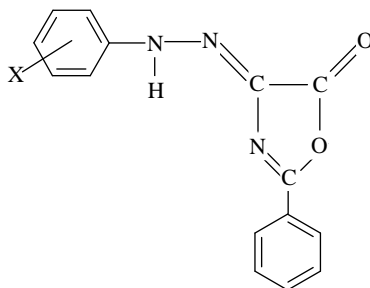
Summary: The electronic absorption spectra of some 4-arylhydrazo-2-phenyl-2-oxazoline-5-one derivatives are studied in organic solvents of different polarity and in solutions of varying pH values. The spectral study is utilized for the determination of the ionization constants (pK) of the derivatives. The five derivatives (I-V) containing H, p-Br, p-NO₂, p-CH₃ and p-OCH₃ exhibit one ionization step with pK values in the range 7.12-10.75, while p-COOH (VI) and o-COOH (VII) derivatives show two ionization steps (pK₁ = 3.01-7.53 and pK₂ = 8.09-10.05). The different absorption bands are assigned to the corresponding electronic transitions and the solvent effect on the CT band energy is also discussed. The effects of substituent and the solvent polarity on electronic spectra were discussed.

Introduction

Many hydrazo-compounds have been applied as chromogenic reagents for the determination of several metal ions^(1,2). The use of such reagents was found to depend essentially on their UV-vis spectral properties. Various methods available for pK determination have been summarized during the past decades⁽³⁾. King⁽⁴⁾ provides a discussion of the relative merits of some of these methods and the degree of precision attainable with them. Albert and Serjeants⁽⁵⁾, extended and brought up to date detailed information on the two most useful methods. Many articles have been published concerning the spectral characteristics of azo-compounds⁽⁶⁻⁸⁾, which dealt with spectral-structure correlations as well as the effects of the medium on the band position. However, it seems that no studies were carried out concerning hydrazo-compounds based on oxazolones. The UV spectra of some 4-arylhydrazo-2-phenyl-2-oxazoline-5-one derivatives were not the subject of many investigations.

The present article is concerned with UV-vis spectra studies of some derivatives of 4-arylhydrazo-2-phenyl-2-oxazoline-5-one in organic solvents of different polarity and in buffer solutions of varying pH.

The oxazolone compounds under investigation have the following structural formula:



where; X =H (I), p-Br (II), p-NO₂ (III), p-CH₃ (IV), p-OCH₃ (V), p-COOH (VI) and o-COOH (VII)

Experimental

Chemicals and Equipments

All chemicals used were of analytical reagent grade and need no further purification. Hippuric acid, aniline, p-methoxyaniline and p-bromoaniline from (Merck, Germany). p-nitroaniline (Riedel de Haen AG, Germany). p-toluidine, p-aminobenzoic acid, and anthranilic acid from (B.D.H, England). Different acid solutions (nitric, hydrochloric and sulphuric acids) and also potassium nitrate were prepared by dissolving A. R. grade chemicals in doubly distilled water. The acids were standardized by using primary standard base.

All spectral measurements were obtained at room temperature by using SHIMADZU UV visible spectrophotometer (UV-1601 PC). The absorption spectra of the oxazolone derivatives were studied in solution of varying pH-values. The pH was adjusted using a digital GENCO pH-meter with an accuracy of ± 0.005 units. The pH-meter was calibrated regularly before use with standard buffer solution of pH 4.00 ± 0.01 and 7.00 ± 0.01 at 25°C.

Preparation of Organic Ligands

To a solution of hippuric acid (0.1 mole) in 150 mL cold acetic anhydride containing freshly fused sodium acetate, a solution of ice cold (0.1 mole) diazonium

chloride of the different amines was added with stirring at -5°C , and the mixture was left for two hours at -5°C , then the hydrazone was precipitated by adding water, filtered, washed, and dried. The precipitate was recrystallized with acetic acid, the melting points were measured and were found as reported in literature^(9,10), for oxazolone derivatives [(H (I), p-Br (II), p-NO₂ (III), p-CH₃ (IV), p-OCH₃ (V), p-COOH (VI) and o-COOH (VII)], the melting point values were 203, 200, 220, 218, 205, 255 and 265 °C, respectively.

Solutions for Spectral Measurements

A solutions stock 5×10^{-2} M of the oxazolone derivatives (I-VII) were prepared by dissolving the appropriate amount of the hydrazone in the proper volume of mixed water-solvent (ethanol, methanol, acetone, dioxane and DMF).

Procedure for Spectrophotometric Determination of the Dissociation Constants of the Studied Ligands

The visible and ultraviolet spectra of 5×10^{-5} M solutions of the oxazolone derivatives were scanned on the range 200 to 600 nm. The ionic strength of the solution was kept constant at 0.1 M using KNO₃. All the studied solutions were diluted with bidistilled water and organic solvent of the required %. The pH was adjusted to the required value using dilute solutions of either HCl or KOH. The spectra of the solutions at different pH values were recorded using the same solvent mixture as a blank in a 1 cm quartz cell. The pH values were corrected using Dauhéret corrections values for mixed solvents using the following equation⁽¹¹⁾: $\text{pH}^* = \text{pH}(\text{R}) - \delta$, the quantity, δ is found to be approximately constant for a given solvent concentration. The methods applied for the determination of pKa values of the different synthesized ligands are Half height⁽¹²⁾ and Modified limiting absorbance methods⁽¹²⁾.

Results and Discussion

Spectra in Solutions of Varying pH Values

At high pH values the ionic form of the compound becomes the predominate species and the intramolecular charge transfer is enhanced causing an easier

electronic excitation of the π -electrons and consequently the absorption band of the ionic form is located at longer wavelengths. The dissociation of these oxazolone derivatives were found, however, to be affected to certain extent by the presence of organic solvents, due to the changed in the dielectric constant of the medium and the possibility of solute-solvent interaction. The study of the absorption spectra of oxazolone derivatives was performed at different pH values in solutions containing different percentages of ethanol, methanol, acetone, dioxane and DMF. It is aimed to study the spectral behavior of these derivatives in relation to the nature and composition of the medium utilized. For this purpose the absorption spectra of compounds (I-VII) are investigated in solutions of varying pH (2-10) values containing 20-80% by volume of the above mentioned solvents.

The absorption spectra of the oxazolone derivatives I and (V-VII) are represented in Figs. (1-4) in solutions of varying pH values (2–10) containing 60% (V/V) ethanol. It is to be mentioned that in some of the spectra of compounds (I-VII) one absorption band is observed, while in the other two bands were observed. For compounds (I, II, III and VII) one absorption band is observed within the whole pH range.

These bands are characterized by gradualness lower shift with increasing pH may be due to the transformation from one form to another. While compounds IV, V and VI have two absorption bands, these bands show the same gradualness lower shift with increasing pH.

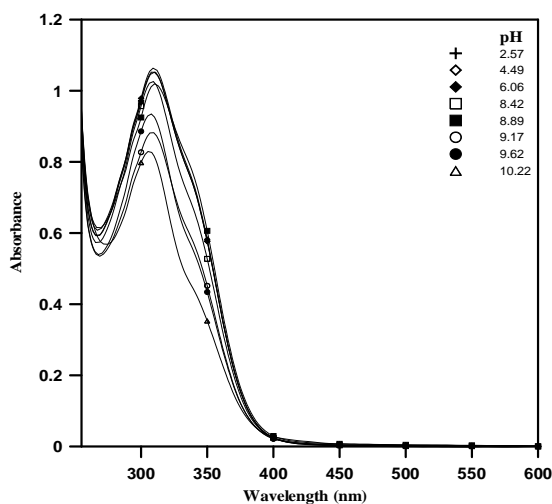


Fig. (1) Absorption spectra of (I) in 60% ethanol of varying pH.

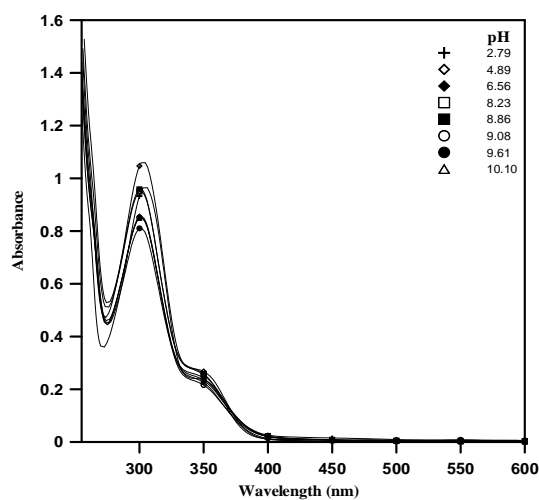


Fig. (2) Absorption spectra of (VII) in 60% ethanol of varying pH.

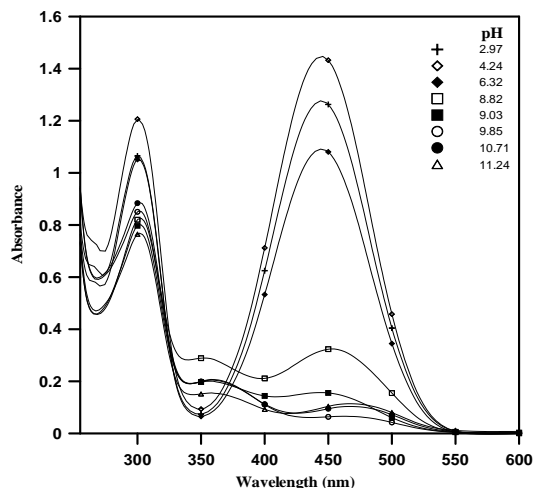


Fig. (3) Absorption spectra of (V) in 60% ethanol of varying pH.

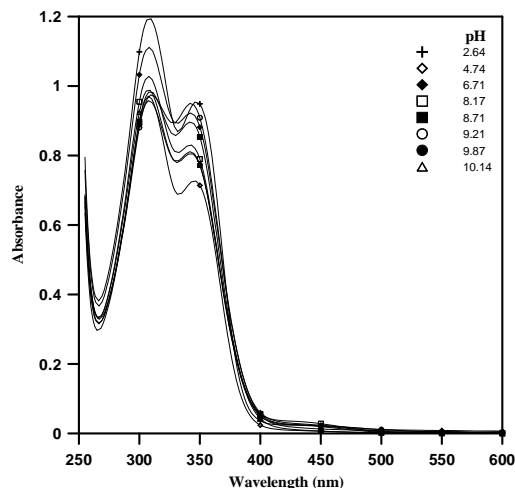


Fig. (4) Absorption spectra of (VI) in 60% ethanol of varying pH.

The first band is may be due to the nonionized form, whereas the second band is due to the ionized species. The $p\text{-NO}_2$ derivative show a district change in different media e.g. in ethanol and methanol water solvent mixtures as solvents one band only appeared, while in dioxane and DMF water solvent mixtures as solvents two bands were appeared due to the effect of solvent and medium pH. A remarkable change in the spectra of the studied derivatives is observed in the pH range 6-8.5 with a change in color from orange to faint yellow, the change in absorbance with varying pH attains a limiting value in solutions of pH 10 indicating that most of the acid form is transferred to its conjugate base Figs (5 and 6). Such changes are used for calculating pK values, the values are given in Table (1).

The spectra of compound (I) show one band within the pH range 2.5–10 which is characterized by a decrease in absorbance with increasing pH of the medium indicating the transformation of the form at lower pH into another form in which the CT interaction occurs at somewhat lower energy. Also an obvious change in color from orange to yellow of this compound is observed on changing pH from 6 to 10, which reveals its possible use as an acid base indicator. The calculated pK values for the derivatives (I-VI) are in the range 7.25-10.21, Table 1. Some spectra of compounds did not show regular changes with change of pH, this behavior may be attributed to overlap of the ionization steps and antagonizing effects on the

intramolecular charge transfer, the spectra of these compounds displayed their bands and no obvious isobestic points are observed.

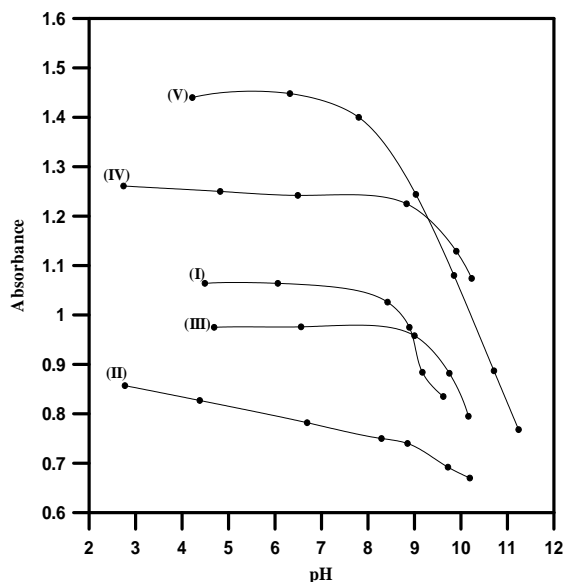


Fig. (5) Absorbance-pH curves for (I-V) oxazolone derivatives in 60% ethanol.

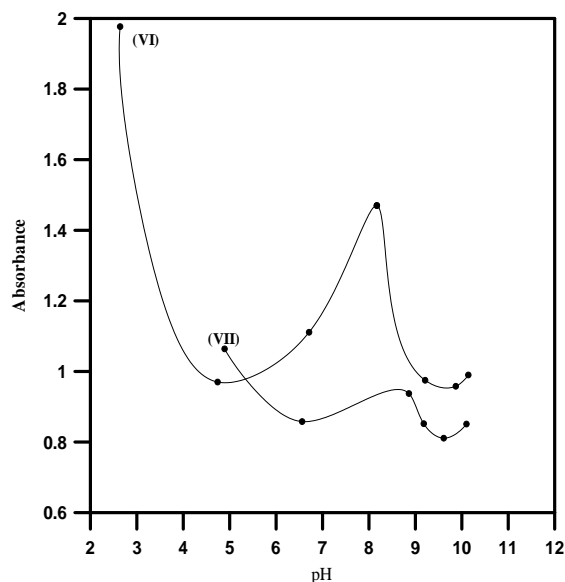


Fig. (6) Absorbance-pH curves for (VI-VII) oxazolone derivatives in 60% ethanol.

The pH-absorbance curves showed a single step on the acid side Figs. (5 and 6). The plots of absorbance values at some different wavelengths, corresponding to the absorption of the equilibrium species, was typical Z shaped for compounds (I-V), hence having the appearance of dissociation curves. These curves were used for the determination of the acid ionization constants of the compounds under study. The values obtained by the different methods are depicted in Table 1.

Structure-Acidity Relationships

The present part includes the study of the absorption spectra of the oxazolone derivatives (I-VII) in (20%-80%) by volume water-organic solvent mixtures. The dissociation constants (pK) values of the derivatives were investigated using Hammett equation in the form:

$$pK_x = pK_H - \rho\sigma$$

Both ρ and σ have their usual meaning, whereas x and H refer to the substituted and unsubstituted derivatives, respectively. The values were taken from the tabulation by Richie and Sager⁽¹³⁾.

Table (1) pK values for 4-arylhydrazo-2-phenyl-2-oxazolin-5-one derivatives in different solvent-water mixtures of different percentage.

(mean pKa values)										
Solvent	X	H (I)	p-Br (II)	p-NO ₂ (III)	p-CH ₃ (IV)	p-OCH ₃ (V)	p-COOH (VI)		o-COOH (VII)	
	σ_X	0	0.232	0.778	- 0.170	- 0.268	0.45		—	
Ethanol	20%	9.13	8.51	9.09	9.16	9.86	6.49	8.02	3.12	8.12
	40%	9.22	9.51	9.74	9.4	9.96	6.02	8.18	3.14	8.99
	60%	9.34	9.84	9.95	9.53	9.97	3.22	8.41	5.72	9.21
	80%	10.37	10.48	10.08	9.55	10.01	4.18	8.96	6.03	9.59
Methanol	20%	8.99	9.68	9.08	9.65	9.21	5.69	9.28	2.9	8.99
	40%	9.09	9.69	10.84	9.66	9.81	5.62	9.31	2.91	9.13
	60%	9.9	9.88	9.35	9.77	9.89	3.45	9.36	3.15	9.66
	80%	9.97	9.9	9.47	9.92	10.09	3.29	9.77	3.77	9.89
Acetone	20%	9.08	9.21	—	9.01	9.02	5.9	9	3.64	9.35
	40%	9.21	9.38	—	9.24	9.21	5.79	9.09	5.35	9.42
	60%	9.25	9.77	—	9.32	9.69	5.66	9.15	5.81	9.45
	80%	9.75	9.79	—	9.71	9.76	6.05	9.19	4.52	9.46
Dioxane	20%	9.05	9.34	9.02	8.79	9.25	4.86	8.23	2.75	8.12
	40%	9.74	9.41	9.13	8.98	9.42	4.67	9.08	3.78	9.08
	60%	9.88	9.58	9.23	9.02	9.56	5.4	9.25	5.24	9.49
	80%	9.99	9.74	9.4	9.29	9.89	5.26	9.64	5.51	9.51
DMF	20%	10.11	9.68	9.18	9.12	9.25	3.03	8.85	5.07	8.88
	40%	10.34	9.75	9.58	9.45	9.79	5.49	9.42	5.33	9.12
	60%	10.42	10.01	9.65	9.6	9.96	5.75	9.46	6.03	9.6
	80%	10.44	10.02	9.7	10.22	10.21	5.77	9.55	7.43	10.1

In Table (1), the mean pK values of oxazolone derivatives (I-VI) with the sigma constant of the para substituents are given in mixed water-organic solvent. The plot of

the average values of pK calculated by aid of the methods mentioned above versus the substituent sigma constant is linear Figs (7 and 8). The equation of the straight line is represented as follows:

$$pK_x = 9.11 - 2.55 \sigma$$

$r = 0.996$, $s = \pm 0.10$, for 60% (v/v) ethanol, where (r) and (s) are the correlation coefficient and the standard deviation, respectively. The slope and intercept were computed by the method of least squares⁽¹⁴⁾.

Table (2) Slope values of the $pK-\sigma^*$ plots in different percentage of different organic solvents

Solvent	Slope			
	20% (v/v)	40% (v/v)	60% (v/v)	80% (v/v)
Eth-OH	0.798	0.435	0.426	0.666
Me-OH	0.314	0.139	0.296	0.326
Acetone	0.290	0.224	0.199	0.241
Dioxane	0.368	0.702	0.333	0.613
DMF	0.820	0.844	0.915	0.075

It is obvious from the value of (r) that the values of pK are correlated well with Hammett sigma constants. From the sigma and magnitude of (ρ) it is evident that the electron withdrawing substituent increases the ionization of hydrazone. The plot of pK versus the substituent sigma constant (σ) for each compound in Table (1) should give a straight line.

The slopes of the straight lines correlating the pK values with the substituent constant σ at different percentages of solvent are not the same, Table (2). This supports the opinion that the change in pK is not only due to dielectric effects but also the solvation is an important factor.

From the data obtained we observed that two pK's values for the derivative containing carboxylic group VI and VII in different percentage of solvent-water mixtures, the first may be due the ionization of COOH group and the other for the oxazolone derivative.

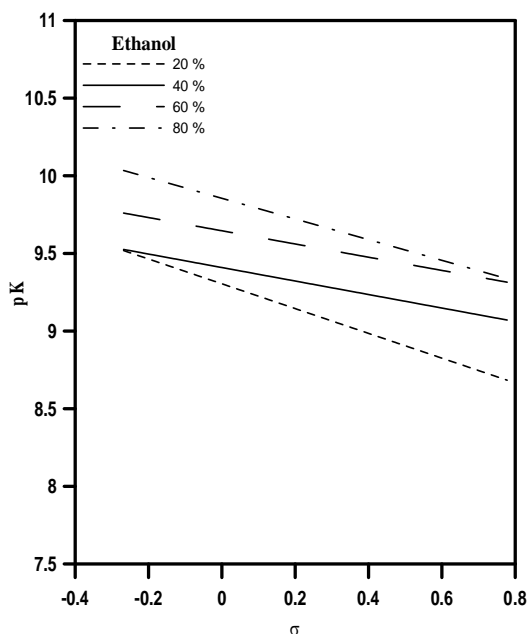


Fig. (7) Dependence of acid dissociation constant (pK) on the Hammett substituent constant (σ) for 4-arylhydrazo-2-phenyl-2-oxazolin-5-one derivatives in ethyl alcohol-water mixtures (v/v) 20-80%.

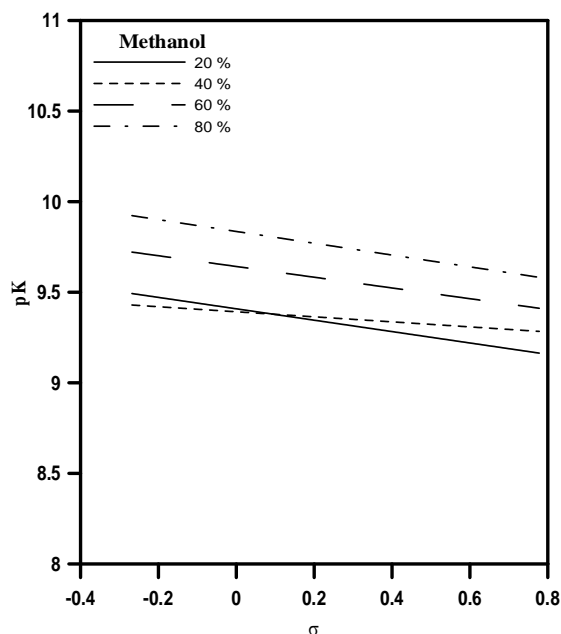


Fig. (8) Dependence of acid dissociation constant (pK) on the Hammett substituent constant (σ) for 4-arylhydrazo-2-phenyl-2-oxazolin-5-one derivatives in methyl alcohol-water mixtures (v/v) 20-80%.

Effect of Some Organic Solvents on the Acid Dissociation Constant of Some Oxazolone Derivatives

The equilibria set in solution are apparently affected by the presence of organic solvents. Since the pK values are obtained in mixed water-organic solvents the presence of the latter is thus expected to decrease the ionization. The rate at which the ionic form is produced, is influenced by both the nature and amount of organic solvent used. The elimination of the protons from all derivatives studied decreases as the amount of organic solvent increases.

The variation of pK values with solvent concentration is due to some factors such as changes in the dielectric constant of the medium, solvolysis of ions and basicity of the solvent mixtures⁽¹⁵⁾. The variation of pK values with dielectric constant (D) in solvent mixtures is given by the relation⁽¹⁶⁾,

$$pK = pK_o + [(0.43Ne^2)/RT] * [(Z_1Z_2)/(r_1r_2)] * (1/D)$$

where pK_a and pK_o are the acid dissociation constants in the solvent mixture and in pure water, respectively, Z_1 and Z_2 are the charges carried by the ions in equilibrium, and $(r_1$ and $r_2)$ are the radii of the ions.

From this equation it is evident that if the dielectric constant of the medium is the predominate factor affecting the change of pK values with solvent concentration, the plot of pK_a against $1/D$ must be linear. In the studied derivatives, however, the plots of pK as a function of $1/D$ are not strictly linear relationships, Figs. (9 and 10) of compound I and VI. This behavior indicates that the changes in pK with the organic solvent proportion⁽¹⁷⁻¹⁹⁾, though mainly governed by the dielectric constant, yet influenced by solvent basicities and as well by the solvation of the solute by organic solvent molecules. Decrease in solvent basicity is quite apparent with alcohol and this in turn leads to decrease in the releasing tendency of the proton from the derivatives investigated.

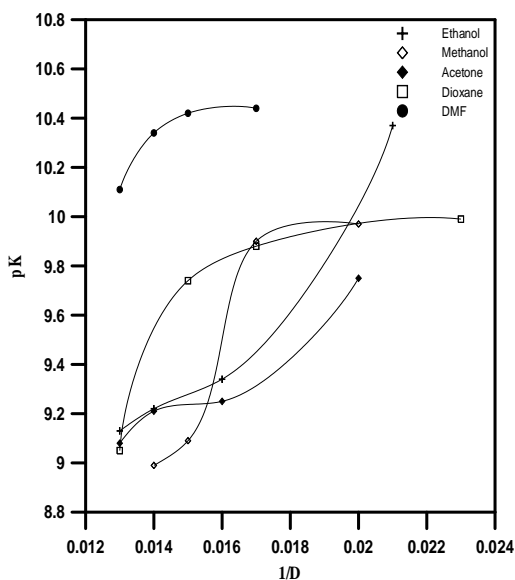


Fig. (9) Dependence of acid dissociation constant (pK) on the dielectric constant ($1/D$) for 4-arylhydrazo-2-phenyl-2-oxazolin-5-one of solvent-water mixture.

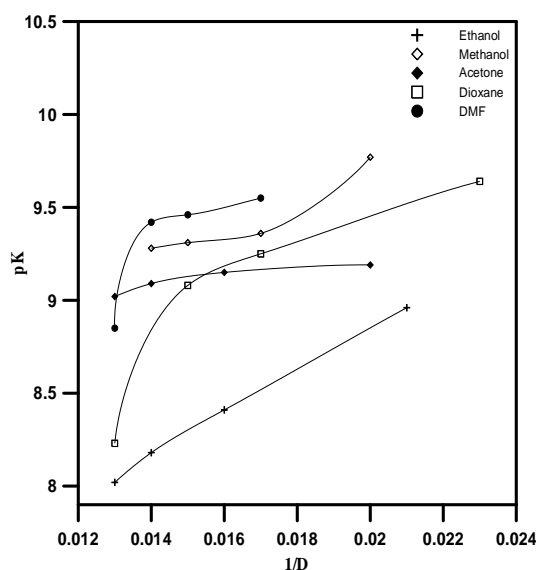


Fig. (10) Dependence of acid dissociation constant (pK) on the dielectric constant ($1/D$) for p-carboxy-4-arylhydrazo-2-phenyl-2-oxazolin-5-one of solvent-water mixture.

References

1. R.M. Issa, M. Gaber, A.M. Khedr, *Egypt. J. Anal. Chem.* 10, 23 (2002).
2. A.S. Amin, M.M. Mostafa, R.M. Issa, *Talanta* 44, 311 (1996).
3. R. F. Cookson, *Chem. Revs.*, 74, 5 (1974).
4. E. J. King "Acid-Base Equilibria" Pergamon press, Oxford (1965).
5. A. Albert and E. P. Serjeant, "The determination of ionization constants" 2nd. Ed. Champan and Hall, London, (1971).
6. R.M. Issa, S.S. Assar, H.A. Dessouki, *Egypt. J. Chem.*, 35, 321 (1992).
7. R. Haessener, H. Mustroph, B. Borsdort, *J. Prakt. Chem.* 327, 555 (1985).
8. V.F. Trawen, A.M. Tsygchenkova, B.I. Strepanov, *Zh. Org. Khim.*, 21, 1539 (1985).
9. E. J. Browne and Poly, J. B., *J. Chem. Soc.*, 575 (1962).
10. A. M. Khalil, I. I. Abd El-Gawad and H. M. Hasan, *Aust. J. Chem.*, 27, 2509-10 (1974).
11. G. Douhréret, *Bull. Soc. Chem.*, (France) 3122 (1968).
12. R. M. Issa and A. H. Zewail, *J. Chem. U. A. R.*, 14, 461 (1971).
13. C. D. Ritchie and W. F. Sager, "Progress in Physical Organic Chemistry", Vol. 2, Interscience publishers, N. Y., P. 334 (1964).
14. H. H. Jaffé, *Chem. Rev.*, 53, 191 (1953).
15. S. Karboune, M. Safari, Bena-Marie Lue, F.K. Yeboah and S. Kermasha, *J. of Biotechnology*, 119, 281 (2005).
16. G. Charlot and B. Termillon, "Chemical Reactions in Solvents and Melts", pergamon press. N. Y., 306 (1969).
17. A.M. Khedr, M. Gaber, R.M. Issa and H. Erten, *Dyes and Pigments*, 67, 117 (2005).
18. M. Gaber, I.A. Mansour, Y.S.Y. El-Sayed, *Spectrochimica Acta, Molecular and Biomolecular Spectroscopy*, 68, 305 (2007).
19. M.B. Gholivand, J.B. Ghasemi, S. Saaidpour and A. Mohajeri, *Spectrochimica Acta*, In Press, (2008).