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Evidences for zwitter ions formation during determination of pKa values for o-amino benzylidene o, m, p- hydroxyl anilines

A.S.P.Azzouz*, A.K.E.AL-Abassy
Chemistry Department, College of Education, Mosul University, (IRAQ)
E-mail : azzouz20042001@yahoo.com

ABSTRACT

o- Aminobenzylidene o, m, p- hydroxyl anilines as numbered I, II, III respectively were prepared by astandard method, Their chemical structures were confirmed by physical method, namely by using melting points, UV and IR spectra, beside some chemical tests.

The pKa values for imines I, II and III and were determined by using a potentiometric titration method in 10% ethanol at a temperature range (20-60)°C. Imines I and III show anomalous pKa values in the range between (5-6.5). These were unexpected results and confirmed by the formation of zwitter ions at all temperatures stated. Imine II showed a similar result at temperatures (20-30)°C and other different results at other higher temperature range between (40-60)°C. All evidences supporting zwitter ions formation were given and discussed.

KEYWORDS

Schiff base;
Zwitter ions;
pKa;
Potentiometry.

INTRODUCTION

The chemistry of imines in a forms of Schiff bases and oximes had faced a great deal of attentions by many workers[1-4] during the last years. This was for their importance in kinetic[5,6], stability[7] constants of dye formation, kinetic and thermodynamic study[8] on tautomerism of dyes and association study[9] between Schiff base with phenols. In 2012, Azzouz etal had focused their works on pKa study[10-12] of oximes and Schiff bases prepared from different carbonyl compounds and primary amines. These were for their importance of imines in many fields[13].

This manuscript was a continuation of last topic. It deals with determination of pKa study for o-aminobenzylidene o, m, p- hydroxyl anilines.

These interesting imines had acidic phenol group and aromatic amine groups in theit structures, hence their pka values evaluation by potentionetric method, had a significant importance from chemistry point of view The study showed a comparison between pKa value in these imines before and after addition of NaOH as a titrant during pKa determination.

EXPERIMENTAL

o- Aminobenzaldehyde and o, m, p- aminophenols were supplied from Fluka chemical company. Pure ethanol, sodium hydroxide were bought from local market and supplied originally from Aldrich company.

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All imines under investigation were prepared by a standard method[2,3], or by mixing equivalent amounts i.e 10^{-2} mole of o- amino benzaldehyde with o, m, p-aminophenol. The mixture was refluxed for 2 hours, followed by cooling and filtration. Pure imines I, II and III were purified by recrystallization from absolule ethanol. TABLE 1 showed, the imine number, nomenclature, and U. V and IR spectra of imines.

pKa determination

The pKa of Schiff bases were determined by manufacturing glass cylindrical cell of maximum capacity about 30ml. The cells contains two walls for insertion of pumbed water from thermostat, to maintain a fixed temperature in the range (20-60)°C, during pKa determination.

The whole assembly was completely isolated from surrounding by thick insulation material. 20ml of 0.01M solution of any Schiff base in 10% ethanol was placed in the cell. After equilibrium temperature was attained, a successive 0.2ml of 0.1N NaOH was added till about 1.2ml or 1.6ml was totally added, followed by measuring the final equilibrium pH of solution. An average single pKa value for Schiff bases I and III were determined at temperature range mentioned. Similar measurements were obtained for Imine III at temperature (20-30)°C.

At other higher temperature range (40-60) °C, Imine III gave two pKa values at volume of titrant 0.8 and 1.6ml respectively.

The pKa was determined by standard method[14] using an equation of the form:-

$$\mathbf{pka = pH + Log}\frac{[acid]}{[salt]}$$

INSTRUMENTATION

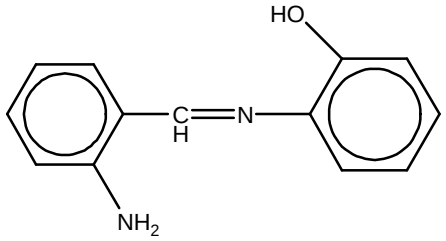
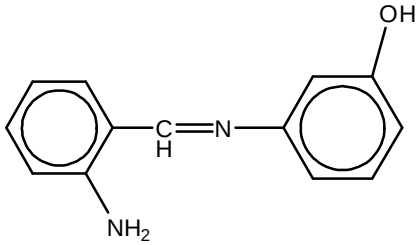
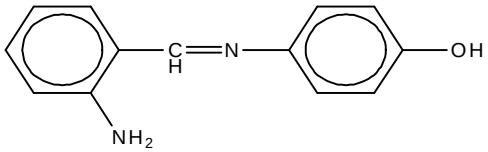
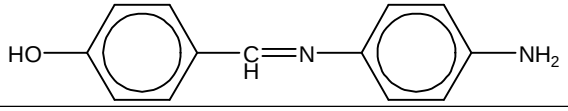
1 The UV spectra of imines I, II and III were measured by a double beam computerized UV 1601 Shimadzu spectrophotometer using matched quartz cells of dimensions $1\times1\times3$ cm^3. solutions of 10^{-3}M in ethanol were prepared.

2 The IR spectra of solid imines were measured by computerized FTIR Bruker Tensor 27 spectrophotometer.

3 Memmert Searl L200 water thermostat, having water pump for pumping water to glass cell mentioned.

4 The melting points of imines under study were measured by using STUART SMP 30.

TABLE 1 : Structures and nomenclature of imines

Imine No.	Structure	Nomenclature
I		o- Amino benzylidene -o- hydroxyaniline
II		o-Amino benzylidene -m- hydroxyaniline
III		o-Amino benzylidene -p- hydroxyaniline
IV		p-Hydroxy benzylidene-p-amino aniline

5 The pH of any solution during potentiometric titration was measured by pH meter JENWAY3510.

RESULTS AND DISCUSSION

At the beginning of this investigation, it was thought of a great importance to confirm the structure of imines by physical method, namely by using IR-UV spectra as TABLE 2, beside some chemical tests.

The IR showed the following stretching vibrations as follows:

1 Astrong asymmetric absorptions of primary amine in the range (3461.06-3461.18) cm^{-1}, with similar amine symmetric absorptions in the range (3363.89-3381.56) cm^{-1}.

These two absorptions confirm[16] the existence of primary aromatic amine groups in imines.

2 A medium stretching absorption bands for OH groups in the range (3305.18-3363.02) cm^{-1}.

3 A weak or medium stretching bands for hydrogen bandings in the range (3272.7-3297.23) cm^{-1}.

4 A medium or weak absorptions of stretching C-H grouping in the range (2963.71-3052.57) cm^{-1}.

5 A medium stretching absorptions for carbonyl group in the range (1663.50-1664.57) cm^{-1}. These were arising for tautomerism reactions of type enol $\rightleftharpoons$ keto in Schiff bases having phenolic groupings.

6 A strong storetching absorptions bands for imines in the range (1624.29-1624.42) cm^{-1}. These confirm the existence of azomethine linkages in imines.

7 A strong stretching absorptions for aromaticity in imines were abserved in the range (1600.77-1601.84) cm^{-1}.

TABLE 2 : IR and UV spectra of imines

Imine No.	NH_2 asymm.	NH_2 symm.	OH	H.B	C.H	C=O	C=N	AROM	λ(nm)	Σ_{max}	λ(nm)	Σ_{max}
I	3461.11 (s)	3375.92 (s)	3305.18 (s)	32727 (w)	1664.57 (m)	1624.42 (m)	1624.42 (s)	1601.84 (s)	290.6	19250	222.6	13020
I I	3461.06 (s)	3381.56 (s)	3363.62 (s)	3297.23 (m)	2964.42 (w)	1663.50 (m)	1624.42 (s)	1600.77 (s)	292.6	31660	215.2	19740
I I I	3461.181(s)	3363.89 (s)	3342.83 (s)	3282.65 (m)	2963.71 (w)	1664.39 (s)	1624.29 (s)	1601.01 (s)	292.2	19580	226.4	13500
I V	3359.08 (s)	3287.80 (s)	3287.8 (b)		3077.87 (w)	1714.94 (w)	1625.78 (s)	1606.28 (s)	300	15300	234.4	18060

Σ_{max} **in unit of Liter.mole^{-1}.cm^{-1}**

The UV spectra of 10^{-4}M of imines (I-IV) showed tdwo absorption bands as in TABLE 2 with molar extension coefficient values of more than 1000 in units Liter.mole-^{1}.cm^{2}.these meashrement were in agreement with previous study[3].

The last mean that aldehydic phenyl with azomethine group in one plane, the rest of molecule was in other plane.

The melting points of imines I, II and III showed the following range values of (145-147, 120-122 and 148-150)°C. The greater melting point value of imine III can be interpreted by the higher tendency of association by intermolecular hydrogen bonding.

The chemical method included the use of diazotization test and ferric chloride solution as a specific tests for aromatic amino and phenol groups respectively.

All these physical and chemical methods confirm the chemical structures of imines under study and agreed with literature[15,16].

The second part of the study deals with interpretation of $\overline{pKa}$ for imines having ortho NH_2 group on aldehyde part and phenolic groups in ortho, meta and para positions of amine part in Schift bases. Before starting the interpretation of result, it was thought of a great importance to know the $\overline{pKa}$ values of groups mentioned. They had $\overline{pKa}$ values of 4.6 and 9.99 respectively as measured in water solvent and 25°C.

A- The $\overline{pKa}$ values of imine I at a range of temperature between (20-60)°C having

o-NH_2 and o-OH groups on aldehyde and amine parts of molecule, showed the following results:-

1 The increase of temperature from 20°C to 60°C resulted in decreasing $\overline{pKa}$ values or increasing acidity of imine. In other words, the increase of temperature was accompanied by a greater ionization process or liberation of hydrogen ions. This was in agreement with endothermic ionization process of acid imine.

2 The pKa values collected at temperature range (20-60)°C having a range of value (5.6651-6.0452).

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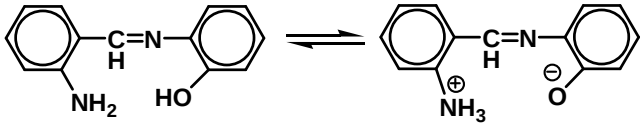
TABLE 3 : pKa Values of imines I, II and III and IV in 10% ethanol at temperature range (20-60)°C

Imine number	Temp°C	ml of (0.1 M) NaOH	pH	pKa	$\overline{pKa}$
I	293	0.0	5.06		6.0452
		0.2	5.20	6.1511	
		0.4	5.32	5.9207	
		0.6	5.48	5.8472	
		0.8	5.67	5.8445	
		1	5.95	5.9477	
		1.2	6.74	6.5600	
I	303	0.0	4.65		5.9065
		0.2	5.09	6.04	
		0.4	5.23	5.8304	
		0.6	5.35	5.7170	
		0.8	5.55	5.7244	
		1	5.83	5.8277	
		1.2	6.48	6.2999	
I	313	0.0	4.83		
		0.2	4.96	5.9089	
		0.4	5.09	5.6898	
		0.6	5.28	5.6468	
		0.8	5.49	5.6643	
		1	5.78	5.7776	
		1.2	6.61	6.4300	
I	323	0.0	4.72		5.7380
		0.2	4.84	5.7810	
		0.4	5.00	5.5992	
		0.6	5.15	5.5164	
		0.8	5.35	5.7041	
		1	5.65	5.6475	
		1.2	6.36	6.1799	
I	333	0.0	4.65		5.6651
		0.2	4.78	5.7262	
		0.4	4.94	5.5388	
		0.6	5.19	5.5566	
		0.8	5.40	5.5742	
		1	5.84	5.9300	
		1.2	5.43	5.6651	
II	20	0.0	4.36		5.0654
		0.2	4.49	5.4286	
		0.4	4.62	5.2152	
		0.6	4.75	5.1141	
		0.8	4.88	5.0524	
		1	4.99	4.9861	
		1.2	5.13	4.9485	
		1.4	5.32	4.9531	
		1.6	5.44	4.8249	
II	30	0.0	4.29		5.1375
		0.2	4.44	5.3768	
		0.4	4.56	5.1544	
		0.6	4.69	5.0536	
		0.8	4.81	4.9820	
		1	4.94	4.9358	
		1.2	5.06	4.8783	
		1.4	5.43	5.0634	
		1.6	6.27	5.6558	
II	40	0.0	4.22		10.1773
		0.2	4.60	5.5421	
		0.4	4.93	5.5288	
		0.6	5.31	5.1545	
		0.8	5.95	6.1247	
		1	9.49	9.4936	
		1.2	10.22	10.0718	
		1.4	10.75	10.5030	
		1.6	11.00	10.6409	
II	50	0.0	4.16		9.8546
		0.2	4.57	5.4961	
		0.4	4.91	5.5086	
		0.6	5.27	5.6368	
		0.8	5.88	5.9946	
		1	9.27	9.2713	
		1.2	9.99	9.8288	
		1.4	10.44	10.1337	
		1.6	10.67	10.1847	
II	60	0.0	4.10		9.8938
		0.2	4.57	5.5115	
		0.4	4.97	5.5690	
		0.6	5.37	5.7370	
		0.8	5.86	6.0347	
		1	9.09	9.0902	
		1.2	9.80	9.6321	
		1.4	10.22	9.8904	
		1.6	10.44	9.9043	
III	20	0.0	5.53		6.4392
		0.2	5.66	6.6131	
		0.4	5.84	6.4416	
		0.6	5.94	6.3077	
		0.8	6.12	6.2948	

Imine number	Temp°C	ml of (0.1 M) NaOH	pH	pKa	$\overline{pKa}$
		1	6.36	6.3579	
		1.2	6.80	6.6200	
		0.0	5.39		
		0.2	5.50	6.4527	
		0.4	5.62	6.2213	
III	30	0.6	5.77	6.1376	6.2557
		0.8	5.96	6.1347	
		1	6.18	6.1778	
		1.2	6.59	6.4100	
		0.0	5.30		
		0.2	5.40	6.3523	
		0.4	5.52	6.1212	
III	40	0.6	5.69	6.0575	6.1989
		0.8	5.87	6.0447	
		1	6.12	6.1178	
		1.2	6.68	6.5000	
		0.0	5.15		
		0.2	5.25	6.2015	
		0.4	5.38	5.9809	
III	50	0.6	5.53	5.8973	6.0704
		0.8	5.73	5.9046	
		1	6.01	6.0078	
		1.2	6.61	6.4300	
		0.0	5.13		
		0.2	5.27	6.2216	
		0.4	5.39	5.9909	
III	60	0.6	5.53	5.8973	6.0387
		0.8	5.71	5.8845	
		1	5.95	5.9477	
		1.2	6.47	6.2899	
		0.0	6.81		
		0.2	7.58	8.53	
		0.4	8.29	8.89	
IV	293	0.6	9.24	9.61	9.8114
		0.8	9.56	9.74	
		1	10.36	10.39	
		1.2	10.70	10.61	
		1.4	11.05	10.91	
		0.0	6.44		
		0.2	7.30	8.25	
		0.4	7.81	8.41	
IV	303	0.6	8.37	8.73	8.9600
		0.8	8.82	8.99	
		1	9.09	9.09	
		1.2	9.77	9.60	
		1.4	10.00	9.65	
		0.0	6.62		
		0.2	7.07	8.02	
		0.4	7.48	8.08	
IV	313	0.6	7.80	8.16	8.500
		0.8	8.13	8.30	
		1	8.63	8.62	
		1.2	9.12	8.94	
		1.4	9.74	9.38	
		0.0	6.49		
		0.2	6.98	7.93	
		0.4	7.27	7.87	
IV	323	0.6	7.56	7.92	8.1114
		0.8	7.74	7.91	
		1	8.02	8.01	
		1.2	8.50	8.32	
		1.4	9.19	8.82	
		0.0	6.38		
		0.2	6.79	7.74	
		0.4	7.02	7.62	
IV	333	0.6	7.14	7.50	7.4271
		0.8	7.24	7.41	
		1	7.40	7.39	
		1.2	7.58	7.40	
		1.4	7.80	7.43	

These values were far away from the pKa values of NH_2 aromatic and OH phenol mentioned before. The question can be raised here, why there were a decrement between experimental findings and theortical pKa values. The only answer could be given here, was due to the existence of imine I in zwitter ions formation according to the following reaction as:

The zwitter ions formation had been stated to exist previously in o,m, p… amino phenols[14]. Their structures were resemble or similar to imine I and other imines by having NH_2 and phenol grops.



The $^{\oplus}_{NH3}$ act as electrophile group and regarded as a strong acid conjugate of amine, hence their pKa value collected in TABLE 2 seem accepted from experimental and theortical points of view.

B- The pka value of imine II at temperature range (20-60) °C showed the following results

1 An increase in temperature from (20-60)°C resulted to an increase of acidity. This was a good agreement to result listed in imine I.
2 At temperatures 20°C and 30°C, the pKa value of imine II were interpretied similarly to those mentioned earlier in imine I.
3 At other higher temperature of 40°C, 50°C and 60°C, two sets of different results were collected. The first one after adding 0.1N titrant NaOH in the range between(0.2-0.8) ml resulted to pH range 4-6, or pka range value around 5-6 as in TABLE 2. These value were reffered to zwitter ions formation listed above, or zwitter ions were stable at last pH range stated. The second set of result were obtained after an increase of titrant volume in the range (1.0-1.6)ml. These were accompanied by a sudden elevation of pH in a range 9-11 or pKa range value 9-11.

These higher pKa values were close or near to pKa of phenol.

Hence it was concguded in this investigation that during determination of $\overline{pKa}$ values of imine (II) at pH value of 9 or more, the zwitter ions formation were unstable and resulted to the conversion of zwitter ions forms to normal phenol and amine forms as in its structure. This resulted to the evaluation of $\overline{pKa}$ values near to phenol and agreed with experimental findings.

C- The $\overline{pKa}$ values of imine III showed a similar results to imine I with the formation of zwitter ions in the range of 6.0387-6.4392 $\overline{pKa}$ values

These results confirm previous results mentioned in imines I and II.

In order to confirm the existence of imines I, II and III and IV in zwitter ions formation, hence this encourage to measure the uv spectra of these imines in ethanol. These were followed by addition of 2 drops of 0.1N NaOH to uv cells.These resulted to a blue shift in the spectra of $\Delta\lambda$ values 49.8,26.8,38 and 16.7 nm respectively.

These findings come in agreement[14] with similar compounds in amino phenols,as shown in typical for 10^{-4}M imines 1-2 solutions in ethanol as in Figure (1-2)

The resulted mixtures were subjected to measure their uv spectra as in Figure 1. These resulted to the generation of blue shift in the spectra after addition of alkali. These interesting results were agreed with[14] literature.

Finally, it was though of a great importence to check the pH of original 10^{-2}M ethanolic solution of imines I,II and III before adding 0.1M NaOH at a range of temperature (20-60)°C. Data collected were shown in TABLE 3.

TABLE 3. pH of 10^{-2}M imines I,II and III in ethanol at temperature range (20-60) °C

TABLE 4, showed the pH values of imines I,II and III in ethanol at temperature range (20- 60)°C. were in comparable to those listed in TABLE 2 after adding 0.1M titrant NaOH. This means that all imines mentioned were exist originally in zwitter ions forms before adding alkali.

TABLE 4 : pH of 10^{-2}M imines 1, II and III in ethanol at Temperature range (20-60) °C

Temp.°C	pH of imine number		
	I	II	III
20	5.06	4.36	5.53
30	4.86	4.29	5.39
40	4.82	4.22	5.30
50	4.7	4.16	5.15
60	4.65	4.10	5.13

CONCLUSIONS

1 Imines I,II and III were prepared by a standard method[2,3] Their chemical structures were confirmed by chemical method using ferric chloride and diazotization reagents and physical method by using m.p, IR and uv spectra.
2 The original 10^{-2}M of Schiff bases in ethanol, had been proved to exist oringally in zwitter ions forms. These were in agreement[14] with o, m, p- amino phenols.
3 The zwitter ions formation in imines after adding 0.1M NaOH as a titrant during $\overline{pKa}$ determination, was confirmed to exist also experimentally by the

following methods:-

i By $\overline{pKa}$ values estimated in these Schiff bases having a range of values around (5-6) pKa units.

ii A blue shiff in uv spectra of 10^{-4}M solution of imines were observed, after adding 2 drops of 0.1N NaOH.

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