

Comparison of pKa values for some phenols imines derived from 3-acetyl and 4-acetyl pyridines.

A.S.P.Azzouz and R.D.S.Uezbak

Chemistry Department / College of Education

University of Mosul

خلاصة

يشتمل البحث على تحضير ستة ايمينات مشتقة من الكيتونات الام والمسمات بريدينات 3-اسيتال و 4-اسيتال. هذه الايمينات تحتوي المجاميع الفينولية في مواقع اورثو، ميتا وبارا في جانب الامين الاروماتي للجزيئات. تم اثبات الهيئات التركيبية سابقاً بواسطة اطياف UV, IR ودرجات الانصهار هذا بالاضافة الى الكشوفات النوعية الكيميائية.

الهدف الرئيسي للدراسة هو تعيين قيم pKa للايمينات الفينولية و - pKa لاحماضها القرينة (ايونات النتريليوم) بالطريقة المجهادية. الاخيرة وجد انها بسيطة، سريعة ودقيقة و قد لوحظ عموماً ان قيم ثوابت التاين للاحماض المدروسة تعتمد على ثلاثة عوامل رئيسية وهي :-

1. الهيئة التركيبية للايمين.
2. درجة الحرارة اثناء تعيين pKa.
3. نوع الاواصر الهيدروجينية الموجودة في الايمينات.

Abstract

The study includes the preparation of a new six imines derived from the mother ketones, namely the 3-acetyl and 4-acetyl pyridines. These imines containing phenols groups in ortho, meta and para positions on aromatic amine side of the molecules. The structures of these compounds were confirmed previously by UV, IR spectra, melting points in addition to the examination of specific chemical tests.

The main object of this study is the determination of pKa values for these phenolic imines and pKa⁻ for their conjugate acids (nitrilium ions) by potentiometric method. The last as found to be simple, rapid and precise.

Generally, it was observed that, ionization constants values in these acids depend on three main factors :-

1. The chemical structures of imines.
2. The ambient temperature during pKa determination.
3. The type of hydrogen bonding present in these imines.

Introduction

The spectrophotometric and potentiometric methods were applied previously for the determination¹ of pKa values of monoxime and

**Presented at the second conference on Chemistry, University of Mosul, college of Education, 17-18 November-2013.*

dioxime in oxo phenyl pyridinium chloride with values of 4.32 and 4.27 respectively. During the last decades, many aliphatic and aromatic imines were prepared²⁻⁶. These were for their wide applications in different fields^{5,7}.

The potentiometric method for the determination of pKa was reviewed by cookson⁸.

Azzouz⁹⁻¹¹ etal had applied the potentiometric method for determination of pKa for oximes and Schiff bases derived from benzil⁹⁻¹⁰, N-formyl pipyridine¹¹. This method as found to be simple, rapid and precise.

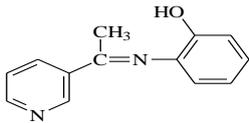
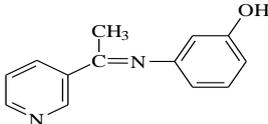
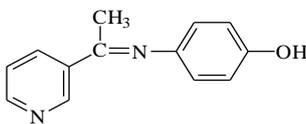
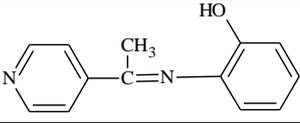
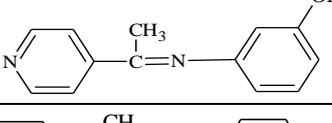
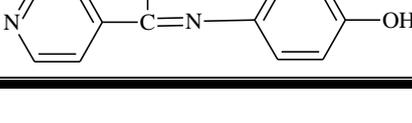
The lack of publications in the field of pKa studies, encouraged the workers, to deal with pKa determination of phenolic imines derived from 3-acetyl and 4-acetyl pyridines.

Experimental

All chemical used in this study was supplied from Fluka, BDH and Molckula companies.

All Schiff bases were prepared by standard method², or by the reactions of equimolar amounts from 3-acetyl and 4-acetyl pyridines with o, m, p-amino phenols. Table (1) shows, the number, nomenclature and structures of imines prepared.

Table (1) : Number, nomenclature and structures of imines

Comp. No.	Nomenclature	Structure
1	Methyl-3-pyridyl ketonylidene <i>o</i> -amino phenol	
2	Methyl-3-pyridyl ketonylidene <i>m</i> -amino phenol	
3	Methyl-3-pyridyl ketonylidene <i>p</i> -amino phenol	
4	Methyl-4-pyridyl ketonylidene <i>o</i> -amino phenol	
5	Methyl-4-pyridyl ketonylidene <i>m</i> -amino phenol	
6	Methyl-4-pyridyl ketonylidene <i>p</i> -amino phenol	

Solutions required

0.1M NaOH and HCl were prepared by standard procedure¹². 0.01M of benzoic acid as standard¹³ for the calibration of potentiometric method used for pKa determination of imines under study.

This required a calibration of pH meter used, by using a buffer solution of pH nine. For determination of pKa for any imine under study at any desired temperature, following the procedure as:

Pipette 50ml of 10⁻²M of any acid imines and placed in a special titration cell containing double layers, for circulating water inside the cell. Water was pumped from any thermostat at certain temperature in the range between (10-50)C°. When the of imine reached the required temperature, addition of 0.5ml successive quantities of 0.1M NaOH was done. The mixture was stirred with magnetic bar placed inside the cell after each addition, followed by measurement of pH after each addition. Titration was continued for about seven times, then followed by calculation of pKa from Handerson-Hasselbach equation of the form :-

$$pK_a = pH + \log \frac{[HA]}{[A^-]}$$

Instrumentation

1. Electrothermal melting point apparatus was used for measurement of melting points of imines.
2. FTIR spectrophotometer was used for measurement of IR spectra of solid imines by KBr disc method or in solution after dissolving imines in dry benzene.
3. A computerized double beam Shimadzu 1601 for measurement of UV spectra of imines solutions by using ethanol and dry benzene as solvents.
4. A memmert thermostat manufactured by Searle company model L200, for fixation the temperature of imines solution. Water is pumped out from thermostat to cell by using water pump.
5. A digital Philips pH meter model pw 9421 was used for measuring pH of solutions during potentiometric titration.

Result and Discussion

All phenolic Schiff bases (1-6) are regarded as weak acids, having phenol groups in o, m and p-positions. They are considered as positional²⁴ isomers. As well known phenol has two reverse behaviors, inductive and mesomeric effects. In order to know the net behavior of the last two effects, it is advisable to use the sigma constant(σ) from Hammett equation as shows in Table(2).

Table (2) : Sigma constants for substituents

Substituent	σ_p	σ_m
NH ₂	-0.66	-0.16
OH	-0.37	+0.121

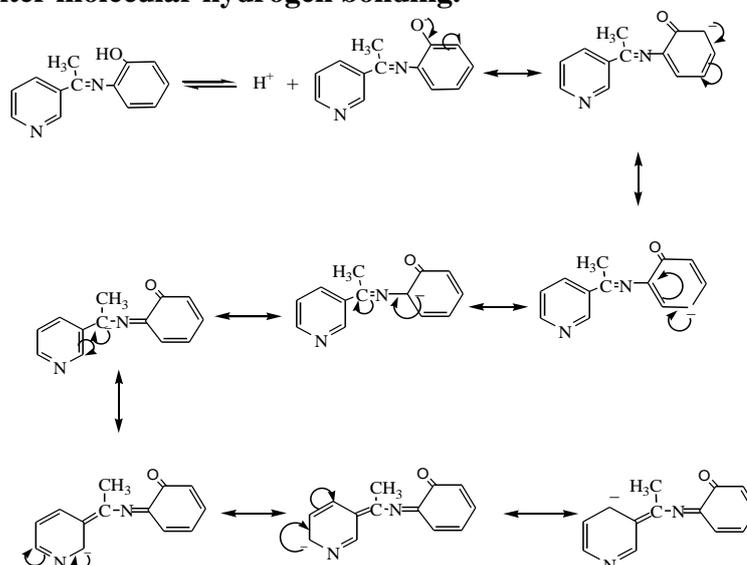
The negative and positive signs of σ constant, means an electron donor and acceptor property of substituents NH₂ and OH at meta or para positions.

Comparison of pKa for phenolic Schiff bases derived from 3-acetyl pyridine

This includes pKa for Schiff bases 1-3, as in Table (3-5), with the following results :-

1. An inverse relation between pKa and T. This means that raising the temperature was accompanied by an increase of acidity or lowering the pKa value.
2. At constants temperature, the study showed that Schiff bases (1) had higher acidity among others, with an order of increasing acidity with the following arrangement 1>2>3. When dilution method from the IR spectrum was applied to Schiff bases 1, 2, 3. These showed the occurrence of intra, inter and inter molecular hydrogen bonding in these molecules respectively. The result of intra molecular hydrogen bonding in Schiff bases 1 is accompanied by an increase of stability of molecule and hence its acid anion by resonance as in Scheme (1).

Scheme (1) : Resonance structures of acid (1) anion phenolic acid 2 and 3 had an inter molecular hydrogen bonding.



It was observed that acidity of 2 was greater than 3 at temperatures range (288-298)K. This was in agreement with electron acceptor and donor properties of OH groups in meta and para positions in these acids. The reverse of these results were obtained at absolute temperatures 308, 318 and 328. The last could be due to the weakening property of hydrogen bonding in acids 2 and 3 at these relatively elevated temperatures. This comes in agreement with pKa study²⁵ of imines and dibenzamide collected previously.

Table (3) : pKa values for imine 1 in 10% ethanol at different temperatures

T (K)	ml of (0.1 M) NaOH	pH	pKa	$\overline{\text{pKa}}$
288	0.2	8.34	9.3051	9.4174
	0.4	8.72	9.3346	
	0.6	9.02	9.4032	
	0.8	9.31	9.5040	
	1.0	9.41	9.4311	
	1.2	9.59	9.5932	
	1.4	9.68	9.3503	
298	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	
308	0.2	8.38	9.3453	9.2555
	0.4	8.75	9.3648	
	0.6	8.93	9.3127	
	0.8	9.07	9.2623	
	1.0	9.23	9.2495	
	1.2	9.32	9.1685	
	1.4	9.42	9.0857	
318	0.2	8.25	9.2149	9.1406
	0.4	8.65	9.2645	
	0.6	8.86	9.2424	
	0.8	8.95	9.1418	
	1.0	9.10	9.1187	
	1.2	9.20	9.0476	
	1.4	9.29	8.9542	
328	0.2	8.00	8.9646	8.8983
	0.4	8.33	8.9438	
	0.6	8.58	8.9617	
	0.8	8.76	8.9512	
	1.0	8.87	8.8878	
	1.2	8.98	8.8264	
	1.4	9.09	8.7527	

Comparison of pKa values for some phenols imines derived from

Table (4) : pKa values for imine 2 in 10% ethanol at different temperatures

T (K)	ml of (0.1 M) NaOH	pH	pKa	$\overline{\text{pKa}}$
288	0.2	8.72	9.6867	9.9488
	0.4	9.38	10.0000	
	0.6	9.61	9.9997	
	0.8	9.79	9.9918	
	1.0	9.93	9.9619	
	1.2	10.15	10.0213	
	1.4	10.28	9.9805	
298	0.2	8.81	9.7773	9.8893
	0.4	9.24	9.8581	
	0.6	9.52	9.9080	
	0.8	9.73	9.9303	
	1.0	9.90	9.9309	
	1.2	10.05	9.9158	
	1.4	10.21	9.9045	
308	0.2	8.79	9.7571	9.8518
	0.4	9.24	9.8581	
	0.6	9.51	9.8979	
	0.8	9.72	9.9200	
	1.0	9.86	9.8897	
	1.2	9.98	9.8426	
	1.4	10.11	9.7975	
318	0.2	8.66	9.6264	9.7148
	0.4	9.12	9.7369	
	0.6	9.34	9.7256	
	0.8	9.53	9.7265	
	1.0	9.73	9.7992	
	1.2	9.86	9.7183	
	1.4	9.99	9.6709	
328	0.2	8.43	9.3954	9.5097
	0.4	8.93	9.5456	
	0.6	9.20	9.5843	
	0.8	9.36	9.5544	
	1.0	9.51	9.5323	
	1.2	9.66	9.5132	
	1.4	9.77	9.4427	

Table (5) : pKa values for imine 3 in 10% ethanol at different temperatures

T (K)	ml of (0.1 M) NaOH	pH	pKa	$\overline{\text{pKa}}$
288	0.2	9.07	10.0399	10.1598
	0.4	9.59	10.2143	
	0.6	9.84	10.2359	
	0.8	10.03	10.2405	
	1.0	10.16	10.2028	
	1.2	10.27	10.1497	
	1.4	10.33	10.0353	
298	0.2	9.03	9.9994	10.0161
	0.4	9.45	10.0712	
	0.6	9.70	10.0917	
	0.8	9.86	10.0639	
	1.0	10.00	10.0347	
	1.2	10.09	9.9578	
	1.4	10.20	9.8938	
308	0.2	8.85	9.8176	9.7745
	0.4	9.31	9.9289	
	0.6	9.46	9.8471	
	0.8	9.62	9.8179	
	1.0	9.75	9.7767	
	1.2	9.82	9.6771	
	1.4	9.88	9.5563	
318	0.2	8.54	9.5058	9.5251
	0.4	9.00	9.6160	
	0.6	9.24	9.6246	
	0.8	9.39	9.5847	
	1.0	9.53	9.5526	
	1.2	9.60	9.4521	
	1.4	9.67	9.3401	
328	0.2	8.34	9.3052	9.3131
	0.4	8.82	9.4351	
	0.6	9.04	9.4232	
	0.8	9.17	9.3629	
	1.0	9.30	9.3201	
	1.2	9.39	9.2392	
	1.4	9.44	9.1059	

Comparison of pKa for Schiff bases 4-6 derived from 4-acetyl pyridine

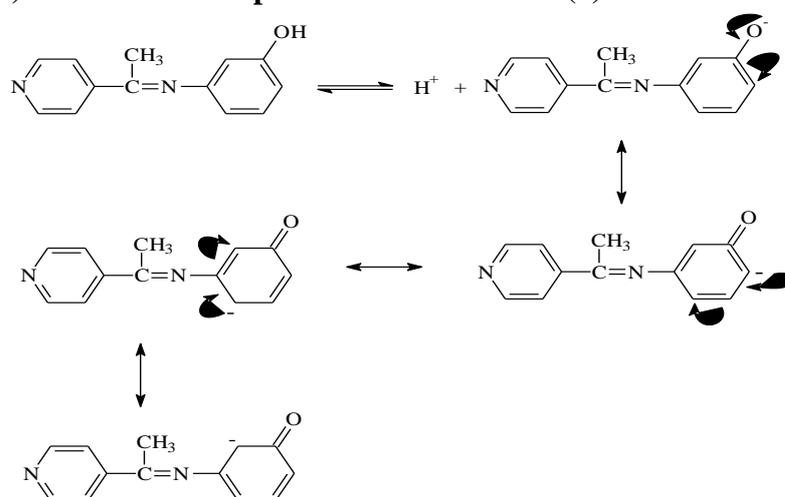
In these 4-6 phenolic acids, the following summarized results were collected from Tables 6-8

1. The pKa values of these acids were decreased by an increase of temperatures. This is in full agreement with acids 1-3 and with previous studies^{11,16}.

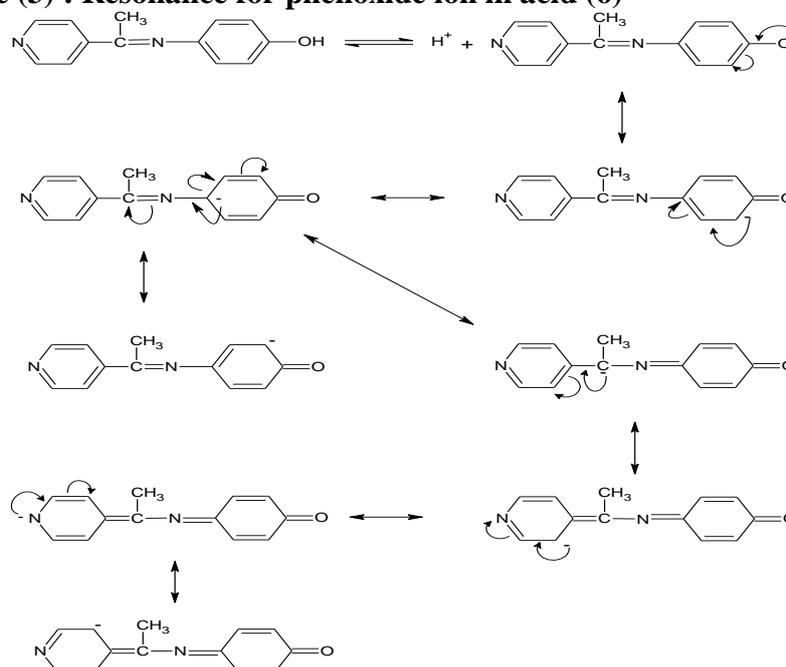
2. The arrangement of increasing acidity was in order of acid number 4>6>5. The increase of acidities of acid number 4 at all temperatures were due to the capability to occur in a form of intramolecular hydrogen bonding. The last would accompanied by the increase of stability of its phenoxide ion by resonance similar to that cited in Scheme (1). The increase of acidity of acid number 6 as compared to acid 5 at all temperatures, does not agreed with values of sigma constant listed in Table (2). A suitable interpretation to the last was due to the following two reasons :-

1. The variation of strength of intermolecular hydrogen bonding in acids 5 and 6 due to their molecular linearity.
2. The difference in resonance number for phenoxide ions in Scheme (2-3) for acids 4 and 5 respectively.

Scheme (2) : Resonance for phenoxide ion in acids (5)



Scheme (3) : Resonance for phenoxide ion in acid (6)



These Scheme show a resonance numbers of 4 and 8 for acid 5 and 6 respectively.

Finally these two last reasons might explain the variation of pKa for acid 5 and 6 at all temperatures.

Table (6) : pKa values for imine 4 in 10% ethanol at different temperatures

T (K)	ml of (0.1 M) NaOH	pH	pKa	$\overline{\text{pKa}}$
288	0.2	8.60	9.5661	9.5237
	0.4	9.05	9.6664	
	0.6	9.18	9.5641	
	0.8	9.36	9.5544	
	1.0	9.47	9.4918	
	1.2	9.60	9.4521	
	1.4	9.70	9.3708	
298	0.2	8.30	9.2651	9.2559
	0.4	8.63	9.2444	
	0.6	8.87	9.2524	
	0.8	9.05	9.2422	
	1.0	9.28	9.2999	
	1.2	9.41	9.2594	
	1.4	9.56	9.2278	
308	0.2	8.25	9.2149	9.2486
	0.4	8.62	9.2344	
	0.6	8.96	9.3428	
	0.8	9.13	9.3226	
	1.0	9.22	9.2395	
	1.2	9.39	9.2392	
	1.4	9.48	9.1465	
318	0.2	8.13	9.0947	9.1522
	0.4	8.61	9.2244	
	0.6	8.83	9.2123	
	0.8	9.03	9.2221	
	1.0	9.14	9.1589	
	1.2	9.28	9.1282	
	1.4	9.36	9.0249	
328	0.2	8.01	8.9746	8.9441
	0.4	8.40	9.0139	
	0.6	8.64	9.0218	
	0.8	8.80	8.9913	
	1.0	8.94	8.9580	
	1.2	9.01	8.8565	
	1.4	9.13	8.7929	

Comparison of pKa values for some phenols imines derived from

Table (7) : pKa values for imine 5 in 10% ethanol at different temperatures

T (K)	ml of (0.1 M) NaOH	pH	pKa	$\overline{\text{pKa}}$
288	0.2	8.95	9.9185	10.4025
	0.4	9.65	10.2745	
	0.6	9.99	10.3922	
	0.8	10.30	10.5283	
	1.0	10.50	10.5743	
	1.2	10.65	10.5783	
	1.4	10.77	10.5514	
298	0.2	9.02	9.9893	10.1629
	0.4	9.46	10.0814	
	0.6	9.78	10.1739	
	0.8	10.02	10.2300	
	1.0	10.16	10.2028	
	1.2	10.36	10.2478	
	1.4	10.49	10.2150	
308	0.2	8.87	9.8378	9.9943
	0.4	9.32	9.9391	
	0.6	9.65	10.0405	
	0.8	9.84	10.0432	
	1.0	10.03	10.0659	
	1.2	10.17	10.0425	
	1.4	10.29	9.9914	
318	0.2	8.65	9.6156	9.7554
	0.4	9.13	9.7470	
	0.6	9.43	9.8167	
	0.8	9.62	9.8179	
	1.0	9.78	9.8074	
	1.2	9.90	9.7596	
	1.4	10.04	9.7235	
328	0.2	8.30	9.2651	9.3727
	0.4	8.73	9.3447	
	0.6	8.98	9.3629	
	0.8	9.25	9.4434	
	1.0	9.42	9.4412	
	1.2	9.57	9.4216	
	1.4	9.66	9.3298	

Table (8) : pKa values for imine 6 in 10% ethanol at different temperatures

T (K)	ml of (0.1 M) NaOH	pH	pKa	$\overline{\text{pKa}}$
288	0.2	8.94	9.9084	10.0783
	0.4	9.50	10.1222	
	0.6	9.70	10.1122	
	0.8	9.93	10.1363	
	1.0	10.14	10.1816	
	1.2	10.21	10.0852	
	1.4	10.30	10.0024	
298	0.2	8.90	9.8680	9.9275
	0.4	9.36	9.9797	
	0.6	9.64	10.0303	
	0.8	9.82	10.0226	
	1.0	9.92	9.9516	
	1.2	9.99	9.8531	
	1.4	10.10	9.7869	
308	0.2	8.88	9.8479	9.7966
	0.4	9.26	9.8784	
	0.6	9.52	9.9080	
	0.8	9.62	9.8179	
	1.0	9.77	9.7972	
	1.2	9.85	9.7079	
	1.4	9.94	9.6187	
318	0.2	8.64	9.6063	9.5581
	0.4	9.10	9.7168	
	0.6	9.29	9.6751	
	0.8	9.41	9.6049	
	1.0	9.53	9.5526	
	1.2	9.59	9.4419	
	1.4	9.64	9.3094	
328	0.2	8.52	9.4857	9.1720
	0.4	8.80	9.4150	
	0.6	8.86	9.2424	
	0.8	8.98	9.1719	
	1.0	9.00	9.0183	
	1.2	9.13	8.9771	
	1.4	9.23	8.8937	

Comparison between pKa and pKa⁻ for phenolic Schiff bases derived 3-acetyl and 4-acetyl pyridines

Both pKa and pKa⁻ values for these acids were obtained after titration of these acid compounds with NaOH and HCl respectively. Hence pKa⁻ value represent the acidity of nitrilium ion (conjugate acid) produced for each acid.

Comparison of pKa values for some phenols imines derived from

This study encourage the worker to evaluate the relative pKa values, denoted Kr as define in the following equation :-

$$K_r = \frac{\bar{K}_a}{K_a}$$

\bar{K}_a = Ionization constant of nitrilium ion acid

K_a = Ionization constant of phenolic acid

K_r was calculated at fix temperature, solvent and position of phenol group at ortho, meta and para positions as in Table (9).

Table (9) shows that relative acidity K_r of acid phenols have higher values between 2832.69-296073.82. These numbers shows the higher acidity of nitrilium ion produced after titration of phenolic Schiff bases with HCl titrant relative to phenolic acid and agreed with literature¹⁷⁻¹⁸.

Table (9) : The relative K_r values for phenolic Schiff bases at different temperatures

Comp.No.	T(K)	K_r
1	288	3480.17
	298	4080.37
	308	6115.05
	318	7524.89
	328	6120.68
2	288	6845.18
	298	87377.58
	308	111532.13
	318	115771.06
	328	114788.93
3	288	4716.28
	298	5353.03
	308	4832.81
	318	3896.73
	328	3379.87
4	288	6975.89
	298	6054.80
	308	9268.29
	318	10399.20
	328	11038.24
5	288	296073.82
	298	187845.16
	308	176725.82
	318	138324.78
	328	79836.23
6	288	5086.28
	298	5078.09
	308	6015.89
	318	5225.16
	328	2832.69

References

1. L.T.Milovanovi, K.D.K.Raji and B.S.Stankovi, Monatshefte, 2004, **119**, 100.
2. Ed.S.Patai, The Chemistry of Carbon Nitrogen Double Bond, 1970 Wiley, New York.
3. A.S.P.Azzouz, Z.Phys.Chem., 2002, **216**, 1.
4. A.S.P.Azzouz, K.A.Abdalla and Kh.I.Al-Niemi, MicroChem.J. 1991, **43**, 45.
5. A.S.P.Azzouz, S.A.Ahmed and R.H.Al-Hyall, Nat.J.Chem., 2010, **39**, 499.
6. A.S.P.Azzouz and B.O.Kashmda, Nat.J.Chem., 2011, **41**, 1.
7. A.S.P.Azzouz and S.S.Othman, J.Edu.Sci., 2001, **48**, 32.
8. R.F.Cookson, Chem.Rev., 1974, **74**, 5.
9. A.S.P.Azzouz, M.S.Saeed and Kh.I.Al-Niemi, Nat.J.Chem., 2007, **25**, 38.
10. A.S.P.Azzouz, M.S.Saeed and Kh.I.Al-Niemi, J.Edu.Sci., 2006, **18(4)**, 1.
11. A.S.P.Azzouz and H.J.Al-Al-Mula, Al-Anbar Univ.J for pure Sci., 2010, **4(2)**, 59.
12. A.I.Vogel and D.S.Lond, A Text Book of Quantitative Inorganic Analysis Including Elementary Instrument Analysis, 1972, 3rd ed., Longman, London.
13. A.Albert and E.P.Serjeant, The Determination of Ionization constant, 1984, 3rd ed., Chapman and Hill, London.
14. C.R.Noller, Text Book of Organic Chemistry, W.B.Saunders Comp., London, pp.252-273.
15. A.S.P.Azzouz and Kh.I.Al-Niemi, J.Edu.Sci.,2004, **16(1)**, 59.
16. A.S.P.Azzouz and F.H.Maree, J.Edu.Sci., 2010, **23(3)**, 17.
17. J.March, Advanced Organic Chemistry, McGraw Hill Book Company, London, pp.63-65, 222-226.
18. A.S.P.Azzouz, A.A.Rahman and A.G.Taki, Nat.J.Chem., 2005, **20**, 568.