Determination of pKa for some Schiff bases derived from benzaldehyde and amino phenols by conductivity measurement

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الخلاصة:

يُعنى هذا البحث بتقدير الـ pKa لبعض قواعد شيف بواسطة الطريقة التوصيلية, حضرت الايمينات قيد الدراسة عن طريق تفاعلات البنزالديهايد مع p,m,o امينو فينول باستخدام الطريقة القياسية. وقد تم التاكد من هيئاتها التركيبية بالاعتماد على قياسات الاشعة فوق البنفسجية وتحت الحمراء بالاضافة الى درجات الانصهار.

لوحظ عملياً في هذه الدراسة ان الاصرة الهيدروجينية قد تساهم في نقصان قيمة الـ pKa لـ benzylidene -o-hydroxy aniline. كما لوحظ ان لوجود مجموعة الفينول في مواقع p,m من جهة الامين الاولي لقواعد شيف التأثير الواضح على قيم الـ pKa المستحصلة.

اخيراً تم حساب المتغيرات الثرموداينميكية لتفاعلات تأين قواعد شيف التي تُظهر الاشارة الموجبة لقيم ΔG° و ΔH° بينما تمتلك قيم ΔS° الاشارة السالبة والتي تم مناقشتها بالتفصيل.

Abstract:

The aim of this work is concerned with the determination of pka for some Schiff bases by conductivity method.These imines are prepared by reactions of benzaldehyde with o,m,p-amino phenols by standard method.

The structures of these imines are confirmed by using some physical methods, namely, U.V,I.R and melting points.

Experimentally it is observed,that intramolecular hydrogen bonding may contribute in decreasing pka value of benzylidene-o-hydroxyaniline. The presence of phenolic groups at m and p-positions of primary amine side of the Schiff bases, have a noticeable influence on the collected pka values.

The thermodynamic of ionization reactions of these Schiff bases are determined. These showed a positive sign values of ΔG° and ΔH° thermodynamic parameters. Also ΔS° value has a negative sign. These positive and negative signs values are discussed in detail.

Keywords: Schiff bases,conductivity, ionization constant, pka and thermodynamic

Introduction:

Schiff bases are named(1) with numerous methods,as ketimines when are derived from ketones and aldimines when are derived from aldehydes. These molecules have intensive importance, as theirs capability to form metal complexes. They have applications in various fields, as pharmaceutical(2,3,4), biological(5,6,7) analytical(8,9) and industrial(7,10,11) applications.

Conductometric method(12) had used extensively for determination of pka for many compounds. Ives(13) used this method to calculate the pka of mono basic acids on the basis of determination of the equivalent conductances at the infinity dilution of their acid solutions.

Several workers had used the same method for determination of pka values for aliphatic and aromatic acids(14), oximes and phenol derived from benzoyl acetone and dimedone(15), formyl(16) pipyridine and others(17).

The lack of pka values for benzylidene-o,m,p-substituted anilines encourage the author to deal with such important topic, using conductivity method.

Experimental part:

Chemicals:

All compounds used in this study were supplied from (Fluka), (BDH) and (Molckula) companies. These were used directly without any extra purification process.

Preparation of Schiff Bases:

Schiff bases compounds were prepared according to a standard method(18), by reactions of equivalent amounts of the benzaldehyde and the primary aromatic amines. The last were in a forms of ortho, meta and para amino phenols. These reactions were carried out in(10-20)ml ethanol solvent. The final mixtures were refluxed for about 1.5hr, cooling and recovery of the products. Purifications of products were performed by recrystallization in ethanol, followed by drying the final products. The melting points of Schiff bases were measured as shown in Table(1).

The I.R. spectra of products under study were measured in the range between (400-4000)cm^{-1} and with KBr disc method. Also the U.V. spectra of products were measured with concentration (10^{-4}M) against a blank.

Preparation of conductivity water:

The usual distilled water was distillated twice to get conductivity water which has specific conductivity value of 1 to 1.2x10^{-6} ohm^{-1}.cm^{-1}.

Preparation of Sodium Hydroxide solution:

A standard 10^{-3}M of potassium hydrogen phthalate was prepared. This solution was titrated with sodium hydroxide using ph.ph indicator.After evaluation of concentration of unknown NaOH, finally diluted to 10^{-3}M.

Preparation of Schiff Bases Solutions:

At the beginning a 10^{-3}M stock solution for each acid Schiff base was prepared. This solution was diluted to prepare a set of solutions having various concentrations (2,4,6,8)x10^{-4}. The conductivites for all solutions were measured at temperatures range(20-60) ºC.

Preparation of the Sodium Salts of Schiff Bases:

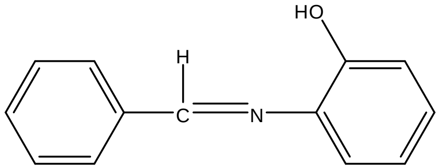
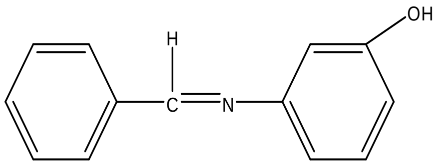
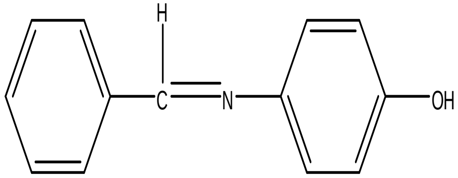
10ml of 10^{-3}M solution of acid Schiff bases was taken and titrated versus 10^{-3} of NaOH, using ph.ph indicator. The final mixture was diluted to 50ml with 50% ethanol-water solvent. From the final solution other solutions mixtures were prepared of concentrations (0.4,0.8,1.2,1.6)x10^{-4}.

The conductivites were measured at a range of temperatures (20-60)ºC.

Instrumentations:

1. The melting points were measured by using Sturart melting point apparatus, model smp30.
2. The desired temperatures under study were fixed by using a water Memmert thermostat model L200.
3. The I.R. spectra of solid Schiff bases compounds were measured by KBr disk method and by using a computerized Bruker Tensor-27.
4. The U.V. spectra of ethanolic solutions of Schiff bases compounds were measured by a double beam computerized U.V.1800 Shimadzu spectrophotometer and using a matched 1x1x3 cm^3 silica cells.
5. The conductivites were measured by using Wissenschaftlich-technisches werkstatten model D8120-Weilheim.

Table (1):Melting points,I.R.and U.V.spectral data for benzylidene-o,m,p-hydroxy aniline

Symbol	Structure	m.p. ºC	I.R.spectra cm^{-1}			U.V. spectra λ_{nm} (ε_{max}) in ethanol
			OH	C=N	Arom	
I		89-91	3328.78	1625.18	1574.10	435(374),420(373),272(1988)
II		222decomp.	3374.60	1622.95	1539.74	407(650)
III		78-80	3327.25	1625.20	1574.26	435(840),422(840),280(895)

Results and Discussion:

Conductometric method had used as important sensitive, fast and accurate method for determination of pka of the mentioned acids. Previously was used in many studies to determination of pka for different acids.(19)

For that reason the equivalent conductance for acid electrolytes must be calculated by using the following equation:

$$\Lambda = \frac{1000\,K}{C} \qquad \ldots\ldots.\ (1)$$

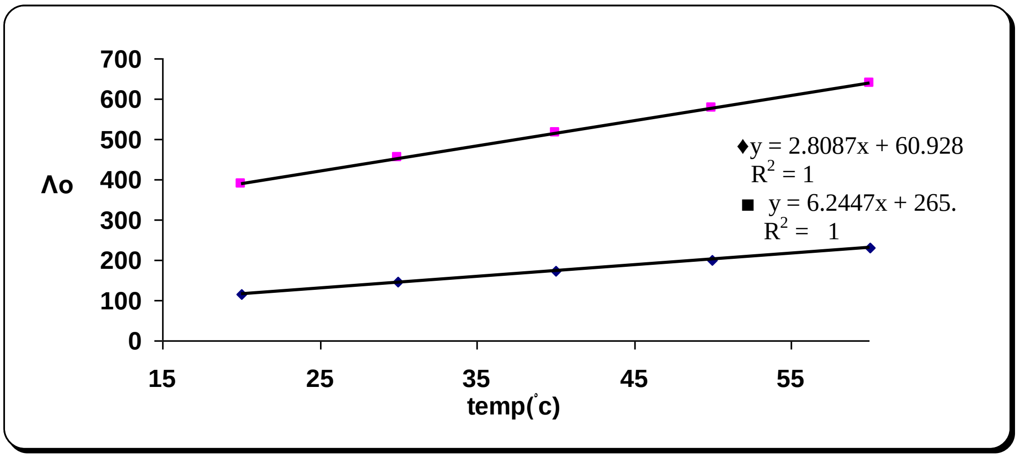
Λ=the equivalent conductance of the electrolyte at any concentration.
K=the specific conductance.
C=the molar concentration.

There are two types of electrolytes, the strong electrolytes which give straight lines when the relationship is drawn between the equivalent conductance of electrolytes at constant temperature against square root of concentration and the weak electrolytes which give curve at the same temperature.

The equivalent conductance of sodium chloride was taken from reference(20) at (20,30,40,50,60)°C. Similarly, also with respect of hydrochloride acid. Finally, the relationship was drawn between Λ_O against the mentioned temperatures as in the Figure (1). Table (2) shows Λ_O values with temperature range between (20-60) °C.

Table(2): The equivalent conductance at infinite dilution for sodium chloride and hydrochloric acid electrolyte.

Temperatures (°C)	Λ_o NaCl $ohm^{-1}\ cm^2\ equiv^{-1}$	Λ_o HCl $ohm^{-1}\ cm^2\ equiv^{-1}$
20	117.102	390.204
30	145.189	452.651
40	173.276	515.098
50	201.363	577.545
60	229.45	639.992



Figure(1): The relationship between Λo and the centigrade temperatures of: ♦ sodium chloride, ■ hydrochloric acid.

Different concentrations of solutions for the organic acids were prepared, the conductances for these solutions were determined and their equivalent conductances were calculated, as shown in Table (3).

Table (3): The equivalent conductances of benzylidene-o,m,p-hydroxy aniline at different temperatures.

Compound Name	**M x10^{-3} √**	**Equivalent conductance:ohm^{-1} cm^{2} equiv^{-1}.**				
		20˚c	30˚c	40˚c	50˚c	60˚c
Benzylidene-o-hydroxyaniline	0.0141	31.50	42.50	65.00	80.00	112.50
	0.0200	16.75	22.50	31.25	46.25	62.50
	0.0245	8.75	12.83	16.50	20.00	26.67
	0.0283	5.19	7.63	10.63	12.38	15.63
	0.0316	3.35	4.20	5.25	6.30	8.30
Benzylidene-m-hydroxyaniline	0.0141	40.00	62.50	85.00	135.00	180.00
	0.0200	15.00	22.25	22.50	35.00	53.75
	0.0245	6.33	8.42	10.42	16.00	19.17
	0.0283	3.38	4.88	6.63	8.88	11.50
	0.0316	2.10	2.80	3.60	4.50	7.10
Benzylidene-p-hydroxyaniline	0.0141	30.00	45.00	77.50	107.50	145.00
	0.0200	11.00	17.50	29.00	40.50	65.00
	0.0245	6.25	9.33	16.50	23.16	36.00
	0.0283	3.25	5.00	9.00	14.75	22.00
	0.0316	1.50	1.80	3.25	4.50	6.50

Similarly Table (4) show the equivalent conductance at various temperatures and concentrations of the sodium salt of organic acids under study.

Table (4): The equivalent conductances for sodium salt of benzylidene-o,m,p-hydroxy aniline at different temperatures

Compound Name	**M x10^{-3} √**	**Equivalent conductance:ohm^{-1} cm^{2} equiv^{-1}.**				
		20˚c	30˚c	40˚c	50˚c	60˚c
Sodium salt of benzylidene-o-hydroxy aniline	6.3200	202.5	210	250	325	400
	8.9000	107.5	125	150	187.50	250
	10.9000	76.67	91.67	116.67	150	191.67
	12.6000	60.63	71.88	90.63	109.38	137.50
	14.1000	47.50	60	77.5	100	122.50
Sodium salt of benzylidene-m-hydroxy aniline	6.3200	100	150	175	210	275
	8.9000	67.50	88.75	120	137.50	175
	10.9000	52.50	61.67	75	108.33	150
	12.6000	47.50	55.63	68.75	93.75	131.25
	14.1000	41.50	45.50	65	90	110
Sodium salt of benzylidene-p-hydroxy aniline	6.3200	82.50	202.50	412.50	600	900
	8.9000	68.75	111.25	218.75	400	500
	10.9000	48.33	75.83	125	166.67	208.33
	12.6000	40.63	60	81.25	106.25	162.50
	14.1000	34.50	50	60	97.50	135

The relationship between Λ against square root of the molar concentrations of electrolytic solutions of the sodium salt of the organic acids at five temperatures gave a straight lines which appears in Figure(2), the intercept of equation represents the equivalent conductance at the infinity dilution of acid salt and a different temperatures.

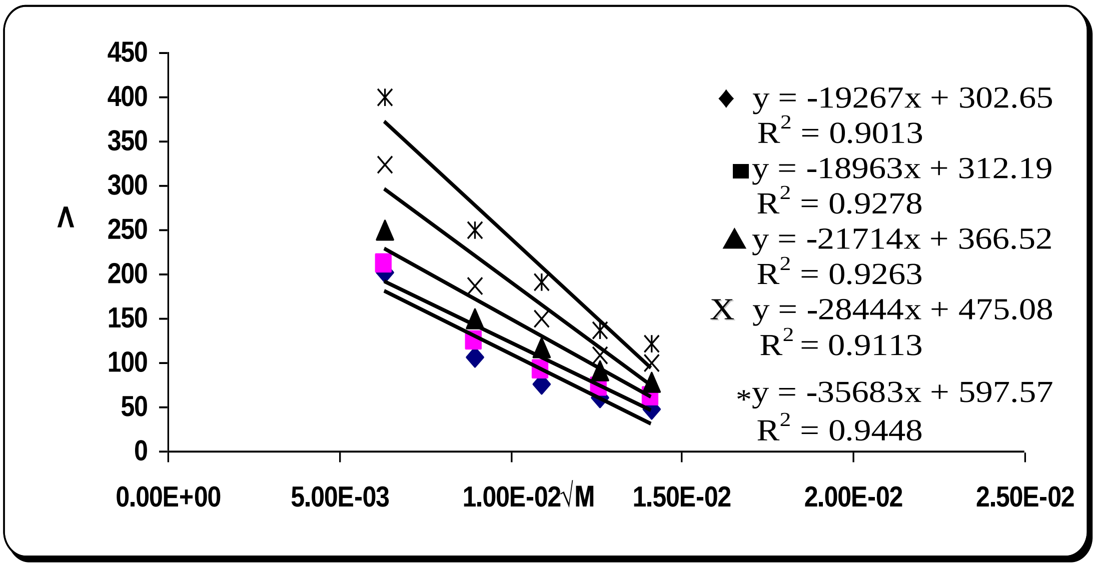


Figure (2):The relationship between Λ versus√M for sodium salt of Benzylidene-O-hydroxyaniline at different temperatures
(♦ 20, ■30, ▲40, X 50, *60) ^{O}C

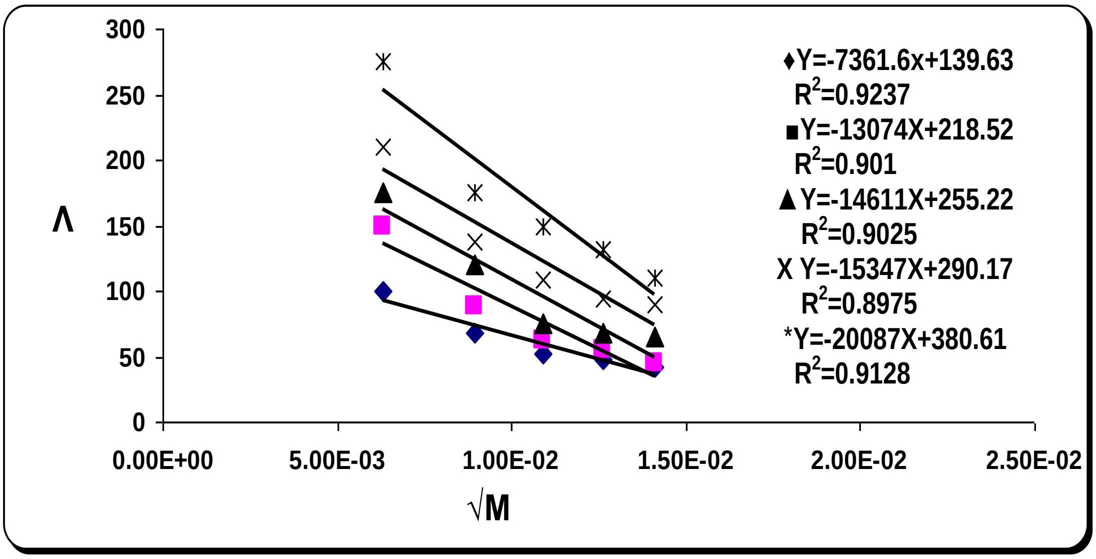


Figure (3):The relationship between Λ versus√M for sodium salt of Benzylidene-m-hydroxyaniline at different temperatures.
(♦ 20, ■30, ▲40, X 50, *60) ^{O}C

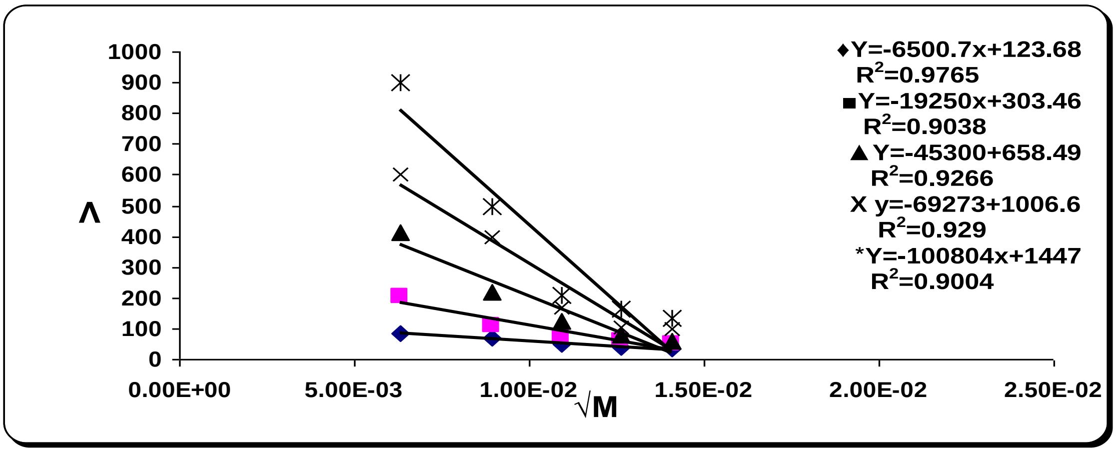


Figure (4): The relationship between Λ versus√M for sodium salt of Benzylidene-P-hydroxyaniline at different temperatures. (♦ 20, ■30, ▲40, X 50, *60) ^{O}C

On the other hand,the relationships between equivalent conductances of organic acids under study,versus √M, show a curved shapes. These finding insist(22) (Figures 5,6 and 7) that Λ_o for each acid cannot determined by this method.

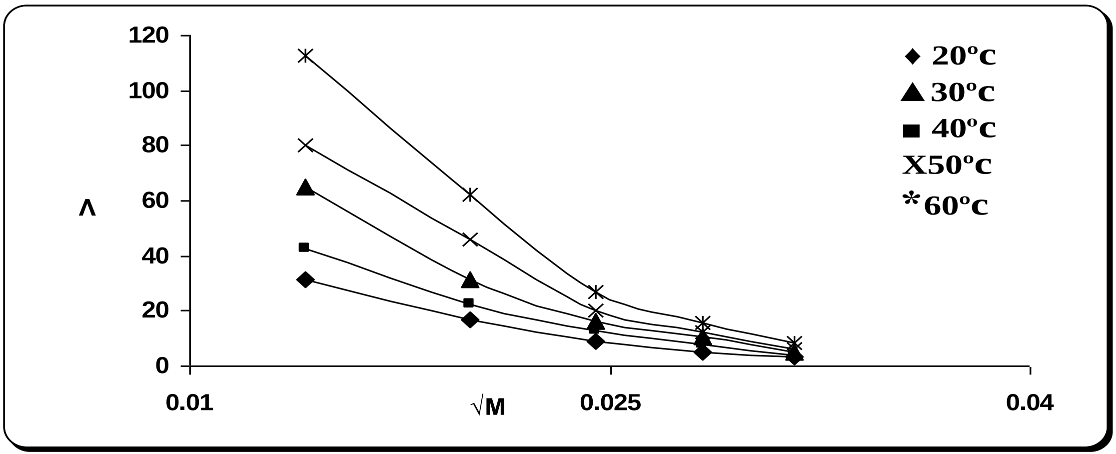


Figure (5): The relationship between Λ versus √M for Benzylidene-o-hydroxyaniline at different temperatures

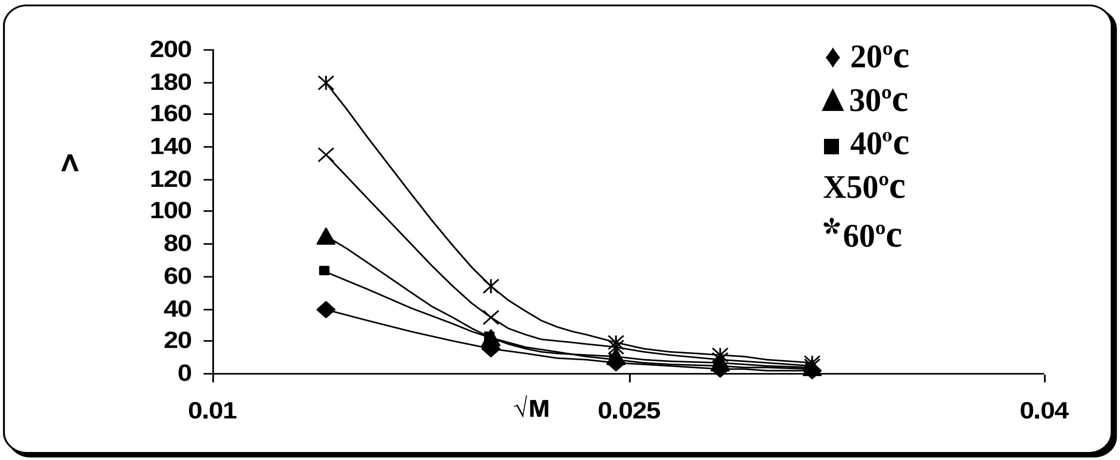


Figure (6):The relationship between Λ versus √M for Benzylidene-m-hydroxyaniline at different temperatures

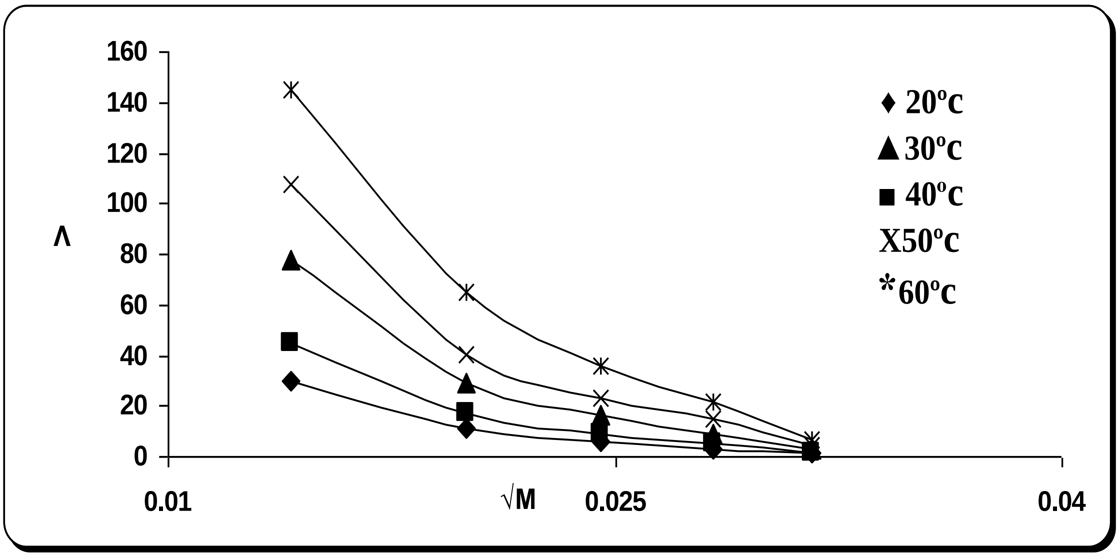


Figure (7): The relationship between Λ versus √M for Benzylidene-p-hydroxyaniline at different temperatures

Another alternative method$^{(21,22,23)}$ according to Kohlrausch assumption was used as in the following equation as:

$\Lambda_o + \Lambda_o = \Lambda_o + \Lambda_o$............ (2)
NaA HCl HA NaCl
$\Lambda_o = \Lambda_o + \Lambda_o - \Lambda_o$ ………. (3)
HA NaA HCl NaCl

This facilitates the evaluation of Λ_O HA at any desired temperature.

Tables (5,6,7) showed the equivalent conductances Λ, Λ_o, Kav and pKa values of acids under study.

Table(5): The equivalent conductance and pka of Benzylidene-o-hydroxyaniline at different temperatures.

t(°c)	Conc x10^{-4} (M)	Λ ohm^{-1} cm^2 equiv^{-1}.	Λ_o ohm^{-1} cm^2 equiv^{-1}.	α X10^{-3}	K_aX10^{-7} Mole.L^{-1}	K_{av}X10^{-7} Mole.L^{-1}	pK_{av}
20	2	31.50	575.8	54.7065	6.3319	2.4443	6.6118
	4	16.75		29.0899	3.4863		
	6	8.75		15.1962	1.4069		
	8	5.19		9.0135	0.6559		
	10	3.35		5.8179	0.3405		
30	2	42.50	585.3	72.6123	11.3706	4.4724	6.3495
	4	22.50		38.4418	6.1471		
	6	12.83		21.9204	2.9476		
	8	7.63		13.0360	1.3775		
	10	4.20		7.1758	0.5187		
40	2	65.00	639.6	101.6260	22.9916	8.0112	6.0963
	4	31.25		48.8587	10.0396		

	6	16.50		25.7974	4.0988		
	8	10.63		16.6198	2.2470		
	10	5.25		8.2083	0.6793		
50	2	80.00	748.2	106.9233	25.6020	9.8479	6.0067
	4	46.25		61.8150	16.2912		
	6	20.00		26.7308	4.4048		
	8	12.38		16.5464	2.2270		
	10	6.30		8.4202	0.7150		
60	2	112.50	870.7	129.2064	38.3424	13.9793	5.8545
	4	62.50		71.7813	22.2045		
	6	26.67		30.6305	5.8071		
	8	15.63		17.9511	2.6252		
	10	8.30		9.5326	0.9174		

Table(6): The equivalent conductance and pka of Benzylidene-m-hydroxyaniline at different temperatures.

t(°c)	Conc x10^{-4} (M)	Λ ohm^{-1} cm^2 equiv^{-1}.	Λ_o ohm^{-1} cm^2 equiv^{-1}.	α X10^{-3}	$K_{aX10}{}^{-7}$ Mole.L^{-1}	$K_{avX10}{}^{-7}$ Mole.L^{-1}	pK_{av}
20	2	40.00	412.7	96.9227	20.8039	5.7044	6.2438
	4	15.00		36.3460	5.4832		
	6	6.33		15.3380	1.4335		
	8	3.38		8.1899	5.4103		
	10	2.10		5.0884	2.6025		
30	2	62.50	491.6	127.1359	37.0341	9.7060	6.0130
	4	22.25		45.2604	8.5828		
	6	8.42		17.1277	1.7908		
	8	4.88		9.9268	0.7962		
	10	2.80		5.6957	0.32627		
40	2	85.00	528.3	160.8934	61.7011	14.6807	5.8333
	4	22.50		42.5894	7.5783		
	6	10.42		19.7236	2.3810		
	8	6.63		12.5497	1.2759		
	10	3.60		6.8143	0.4675		
50	2	135.00	563.3	239.6592	151.0891	35.0399	5.4554
	4	35.00		62.1339	16.4650		
	6	16.00		28.4040	4.9822		
	8	8.88		15.7642	2.0199		
	10	4.50		7.9886	0.6433		
60	2	180.00	653.7	275.3557	209.2762	49.5539	5.3049
	4	53.75		82.2243	2.9465		
	6	19.17		29.3254	5.3156		
	8	11.5		17.5922	2.5202		
	10	7.1		10.8613	1.1927		

Table(7): The equivalent conductance and pka of Benzylidene-p-hydroxyaniline at different temperatures.

t(°c)	Conc x10^{-4} (M)	Λ ohm^{-1} cm^{2} equiv^{-1}.	Λ$_{o}$ ohm^{-1} cm^{2} equiv^{-1}.	α X10^{-3}	K$_{a}$X10^{-7} Mole.L^{-1}	K$_{av}$X10^{-7} Mole.L^{-1}	pK$_{av}$
20	2	30	397.1	75.5477	12.3478	3.5395	6.4511
	4	11		27.7008	3.1568		
	6	6.25		15.7391	1.5100		
	8	3.25		8.1843	0.5403		
	10	1.5		3.7774	0.1432		
30	2	45	576.6	78.0437	13.2128	3.8631	6.4131
	4	17.5		30.3503	3.8001		
	6	9.33		16.1811	1.5968		
	8	5.00		8.6715	0.6068		
	10	1.8		3.1217	0.0775		
40	2	77.5	931.6	83.1902	15.0973	4.3779	6.3587
	4	29.0		31.1292	4.0005		
	6	16.50		17.7115	1.9161		
	8	9.00		9.6608	0.7539		
	10	3.25		3.4886	0.1221		
50	2	107.5	1279.7	84.0041	15.4078	4.5494	6.3420
	4	40.5		31.6480	4.1371		
	6	23.16		18.0979	2.0014		
	8	14.75		11.5261	1.0752		
	10	4.5		3.5164	0.1241		
60	2	145	1720	84.3023	15.5223	5.1225	6.2905
	4	65		37.7907	5.9370		
	6	36		20.9302	2.6845		
	8	22		12.7907	1.3258		
	10	6.5		3.7791	0.1434		

From tables (5,6,7), the following conclusions were deduced:

1- The acidity of any acid was increased by increasing temperature. This means that more protons were liberated from any acid by elevation of temperature between (20-60) ^{0}C. The last is accompanied by decreasing pka value of acid.
2- At any constant temperature the aciditiy was increased in the following order m>o>p, with exception of benzylidene-o-hydroxy aniline at temperature 293K.This may be due to the stronger hydrogen bonding exist at such temperature.

This order can be accepted if we considered the two opposing effect of phenolic group, namely the inductive and resonance effects. It seems possible that resonance effect of (o-OH) group is more effective as compared with inductive effect,beside the hydrogen bonding.Hence these three last effects might be responsible on decreasing the acidity of o-phenolic acid as compared with m-phenolic acid at any temperature.

The lower acidity of benzylidene-p-hydroxy aniline at any temperature can be accepted due to the stronger donation property of phenolic group at p-position supported by the σp value of (-0.37) of Hammet equation.

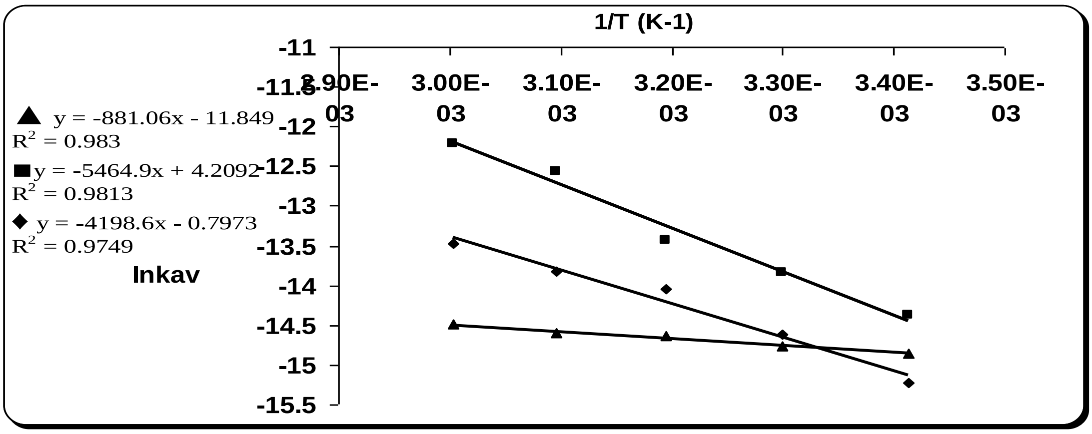
These interesting results encourage the worker to deal with thermodynamic of ionization reactions of acids, namely, ΔG^0, ΔH^0 and ΔS^0.

ΔH^o values are calculated from integrated Vant Hoff equation at all temperatures by using the following equation:

$\mathrm{InKa} = \mathrm{constant} - \Delta H^o/RT$(24) ……….. (4)

Ka =ionization constant.
R=the gas constant =8.314 J.K^{-1}.mole$^{-1.}$
T=absolute temperature.

According to this equation a linear plot was obtained on drawing Ink$_a$ versusT^{-1} with a slope equal ($-\Delta H/R$) as shown in Figure (8).



Figure(8): The relationship between InK$_{av}$ against 1/T of benzylidene- ♦ o, ■m,▲p -hydroxy aniline compounds.

The positive values of heats (enthalpies) (ΔH^o) indicated the ionization reactions were endothermic. These results were accepted theortically.

The change in free energy ΔG^0 for ionization reactions of acids were calculated by equation(25,26):

$\Delta G^{\mathbf{0}} = -RTInK.$ ……………. (5)

The positive values of ΔG^0 listed as in Table (8) indicate that ionization reactions are nonspontaneous. These expected results could be accepted because all organic acids under study have covalent bonding. Thus it was difficult to ionize phenol group as compared with the ionic bonding.

ΔS^0 values were calculated by Gibbs equation:

$\Delta G^{\mathbf{0}} = \Delta H^{\mathbf{0}} - T\,\Delta S^{\mathbf{0}}$ ……………… (6)

Table (8): The thermodynamic parameters and pka of benzylidene-o,m,p-hydroxyaniline at different temperatures.

Compound Name	**Temp K°**	**$K_{avX10}{}^{-7}$ Mole.L^{-1}**	**Ink$_{av}$**	**ΔG° J.mol^{-1}**	**ΔH° J.mol^{-1}**	**ΔS° J.mol^{-1}.K^{-1}**	**$\overline{\Delta G^\circ}$ J.mol^{-1}**	**$\overline{\Delta H^\circ}$ J.mol^{-1}**	**$\overline{\Delta S^\circ}$ J.mol^{-1}.K^{-1}**
Benzylidene-o-hydroxy aniline	293	2.4443	-15.2243	37086.43	35144.20	6.6288-	**36981.786**	**37476.29**	**6.62876-**
	303	4.4724	-14.6202	36830.36	34821.85	6.6287-			
	313	8.0112	-14.0373	36529.01	38603.81	6.6288-			
	323	9.8479	-13.8308	37141.53	39282.62	6.6288-			
	333	13.9793	13.4805-	37321.60	39528.97	6.6287-			
Benzylidene-m-hydroxy aniline	**293**	5.7044	-14.3769	35022.16	24768.54	34.9953-	**34480.886**	**23527.36**	**-34.9953**
	303	9.7060	-13.8453	34878.28	24274.70	34.9953-			
	313	14.6807	-13.4316	34952.81	23999.29	-34.9953			
	323	35.0399	-12.5616	33733.20	22429.72	34.9953-			
	333	49.5539	-12.2150	33817.98	22164.55	34.9953-			
Benzylidene-p-hydroxy aniline	**293**	3.5395	-14.8541	36184.62	65048.81	-98.5126	**38160.364**	**68994.80**	**98.5126-**
	303	3.8631	-14.7666	37199.16	67048.48	-98.5126			
	313	4.3779	-14.6415	38101.31	68935.75	-98.5126			
	323	4.5494	-14.6031	39215.49	71035.05	-98.5126			
	333	5.1225	-14.4845	40.101.24	72905.92	98.5126-			

Table(8) shows that the ΔS^0 values have negative signs. This means that, the ionization products are less random as compared with organic reactants. This was possible for bases having a hydrogen bonding stated before.

All these results were in agreement with other earlier study in the same field (16,17,27).

Conclusions:

1. The conductivities of phenolic acids were increased with increasing of temperatures.
2. The conductivities of phenolic sodium salts of Schiff bases were increased with increasing of temperatures.
3. Generally the acidity of acid phenols was increased with increasing of temperatures.
4. At any constant temperature the acidity of acid phenols was increased in the following order m>o>p, with exception of benzylidene–o-hydroxy aniline at temperature293K. This may be due to the stronger hydrogen bonding exist at such temperature.

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