



Determination of pKa values for new Schiff bases derived from benzaldehyde and salicylaldehyde with glycine and β - alanine

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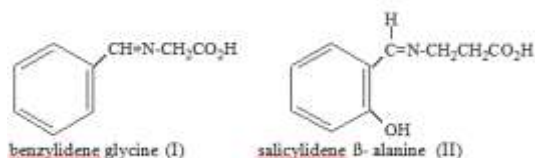
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Abstract

Two new Schiff base acids, namely benzylidene glycine(I) and salicylidene β - alanine(II) were prepared by new procedure using sodium hydroxide as catalyst.

The main aim of the project was the determination of pKa values for these acidic imines using conductivity method, the method as found simple, precise and accurate for determination of pKa of compounds, All conductivities parameters of benzylidene glycine and salicylidene β -alanine and their sodium salts in deionized water were mentioned . The variation of acidities of acids(I) and(II) were also included. The thermodynamic reactions parameters namely ΔG° , ΔH and ΔS° for these ionization reactions of acids were discussed and interpreted .



Introduction

The acid dissociation constant was among the most frequently used physio chemical parameters and its determination was of interest to a wide range of research fields.

The conductivity method was applied originally and previously for the determination of ionization constants for numerous mono basic carboxylic acid[1]. Also conductivities were applied for the determination of thermodynamic dissociation constants for salicylic [2] acid in binary mixed solvent systems at 298K. Electric conductivity was used in the determination of acidity constants of perfluoroalkanoic [3] acids, The previous method was used in the determination of acid dissociation constants of some mono basic organic acids [4] in acetonitril and dissociation constants of cysteine[5] in aqueous solutions .Conductance measurements were applied in studying dissociation and association constants with thermodynamic functions of alanine [6] in DMF mixtures. In 2013 a group of workers[7] were developed and compared fourteen methods of pKa values Azzouz and Maree had determined pKa values for anumber of acid imines

derived from benzoyl acetone –dimedone[8] and benzoyl acetonitrile[9].

This manuscript was a continuation of previous study[10]. It deals with synthesis of Schiff bases derived from benzaldehyde and salicylaldehyde with some amino acids by a new developed method.

The main purpose of this investigation was to determine the influence of temperature in the range (293-333) K^o on pKa values for ionization reactions of imines with particular attention to the thermodynamic parameters namely ΔG° , ΔH and ΔS° which were included and discussed.

Experimental

All chemicals used throughout this work were supplied from Fluka, Aldrich and Molecule companies.

They were benzaldehyde, salicylaldehyde, glycine and β -alanine while ethanol was bought (pure) from local market.

Schiff bases (I) and (II) under study were prepared by using standard method[11], or by mixing equimolar (10^{-2} mole) amounts of benzaldehyde, salicylaldehyde with appropriate amount of glycine and β -alanine

respectively. About 15 ml of absolute ethanol with 0.01 mole of sodium hydroxide were added. The final mixture was refluxed, cooled, followed by filtration and recrystallization from ethanol. Pure Schiff bases[8] (I) and (II) had a melting points of 195C° (decomp.) and 120C° respectively.

Deionized water was prepared after multiple redistillation of water. It has a conductivity range value of $(0.2-1.0) \times 10^{-6} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$.

A stock solutions of Schiff bases (I)-(II) of concentration $(10^{-3}) \text{ mol} \cdot \text{dm}^{-3}$ were prepared, followed by dilution to the required concentration as in Tables 3-4. Similarly the sodium salt of Schiff bases (I)-(II) were prepared using a similar procedure adopted elsewhere [9]. A stock solution of each salt was prepared of concentration $(10^{-3}) \text{ mol} \cdot \text{dm}^{-3}$ and diluted to the required concentration range as in Table (1-2).

All solutions of Schiff bases and their sodium salts were maintained at fixed temperature range (293-333)K° by using a thermostat.

Instrumentation

1-The conductance of any solution was measured using conductivity bridge model LF 42,NO.87CW

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2- The temperature was controlled for any solution using thermostat model L200 type Memmert, manufactured by Searle.

3- All graphs were preformed using Microsoft excel program 2010 .

Results and discussion

At the beginning of this investigation , it was thought of great importance to confirm the chemical structures of Schiff bases (I)-(II). These were accomplished by physical method using melting points beside UV-IR spectra mentioned in a previous manuscript[10].

This encourage the workers in this investigation to determine the acidities of Schiff bases (I)-(II) as measured by pKa at temperature range (293-333)K° in deionized water, using a conductivity measurements.

The equivalent conductance versus the square root of concentration solutions of sodium salts of Schiff bases (I)-(II) at temperatures stated were shown in Tables (1-2).

Table (1): specific conductance and equivalent conductance of salicylidene β -alanine at different temperatures

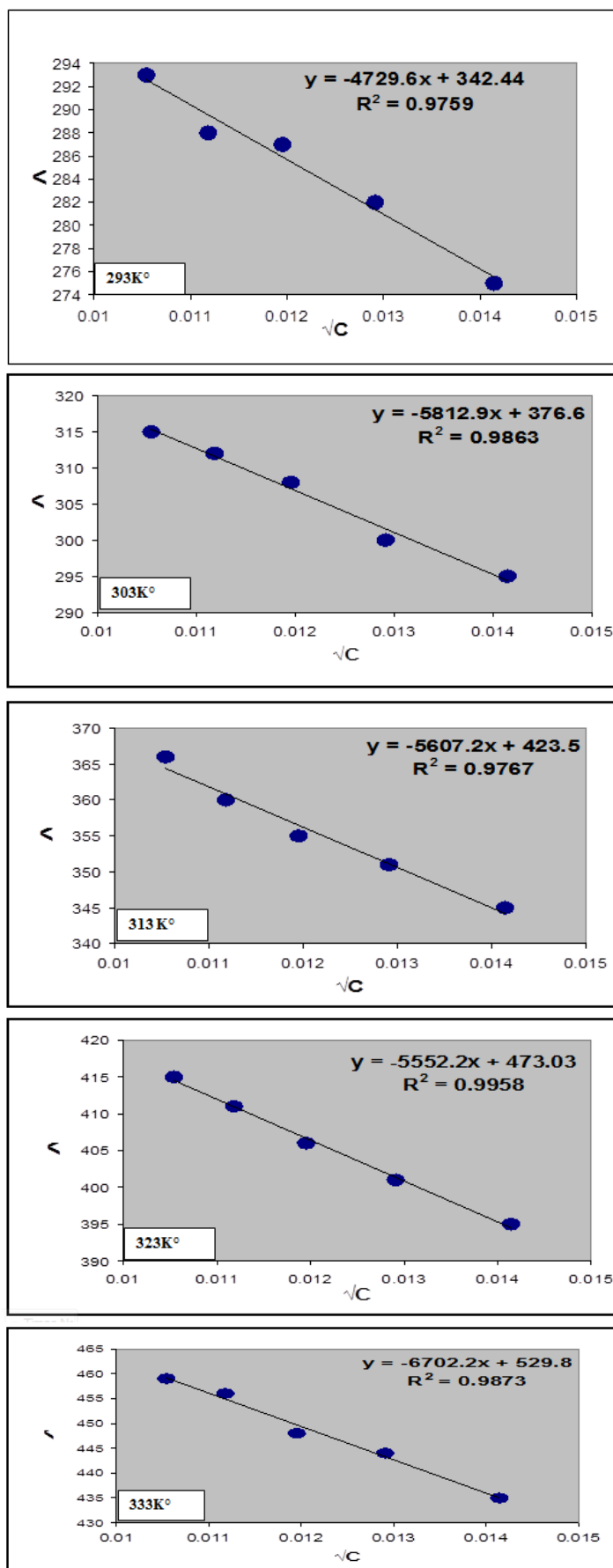
293 K°			
$K \cdot 10^{-6}$ $\text{ohm}^{-1} \cdot \text{cm}^{-1}$	Λ $\text{Ohm}^{-1} \cdot \text{cm}^2 \cdot \text{equi}^{-1}$	Conc. $\text{mol} \cdot \text{dm}^{-3}$	\sqrt{C}
5.5	275	0.0002	0.014142135
4.7	282	0.00016	0.012909918
4.1	287	0.00014	0.01195228
3.6	288	0.00012	0.011180339
3.2	293	0.00011	0.01054092
303 K°			
$K \cdot 10^{-6}$ $\text{ohm}^{-1} \cdot \text{cm}^{-1}$	Λ $\text{Ohm}^{-1} \cdot \text{cm}^2 \cdot \text{equi}^{-1}$	Conc. $\text{mol} \cdot \text{dm}^{-3}$	\sqrt{C}
5.9	295	0.0002	0.014142135
5.1	311	0.00016	0.012909918
4.4	318	0.00014	0.01195228
3.9	312	0.00012	0.011180339
3.5	315	0.00011	0.01054092
313 K°			
$K \cdot 10^{-6}$ $\text{ohm}^{-1} \cdot \text{cm}^{-1}$	Λ $\text{Ohm}^{-1} \cdot \text{cm}^2 \cdot \text{equi}^{-1}$	Conc. $\text{mol} \cdot \text{dm}^{-3}$	\sqrt{C}
6.9	345	0.0002	0.014142135
5.8	351	0.00016	0.012909918
5.1	355	0.00014	0.01195228
4.5	361	0.00012	0.011180339
4.1	366	0.00011	0.01054092
323 K°			
$K \cdot 10^{-6}$ $\text{ohm}^{-1} \cdot \text{cm}^{-1}$	Λ $\text{Ohm}^{-1} \cdot \text{cm}^2 \cdot \text{equi}^{-1}$	Conc. $\text{mol} \cdot \text{dm}^{-3}$	\sqrt{C}
7.9	395	0.0002	0.014142135
6.6	411	0.00016	0.012909918
5.7	416	0.00014	0.01195228
5.1	411	0.00012	0.011180339
4.6	415	0.00011	0.01054092

Table (2): Specific conductance and equivalent conductance of benzylidene glycine at different temperatures.

293 K°			
$K \cdot 10^{-6}$ $\text{ohm}^{-1} \cdot \text{cm}^{-1}$	Λ $\text{Ohm}^{-1} \cdot \text{cm}^2 \cdot \text{equi}^{-1}$	Conc. $\text{mol} \cdot \text{dm}^{-3}$	\sqrt{C}
6.5	325	0.0002	0.014142135
5.6	336	0.00016	0.012909918
5.1	357	0.00014	0.01195228
4.6	368	0.00012	0.011180339
4.4	396	0.00011	0.01054092
303 K°			
$K \cdot 10^{-6}$ $\text{ohm}^{-1} \cdot \text{cm}^{-1}$	Λ $\text{Ohm}^{-1} \cdot \text{cm}^2 \cdot \text{equi}^{-1}$	Conc. $\text{mol} \cdot \text{dm}^{-3}$	\sqrt{C}
6.9	345	0.0002	0.014142135
6.1	366	0.00016	0.012909918
5.3	371	0.00014	0.01195228
4.9	392	0.00012	0.011180339
4.6	414	0.00011	0.01054092
313 K°			
$K \cdot 10^{-6}$ $\text{ohm}^{-1} \cdot \text{cm}^{-1}$	Λ $\text{Ohm}^{-1} \cdot \text{cm}^2 \cdot \text{equi}^{-1}$	Conc. $\text{mol} \cdot \text{dm}^{-3}$	\sqrt{C}
8.1	415	0.0002	0.014142135
7.1	421	0.00016	0.012909918
6.1	427	0.00014	0.01195228
5.6	448	0.00012	0.011180339
5.3	477	0.00011	0.01054092
323 K°			
$K \cdot 10^{-6}$ $\text{ohm}^{-1} \cdot \text{cm}^{-1}$	Λ $\text{Ohm}^{-1} \cdot \text{cm}^2 \cdot \text{equi}^{-1}$	Conc. $\text{mol} \cdot \text{dm}^{-3}$	\sqrt{C}
9.1	451	0.0002	0.014142135
7.7	462	0.00016	0.012909918
6.7	469	0.00014	0.01195228
6.5	521	0.00012	0.011180339
6.1	541	0.00011	0.01054092
333 K°			
$K \cdot 10^{-6}$ $\text{ohm}^{-1} \cdot \text{cm}^{-1}$	Λ $\text{Ohm}^{-1} \cdot \text{cm}^2 \cdot \text{equi}^{-1}$	Conc. $\text{mol} \cdot \text{dm}^{-3}$	\sqrt{C}
9.3	465	0.0002	0.014142135
8.7	522	0.00016	0.012909918
7.5	525	0.00014	0.01195228
7.1	568	0.00012	0.011180339
6.8	612	0.00011	0.01054092

Now when such data were plotted versus each other, these showed an inverse straight lines as in fig.1 of correlation coefficient range value 0.9759-0.9958.

These confirm the idea of strong electrolyte[12] for these sodium salts.



Fig(1): The relationship between equivalent conductances and square root of concentration for salicylidene β -alanine at different temperatures.

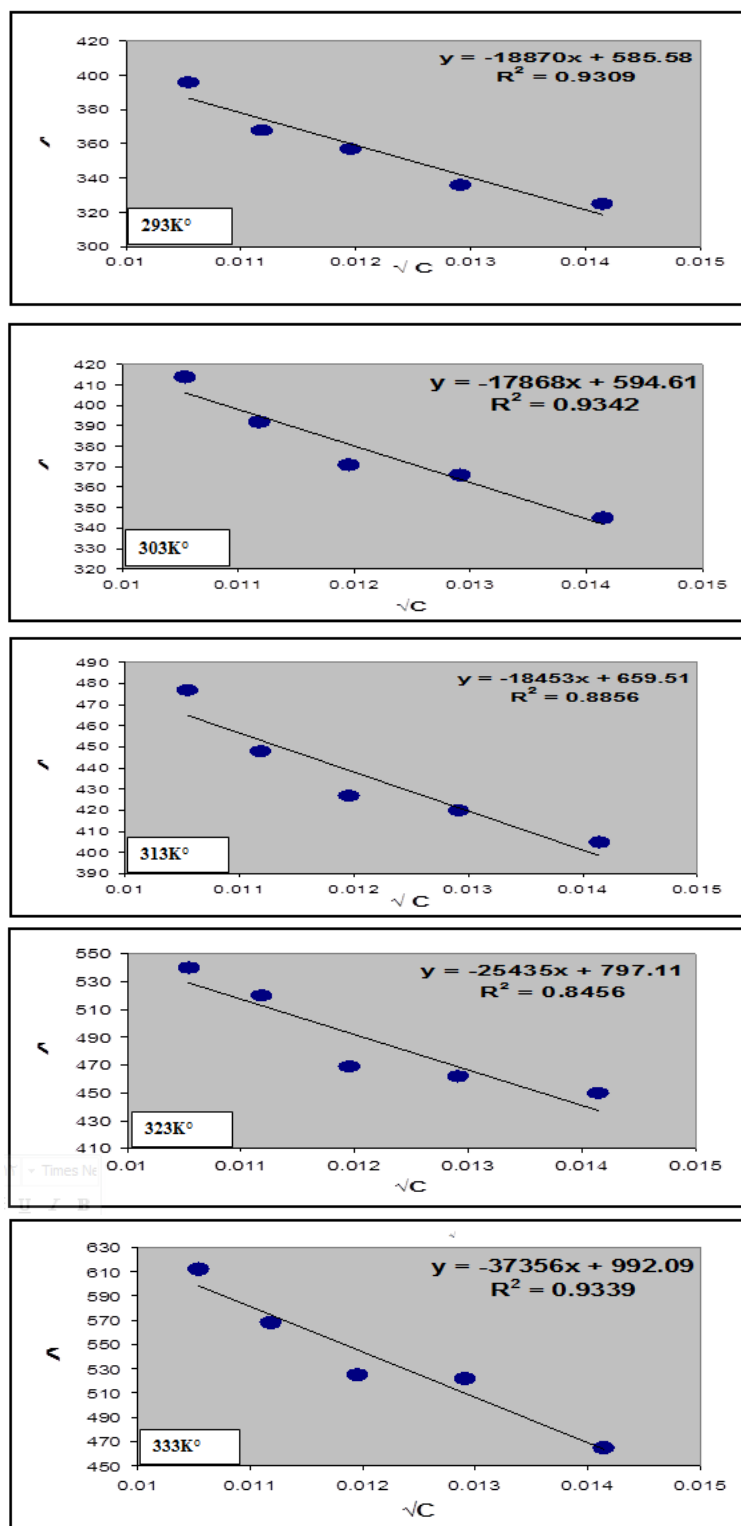


fig (2): The relationship between equivalent conductances and square root of concentration for benzylidene glycine at different temperatures.

The intercepts of these lines as fixed on each plot represent the equivalent conductances of the salt at infinite dilution (Λ°) at any temperature under study.

Similarly various concentrations of Schiff bases (I)-(II) as in tables (3-4) were prepared, followed by measurements of their specific and equivalent conductances at temperature range (293-333)K $^\circ$.

Table (3): Specific conductivity / equivalent conductivity , degree of dissociation and ionization constant for benzylidene glycine

T=293K°									
Conc. mol.dm ⁻³	K*10 ⁻⁶ ohm ⁻¹ .cm ⁻¹	Λ Ohm 1.cm ² .equi ⁻¹	Λ° Ohm ⁻¹ cm ² .equi ⁻¹	α	α^2	$\alpha^2 C$	1- α	Ka *10 ⁻⁵	Ka ⁻ *10 ⁻⁵
0.001	5390	59	813	0.0725	0.0052562	0.0000052	0.9275	0.56	0.52
0.0009	5350	61		0.0749	0.00561	0.000005	0.9251	0.54	
0.0008	5.0	63		0.0774	0.0059907	0.0000047	0.9226	0.50	
0.0007	4.7	67		0.0823	0.0067732	0.0000047	0.9177	0.51	
0.0006	4.3	72		0.0885	0.0078322	0.0000046	0.9115	0.50	
0.0005	4.0	80		0.0983	0.0096628	0.0000048	0.9017	0.53	
0.0004	3.5	88		0.1081	0.0116856	0.0000046	0.8919	0.51	
T=303K°									
Conc. mol.dm ⁻³	K*10 ⁻⁶ ohm ⁻¹ .cm ⁻¹	Λ Ohm 1.cm ² .equi ⁻¹	Λ° Ohm ⁻¹ cm ² .equi ⁻¹	α	α^2	$\alpha^2 C$	1- α	Ka *10 ⁻⁶	Ka ⁻ *10 ⁻⁶
0.001	5.6	56	847	0.0660	0.004356	0.000004356	0.934	4.663	4.36
0.0009	5.21	58		0.0684	0.00467856	0.00000421	0.9316	4.519	
0.0008	4.80	60		0.0707	0.00499849	0.000003998	0.9293	4.302	
0.0007	4.41	63		0.0743	0.00552049	0.000003864	0.9257	4.174	
0.0006	4.11	69		0.0813	0.00660969	0.000003965	0.9187	4.315	
0.0005	3.81	76		0.0896	0.00802816	0.000004014	0.9104	4.409	
0.0004	3.27	82		0.0967	0.00935089	0.00000374	0.9033	4.140	
T=313K°									
Conc. mol.dm ⁻³	K*10 ⁻⁶ ohm ⁻¹ .cm ⁻¹	Λ - Ohm 1.cm ² .equi ⁻¹	Λ° Ohm ⁻¹ cm ² .equi ⁻¹	α	α^2	$\alpha^2 C$	1- α	Ka *10 ⁻⁵	Ka ⁻ *10 ⁻⁵
0.001	54	54	930	0.0580	0.003364	0.0000033	0.942	0.35	0.307
0.0009	55	55		0.0591	0.0034928	0.0000031	0.9409	0.32	
0.0008	56	56		0.0601	0.003612	0.0000028	0.9399	0.29	
0.0007	60	61		0.0644	0.0041473	0.0000029	0.9356	0.3	
0.0006	63	63		0.0677	0.0045832	0.0000027	0.9323	0.28	
0.0005	70	71		0.0752	0.005655	0.00000282	0.9248	0.304	
0.0004	78	78		0.0838	0.0070224	0.0000028	0.9162	0.305	
T=323K°									
Conc. mol.dm ⁻³	K*10 ⁻⁶ ohm ⁻¹ .cm ⁻¹	Λ - Ohm 1.cm ² .equi ⁻¹	Λ° Ohm ⁻¹ cm ² .equi ⁻¹	α	α^2	$\alpha^2 C$	1- α	Ka *10 ⁻⁵	Ka ⁻ *10 ⁻⁵
0.001	5.3	53	1102	0.0480	0.002304	0.0000023	0.952	0.24	0.257
0.0009	5.0	55		0.0498	0.00248	0.0000022	0.9502	0.23	
0.0008	4.8	61		0.0544	0.0029593	0.0000023	0.9456	0.24	
0.0007	4.5	64		0.0580	0.003364	0.0000023	0.942	0.24	
0.0006	4.3	71		0.0643	0.0041344	0.0000023	0.9357	0.25	
0.0005	4.1	82		0.0743	0.0055204	0.0000027	0.9257	0.29	
0.0004	3.8	95		0.0861	0.0074132	0.0000029	0.9139	0.31	
T=333K°									
Conc. mol.dm ⁻³	K*10 ⁻⁶ ohm ⁻¹ .cm ⁻¹	Λ - Ohm 1.cm ² .equi ⁻¹	Λ° Ohm ⁻¹ cm ² .equi ⁻¹	α	α^2	$\alpha^2 C$	1- α	Ka *10 ⁻⁶	Ka ⁻ *10 ⁻⁶
0.001	4.51	45	1318	0.0341	0.00116281	0.000001162	0.9659	1.203	1.271
0.0009	4.23	47		0.0356	0.00126736	0.00000114	0.9644	1.182	
0.0008	4.11	51		0.0386	0.00148996	0.000001191	0.9614	1.238	
0.0007	3.87	55		0.0417	0.00173889	0.000001217	0.9583	1.269	
0.0006	3.55	59		0.0447	0.00199809	0.000001198	0.9553	1.254	
0.0005	3.21	64		0.0485	0.00235225	0.000001176	0.9515	1.235	
0.0004	3.17	79		0.0598	0.00357604	0.00000143	0.9402	1.52	

Table (4): Specific conductivity / equivalent conductivity, degree of dissociation and ionization constant for Salicylidene β-alanine

T=293K°									
Conc. mol.dm ⁻³	K*10 ⁻⁶ ohm ⁻¹ .cm ⁻¹	Λ - ohm 1.cm ² .equi ⁻¹	Λ ^o Ohm ⁻¹ cm ² .equi	α	α ²	α ² C	1-α	Ka *10 ⁻⁶	Ka ⁻ *10 ⁻⁶
0.001	5.1	51.0	570	0.0894	0.00799236	0.000007992	0.9106	8.776	6.969
0.0009	4.6	51.1		0.0896	0.00802816	0.000007225	0.9104	7.936	
0.0008	4.3	53.8		0.0943	0.00889249	0.000007113	0.9057	7.853	
0.0007	3.8	54.2		0.0950	0.009025	0.000006317	0.905	6.980	
0.0006	3.4	56.6		0.0992	0.00984064	0.000005904	0.9008	6.554	
0.0005	2.9	58.0		0.1016	0.01032256	0.00000161	0.8984	5.744	
0.0004	2.4	60.0		0.1052	0.01106704	0.000004426	0.8948	4.946	
0.0004	2.4	60.0		0.1052	0.01106704	0.000004426	0.8948	4.946	
T=303K°									
Conc. mol.dm ⁻³	K*10 ⁻⁶ ohm ⁻¹ .cm ⁻¹	Λ - Ohm 1.cm ² .equi ⁻¹	Λ ^o Ohm ⁻¹ cm ² .equi	α	α ²	α ² C	1-α	Ka *10 ⁻⁵	Ka ⁻ *10 ⁻⁵
0.001	5.7	57	629	0.0905	0.0081902	0.0000081	0.9095	0.89	0.75
0.0009	5.2	58		0.0920	0.008464	0.0000076	0.908	0.83	
0.0008	4.7	59		0.0936	0.0087609	0.0000070	0.9064	0.77	
0.0007	4.2	61		0.0968	0.0093702	0.0000065	0.9032	0.71	
0.0006	3.8	63		0.1000	0.0101011111111111000000000000	0.000006	0.9000	0.66	
0.0005	3.5	71		0.1127	0.0127012	0.0000063	0.8873	0.71	
0.0004	3.1	78		0.1238	0.0153264	0.0000061	0.8762	0.69	
0.0004	3.1	78		0.1238	0.0153264	0.0000061	0.8762	0.69	
T=313K°									
Conc. mol.dm ⁻³	K*10 ⁻⁶ ohm ⁻¹ .cm ⁻¹	Λ - Ohm 1.cm ² .equi ⁻¹	Λ ^o Ohm ⁻¹ cm ² .equi	α	α ²	α ² C	1-α	Ka *10 ⁻⁵	Ka ⁻ *10 ⁻⁵
0.001	6.7	67	694	0.0965	0.0093122	0.0000093	0.9035	1.02	0.88
0.0009	6.3	70		0.1008	0.0101606	0.0000091	0.8992	1.01	
0.0008	5.7	73		0.1051	0.0110460	0.0000088	0.8949	0.98	
0.0007	5.2	74		0.1065	0.0113422	0.0000079	0.8935	0.99	
0.0006	4.5	75		0.1080	0.011664	0.0000069	0.892	0.77	
0.0005	4.2	83		0.1195	0.0142802	0.0000071	0.8805	0.80	
0.0004	3.6	90		0.1296	0.0167961	0.0000067	0.8704	0.76	
0.0004	3.6	90		0.1296	0.0167961	0.0000067	0.8704	0.76	
T=323K° T=313K°									
Conc. mol.dm ⁻³	K*10 ⁻⁶ ohm ⁻¹ .cm ⁻¹	Λ - Ohm 1.cm ² .equi ⁻¹	Λ ^o Ohm ⁻¹ cm ² .equi	α	α ²	α ² C	1-α	Ka *10 ⁻⁵	Ka ⁻ *10 ⁻⁵
0.001	7.7	77	778	0.0989	0.0097812	0.0000097	0.9011	1.07	0.90
0.0009	7.1	79		0.1014	0.0102819	0.0000092	0.8986	1.02	
0.0008	6.5	81		0.1040	0.010816	0.0000086	0.896	0.95	
0.0007	5.8	84		0.1079	0.0116424	0.0000081	0.8921	0.90	
0.0006	5.2	87		0.1117	0.0124768	0.0000074	0.8883	0.83	
0.0005	4.7	94		0.1207	0.0145684	0.0000072	0.8793	0.81	
0.0004	4.0	100		0.1284	0.0164865	0.0000065	0.8716	0.74	
0.0004	4.0	100		0.1284	0.0164865	0.0000065	0.8716	0.74	
T=333K°									
Conc. mol.dm ⁻³	K*10 ⁻⁶ ohm ⁻¹ .cm ⁻¹	Λ - Ohm 1.cm ² .equi ⁻¹	Λ ^o Ohm ⁻¹ cm ² .equi	α	α ²	α ² C	1-α	Ka *10 ⁻⁵	Ka ⁻ *10 ⁻⁵
0.001	8.6	86	856	0.1004	0.0100801	0.00001	0.8996	1.11	1.042
0.0009	8.1	91		0.1050	0.011025	0.0000099	0.8950	1.10	
0.0008	7.4	93		0.1085	0.0117722	0.0000094	0.8915	1.05	
0.0007	6.6	95		0.1109	0.0122988	0.0000086	0.8891	0.96	
0.0006	5.8	97		0.1132	0.0128142	0.0000076	0.8868	0.85	
0.0005	5.6	113		0.1319	0.0173976	0.0000086	0.8681	0.99	
0.0004	5.1	128		0.1494	0.0223203	0.0000089	0.8506	1.04	
0.0004	5.1	128		0.1494	0.0223203	0.0000089	0.8506	1.04	

Now the equivalent conductances at infinite dilution (Λ^o) of Schiff bases (I)-(II)

were calculated [12,13] on the basis of independent ion migration of ions. The last was applied in the determination of Λ^o for some imines derived

benzoyl acetone and dimedon, as explained in our previous communication[14].

Now it become possible to evaluate the degree of dissociation (α) and the ionization constant of

acids (I)-(II) using equations (1-2) at temperature range (293-333)K°, as in tables (3-4) .

$$\alpha = \frac{\Lambda}{\Lambda^\circ} \dots\dots(1)$$

$$K_a = \frac{\alpha^2 C}{1-\alpha} \dots\dots(2)$$

These tables (3-4) showed that Λ° value for any acid (I) or (II) was increased by increasing temperature, These results confirm [15] the previous study on Λ° of phenolic imines derived from benzoyl acetonitrile upon elevation of temperatures. It was cleared from table (3) that ionization constants values of benzylidene glycine were depressed by an elevation of temperatures in the range (293-333)K°. These means that ionization reactions of such acidic compound were directed toward reactant product. On the contrary to that ionization constants values of salicylidene β -alanine were increased by elevation of temperature. The reason for such variation in results were due to the difference in structures of acids (I) and (II), as agreed with theoretical expectation. Table (5) showed a comparison between pKa values for acids (I) and (II) at temperature range (293-333)K°.

Table (5): pKa values of benzylidene glycine with salicylidene β -alanine at various temperatures .

T(K)	benzylidene glycine	salicylidene β -alanine
293	532839	531568
313	533615	531249
313	535128	531555
323	535911	531457
333	538958	439829

At any constant temperature, the acidity of salicylidene β -alanine was greater than benzylidene glycine .In order to interpret the values collected in table (5), this need to consider the pKa values of glycine and β -alanine from literature as in table (6)

Table(6) : pKa values of some amino acids

Amino acids	ton gained(pKa)	Proton lost (pKp)
glycine	233513	937796
β -alanine	2334	9387

The isoelectric point (pI) for glycine and β -alanine was determined[13] from an equation (3).

$$pI = \frac{pK_1 + pK_2}{2} \dots\dots(3)$$

Whene applying last equation to glycine and β -alanine, resulted to pI values of 6.0650 and 6.105 respectively. These values were closed to pKa values of benzylidene glycine and salicylidene β -alanine, bearing in mind the difference in structures between Schiff bases under investigation and amino acids mentioned.

Hence the near pKa values of benzylidene glycine and salicylidene β -alanine with pI values of glycine and β -alanine, led the workers in this investigation to confirm the existence of acids (I)-(II) as in isoelectric points. At such point the carboxyl proton was lost and combined with nitrogen Schiff base 1 resulted to the formation of nitrilium ion as conjugated acid of amine in Schiff base $HN = C$.

The change of free energy ΔG° ionization reactions of acid Schiff base (I) and (II) were calculated from equation (4). $\Delta G^\circ = -RT \ln K_a \dots\dots(4)$. All ΔG° values tabulated in tables (7-8) had apositive signs. This means, that ionization reactions occurred in non spontaneous process.

Since Schiff bases (I)-(II) have a convalent bonding, therefore, they were difficult to be ionized as compared with ionic bonds.

The heats of ionizations reactions of acids under investigation were also calculated from intergrated Vant Hoff equation number (5) .

$$\ln K_a = \text{constant} - \frac{\Delta H^\circ}{RT} \dots\dots (5)$$

The plot of $\ln K_a$ versus T^{-1} for salicylidene β -alanine and benzylidene glycine at different temperatures showed a straight lines of correlation coefficient range value of 0.9668-0.9108.

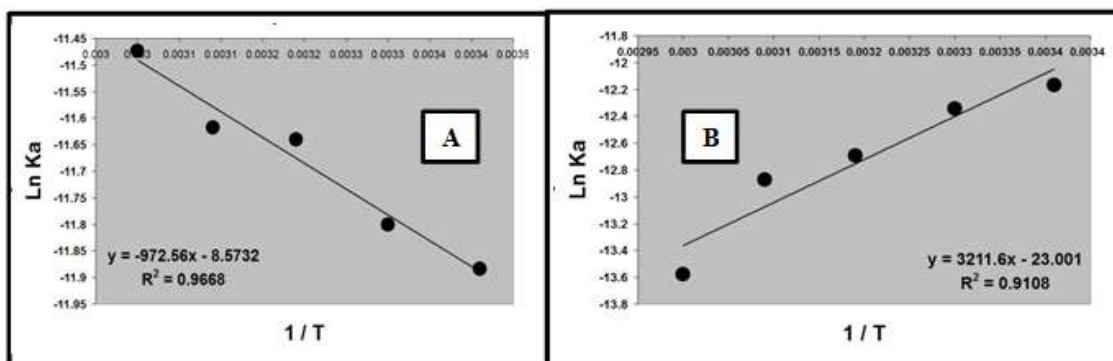


Fig. (3): Effect of temperature on the equilibrium constant of value for ionization reaction of salicylidene- β -alanine (A) and benzylidene glycine (B).

Table (7): The influence of temperature and thermodynamic parameters on equilibrium constant values for ionization reactions of salicylidene β -alanine

T	1/T	$K_a \times 10^{-6}$ $L.mol^{-1}$	$\ln K_a$	ΔG° $kJ.mol^{-1}$	$\Delta G^{\circ-}$ $kJ.mol^{-1}$	ΔH $kJ.mol^{-1}$	ΔH^- $kJ.mol^{-1}$	ΔS° $J.mol^{-1}.K^{-1}$	$\Delta S^{\circ-}$ $J.mol^{-1}.K^{-1}$
293	0.00314	6.9	-11.883	+28.94	+30.38	+8.064	+8.0272	-71.249	-71.404
303	0.0033	7.5	-11.811	+29.72		+8.129		-71.257	
313	0.00319	8.8	-11.641	+31.29		+7.981		-71.274	
323	0.00309	9.1	-11.618	+31.19		+8.175		-71.253	
333	0.003	10.4	-11.473	+31.76		+7.787		-71.990	

Table (8): The influence of temperature and thermodynamic parameters on equilibrium constant values of benzylidene glycine.

T	1/T	$K_a \times 10^{-7}$ $L.mol^{-1}$	$\ln K_a$	ΔG° $kJ.mol^{-1}$	$\Delta G^{\circ-}$ $kJ.mol^{-1}$	ΔH $kJ.mol^{-1}$	ΔH^- $kJ.mol^{-1}$	ΔS° $J.mol^{-1}.K^{-1}$	$\Delta S^{\circ-}$ $J.mol^{-1}.K^{-1}$
293	0.00341	52	-12.166	+29.63	+33.178	-26.392	-26.667	-191.211	-191.199
303	0.0033	43.6	-12.343	+31.09		-26.847		-191.211	
313	0.00319	30.7	-12.693	+33.03		-26.819		-191.211	
323	0.00309	25.7	-12.871	+34.56		-27.19		-191.176	
333	0.003	12.71	-13.575	+37.58		-26.189		-191.198	

The average enthalpy or heat for ionization ΔH^+ was +8.0272 KJ.mole. This means ionization reaction was occurred after absorption of heat. On the contrary to that, the average enthalpy for ionization of benzylidene glycine has a negative sign of average value -26.667, or the ionization in benzylidene glycine was occurred after liberation of heat energy.

These positive or negative values of enthalpies of ionization in salicylidene β -alanine and benzylidene glycine could be interpreted due to the presence of intramolecular and intermolecular hydrogen bonding in these systems respectively. This last observation was confirmed in literature [17] by the fact the salicylaldehyde nucleus which has the same intramolecular hydrogen bond. Hence its derivative was expected to contain the intramolecular hydrogen bonding.

The change in entropy ΔS° for this ionization reaction was calculated from Gibbs energy of from as in equation (6) $\Delta G^\circ = \Delta H - T \Delta S^\circ \dots (6)$. For mono protoic acid HA, the ionization reaction was directed toward an increase in random of the system. Hence ΔS° as expected theoretically has apposite sign. These negative signs of ΔS° values for salicylidene β -alanine and benzylidene glycine as in tables (7-8) were contrary to our expectation. This only happened by strong interaction between polar solvent deionized water molecule with negative anion

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(A⁻) for mono protoic acid HA. While other systems, such as association[18] reaction between phenols with benzyl mono benzylidene aniline and ionization[19] reactions of some acids and basic imines derived from 3 and 4 acetyl pyridines.

This investigation was in agreement with other pKa studies on imines derived from benzoyl acetone with dimedone [9] and benzoyl acetonitrile using conductivity measurements.

Conclusion

- 1- Two acid Schiff bases benzylidene glycine and salicylidene β -alanine were prepared [8] by developed method using sodium hydroxide as a new catalyst.
- 2- The conductance measurements were applied to the determination of pKa values for these acid Schiff bases. This method was found simple, precised and accurate.
- 3- The determination of pKa by conductance method, led to the believe of existence of acid Schiff bases in isoelectric point.
- 4- The thermodynamic parameters of ionization of acid Schiff bases confirmed that ionization reactions occurred in non-spontaneous process, in endothermic or exothermic reaction depending on structure of acid and accompanied by a decrease of random of systems.

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حساب قيم ثابت التفكك لقواعد شيف جديدة مشتقة من بنزالدهايد وسالسالدهايد مع

الكلايسين والبيتا-الانين

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الملخص

حضرت قواعد شيف جديدة وهي البنزالدين كلايسين (I) والسالسيلايدين بيتا-الانين (II) باستخدام طريقة جديدة تتمثل باستخدام هيدروكسيد الصوديوم كعامل محفز. الهدف الرئيسي من هذا البحث هو حساب قيم ثابت التفكك (pKa) لتلك الايمينات الحامضية باستخدام طريقة التوصيل الكهربائي اذ تمتاز هذه الطريقة بانها بسيطة، رخيصة ودقيقة لحساب قيم ثابت التفكك للمركبات وقد اجريت كافة قياسات التوصيل الكهربائي للبنزالدين كلايسين، السالسيلايدين بيتا-الانين واملاح الصوديوم لكليهما في ماء خالي من الايونات وقد تضمن البحث استخدام احماض مختلفة الحامضية (I) و (II) وتم ايضا مناقشة القيم الثيرموديناميكية ΔG° ، ΔH ، ΔS° للتفاعلات الايونية لهذه الاحماض.