Influence of different of ethanol percentages on pKa values for some imines derived from 3-acetyl and 4-acetyl pyridines

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Abstract

The work is concerned with the influence of different ethanol percentages in the range (10-50)vol. % at fixed 25C° temperature on the values of ionization constants pK_a for some acidic and basic imines . These imines are derived 3-acetyl and 4-acetyl pyridines in a forms of syn or anti oxime and phenolic or amino Schiff bases , containing phenol and primary amine groups in ortho , meta and p-positions on the aromatic ring of primary amine sides

The plots of pK_a values of acids versus the dielectric constants (D) of different alcoholic media show a different linear or curve shapes . These results were interpreted and discussed in details in this topic .

الخلاصة

يعنى البحث بدراسة تأثير النسب المئوية للايثانول في المدى (10–50) ٪ حجماً ، وفي درجة حرارة ثابتة 25ْم على قيم ثوابت التأين pK_a لبعض الاحماض والقواعد الايمينية .
هذه الايمينات مشتقة من بيريدينات 3– اسيتايل و 4– اسيتايل وهي باشكال اوكزيم سين او انتي وقواعد شيف الفينولية او الامينية والحاوية على مجاميع فينول وامين اولي في مواقع اورثو , ميتا وبارا على الحلقات الاروماتية في جهات الامين الاولي .
ان رسم علاقات بين قيم pK_a للاحماض ضد ثوابت العزل الكهربائي (D) لاوساط الكحول المختلفة اعطى عدة اشكال خطية او منحنيات . هذه النتائج تم تفسيرها ومناقشتها بالتفصيل في البحث .

Introduction

Experimentally, the variation of solvent has observed to influence several physical constants [1,2] such as ionization constant, rate constant and others . This encouraged and interested a great numbers of workers to deal with such important topic . Previous works on solvent effect were concerned with destruction[3] of drugs , sulphonation[4] of benzene , 1,3-addition[5] reaction between styrene and tetracyano ethylene , and others[6,7] .

Among the works deal with solvent effects conducted in our laboratory were the influence of solvent on association[8] of some carboxylic acids , tautomerism[9] of some imines derived from 2-hydroxy-1–napthylaldehyde , pK_a values of some acidic imines derived from aromatic and aliphatic carbonyl[10] compounds , benzyol acetone and dimedone[11] .

This work is a continuation of the last topic . It deals with the influence of different ethanol percentages in the range (10-50)vol. % on pK_a values of acidic and basic imines derived from 3-acetyl and 4-acetyl pyridines . The graphs collected between pK_a and dielectric constant of the medium D were discussed and interpreted by a proper scientific way .

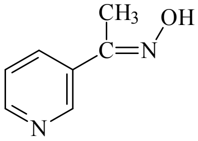
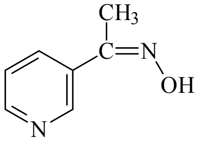
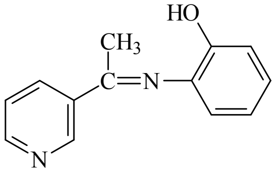
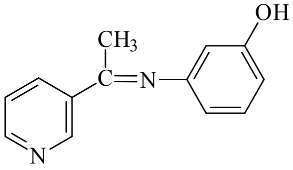
Experimental

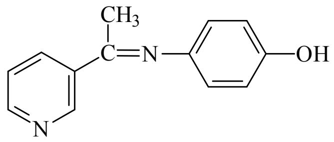
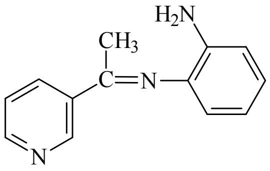
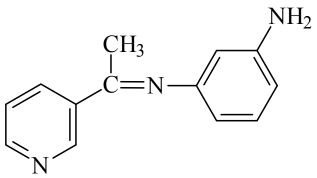
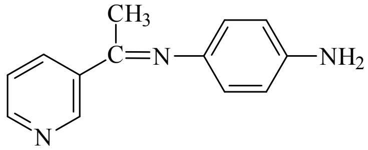
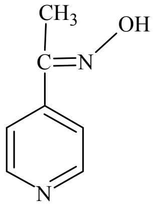
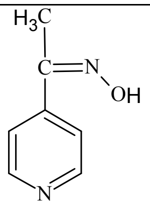
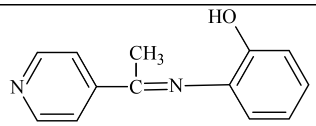
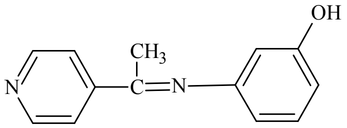
All chemicals used throughout this work were of Fluka , BDH and Molckula origins .

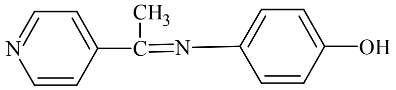
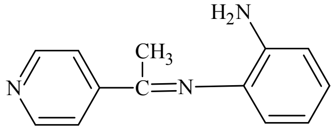
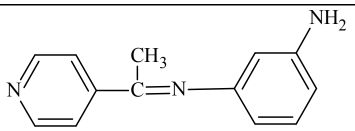
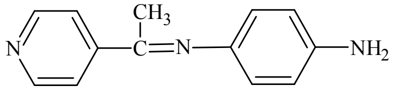
All imines in a forms of oximes syn and Schiff bases were prepared by mixing equimolar amounts of 3-acetyl or 4-acetyl pyridines with suitable primary amine as hydroxyl amine , o, m, p-amino phenol and o, m, p-phenylene diamine , according to standard[9] procedure .

The syn aldoximes were converted to their anti forms by either catalytic HCl gas method[11] or refluxing syn oxime in dry benzene , after addition of dry activated charcoal method[11] .

Table (1) : Shows , names , nomenclature and numbers of imines prepared .

Comp. No.	Nomenclature	Structure
1	syn-Methyl-3-pyridyl ketoxime	
2	anti-Methyl-3-pyridyl ketoxime	
3	Methyl-3-pyridyl ketonylidene *o*-amino phenol	
4	Methyl-3-pyridyl ketonylidene *m*-amino phenol	

5	Methyl-3-pyridyl ketonylidene *p*-amino phenol	
6	Methyl-3-pyridyl ketonylidene *o*-amino aniline	
7	Methyl-3-pyridyl ketonylidene *m*-amino aniline	
8	Methyl-3-pyridyl ketonylidene *p*-amino aniline	
9	syn-Methyl-4-pyridyl ketoxime	
10	anti-Methyl-4-pyridyl ketoxime	
11	Methyl-4-pyridyl ketonyliden *o*-amino phenol	
12	Methyl-4-pyridyl ketonyliden *m*-amino phenol	

13	Methyl-4-pyridyl ketonyliden *p*-amino phenol	
14	Methyl-4-pyridyl ketonyliden *o*-amino aniline	
15	Methyl-4-pyridyl ketonyliden *m*-amino aniline	
16	Methyl-4-pyridyl ketonyliden *p*-amino aniline	

Results and Discussion

pK_a for all imines were determined at fixed constant temperature value of 25C° , by using a standard method[17]. The pKa of acid HA and conjugate acid BH^+ were calculated by using equations[17].

$$pKa = pH + \log\frac{[HA]}{[A^-]} \quad \dots .\ (1)$$

$$pKa = pH + \log\frac{[BH^+]}{[B]} \quad \dots .\ (2)$$

As known in literature[12] , water was regarded as the proper solvent , during the determination of pK_a for acidic or basic compounds . This was due to highest dielectric constant of 80 Duby value. Experimentally a great numbers of organic compounds were in soluble in water . This was the reason of addition of ethanol to any organic solute during preparation of solutions before pK_a determination. The relative errors by pK_a value caused by the latter is fixed or can be ignored during determination of pK_a values . The work describs the influence of ethanol contents in a range (10-50)% ethanol on pK_a values of acids numbered [1-5,9-13] and pK_a values of acids nitrilium ions for bases numbered [6-8,14-16] .

It is know that change of any ethanol content for any solution is accompanied by the change of dielectric constant of the medium .The last was calculated from specialized literature[13] and from the relationship :-

$D = a\,e^{-bT}$ …. (3)

D = Dielectric constant of the medium

a,b = Constants

T = Absolute temperature

From equation (3) the dielectric constants of (10-50)vol. % ethanol content at 25°c were calculated , results collected are shown in Table (2) .

Table (2) : Relationship between dielectric constant D and % of ethanol content .

% of ethanol content	D
10	40.01
20	36.28
30	32.42
40	28.46
50	24.65

Typical examples on the relationship between pKa and % of ethanol are shown in Tables (3-5)

Table (3) : Experimental $\overline{pKa}$ values for syn 3-pyridyl ketoxime at different ethanol content at 25C° .

Ethanol %	ml of (0.1 M) NaOH	pH	pKa	$\overline{pKa}$
10	0.2	5.20	6.1066	9.4592
	0.4	7.00	7.6133	
	0.6	9.91	10.3085	
	0.8	10.30	10.5283	
	1.0	10.48	10.5517	
	1.2	10.63	10.5546	
	1.4	10.77	10.5514	
20	0.2	5.24	6.2012	9.9566
	0.4	9.34	9.9594	
	0.6	10.16	10.5725	
	0.8	10.47	10.7169	
	1.0	10.64	10.7365	
	1.2	10.82	10.7879	
	1.4	10.90	10.7216	
30	0.2	5.10	6.0680	9.7715
	0.4	7.54	8.1533	
	0.6	10.25	10.6699	
	0.8	10.62	10.8909	
	1.0	10.78	10.9073	
	1.2	10.93	10.8356	
	1.4	11.01	10.8756	
40	0.2	4.98	5.9389	9.7017
	0.4	6.15	6.7630	
	0.6	10.21	10.6265	
	0.8	10.73	11.0250	
	1.0	10.96	11.1456	
	1.2	11.13	11.2251	
	1.4	11.21	11.1880	
50	0.2	4.94	5.8984	9.5513
	0.4	5.86	6.4728	
	0.6	9.49	9.8775	
	0.8	10.68	10.9632	
	1.0	10.95	11.1317	
	1.2	11.14	11.2409	
	1.4	11.26	11.2748	

Table (4) : Experimental $\overline{pKa}$ values for anti 3-pyridyl ketoxime at different ethanol content at 25C^o .

Ethanol %	ml of (0.1 M) NaOH	pH	pKa	$\overline{pKa}$
10	0.2	9.78	10.7749	10.8361
	0.4	10.21	10.8704	
	0.6	10.46	10.9051	
	0.8	10.60	10.9217	
	1.0	10.74	10.8574	
	1.2	10.82	10.7879	
	1.4	10.91	10.7352	
20	0.2	9.34	10.3150	10.8008
	0.4	10.24	10.9039	
	0.6	10.49	10.9399	
	0.8	10.68	10.9632	
	1.0	10.78	10.9073	
	1.2	10.84	10.8136	
	1.4	10.93	10.7626	
30	0.2	7.02	7.9841	10.5498
	0.4	10.21	10.8704	
	0.6	10.53	10.9868	
	0.8	10.77	11.0755	
	1.0	10.86	11.0101	
	1.2	10.98	11.0021	
	1.4	11.04	10.9195	
40	0.2	5.93	6.8935	10.5254
	0.4	10.16	10.8151	
	0.6	10.63	11.1099	
	0.8	10.87	11.2071	
	1.0	11.02	11.1559	
	1.2	11.15	11.2569	
	1.4	11.24	11.2396	
50	0.2	5.72	6.6831	10.5036
	0.4	9.54	10.1630	
	0.6	10.65	11.1323	
	0.8	10.95	11.3189	
	1.0	11.14	11.4174	
	1.2	11.26	11.4441	
	1.4	11.31	11.3662	

Table (5) : Experimental $\overline{pKa}$ values for methyl 3-pyridyl ketonylidene o-aminophenol at different ethanol content at 25C° .

Ethanol %	ml of (0.1 M) NaOH	pH	pKa	$\overline{pKa}$
10	0.2	8.44	9.4054	9.2958
	0.4	8.79	9.4049	
	0.6	8.93	9.3127	
	0.8	9.12	9.3126	
	1.0	9.23	9.2495	
	1.2	9.37	9.2189	
	1.4	9.50	9.1668	
20	0.2	7.87	8.8344	9.3514
	0.4	8.82	9.4351	
	0.6	9.10	9.4836	
	0.8	9.31	9.5039	
	1.0	9.44	9.4615	
	1.2	9.57	9.4216	
	1.4	9.65	9.3196	
30	0.2	7.01	7.9741	9.3778
	0.4	8.98	9.5959	
	0.6	9.27	9.6549	
	0.8	9.47	9.6657	
	1.0	9.61	9.6339	
	1.2	9.73	9.5847	
	1.4	9.86	9.5356	
40	0.2	6.16	7.1237	9.4505
	0.4	8.95	9.5657	
	0.6	9.46	9.8471	
	0.8	9.73	9.9303	
	1.0	9.91	9.9309	
	1.2	10.04	9.9053	
	1.4	10.16	9.8508	
50	0.2	6.27	7.2338	9.3908
	0.4	8.60	9.2143	
	0.6	9.42	9.8065	
	0.8	9.72	9.9200	
	1.0	9.88	9.9103	
	1.2	9.98	9.8426	
	1.4	10.12	9.8081	

Table (2) shows an inverse relationship between dielectric constant versus percentage of ethanol for a different percentages of ethanol solutions . This led and encouraged to plot pK_a or $\overline{pK_a}$ for imines under study versus the dielectric constant D by using Microsoft excel program , and the following graphs were obtained as shown in Fig. 1-6 .

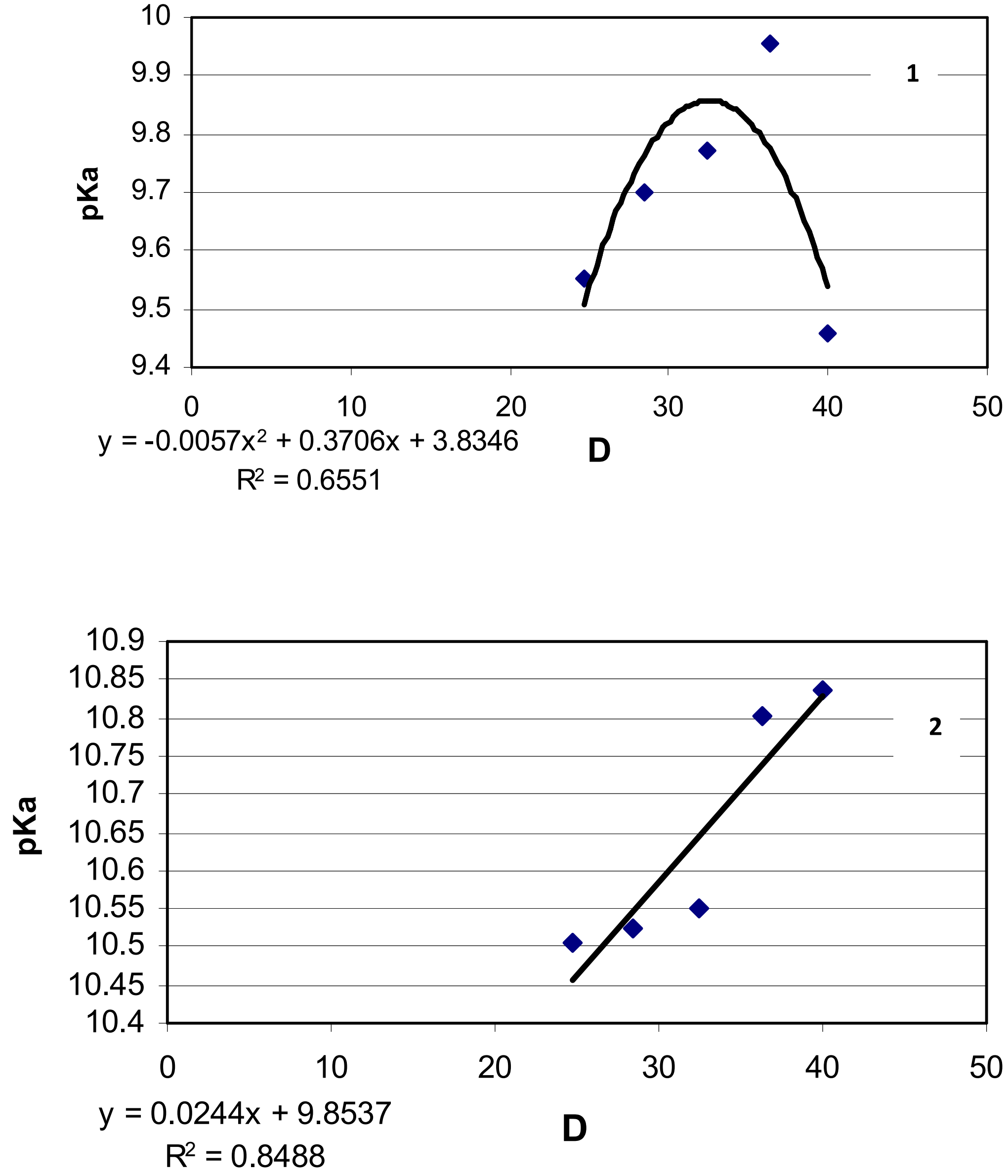


Fig. (1) : pKa versus D for geometrical isomers in :

1. **syn methyl 3-pyridal ketoxime**
2. **anti methyl 3-pyridal ketoxime**

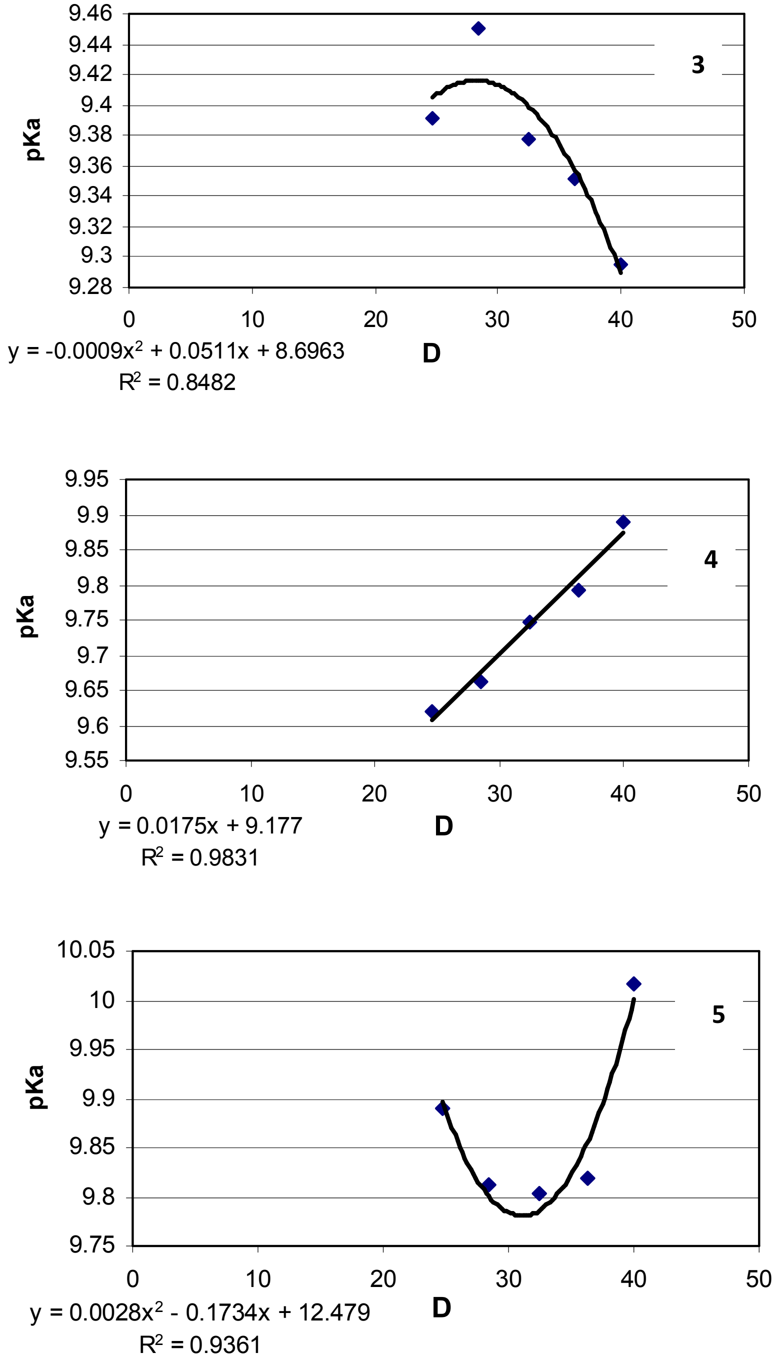


Fig. (2) : pKa versus D of phenolic Schiff bases for :

3. **methyl-3-pyridal–o-amino phenol**
4. **methyl-3-pyridal–m-amino phenol**
5. **methyl-3-pyridal–p-amino phenol**

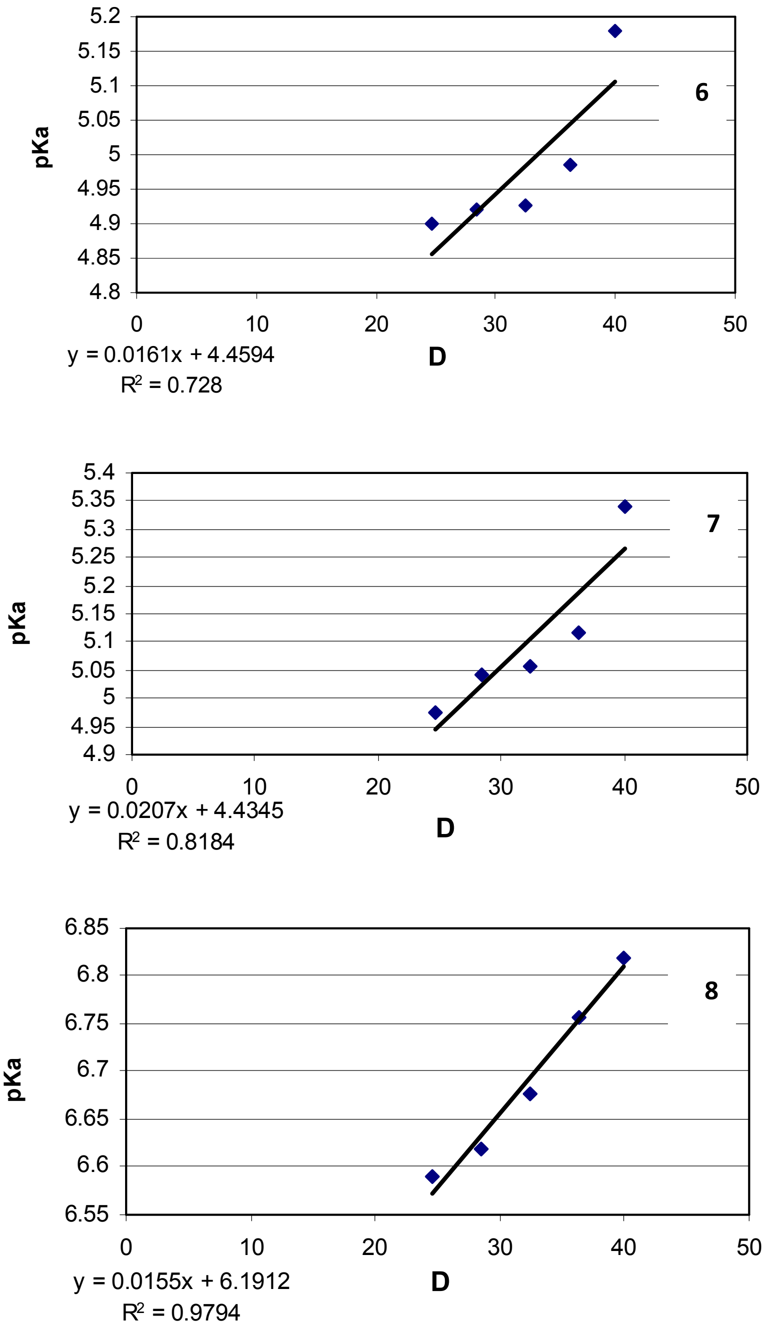


Fig. (3) : pKa` versus D of amino Schiff bases for :

6. **methyl-3-pyridal–o-amino aniline**
7. **methyl-3-pyridal–m-amino aniline**
8. **methyl-3-pyridal–p-amino aniline**

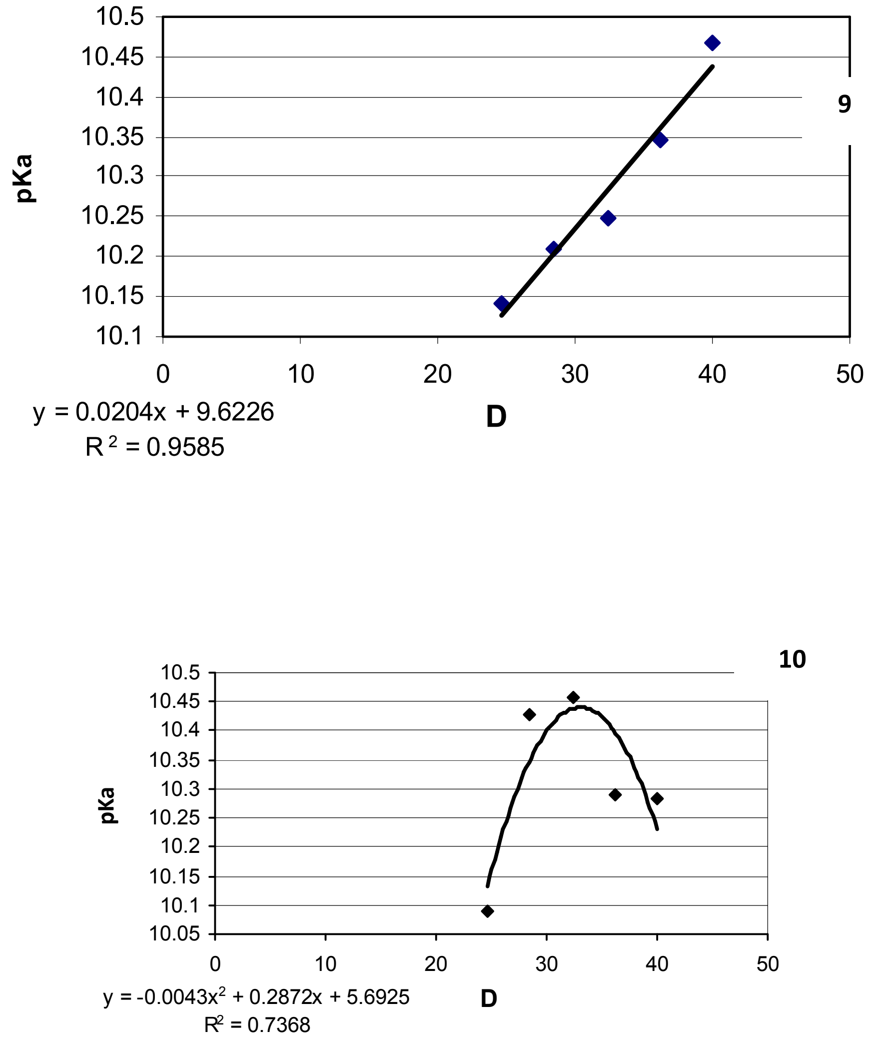


Fig. (4) : pKa versus D of geometrical isomers for :
9. syn methyl-4-pyridal ketoxime
10. anti methyl-4-pyridal ketoxime

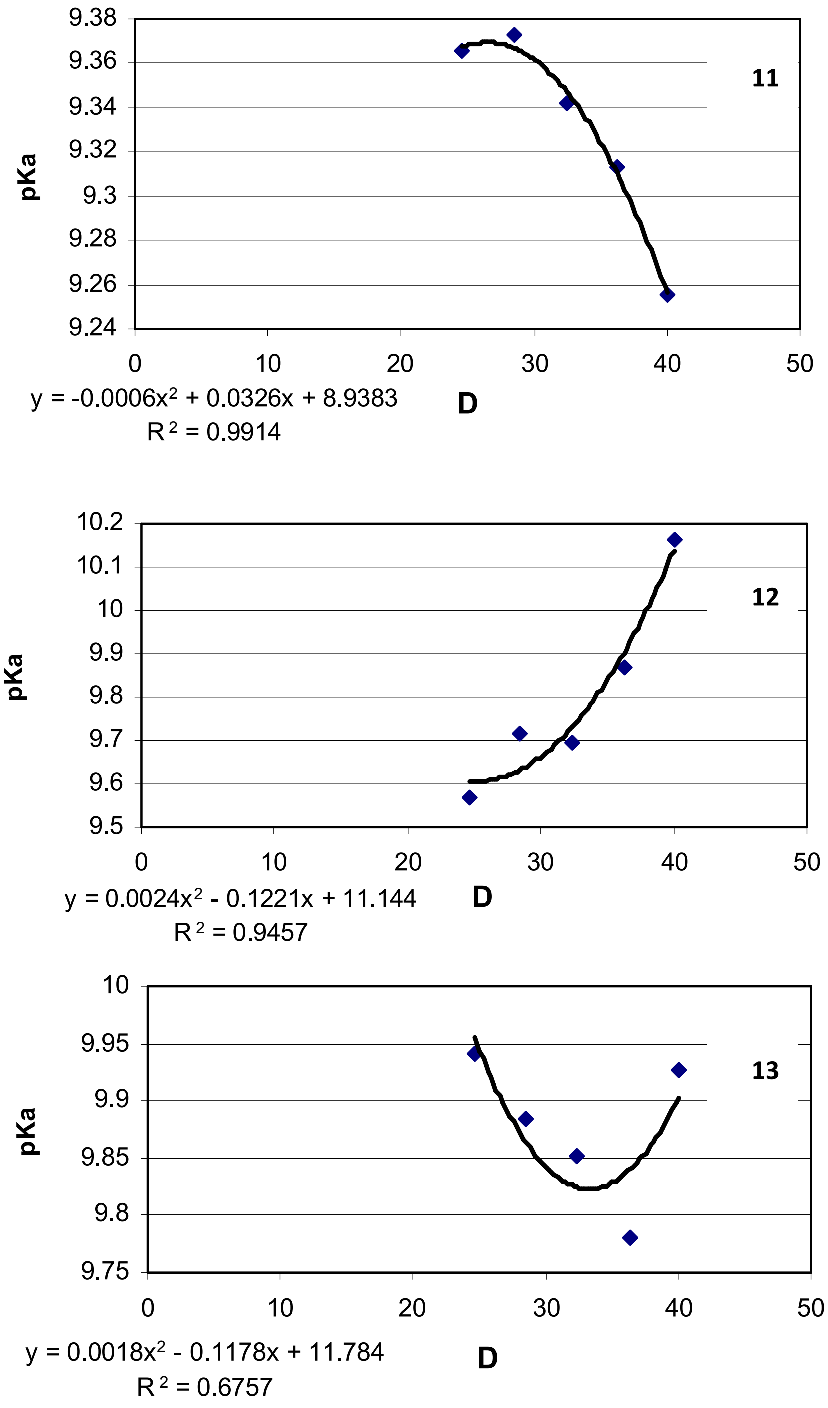


Fig. (5) : pKa versus D of phenolic Schiff bases for :
11. methyl-4-pyridal–o-amino phenol
12. methyl-4-pyridal–m-amino phenol
13. methyl-4-pyridal–p-amino phenol

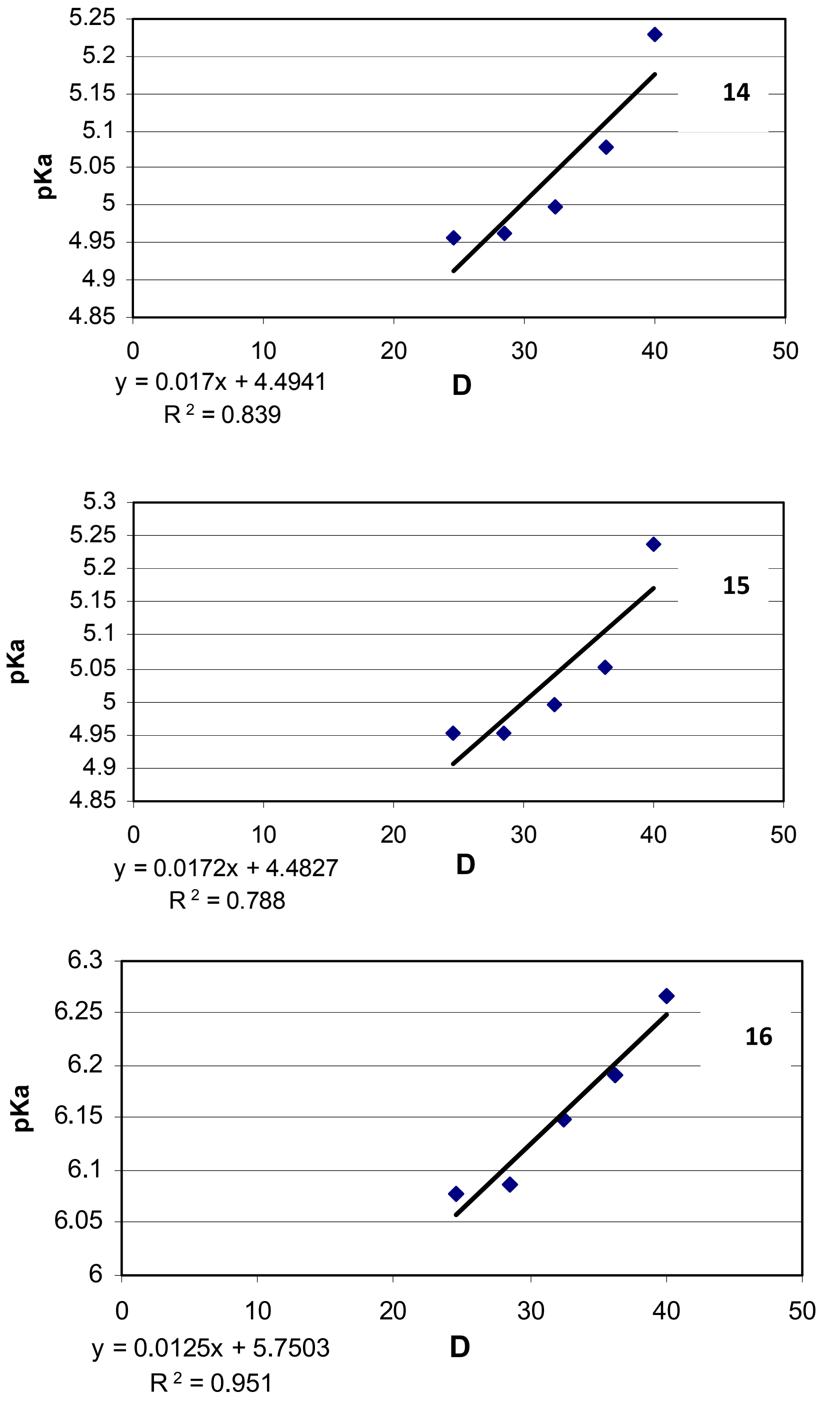


Fig. (6) : pKa` versus D of amino Schiff bases for :
14. methyl-4-pyridal–o-amino aniline
15. methyl-4-pyridal–m-amino aniline
16. methyl-4-pyridal–p-amino aniline

Careful examination of Fig. 1-6 , show three different categories of shapes for the relation mentioned as follows :-

1- A direct linear relationships between pK_a or pK_a versus D for acids numbered 2,4,9 and nitrilium ions 6,7,8,14,15,16. This mean increasing D were accompanied by an increase of pK_a or diminishing the acidites of acid imines. In imine 12 the direct relationship just mentioned converted in to a curve in stead of line . These results were in contrary with theoretical expectation found in equation (4) , as will explain later in this paper .

$F = q_1q_2 \ / \ Dr^2$ ….(4)

F = Force binding the positive and negative ions in acid .

q_1 = Charge of positive ion .

q_2 = Charge of negative ion .

r = Distance between positive and negative ions .

2- The presence of two relationships , the first is a direct curve , then it converted into an inverse curve in the second as in acids numbered 1,3,10,11 . The net shape was in the form of bell as confirmed[14,15] by workers in similar studies .

3- The presence of inverted bell shape as in acids numbered 5,13 .

A question can be raised in this event , why acidity was increased with increasing D in the first part of the curve then suddenly decreased in the second part of the curve . A proper answered to that by considering a high degree of solvation process for ions products as compared with reactant ion . Solvation mean a surrounding of ions products by greater numbered of solvent molecule as compared with reactant molecule . This caused a higher stability of ions product , leading to an increase of ionization process of acid HA . The last can happen in accordance to the principle of Lechalter for an equilibrium reactions . Finally , these results collected were in agreement with literature[16] .

Conclusion

The influence of different ethanol percentages in the rang (10-50)% on pK_a or pK_a^- for some acids derived from 3-acetyl and 4-acetyl pyridines were studied in this work . This needed conversion of ethanol percent in to dielectric constant D of the medium by using specialized equation from literature[13]. When pK_a or pK_a^- values were plotted versus D for all imines , resulted to appearance of three types of relationships as follows:-

1- Direct relations in a forms of lines for nine acids and one curve .

2- Bell shape relationships for four acids .

3- Inverted bell shapes for two acids .

The increase in acidity for any acid by increasing the value of dielectric constant of the medium was interpreted by the favored solvation process of ions products . The reverse of this result was line by decreasing the value of dielectric constant . This interpreted by the favored solvation for reactant molecules relative to ions products .

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