

## **pH-metric Study of the Acid-Base Properties of some Bisazo-dianil Compounds Containing the Pyrimidine Nucleus**

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**Summary:** The  $pK_{a1}$  and  $pK_{a2}$  of a new series of bis-azodianil compounds based on pyrimidinylazohydroxy benzaldehydes and aliphatic diamines are determined from pH-titration. The solutions used for titration have 75, 80, 85, 90 and 95% by volume methanol. The colour of these compounds were tested in 0.1 M HCl, 0.1 M NaOH and 0.1 M KCl. The UV spectra of some compounds were also measured in these three solutions.

### **Introduction**

Many of the known azo compounds function readily as chromogenic reagents for transition metal ions based on their ability to form stable complexes<sup>(1)</sup>. The spectrometric study of the acid-base characteristics of the reagent obtained by coupling 3-methyl-1-phenylpyrazolin-5-one with diazotized amino-aryl-sulfonic acid was described<sup>(2)</sup>, the apparent  $pK_a$  values were evaluated and this reagent was used as visual indicator in acid-base titration. Azomethines containing an OH-group in o-position to the C=N linkage form readily metal chelates with transition metal ions<sup>(3,4)</sup>. The effect of medium on the ionization constant of organic compounds having acidic character was the subject of some recent studies. Hashem and Saleh<sup>(5)</sup> determined the  $pK_a$  of some substituted pyridolines in water ethanol mixture from spectrophotometric measurements. The values obtained were discussed in terms of molecular structure of the studied pyridolines and composition of the solvent used. Ertan<sup>(6)</sup> investigated the acid dissociation constant of some hetaryl azo pyrazolone dyes in various water ethanol mixtures spectrophotometrically. The effect of solvent, temperature and reagent concentration were studied. Kgilic et. Al.<sup>(7)</sup> evaluated the protonation constants of some substituted salicylidene anilines in ethanol-water mixtures at 25 °C by potentiometric titration. The trend in the  $pK_a$  values was explained in terms of the nature of substituent and the dielectric constant of the medium.

Recently, we prepared a series of bisazo-dianils based on 5-(2-carboxy phenylazo)-salicylaldehyde and primary amines and studied their UV/Vis, IR,  $^1\text{H}$  NMR spectra<sup>(8)</sup> as well as their chelates with Mn(II), Co(II) and Cu(II)<sup>(9)</sup>. Chelate formation with the bisazo-dianils occurs through proton displacement from the phenolic and carboxylic OH-groups<sup>(9)</sup>. A similar work has been conducted on a series of bisazo-dianils containing the pyrimidine nucleus<sup>(10)</sup>.

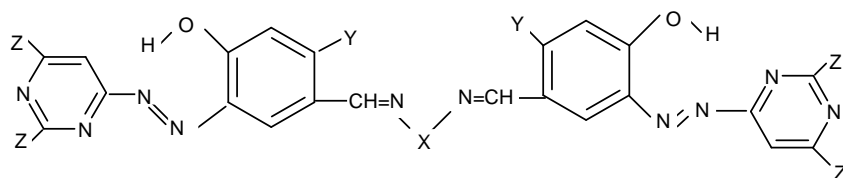
In the present article, the acid properties of the bisazo-dianils having two pyrimidine rings are studied applying potentiometric titration in water methanol mixtures. The  $\text{pK}_a$  values for the various equilibria are determined.

### Experimental

All compounds used were pure grade chemicals obtained from Aldrich and BDH, and used without further purification.

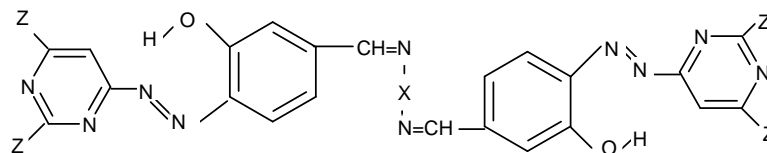
Azo dye derivatives of amino/pyrimidines and hydroxybenzaldehydes were synthesized according to the procedure given previously<sup>(11)</sup>. The bisazo-dianil compounds (I-XII) were obtained by condensation of the azo compounds with 1,3-diaminopropane or 1,6 diaminohexane in the usual way for the preparation of Schiff Bases<sup>(10,12)</sup>. The purity of the compounds obtained was gained from data of elemental analysis.

The bisazo-dianils involved in the present investigation have the general structural formulae given in schemes I and II.



Scheme I

compounds	x	Y	z
I	(CH <sub>2</sub> ) <sub>3</sub>	OH	OH
II	(CH <sub>2</sub> ) <sub>6</sub>	OH	OH
III	(CH <sub>2</sub> ) <sub>3</sub>	H	CH <sub>3</sub>
IV	(CH <sub>2</sub> ) <sub>6</sub>	H	CH <sub>3</sub>
V	(CH <sub>2</sub> ) <sub>3</sub>	H	OH
VI	(CH <sub>2</sub> ) <sub>6</sub>	H	OH
VII	(CH <sub>2</sub> ) <sub>3</sub>	OH	CH <sub>3</sub>
VIII	(CH <sub>2</sub> ) <sub>6</sub>	OH	CH <sub>3</sub>



Scheme II

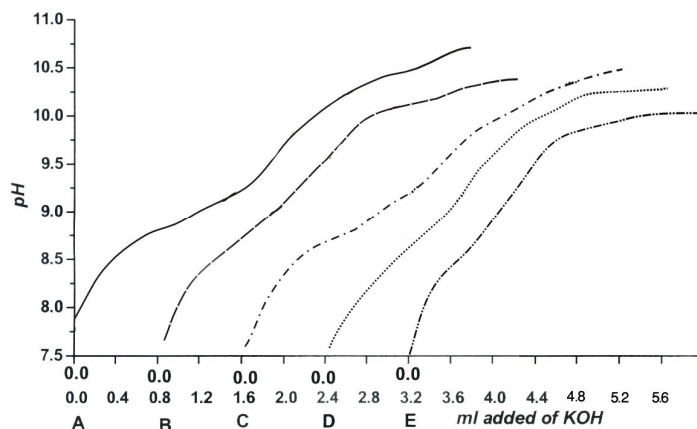
compounds	x	z
IX	(CH <sub>2</sub> ) <sub>3</sub>	OH
X	(CH <sub>2</sub> ) <sub>6</sub>	OH
XI	(CH <sub>2</sub> ) <sub>3</sub>	CH <sub>3</sub>
XII	(CH <sub>2</sub> ) <sub>6</sub>	CH <sub>3</sub>

Due to the low solubility of the bisazo-dianils in organic solvents, saturated solutions were first prepared by heating the compounds in methanol, after allowing to cool the solid was filtered off to get a clear solution. Volumes of the clear solution were mixed with twice distilled water to give the required solvent composition (75, 80, 85, 90, and 95% by volume methanol). The solutions thus obtained were then titrated with  $8.6 \times 10^{-3}$  M KOH containing the same proportion of methanol as that of the bisazo-dianils solution. The titration was carried out under continuous stirring. The pH of the reaction mixture was measured by the aid of an Accemet 830 pH-Meter (range 0-14 accurate to 0.10 pH unit). After each addition of the titrant, sufficient time was given to attain the equilibrium. The pH values recorded were then corrected for the effect of methanol using the relation given by Van Uitert and Haas<sup>(13)</sup>.

### Results and Discussion

On plotting the pH of the reaction mixture as a function of the volume of the titrant added, the titration curves (represented in Fig.1) were obtained. The curves displayed one (III, IV, XI & XII or two inflections (I, II & V-X) depending on the molecular structure of the bisazo-dianils titrated. As a matter

of fact the two neutralization steps observed for VII and VIII represent the reaction of the OH-groups in o-position to the azo groups in the first step while the OH-groups involved in hydrogen bonding with the C=N group are neutralized in the second stage. This is similar to previous observations with simple azo-azomethine compounds<sup>(14)</sup>.

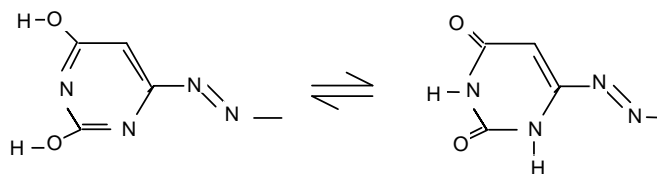


- A) 7.5 ml of ligand solution + 2.5 ml of H<sub>2</sub>O
- B) 8.0 ml of ligand solution + 2.0 ml of H<sub>2</sub>O
- C) 8.5 ml of ligand solution + 1.5 ml of H<sub>2</sub>O
- D) 9.0 ml of ligand solution + 1.0 ml of H<sub>2</sub>O
- E) 9.5 ml of ligand solution + 0.5 ml of H<sub>2</sub>O

Fig. (1) : The Titration Curves of compound VI with  $6.8 \times 10^{-3}$  M KOH

Thus, the first group of OH has  $pK_a$  of 8.60-9.45 while the second group has  $pK_a$  of 9.70-10.20. This finds support from the values of  $pK_a$  for compounds III,IV,XI and XII containing only OH-groups in o-positions to the azo groups having  $pK_a$  of 8.6.-9.10 .

For compounds V, VI, IX and X , the first step corresponds to the ionization of the of OH-groups in o-position to the N=N group ( $pK_a = 8.6-9.1$ ), while the second one is that for the OH-groups of the dihydroxy pyrimidine ring (9.5-10.25). Despite the fact that the OH-groups on the pyrimidine rings are not contributing to hydrogen bonding, yet the possible tautomeric shift of the type:



leads to a decrease of the acidic character of the dihydroxy pyrimidine OH-groups. This is also gathered from the volumes of alkali needed for the neutralization steps, which is two equivalents for the first step and four equivalents for the second one. For compounds I and II, two neutralization steps are obtained, the first one for the OH-groups in the o-position to the N=N groups while the second one is due to neutralization of the remaining OH-groups (azomethine OH and pyrimidine OH). Accordingly, for these two compounds the neutralization of the azomethine OH-groups occurs simultaneously with those of the hydroxy pyrimidine moiety.

#### Determination of $pK_a$ :

The  $pK_a$  values for the various neutralization steps were determined from the data of pH-metric titration, making use of the relation:

$$pH = pK_a + \log \frac{(Salt)}{(Acid)}$$

Whereby  $pK_a$  will be the pH at half neutralization for each step .

Also the  $pK_a$  was determined by analyzing the titration curve. Substituting for salt and acid concentrations by volumes of alkali added during the titration then

$$pH = pK_a - \log \frac{(V_{ep} - V)}{(V)}$$

$V_{ep}$ : volume of alkali at end point (complete neutralization)

$V$ : Volume of alkali added at any point before neutralization

pH: measured value at volume of alkali  $V$

The plot of  $\log \frac{(V_{ep} - V)}{(V)}$  vs pH yields linear relations with negative slopes; the

$pK_a$  values were determined from the intercepts of these plots (second method).

The mean  $pK_a$  obtained for all compounds at 75 % by volume of methanol are given in the table I.

**Table 1: The values of pK<sub>a</sub> for ligands and the colour change with media**

Comp. no.	Colour in different media				pK <sub>a</sub> in 75% methanol water			pK <sub>a</sub> in pure methanol			pK <sub>a</sub> in pure water		
	Solid	0.1 M HCl	0.1 M KCl	0.1 M NaOH	pK <sub>a1</sub>	pK <sub>a2</sub>	pK <sub>a3</sub>	pK <sub>a1</sub>	pK <sub>a2</sub>	pK <sub>a3</sub>	pK <sub>a1</sub>	pK <sub>a2</sub>	pK <sub>a3</sub>
I	Pale red	Yellow	Yellow	Orange	8.75	9.70		9.5	10	-	8.0	9.20	
II	Red	Brown	ppt	Dark brown	8.80	10.15		9.9	10	-	8.6	10.0	
III	Pale yellow	Orange	Yellow	Yellow	8.80	-	-	9.7	-	-	8.2	-	-
IV	Pale yellow	Dark yellow	Yellow	Yellow	8.60	-	-	4.0	-	-	8.5	-	-
V	Light red	Faint yellow	Yellow	Orange	8.7	-	9.5	8.9	-	10.5	8.6	-	10.5
VI	Pale yellow	Yellow	Yellow	Yellow	8.6	-	9.75	8.7	-	9.9	8.6	-	9.9
VII	Pale yellow	Yellow	Yellow	Yellow	9.10	10.05	-	9.5	10.4	-	9.0	9.3	-
VIII	Brown	Brown	Brown	Brown	9.45	10.20	-	10.0	10.5	-	9.1	10.2	-
IX	Light red	Yellow	Yellow	Dark yellow	9.00	-	10.25	9.3	-	10.5	8.7	-	9.5
X	Brown	Brown	Brown	Dark brown	9.10	-	9.95	9.4	-	10.5	9.2	-	9.8
XI	Pale yellow	Yellow	Yellow	Faint yellow	9.10	-	-	9.3	-	-	9.0	-	-
XII	Pale yellow	Yellow	Yellow	Faint yellow	8.90	-	-	9.6	-	-	8.9	-	-

The effect of proportion of methanol was then investigated by titrating the bisazo-dianil compounds under study in media containing varied proportions of methanol (75-95 % by volume). The titration curve display more obvious inflections at higher methanol proportion. The titration curves shifted to higher pH values as the proportion of methanol in the media was increased, thus  $pK_a$  increases with increased proportions of methanol. Medium effect or solvent composition influence on acid-base equilibria are usually interpreted on the basis of changes in electrostatic effect (permitivity or  $1/\epsilon$ ) and nonelectrostatic effect (basicity in hydrogen bond acceptance)

The increase of  $pK_a$  with increased methanol proportion in the medium can be explained in the light of both factors. The nonelectrostatic effect results from decreased solvent hydrogen bond acceptance<sup>(15,16)</sup>, hence the intramolecular H-bond in the solute molecule will increase resulting in a higher  $pK_a$  value. Also, the decrease of the dielectric constant of the medium on increasing the methanol content will lower the ionization of the bis azo dianil molecules, hence shifts the ionization equilibrium in the direction of the nonionised molecules resulting in an increase of  $pK_a$ .

The increase of  $pK_a$  with increased proportion of methanol in the medium can be explained on the bases of the relation<sup>(17,18)</sup> :

$$pK_a^{(m)} = pK_a^{(w)} + \log (m_{\gamma H^+} \cdot m_{\gamma B^-} / m_{\gamma HB})$$

In which  $m_{\gamma}$  is the activity coefficient of the subscription species in water-methanol medium relative to that in pure water.

The electrostatic effect will operate only on the activity coefficient of the ionized species, hence the increased proportion of methanol will exert its effect on an increase of the relative reactivity coefficient of both  $H^+$  and  $B^-$  ions, which in tern results in a higher  $pK_a(s)$  values.

The plot of  $pK_a$  as a function of the reciprocal of the dielectric constant of the medium ( $\frac{1}{\epsilon_{mix}}$ ) gave satisfactory linear relationships (Fig 2) indicating the validity of the relation

$$pK_{a(mix)} = pK_{a(w)} + c \left( \frac{1}{\epsilon_{mix}} \right) = pK_{a(Meth)} - c \left( \frac{1}{\epsilon_{mix}} \right)$$

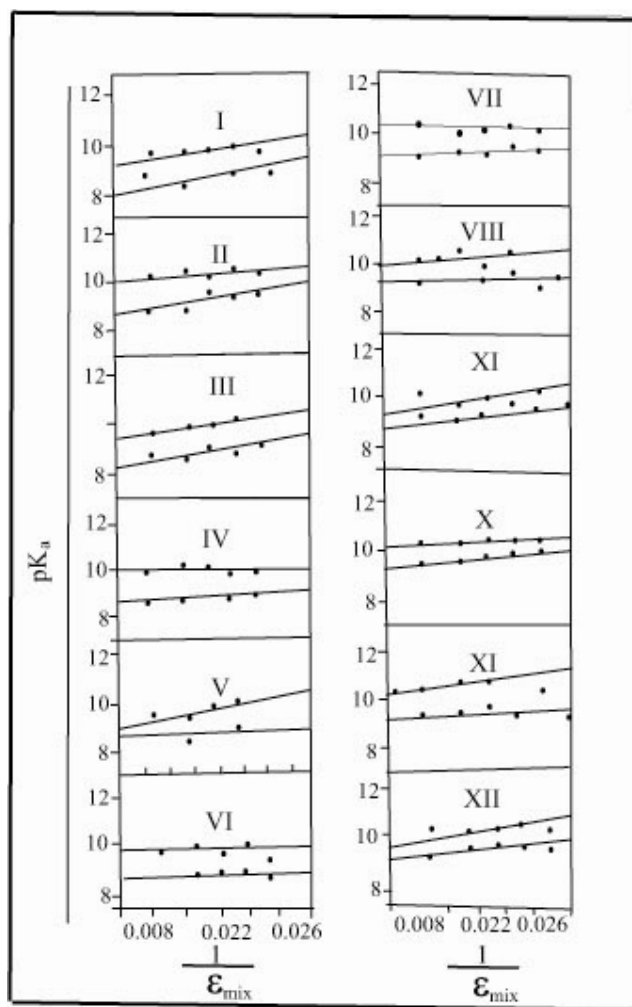


Fig. (2) The relation between  $pK_a$  and  $\frac{1}{\epsilon_{mix}}$  for different ligand

The values of  $(\frac{1}{\epsilon_{mix}})$  at various of proportions of methanol were calculated using

the Poisson equation in the form:

$$\left(\frac{1}{\epsilon_{mix}}\right) = \frac{1}{\epsilon_w} f_w + \frac{1}{\epsilon_{Meth}} f_{Meth}$$

in which the  $\epsilon_{mix}$ ,  $\epsilon_w$  and  $\epsilon_{meth}$  are the dielectric constants of the solvent mixture titrated, pure water and pure methanol;  $f_w$  and  $f_{Meth}$  are the mol fractions of water and methanol in the solvent mixture.



The satisfactory linear plots of  $pK_a$  vs  $(1/\epsilon_{mix})$  made it possible to determine the values of  $pK_a$  in both pure methanol and water by extrapolation. The values thus obtained are given in table 1.

For using these compounds as acid-base indicators, the colour of all compounds was tested in 0.1 M HCl, 0.1 M NaOH and 0.1 M KCl. It was noticed that the color of most compounds slightly changed in the three media. There was a wide range for the change of colour when these compounds were used as acid-base indicators.

The colour of compound I changed from yellow in acid medium to orange in basic media; that of compounds III and V changed from orange in acid medium to yellow in basic ones. So we tested the use of these two compounds as indicators in titration of 0.1 M NaOH against 0.1 M HCl. The results were compared with those obtained when using phph and MO as indicators. There was an obvious difference between the two results because no sharp end point was observed, so these compounds cannot be used as acid-base indicators. The changes of the color in different media are listed in table (1).

To get a deeper insight in the nature of the species present in solution and the origin of colour change for the bisazo-dianil compounds under study, their UV-Vis spectra of compounds III and V were measured in 0.1 M solutions of HCl, KCl, or NaOH and in methanol. The spectra for compound III are shown in Fig. 3. The absorption spectra showed the  $\lambda_{max}$  of bands at 282 and 284 nm in methanol, at 285 and 288 nm in 0.1 M HCl, at 330 and 333 nm in 0.1 M NaOH. In 0.1M KCl, the spectra displayed two bands for each compound at (285,330nm) and (282,333 nm) for III and V respectively. The two bands observed were assigned to the medium energy  $\pi-\pi^*$  transition of the aromatic rings and the  $\pi-\pi^*$  of both N=N and C=N centers influenced by an intramolecular charge transfer from the aromatic rings as source to the N=N and C=N bands as sink<sup>(16)</sup>.

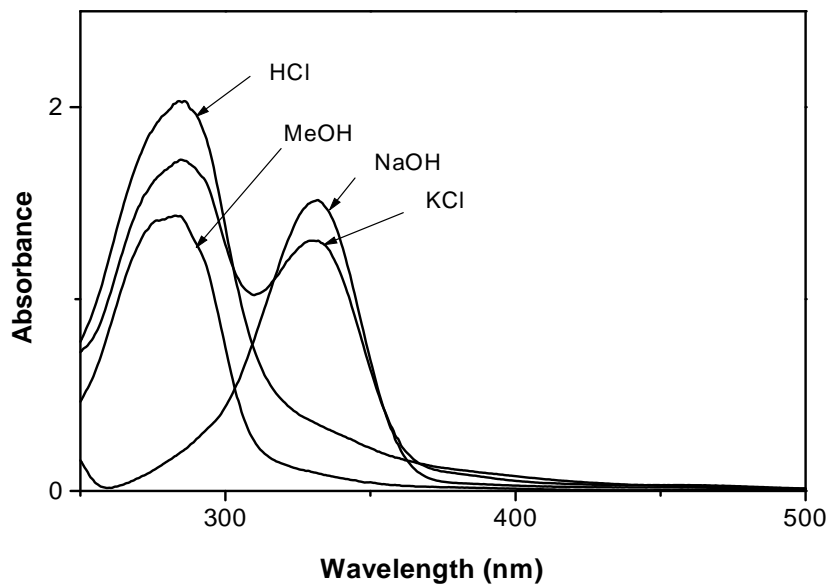


Fig.(3) The UV/Vis Spectra of compound III in 0.1 M HCl, 0.1 M KCl and 0.1 M NaOH

It is noticed that the bands in case of methanol and HCl are at the same position, which indicates that these compounds are existing in the nonionic state in the acid medium. The band positions changes in case of NaOH as a result of complete ionization in the basic medium, but when using KCl as a medium the spectra show two bands, the first one at almost the same position for HCl or methanol and the second band is typical to that in alkaline medium. This revealed that in neutral medium, these compounds are present as a mixture of nonionized and ionized forms or as partly ionized species. Accordingly, the bands observed below 300 nm are due to absorption of the nonionic form of the compounds under study while those bands above 300 nm correspond to absorption by the ionic forms. Thus, the colour change occurring during the titration of the compounds with KOH solutions is due to the change of the nonionised bisazo-dianils to the ionic state in which the intramolecular charge transfer requires lower energy than for the nonionised species.

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