



The Effect of Temperature and Thermodynamic Parameters on the Ionization Constants of Some Imines Derived from Vanillin with substituted aniline

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ABSTRACT

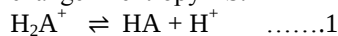
This work presents a method for the preparation of imine compounds including Schiff bases derived from vanillin with aniline, o-nitroaniline, o-tolidene and o-chloroaniline. Compounds' structures of the prepared compounds were confirmed by physical methods like melting point, infrared spectroscopy (IR), electronic spectroscopy (U.V), and nuclear magnetic resonance spectroscopy (NMR).

The ionization constants of the imine nitrogen proton K_{a1} and the phenol hydroxyl group proton K_{a2} were determined using the spectrometric titration method at five temperatures including 293,298,303,308 and 313K in a buffer solution medium. The thermodynamic of ionization for imines confirm that ionization reactions in these imines are accompanied by an increase of parameters ΔG° and ΔH° . These mean that ionization reactions in these imines are non-spontaneous and endothermic respectively. ΔS° values of ionization reactions estimated have a negative and a positive signs.

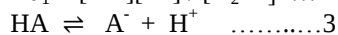
Introduction

Schiff [1] bases are compounds containing the imine group or what is known azomethine group ($CH=N-$). Schiff [3, 2] was the first to prepare these compounds in 1864, by condensing primary amines with aldehydes or ketones [5, 4]. Schiff bases have the general formula of $R_1R_2C=N-R_3$. Imines can be further characterized as primary ($R_3 = H$) or secondary ($R_3 = \text{alkyl or aryl}$) aldimines ($R_1 = H$, $R_2 = \text{alkyl or aryl}$), or ketimines ($R_1 = \text{alkyl or aryl}$, $R_2 = \text{alkyl or aryl}$) depending on the specific identities of R_1 , R_2 and R_3 [7,6].as the Because of their ability to form complexes with transition metal ions, Schiff bases are considered as a very important class of compounds [8]. Temperature is a parameter that affects many chemical reactions, and it also affects the physical constants, including the ionization constant. It was found that the dpK_a/dT changes by -0.4 to -0.2 per 10 K for each of the phenols and amines [9]. Therefore, the effect of temperature on the pK_{a1} and pK_{a2} values was studied and calculated at five temperatures including 293,298,303,308 and 313K. the change of ionization constants with temperature has importance in thermodynamic studies[10]. Therefore, in this study, the

thermodynamic parameters were determined for the ionization constants of the imine nitrogen proton and the proton of the hydroxyl phenol group as shown in equations 1 and 3 respectively, among these important parameters are the change in the Gibbs free energy ΔG° , the change in the enthalpy ΔH° , and the change in entropy ΔS° .



$$K_{a1} = [HA][H^+] / [H_2A^+] \dots\dots\dots 2$$



$$K_{a2} = [A^-][H^+] / [HA] \dots\dots\dots 4$$

Experimental method

Chemicals

Chemicals and solvents were supplied from Fluka and BDH companies were used without further purification.

Preparation of Schiff bases

Schiff bases were prepared by mixing equimolar amounts of aldehyde vanillin and primary aromatic amines including aniline, ortho-nitroaniline, ortho-tolidene and ortho-chloroaniline dissolved in 10-15 ml of ethanol. The mixture was mixed in a 250ml conical flask and refluxed for two hours The resulting

solid was separated and washed and recrystallized with ethanol and dried [11, 12,].
Melting points were determined using a melting point meter (Stuart melting point /smp 30).

All the structural formulas and melting points are listed in Table 1

Table 1: Numbers, names, structural formulas and melting points of the prepared imines

Compound no	Structural Formulas	Name	Melting Point
1		2-Methoxy-4-((phenyl imino) methyl) phenol	150 – 153
2		2-Methoxy-4-((o-nitro phenyl imino) methyl) phenol	51
3		2-Methoxy-4-((o-tolyl imino) methyl) phenol	113
4		2-Methoxy-4-((o-chloro phenyl imino)methyl) phenol	68

FTIR Spectra

Infrared spectra of the prepared imines in the solid state were measured in the range 400-3800 cm^{-1} in the

form of KBr disks. The results are included in Table (2).

Table 2: The important wavenumber in the IR spectrum of the prepared imines

Comp. No.	OHstr. cm^{-1}	C=Nstr. cm^{-1}	C=Cstr. aromatic cm^{-1}	C-Hstr. aromatic cm^{-1}	C-Hstr. aliphatic cm^{-1}	C-O-C str. cm^{-1}	C-H bend cm^{-1}	NO_2 cm^{-1}	Cl cm^{-1}
1	3228.62 w	1622.02 m	1427.23 1514.02 1583.45 s	3089.75 w	2958.6 w	1161.07 s	690.47 765.69 s		
2	3475.49 M	1625.88 M	1427.23 1510.16 M	3114.82 W	2825.52 M	1124.42 M	761.83 m	1352.01 s	
3	3159.18 w	1623.95 S	1431.08 1514.02 1591.16 S	3012.60 M	2925.81 2970.17 M	1217.0 S	761.83 s		
4	3454.27 w	1625.88 M	1429.15 1463.87 1515.94 M	3205.47 W	2810.09 M	1122.49 M	761.83 m		586.32 M

Weak = W, Medium = M, Strong = S, Bending Vibration = bend, Stretching Vibration = str

Electronic Spectra

The electronic spectra of the prepared imines were measured at a concentration of 10^{-4} molarity in

ethanol solvent. the main peaks lambds with the corresponding transition listed in Table (3).

Table 3: Important bands in the U.V spectrum of the prepared Schiff bases

Comp. No.	λ_{max}	ϵ_{max}	Transition type	λ_{max}	ϵ_{max}	Transition type
1	285	4300	$\pi \rightarrow \pi^*$	325.5	6920	$\pi \rightarrow \pi^*$
2	278.5	7940	$\pi \rightarrow \pi^*$	308.5	6580	$\pi \rightarrow \pi^*$
3	281.8	6400	$\pi \rightarrow \pi^*$	319.2	8050	$\pi \rightarrow \pi^*$
4	282	7650	$\pi \rightarrow \pi^*$	314.5	8960	$\pi \rightarrow \pi^*$

NMR spectra

The following figures show the measurements of the NMR spectra of the prepared imines.

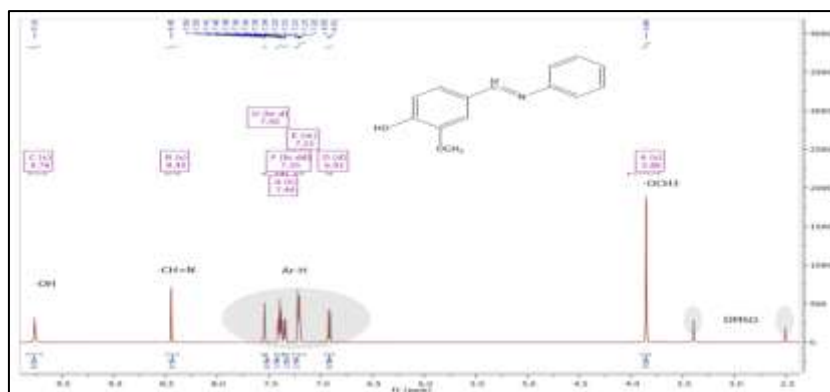


Fig. 1: NMR spectrum of compound No. 1

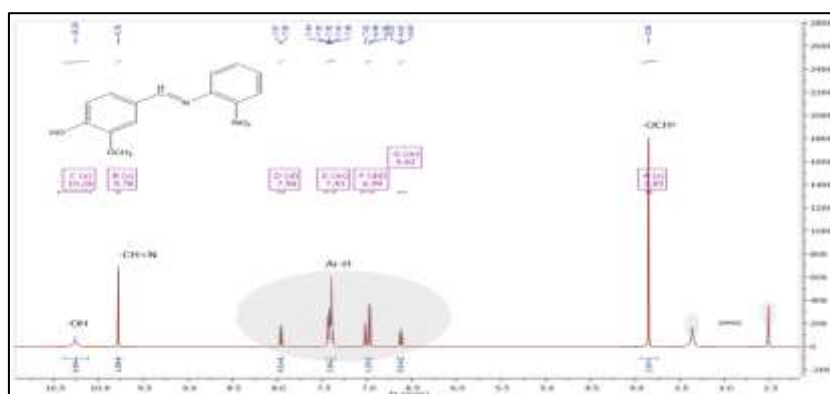


Fig. 2: NMR spectrum of compound No. 2

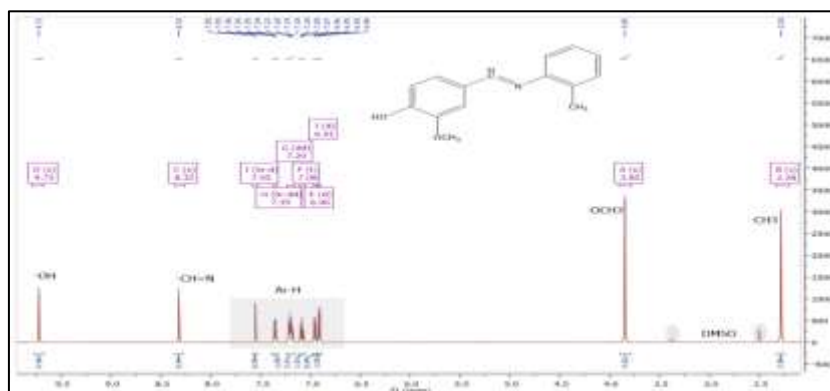


Fig. 3: NMR spectrum of compound No. 3

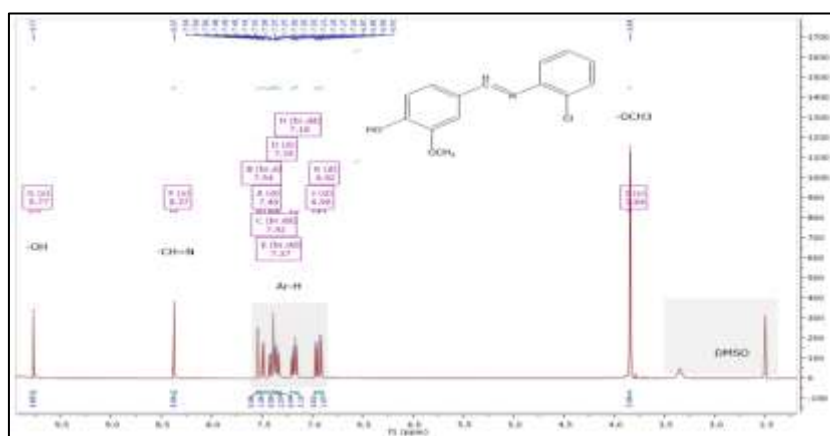


Fig. 4: NMR spectrum of compound No. 4

Determination of the pKa : The pKa of the prepared imines were determined using the spectrophotometric

titration method that depends on the measurement of the ultraviolet and visible spectrum of the imine

solution which is prepared at a concentration of 5×10^{-5} in a buffer solution medium [13] consisting of chloroacetic acid, piperazine, boric acid, succinic acid, Tris(hydroxymethyl)aminomethane, di-Sodium hydrogen phosphate anhydrous, potassium hydroxide, ethylenediamine, and n-butylamine.

This solution has a pH of 12 and by the gradual addition of 0.5 milliliters of 10 N hydrochloric acid the pH reaches 1.6 [15.14], the values of the K_{a1} and K_{a2} are obtained from equations 5 and 6 [15.14], respectively.

$$(A_{\lambda} - A_{\lambda H_2A}) \cdot 10^{-pH} = -K_1 \cdot A_{\lambda} + K_1 \cdot A_{\lambda HA} \dots 5$$

$$(A_{\lambda} - A_{\lambda A}) \cdot 10^{pH} = -1/K_2 \cdot A_{\lambda} + 1/K_2 \cdot A_{\lambda HA} \dots 6$$

Where $A_{\lambda H_2A}$, $A_{\lambda HA}$ and $A_{\lambda A}$ are the absorbance of the types H_2A^+ , HA and A respectively. The value of $A_{\lambda H_2A}$ is assigned to the region of the lowest pH, while $A_{\lambda A}$ is assigned to the region of the highest pH.

Results and discussion

Measurements of the IR spectra of the four prepared imines showed the frequencies of stretch bands belonging to the azomethane group in the range $1622.02 - 1625.88 \text{ cm}^{-1}$ with medium intensity. All the frequencies listed in Table 2 are in agreement with the literature [16]. Also, the proton beams belonging to the azomethane group of the four compounds appeared in the range (8.32-9.78) ppm in the NMR spectrum. As for the electronic spectra, the values of $\epsilon_{\max}$ were > 1000 , which attribute to the transition of $\pi \rightarrow \pi^*$ since the prepared imines tend to adopt a configuration in space of two aromatic rings are hardly coplanar. This geometry results in two types of resonance in the molecule, the first taking

place between phenol and the double bond of the imine, the second relating to the lone pair of the nitrogen and the phenyl part of the aniline. [17]. The ionization constants of the four imines were calculated at five temperatures including 293, 298, 303, 308 and 313K. It was found that the values of $\ln K_{a1}$ and $\ln K_{a2}$ of the prepared imines decrease with increasing temperature as shown in Tables 4 and 5. This means that the acidity of the imine increases when the temperature is increased. These results are in agreement with other study [19].

The thermodynamic parameters for the ionization reaction mentioned in equations 1 and 3 were found at five temperatures, The change in the Gibbs free energy was calculated from the following equation [20].

$$\Delta G^\circ = -R T \ln K_a \dots\dots\dots 7$$

As for the heat of enthalpies ΔH° , they were calculated from the following Van't Hoff's integral equation [21].

$$\ln K_a = \text{constant} - \Delta H^\circ / R T \dots\dots\dots 8$$

K_a = ionization constant, R = gas constant, T = absolute temperature.

the relationship between $\ln K_a$ against T^{-1} results in a straight line with a negative slope equal to $-\Delta H^\circ/R$.

From Figures 5 and 6, we determine the values of ΔH° at the five temperatures by knowing the value of the constant and substituting it with Equation 8. As for the entropy change values, they can be obtained from eq.9.

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \dots\dots\dots 9$$

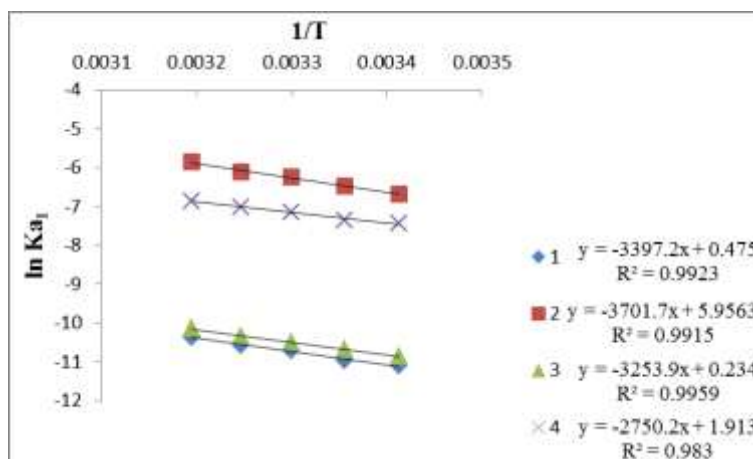


Fig. 5: The relationship of $\ln K_{a1}$ against T^{-1} for the compounds 1, 2, 3 and 4

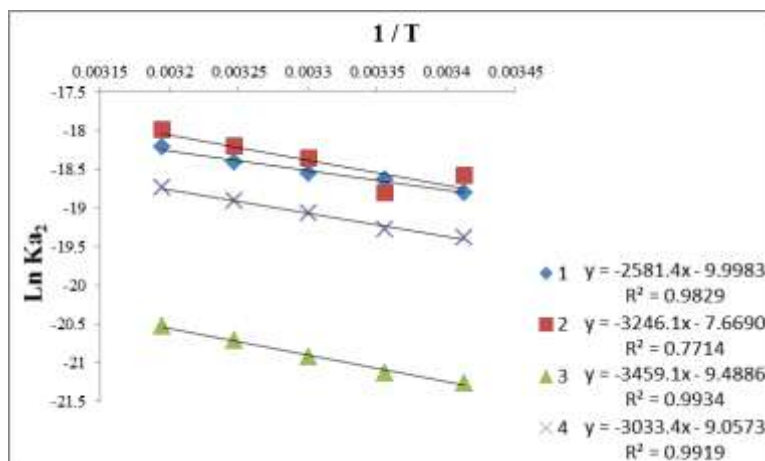


Fig. 6: The relationship of $\ln K_{a2}$ against T^{-1} for the compounds 1, 2, 3 and 4

Table 4: Thermodynamic parameters for the ionization constants (pK_{a1}) of the prepared imines

Compoun.No.	T K	$\ln K_{a1}$	ΔH J.mol ⁻¹	ΔG J.mol ⁻¹	ΔS J.mol ⁻¹ . K ⁻¹	ΔH J.mol ⁻¹	ΔG J.mol ⁻¹	ΔS J.mol ⁻¹ . K ⁻¹
1	293	-11.0985	28192.86	27035.87	3.948	28244.05	27047.58	3.948
	298	-10.9557	28320.27	27143.54	3.948			
	303	-10.7208	28203.78	27007.31	3.948			
	308	-10.5804	28309.52	27093.3	3.948			
	313	-10.3593	28193.86	26957.9	3.948			
2	293	-6.67289	30764.68	16255.18	49.52	30775.82	15771.11	49.52
	298	-6.46336	30770.53	16013.43	49.52			
	303	-6.24922	30747.37	15742.66	49.52			
	308	-6.11106	30900.97	15648.67	49.52			
	313	-5.83936	30695.56	15195.65	49.52			
3	293	-10.8613	27028.26	26458.13	1.945	27053.12	26463.53	1.945
	298	-10.6909	27067.34	26487.48	1.945			
	303	-10.5044	27051.64	26462.06	1.945			
	308	-10.357	27120.68	26521.37	1.945			
	313	-10.1406	26997.7	26388.66	1.945			
4	293	-7.43965	22783.11	18123.01	15.90	22864.90	18045.75	15.90
	298	-7.36597	22989.35	18249.72	15.90			
	303	-7.15413	22841.42	18022.27	15.90			
	308	-7.02058	22876.36	17977.69	15.90			
	313	-6.8617	22834.28	17856.09	15.90			

Table 5: Thermodynamic parameters of ionization constants (pKa₂) for the prepared imines

Compoun. No.	T K	Ln Ka ₁	$\Delta\bar{H}$ J.mol ⁻¹	$\Delta\bar{G}$ J.mol ⁻¹	$\Delta\bar{S}$ J.mol ⁻¹ . K ⁻¹	$\Delta\bar{H}$ J.mol ⁻¹	$\Delta\bar{G}$ J.mol ⁻¹	$\Delta\bar{S}$ J.mol ⁻¹ . K ⁻¹
1	293	-18.8075	21459.39	45815.14	-83.12	21461.96	46648.97	-83.12
	298	-18.6325	21392.02	46163.41	-83.12			
	303	-18.5496	21542.13	46729.14	-83.12			
	308	-18.4069	21532.04	47134.68	-83.12			
	313	-18.2158	21384.25	47402.52	-83.12			
2	293	-18.5796	26578.04	45259.84	-63.7604	26987.74	46307.14	-63.76
	298	-18.8098	27602.08	46602.68	-63.7604			
	303	-18.3539	26916.69	46236.09	-63.7604			
	308	-18.2042	26977.61	46615.81	-63.7604			
	313	-17.9924	26864.29	46821.3	-63.7604			
3	293	-21.2644	28685.75	51800.06	-78.88	28759.28	52662.47	-78.88
	298	-21.1285	28838.68	52347.43	-78.88			
	303	-20.919	28794.7	52697.9	-78.88			
	308	-20.7187	28756.89	53054.52	-78.88			
	313	-20.5252	28720.4	53412.47	-78.88			
4	293	-19.3832	25153.75	47217.42	-75.30	25220.04	48036.73	-75.30
	298	-19.2726	25309.17	47749.35	-75.30			
	303	-19.0677	25217.57	48034.26	-75.30			
	308	-18.9111	25232.75	48425.96	-75.30			
	313	-18.7361	25186.99	48756.71	-75.30			

From Tables 4 and 5, we notice that the values of $\Delta\bar{H}$ due to the ionization reaction of the imine nitrogen proton were positive with a range between (22864.90-30775.82) Joule. Mole⁻¹ and the values of $\Delta\bar{H}$ due to the ionization reaction of the phenol hydroxyl group proton were positive and with a range between (21461.96-25220.04) Joule. Mole⁻¹. Positive values mean that the ionization reaction is endothermic. This means that the breaking of the chemical bond and the separation of molecules into positive and negative ions occurs when the molecule absorbs heat. All values of $\Delta\bar{G}$ had a positive signs. This means that ionization process of imines is non-spontaneous. The last can be accepted, because ionization of ions from phenol or conjugate acid of imines have a covalent bonding properties or are difficult to ionize solutions. It was shown in Table 4 that all $\Delta\bar{S}$ value had a positive signs while all $\Delta\bar{S}$ value in Table 5 had a negative signs. The positive signs of $\Delta\bar{S}$ values are normal for the ionization reaction to change from

regular to irregular ($\bar{S}_2 < \bar{S}_1$) and this means an increase in the entropy of the products compared to the entropy of the reactants.

Negative values mean that the entropy of the products is less than the entropy of the reactants This may be attributed, in general, to the interference of the negative A⁻ ion resulting from ionization with the medium, which may contain H⁺ ions, causing electrostatic attraction which leads to an increase in the regularity.

Conclusion

It can be concluded from the above that the thermodynamic parameters of the ionization reaction in the buffer solution medium of the prepared imines had a positive sign for both $\Delta\bar{G}$ and $\Delta\bar{H}$. This means that the ionization reaction is not spontaneous and endothermic, while the values of $\Delta\bar{S}$ were different between regularity and irregularity.

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تأثير درجة الحرارة والمتغيرات الترموداينميكية على ثوابت تأين بعض الايمينات المشتقة من الفانلين ومعوذات الانلين

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الملخص

يشتمل البحث على تحضير مركبات إيمينية تشمل قواعد شف المشتقة من الفانلين و الانلين أو اورثو نايتروانلين أو اورثو توليديدين أو اورثو كلوروانلين. تم التأكد من الهياكل التركيبية باستخدام الطرائق الفيزيائية مثل درجات الانصهار ،أطياف الاشعة تحت الحمراء (IR) ،الأطياف الالكترونية (U.V) فضلا عن أطياف الرنين النووي المغناطيسي (NMR). تم تعيين ثوابت تأين بروتون نتروجين الإيمين K_{a1} وبروتون مجموعة هيدروكسيل الفينول K_{a2} باستخدام الطريقة التسحيحة الطيفية عند خمس درجات حرارية تشمل 293، 298، 303، 308 و 313 كلفن في وسط المحلول المنظم. ان ثرموداينمك التآين للايمينات يبين ان تفاعل التآين العائد لها مصحوب بزيادة المتغيرات ΔG^- و ΔH^- وهذا يدل على انه تفاعل غير تلقائي وماص للحرارة على التوالي. اما قيم ΔS^- فقد كانت لها اشارتين احدهما موجبة والاخرى سالبة.