

## Determination Of Thermodynamic Functions from the pKa Values of a Number of Schiff Bases by Employing the DFT Method: Theoretical Study

Ra'ed T. Gh. Al-Abady, Fedaa Hasan Meire Altaiea and Emad A. S. Al-Hyali

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Ra'ed T. Gh. Al-Abady, Fedaa Hasan Meire Altaiea and Emad A. S. Al-Hyali

Department of Chemistry – College of Education for Pure Sciences – University of Mosul

Received: 27 January 2022      Accepted: 24 March 2022

DOI: <https://dx.doi.org/10.24237/djps.1802.577C>

ORCID: <https://orcid.org/0000-0002-5090-8485>

Email: [dremadalhyali@uomosul.edu.iq](mailto:dremadalhyali@uomosul.edu.iq)

### Abstract

Thermodynamic functions are normally calculated experimentally through studying the effect of temperature on the equilibrium constant. Such studies may facing experimental errors, they may require the consumption of expensive chemicals, in addition of being time consuming. The development of computer science and programing facilitated the theoretical study of such project. In this work the determination of pKa of several Schiff bases are achieved by statistical analysis using SPSS program (V.12) and by employing parameters based on quantum mechanically derived method. The Chem. Office program (V.12,2010) is used for achieving these studies. The density functional theory (DFT) is applied as an ab initio method, using the method of (B3LYP) at basis set (3-21G). The theoretical pKa values were determined by several derived equations at several temperatures (20,30,40,50, and 60 °C. These equations were obtained from applying multi-parametric regression analysis based on parameters derived from DFT method. The calculated pKa were highly consistent with the practical values in terms of R<sup>2</sup> and SE. These consistency improved as temperature increased from 20-60C°. The best agreement between pKa<sub>(calc)</sub> and pKa<sub>(exp)</sub> are seen

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at 50 and 60 °C. The calculated pKa at various temperatures (20-60°C) were used to calculate the  $\Delta G^\circ$ ,  $\Delta H^\circ$  values, and  $\Delta S^\circ$ . The

**Keywords:** Thermodynamic functions, pKa, DFT, Correlation analysis, Schiff bases.

### حساب الدوال الترموداينميكية من قيم pKa لعدد من قواعد شيف باستخدام طريقة DFT: دراسة نظرية

رائد طارق غانم العبادي، فداء حسن مرعي الطائي و عماد عبد الإله صالح الحياي

قسم الكيمياء – كلية التربية للعلوم الصرفة – جامعة الموصل

#### الخلاصة

تعد الدوال الترموداينميكية من الدوال المهمة للغاية إذ يمكنها تزويد الباحثين بمعلومات قيمة حول النظام المدروس. حيث يتم تحديد تلقائية واتجاه التفاعل المفضل بواسطة قيمة وعلامة  $\Delta G$ . كذلك يتم تقدير نوع وطبيعة القوى التي تتحكم في التفاعل بواسطة  $\Delta H$  وعلامتها. فيما يُشار إلى ترتيب وعشوائية النظام المدروس بقيمة وعلامة  $\Delta S$ . وعادة يتم حساب هذه القيم تجريبياً من خلال دراسة تأثير درجة الحرارة على ثابت الاتزان. وقد تواجه مثل هذه الدراسات أخطاء تجريبية، وقد تتطلب استهلاك مواد كيميائية باهظة الثمن، بالإضافة إلى أنها تستغرق وقتاً طويلاً. وقد سهّل تطوير علوم الكمبيوتر والبرمجة الدراسة النظرية لمثل هذا البحث. في هذا العمل، تم حساب قيم pKa للعديد من قواعد شيف عن طريق التحليل الإحصائي باستخدام برنامج SPSS (V.12) وباستخدام متغيرات تستند على طرق ميكانيك الكم. واستخدم برنامج Office V.12 Chem (2010) لانجاز هذه الدراسة. وقد تم تطبيق نظرية DFT كطريقة أساسية ab initio باستخدام طريقة (B3LYP) وبمستوى اساس (3-21G). وقد تم إيجاد قيم pKa النظرية من خلال عدة معادلات مشتقة عند درجات حرارة متعددة (20، 30، 40، 50، 60 درجة مئوية) تم الحصول على هذه المعادلات من تطبيق التحليل الانحداري متعدد المتغيرات استناداً إلى المتغيرات المشتقة من طريقة DFT. بما يتوافق مع القيم العملية من حيث R2 وSE، وقد تحسن هذا التوافق مع زيادة درجة الحرارة من 20-60 درجة مئوية، وقد كان أفضل توافق بين pKa(calc) و pKa(exp) يظهر عند 50 و 60 درجة مئوية. تم استخدام pKa المحسوب عند درجات حرارة مختلفة (20-60م) لحساب قيم  $\Delta G^\circ$  و  $\Delta H^\circ$  و  $\Delta S^\circ$ . اظهرت النتائج توافق بين القيم المحسوبة للدوال الترموداينميكية بشكل ممتاز مع القيم التجريبية.

**الكلمات المفتاحية:** الدوال الديناميكية الحرارية، pKa، DFT، تحليل الارتباط، قواعد شيف.

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### Introduction

Computational chemistry is an important and commonly used topic in calculating many chemical functions in various fields of chemistry. It was used for calculating the chemical shift of C-13 and N-15 NMR, and in calculating the pK values of many organic compounds. Schiff rules have received great attention in this field. Schiff's bases are compounds of great importance [1]. Their ease of preparation, the presence of variety of substituents, and the imine group (C=N) in their structures, attracted researchers to use it in various industrial applications such as anti-corrosion inhibitors, the manufacture of polymers and dyes [2]. In addition, it has wide scope of biological activities. They were used as selective and sensitive reagents in estimating metals by formation of colored complexes with a number of metal ions [3].

The pKa (dissociation constant of acid) is a valuable chemical function. It helps in estimating the ionization behavior of various kinds of compounds such as Schiff's bases[4]. The extent of ionization of these compounds is determined in aqueous solution that gives the hydrogen ion with the conjugated base for the ionized compound. One of the most important uses of pka values is to estimate the stability, dispensation, and accommodating the drug in the body. The pka function could also be used as an indication of the acidity strength. The pKa value is calculated mathematically by the negative value of logarithm (Ka). The strength of the acidity is inversely proportional to the value of pka although there are many practical methods used to estimate pKa values, the theoretical methods are characterized by their ability to give a quantitative description for the chemical variations, while practical methods are often limited to providing a qualitative description only [5-6].

The pKa value is affected by two factors, electronic and geometrical. The first factor is represented by inductive and mesomeric effects, while the spatial congestion representing the steric effect. Since such factors can be estimated using quantum mechanical methods, this encouraged many researchers in the field to work in this path [7].

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### Method and Calculation

This work is carried out by gathering experimental pKa values for a number of Schiff bases from the literature and used for achieving this research. Two programs, the Chem. Office (V12, 2010) employing the density functional theory (DFT) to undergo the parameters determination which will be used to estimate the pKa by correlation using regression analysis by (SPSS program V.2011). Parameters used as descriptors of the electronic and steric factors such as electronic density, charges, the value of the total energy of the molecule, the energies of the molecular orbitals HOMO, LUMO and other variables will be mentioned and calculated later [6,7].

Simple regression analysis (eq.1) is performed between pKa values with each of the proposed variables. Depending on the results obtained, then multiple linear regression analysis (MLRA) (eq.2) is achieved. Mathematical relationship is derived from variables determined by applying DFT method.

$$Y = b + aX \quad (1)$$

$$Y = b + a_1X_1 + a_2X_2 + a_3X_3 + \dots + a_n X_n \quad (2)$$

Where Y is representing the pKa as a dependent variable,  $X_1, X_2, \dots, X_n$ , are independent parameters and calculated by DFT method,  $a_1, a_2, \dots, a_n$ , are coefficients  $X_1, X_2, X_3, \dots, X_n$  respectively, and b is a reference value. The success of regression and making the correct choice of parameter is indicated by correlation coefficient ( $R^2=1$ ) close to unity, standard error (SE) less than 5% of the experimental error and the consistency with the physical meaning of the subject under consideration [8].

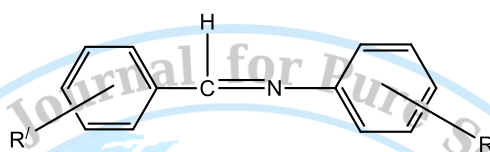
The pKa values of the compounds under study are estimated. The experimental pKa ( $pK_a(\text{exp})$ ) are then compared with the calculated by equations (3-to-7) which will be derived later by regression analysis. The calculated pKa is compared to their experimental results. Then the thermodynamic functions are estimated theoretically under the same practical conditions of

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solvent and temperatures. Regression analysis is carried out at each temperature, pKa and thermodynamic functions are calculated and compared with practical values.

### Results and Discussion



**Figure 1:** Structures of the considered compounds in this study

**Table 1:** Substituents and the experimental values of pKa of the Schiff bases selected from the literature [9] for achieving this study

COMP.NO	Substituents	
	R'	R
1	P-OH	P-NH <sub>2</sub>
2	P-OCH <sub>3</sub>	P-NH <sub>2</sub>
3	P-OCH <sub>3</sub>	m- NH <sub>2</sub>
4	o-NH <sub>2</sub>	o-OH
5	o-NH <sub>2</sub>	m-OH
6	o-NH <sub>2</sub>	p-OH
7	o-F	o-OH
8	o-F	m-OH
9	o-F	p-OH

According to the figure 1, the pKa values are affected by electronic and steric effects and since such parameters could be determined by quantum mechanical methods. The development of computer science, technology and programming facilitate such studies which attracted many researchers in the field and the interest for such calculations is increased [10]. When looking at the literature, a wide scope of various theoretical application can be seen. In this work the density functional theory (DFT) has been applied to achieve this study. It is believed that the DFT method could be the best choice to estimate the pKa by this method of calculation.

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This method of calculation is aimed to estimate the values of pKa of the selected compounds for doing this work by deriving theoretical equations from statistical analysis depending on the calculated parameters by employing DFT method.

The parameters used as descriptors for achieving the statistical analysis are determined by the application of the DFT method employing the method of B3LYP at bases set 3-21G. Several types of parameters are calculated such as kinetic energy (KE), Total energy (TE), potential energy (PE), energy of Highest Occupied Molecular Orbital (HOMO), energy of the Lowest unoccupied Molecular Orbital (LUMO), lowding charge of nitrogen atom of the imine bond (NL) and Mullikan charge of imine bond (NM), In addition to those, lowding charge of O (OL), Mullikan charge of O (OM), length of C=N bond (C=N) and dipole (1),(2) and (3). The values of these parameters are calculated at temperatures 20°C, 30°C, 40°C, 50°C and 60°C as presented in Tables (2-6) respectively. The aim of determining these values at different temperatures is to derive various equations for calculating the thermodynamic functions theoretically [11,12]. Looking at the values in tables (2-6) it can be seen clearly those the values of parameters stay constant except the values of the pKa.

**Table 2:** Results obtained from applying DFT method at 20°C

Comp.	pKa	KE × 10 <sup>3</sup>	TE × 10 <sup>3</sup>	PE × 10 <sup>3</sup>	HOMO	LUMO	N <sub>L</sub>	N <sub>M</sub>
1	5.5703	425.277	-428.666	-853.943	-10.1070	-3.6150	-0.1513	-0.6139
2	12.0071	449.534	-453.181	-902.716	-10.0780	-3.6160	-0.1513	-0.6127
3	12.6649	449.537	-453.179	-902.717	-10.0560	-4.3850	-0.1534	-0.6129
4	6.0452	425.273	-428.674	-853.947	-8.7760	-4.2470	-0.1707	-0.6645
5	5.0654	425.285	-428.673	-853.959	-9.0340	-4.3050	-0.1797	-0.6750
6	6.4392	425.273	-428.674	-853.947	-8.8610	-4.0620	-0.1780	-0.6820
7	10.8390	452.472	-456.049	-908.521	-9.7390	-4.4370	-0.1225	-0.5754
8	12.0386	452.488	-456.051	-908.539	-9.8570	-4.4890	-0.1355	-0.5911
9	11.0559	452.489	-456.052	-908.542	-9.7940	-4.2290	-0.1335	-0.5948
Comp.	O <sub>L</sub>	O <sub>M</sub>	NH <sub>2(L)</sub>	NH <sub>2(M)</sub>	Length of C=N	Dipole1	Dipole2	Dipole3
1	-0.2498	-0.5984	-0.2908	-0.8292	1.2881	-2.8352	0.1903	-0.0928
2	0.0	0.0	-0.2912	-0.8293	1.2883	1.8044	-2.5765	0.3554
3	0.0	0.0	-0.3008	-0.8337	1.2868	-0.1102	-4.2722	0.2627
4	-0.2430	-0.5911	-0.2839	-0.8628	1.2967	1.8803	1.4220	-0.0051
5	-0.2535	-0.6023	-0.2860	-0.8650	1.2997	-1.3461	-0.3110	-0.0248

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6	-0.2502	-0.5978	-0.2908	-0.8660	1.3011	-0.6408	-0.9745	-0.0835
7	-0.2227	-0.5747	0.0	0.0	1.2842	0.6890	1.0316	0.0181
8	-0.2506	-0.5991	0.0	0.0	1.2838	0.1661	2.7525	-0.0050
9	-0.2469	-0.5963	0.0	0.0	1.2859	0.2822	-3.4908	-0.0532

**Table 3:** results obtained from applying DFT method at 30°C

Comp.	pKa	KE × 10 <sup>3</sup>	TE × 10 <sup>3</sup>	PE × 10 <sup>3</sup>	HOMO	LUMO	N <sub>L</sub>	N <sub>M</sub>
1	4.9776	425.277	-428.666	-853.943	-10.1070	-3.6150	-0.1513	-0.6139
2	11.8881	449.534	-453.181	-902.716	-10.0780	-3.6160	-0.1513	-0.6127
3	11.9403	449.537	-453.179	-902.717	-10.0560	-4.3850	-0.1534	-0.6129
4	5.9065	425.273	-428.674	-853.947	-8.7760	-4.2470	-0.1707	-0.6645
5	5.1375	425.285	-428.673	-853.959	-9.0340	-4.3050	-0.1797	-0.6750
6	6.2557	425.273	-428.674	-853.947	-8.8610	-4.0620	-0.1780	-0.6820
7	10.4026	452.472	-456.049	-908.521	-9.7390	-4.4370	-0.1225	-0.5754
8	11.7211	452.488	-456.051	-908.539	-9.8570	-4.4890	-0.1355	-0.5911
9	10.7043	452.489	-456.052	-908.542	-9.7940	-4.2290	-0.1335	-0.5948
Comp.	OL	OM	NH2(L)	NH2(M)	Length of C=N	Dipole1	Dipole2	Dipole3
1	-0.2498	-0.5984	-0.2908	-0.8292	1.2881	-2.8352	0.1903	-0.0928
2	0.0	0.0	-0.2912	-0.8293	1.2883	1.8044	-2.5765	0.3554
3	0.0	0.0	-0.3008	-0.8337	1.2868	-0.1102	-4.2722	0.2627
4	-0.2430	-0.5911	-0.2839	-0.8628	1.2967	1.8803	1.4220	-0.0051
5	-0.2535	-0.6023	-0.2860	-0.8650	1.2997	-1.3461	-0.3110	-0.0248
6	-0.2502	-0.5978	-0.2908	-0.8660	1.3011	-0.6408	-0.9745	-0.0835
7	-0.2227	-0.5747	0.0	0.0	1.2842	0.6890	1.0316	0.0181
8	-0.2506	-0.5991	0.0	0.0	1.2838	0.1661	2.7525	-0.0050
9	-0.2469	-0.5963	0.0	0.0	1.2859	0.2822	-3.4908	-0.0532

**Table 4:** results obtained from applying DFT method at 40°C

Comp.	pKa	KE × 10 <sup>3</sup>	TE × 10 <sup>3</sup>	PE × 10 <sup>3</sup>	HOMO	LUMO	N <sub>L</sub>	N <sub>M</sub>
1	4.8493	425.277	-428.666	-853.943	-10.1070	-3.6150	-0.1513	-0.6139
2	11.3241	449.534	-453.181	-902.716	-10.0780	-3.6160	-0.1513	-0.6127
3	11.1983	449.537	-453.179	-902.717	-10.0560	-4.3850	-0.1534	-0.6129
4	5.8529	425.273	-428.674	-853.947	-8.7760	-4.2470	-0.1707	-0.6645
5	5.5875	425.285	-428.673	-853.959	-9.0340	-4.3050	-0.1797	-0.6750
6	6.1989	425.273	-428.674	-853.947	-8.8610	-4.0620	-0.1780	-0.6820
7	10.0965	452.472	-456.049	-908.521	-9.7390	-4.4370	-0.1225	-0.5754
8	11.2900	452.488	-456.051	-908.539	-9.8570	-4.4890	-0.1355	-0.5911
9	10.3075	452.489	-456.052	-908.542	-9.7940	-4.2290	-0.1335	-0.5948

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Comp.	O <sub>L</sub>	O <sub>M</sub>	NH <sub>2(L)</sub>	NH <sub>2(M)</sub>	Length of C=N	Dipole1	Dipole2	Dipole3
1	-0.2498	-0.5984	-0.2908	-0.8292	1.2881	-2.8352	0.1903	-0.0928
2	0.0	0.0	-0.2912	-0.8293	1.2883	1.8044	-2.5765	0.3554
3	0.0	0.0	-0.3008	-0.8337	1.2868	-0.1102	-4.2722	0.2627
4	-0.2430	-0.5911	-0.2839	-0.8628	1.2967	1.8803	1.4220	-0.0051
5	-0.2535	-0.6023	-0.2860	-0.8650	1.2997	-1.3461	-0.3110	-0.0248
6	-0.2502	-0.5978	-0.2908	-0.8660	1.3011	-0.6408	-0.9745	-0.0835
7	-0.2227	-0.5747	0.0	0.0	1.2842	0.6890	1.0316	0.0181
8	-0.2506	-0.5991	0.0	0.0	1.2838	0.1661	2.7525	-0.0050
9	-0.2469	-0.5963	0.0	0.0	1.2859	0.2822	-3.4908	-0.0532

**Table 5:** results obtained from applying DFT method at 50°C

Comp.	pKa	KE × 10 <sup>3</sup>	TE × 10 <sup>3</sup>	PE × 10 <sup>3</sup>	HOMO	LUMO	N <sub>L</sub>	N <sub>M</sub>
1	4.5346	425.277	-428.666	-853.943	-10.1070	-3.6150	-0.1513	-0.6139
2	10.8871	449.534	-453.181	-902.716	-10.0780	-3.6160	-0.1513	-0.6127
3	10.7135	449.537	-453.179	-902.717	-10.0560	-4.3850	-0.1534	-0.6129
4	5.7380	425.273	-428.674	-853.947	-8.7760	-4.2470	-0.1707	-0.6645
5	5.6590	425.285	-428.673	-853.959	-9.0340	-4.3050	-0.1797	-0.6750
6	6.0704	425.273	-428.674	-853.947	-8.8610	-4.0620	-0.1780	-0.6820
7	9.7394	452.472	-456.049	-908.521	-9.7390	-4.4370	-0.1225	-0.5754
8	11.0213	452.488	-456.051	-908.539	-9.8570	-4.4890	-0.1355	-0.5911
9	9.9751	452.489	-456.052	-908.542	-9.7940	-4.2290	-0.1335	-0.5948

Comp.	O <sub>L</sub>	O <sub>M</sub>	NH <sub>2(L)</sub>	NH <sub>2(M)</sub>	Length of C=N	Dipole1	Dipole2	Dipole3
1	-0.2498	-0.5984	-0.2908	-0.8292	1.2881	-2.8352	0.1903	-0.0928
2	0.0	0.0	-0.2912	-0.8293	1.2883	1.8044	-2.5765	0.3554
3	0.0	0.0	-0.3008	-0.8337	1.2868	-0.1102	-4.2722	0.2627
4	-0.2430	-0.5911	-0.2839	-0.8628	1.2967	1.8803	1.4220	-0.0051
5	-0.2535	-0.6023	-0.2860	-0.8650	1.2997	-1.3461	-0.3110	-0.0248
6	-0.2502	-0.5978	-0.2908	-0.8660	1.3011	-0.6408	-0.9745	-0.0835
7	-0.2227	-0.5747	0.0	0.0	1.2842	0.6890	1.0316	0.0181
8	-0.2506	-0.5991	0.0	0.0	1.2838	0.1661	2.7525	-0.0050
9	-0.2469	-0.5963	0.0	0.0	1.2859	0.2822	-3.4908	-0.0532



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**Table 6:** results obtained from applying DFT method at 60°C

Comp.	pKa	KE × 10 <sup>3</sup>	TE × 10 <sup>3</sup>	PE × 10 <sup>3</sup>	HOMO	LUMO	N <sub>L</sub>	N <sub>M</sub>
1	4.1392	425.277	-428.666	-853.943	-10.1070	-3.6150	-0.1513	-0.6139
2	10.4736	449.534	-453.181	-902.716	-10.0780	-3.6160	-0.1513	-0.6127
3	10.6297	449.537	-453.179	-902.717	-10.0560	-4.3850	-0.1534	-0.6129
4	5.6651	425.273	-428.674	-853.947	-8.7760	-4.2470	-0.1707	-0.6645
5	5.7129	425.285	-428.673	-853.959	-9.0340	-4.3050	-0.1797	-0.6750
6	6.0387	425.273	-428.674	-853.947	-8.8610	-4.0620	-0.1780	-0.6820
7	9.4293	452.472	-456.049	-908.521	-9.7390	-4.4370	-0.1225	-0.5754
8	10.9132	452.488	-456.051	-908.539	-9.8570	-4.4890	-0.1355	-0.5911
9	9.6029	452.489	-456.052	-908.542	-9.7940	-4.2290	-0.1335	-0.5948
Comp.	O <sub>L</sub>	O <sub>M</sub>	NH <sub>2(L)</sub>	NH <sub>2(M)</sub>	Length of C=N	Dipole1	Dipole2	Dipole3
1	-0.2498	-0.5984	-0.2908	-0.8292	1.2881	-2.8352	0.1903	-0.0928
2	0.0	0.0	-0.2912	-0.8293	1.2883	1.8044	-2.5765	0.3554
3	0.0	0.0	-0.3008	-0.8337	1.2868	-0.1102	-4.2722	0.2627
4	-0.2430	-0.5911	-0.2839	-0.8628	1.2967	1.8803	1.4220	-0.0051
5	-0.2535	-0.6023	-0.2860	-0.8650	1.2997	-1.3461	-0.3110	-0.0248
6	-0.2502	-0.5978	-0.2908	-0.8660	1.3011	-0.6408	-0.9745	-0.0835
7	-0.2227	-0.5747	0.0	0.0	1.2842	0.6890	1.0316	0.0181
8	-0.2506	-0.5991	0.0	0.0	1.2838	0.1661	2.7525	-0.0050
9	-0.2469	-0.5963	0.0	0.0	1.2859	0.2822	-3.4908	-0.0532

The relation among the parameters themselves and with values of the pKa was investigated by applying simple regression (eq.1) at different temperatures. The results obtained are listed in tables (7-to-11). The results of the correlation are listed in tables (7-to-11). These results showed variation in the correlation coefficients when studying the relation between the pKa values with T.E, K.E, energy of HOMO, LUMO, Charges and dipole 1,2,3. The rest of relations stay constant i.e., not affected by temperature. In order to derive an equation at each temperature to calculate the pKa. MLRA is used for this purpose. Several attempts were tried table (12) until the best set of parameters in terms of the correlation coefficient (R<sup>2</sup>) and standard error (SE) were obtained at each temperature table (13)

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**Table 7:** Simple regression analysis results of the application of DFT method at 20 °C

parameters	pKa	KE	TE	PE	HOMO	LUMO	N <sub>L</sub>	N <sub>M</sub>	O <sub>L</sub>	O <sub>M</sub>	NH <sub>2(L)</sub>	NH <sub>2(M)</sub>	Length of C=N	Dipole1	Dipole2	Dipole3
pKa	1.000															
KE	0.966	1.000														
TE	-0.966	-1.000	1.000													
PE	-0.966	-1.000	1.000	1.000												
HOMO	-0.674	-0.671	0.671	0.671	1.000											
LUMO	-0.253	-0.314	0.313	0.314	-0.264	1.000										
N <sub>L</sub>	0.712	0.831	-0.830	-0.831	-0.708	-0.199	1.000									
N <sub>M</sub>	0.758	0.846	-0.846	-0.846	-0.832	-0.115	0.977	1.000								
O <sub>L</sub>	0.602	0.437	-0.440	-0.439	-0.509	0.241	0.064	0.215	1.000							
O <sub>M</sub>	0.586	0.415	-0.418	-0.417	-0.502	0.256	0.032	0.187	0.999	1.000						
NH <sub>2(L)</sub>	0.503	0.678	-0.676	-0.677	-0.266	-0.523	0.819	0.707	-0.362	-0.387	1.000					
NH <sub>2(M)</sub>	0.542	0.711	-0.709	-0.710	-0.319	-0.508	0.847	0.743	-0.319	-0.344	0.998	1.000				
Length of C=N	-0.781	-0.838	0.837	0.837	0.871	0.099	-0.938	-0.986	-0.282	-0.260	-0.637	-0.677	1.000			
Dipole1	0.487	0.450	-0.451	-0.450	0.116	-0.213	0.193	0.145	0.362	0.342	0.202	0.195	-0.137	1.000		
Dipole2	-0.347	-0.262	0.264	0.263	0.317	-0.229	0.046	-0.035	-0.643	-0.652	0.270	0.238	0.061	-0.032	1.000	
Dipole3	0.633	0.491	-0.493	-0.492	-0.463	0.186	0.101	0.238	0.969	0.965	-0.276	-0.240	-0.295	0.509	-0.512	1.000

**Table 8:** Simple regression analysis results of the application of DFT method at 30°C

Parameters	pKa	KE	TE	PE	HOMO	LUMO	N <sub>L</sub>	N <sub>M</sub>	O <sub>L</sub>	O <sub>M</sub>	NH <sub>2(L)</sub>	NH <sub>2(M)</sub>	Length of C=N	Dipole1	Dipole2	Dipole3
pKa	1.000															
KE	0.966	1.000														
TE	-0.966	-1.000	1.000													
PE	-0.966	-1.000	1.000	1.000												
HOMO	-0.641	-0.671	0.671	0.671	1.000											
LUMO	-0.258	-0.314	0.313	0.314	-0.264	1.000										
N <sub>L</sub>	0.692	0.831	-0.830	-0.831	-0.708	-0.199	1.000									
N <sub>M</sub>	0.733	0.846	-0.846	-0.846	-0.832	-0.115	0.977	1.000								
O <sub>L</sub>	0.599	0.437	-0.440	-0.439	-0.509	0.241	0.064	0.215	1.000							

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OM	0.583	0.415	-0.418	-0.417	-0.502	0.256	0.032	0.187	0.999	1.000							
NH <sub>2(L)</sub>	0.506	0.687	-0.676	-0.677	-0.266	-0.523	0.819	0.707	-0.362	-0.387	1.000						
NH <sub>2(M)</sub>	0.542	0.711	-0.709	-0.710	-0.319	-0.508	0.847	0.743	-0.319	-0.344	0.998	1.000					
Length of C=N	-0.753	-0.838	0.837	0.837	0.871	0.099	-0.938	-0.986	-0.282	-0.260	-0.637	-0.677	1.000				
Dipole1	0.524	0.450	-0.451	-0.450	0.116	-0.213	0.193	0.145	0.362	0.342	0.202	0.195	-0.137	1.000			
Dipole2	0.337	-0.262	0.264	0.263	0.317	-0.229	0.046	-0.035	-0.643	-0.652	0.270	0.238	0.061	-0.032	1.000		
Dipole3	0.643	0.491	-0.493	-0.492	-0.463	0.186	0.101	-0.238	0.969	0.965	-0.276	-0.240	-0.295	0.509	-0.512	1.000	

**Table 9:** Simple regression analysis results of the application of DFT method at 40°C

parameters	pKa	KE	TE	PE	HOMO	LUMO	N <sub>L</sub>	N <sub>M</sub>	O <sub>L</sub>	O <sub>M</sub>	NH <sub>2(L)</sub>	NH <sub>2(M)</sub>	Length of C=N	Dipole1	Dipole2	Dipole3	
pKa	1.000																
KE	0.970	1.000															
TE	-0.970	-1.000	1.000														
PE	-0.970	-1.000	1.000	1.000													
HOMO	-0.619	-0.671	0.671	0.671	1.000												
LUMO	-0.286	-0.314	0.313	0.314	-0.264	1.000											
N <sub>L</sub>	0.688	0.831	-0.830	-0.831	-0.708	-0.199	1.000										
N <sub>M</sub>	0.725	0.846	-0.846	-0.846	-0.832	-0.115	0.977	1.000									
O <sub>L</sub>	0.578	0.437	-0.440	-0.439	-0.509	0.241	0.064	0.215	1.000								
O <sub>M</sub>	0.562	0.415	-0.418	-0.417	-0.502	0.256	0.032	0.187	0.999	1.000							
NH <sub>2(L)</sub>	0.528	0.687	-0.676	-0.677	-0.266	-0.523	0.819	0.707	-0.362	-0.387	1.000						
NH <sub>2(M)</sub>	0.562	0.711	-0.709	-0.710	-0.319	-0.508	0.847	0.743	-0.319	-0.344	0.998	1.000					
Length of C=N	-0.739	-0.838	0.837	0.837	0.871	0.099	-0.938	-0.986	-0.282	-0.260	-0.637	-0.677	1.000				
Dipole1	0.529	0.450	-0.451	-0.450	0.116	-0.213	0.193	0.145	0.362	0.342	0.202	0.195	-0.137	1.000			
Dipole2	-0.320	-0.262	0.264	0.263	0.317	-0.229	0.046	-0.035	-0.643	-0.652	0.270	0.238	0.061	-0.032	1.000		
Dipole3	0.632	0.491	-0.493	-0.492	-0.463	0.186	0.101	0.238	0.969	0.965	-0.276	-0.240	-0.295	0.509	-0.512	1.000	

**Table 10:** Simple regression analysis results of the application of DFT method at 50°C

parameters	pKa	KE	TE	PE	HOMO	LUMO	N <sub>L</sub>	N <sub>M</sub>	O <sub>L</sub>	O <sub>M</sub>	NH <sub>2(L)</sub>	NH <sub>2(M)</sub>	Length of C=N	Dipole1	Dipole2	Dipole3

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pKa	1.000																
KE	0.966	1.000															
TE	-0.966	-1.000	1.000														
PE	-0.966	-1.000	1.000	1.000													
HOMO	-0.674	-0.671	0.671	0.671	1.000												
LUMO	-0.253	-0.314	0.313	0.314	-0.264	1.000											
N <sub>L</sub>	0.712	0.831	-0.830	-0.831	-0.708	-0.199	1.000										
N <sub>M</sub>	0.758	0.846	-0.846	-0.846	-0.832	-0.115	0.977	1.000									
O <sub>L</sub>	0.602	0.437	-0.440	-0.439	-0.509	0.241	0.064	0.215	1.000								
O <sub>M</sub>	0.586	0.415	-0.418	-0.417	-0.502	0.256	0.032	0.187	0.999	1.000							
NH <sub>2(L)</sub>	0.503	0.678	-0.676	-0.677	-0.266	-0.523	0.819	0.707	-0.362	-0.387	1.000						
NH <sub>2(M)</sub>	0.542	0.711	-0.709	-0.710	-0.319	-0.508	0.847	0.743	-0.319	-0.344	0.998	1.000					
Length of C=N	-0.781	-0.838	0.837	0.837	0.871	0.099	-0.938	-0.986	-0.282	-0.260	-0.637	-0.677	1.000				
Dipole1	0.487	0.450	-0.451	-0.450	0.116	-0.213	0.193	0.145	0.362	0.342	0.202	0.195	-0.137	1.000			
Dipole2	-0.347	-0.262	0.264	0.263	0.317	-0.229	0.046	-0.035	-0.643	-0.652	0.270	0.238	0.061	-0.032	1.000		
Dipole3	0.633	0.491	-0.493	-0.492	-0.463	0.186	0.101	0.238	0.969	0.965	-0.276	-0.240	-0.295	0.509	-0.512	1.000	

Table 11: Simple regression analysis results of the application of DFT method at 60°C

Parameters	pKa	KE	TE	PE	HOMO	LUMO	N <sub>L</sub>	N <sub>M</sub>	O <sub>L</sub>	O <sub>M</sub>	NH <sub>2(L)</sub>	NH <sub>2(M)</sub>	Length of C=N	Dipole1	Dipole2	Dipole3	
pKa	1.000																
KE	0.954	1.000															
TE	-0.955	-1.000	1.000														
PE	-0.954	-1.000	1.000	1.000													
HOMO	-0.555	-0.671	0.671	0.671	1.000												
LUMO	-0.356	-0.314	0.313	0.314	-0.264	1.000											
N <sub>L</sub>	0.642	0.831	-0.830	-0.831	-0.708	-0.199	1.000										
N <sub>M</sub>	0.674	0.846	-0.846	-0.846	-0.832	-0.115	0.977	1.000									
O <sub>L</sub>	0.557	0.437	-0.440	-0.439	-0.509	0.241	0.064	0.215	1.000								
O <sub>M</sub>	0.542	0.415	-0.418	-0.417	-0.502	0.256	0.032	0.187	0.999	1.000							
NH <sub>2(L)</sub>	0.528	0.687	-0.676	-0.677	-0.266	-0.523	0.819	0.707	-0.362	-0.387	1.000						
NH <sub>2(M)</sub>	0.558	0.711	-0.709	-0.710	-0.319	-0.508	0.847	0.743	-0.319	-0.344	0.998	1.000					
Length of C=N	-0.689	-0.838	0.837	0.837	0.871	0.099	-0.938	-0.986	-0.282	-0.260	-0.637	-0.677	1.000				
Dipole1	0.543	0.450	-0.451	-0.450	0.116	-0.213	0.193	0.145	0.362	0.342	0.202	0.195	-0.137	1.000			
Dipole2	-0.296	-0.262	0.264	0.263	0.317	-0.229	0.046	-0.035	-0.643	-0.652	0.270	0.238	0.061	-0.032	1.000		
Dipole3	0.620	0.491	-0.493	-0.492	-0.463	0.186	0.101	0.238	0.969	0.965	-0.276	-0.240	-0.295	0.509	-0.512	1.000	

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**Table 12:** Examples of the attempts of MLRA from these carried out.

Temp.°C	var	Coeff	R <sup>2</sup>	S.E
20	TE	-2.658E <sup>-4</sup>	0.975	0.582
	NH <sub>2(L)</sub>	-6.084		
	TE	-4.820E <sup>-4</sup>	0.979	0.589
NH <sub>2(L)</sub>	-25.951			
O <sub>L</sub>	-21.932			
30	TE	-2.615E <sup>-4</sup>	0.974	0.575
	NH <sub>2(M)</sub>	-2.096		
	TE	-8.835E <sup>-4</sup>	0.982	0.524
NH <sub>2(M)</sub>	-21.778			
O <sub>M</sub>	-24.744			
40	TE	-2.596E <sup>-4</sup>	0.985	0.393
	N <sub>L</sub>	-52.460		
	TE	-2.532E <sup>-4</sup>	0.988	0.381
N <sub>L</sub>	-70.873			
Length of C=N	-70.432			
50	TE	-2.529E <sup>-4</sup>	0.988	0.341
	N <sub>L</sub>	-54.596		
	TE	-2.685E <sup>-4</sup>	0.993	0.289
N <sub>L</sub>	-64.025			
Dipole2	0.095			
60	TE	-2.577E <sup>-4</sup>	0.984	0.382
	N <sub>L</sub>	-63.198		
	TE	-2.799E <sup>-4</sup>	0.994	0.251
N <sub>L</sub>	-76.529			
Dipole2	0.134			

**Table 13:** The best sets of results of MLRA at various temperatures.

Temp.°C	Parameter	Coeff
20	TE	-4.820E <sup>-4</sup>
	NH <sub>2(L)</sub>	-25.951
	O <sub>L</sub>	-21.932
	(Constant) = -213.790 R <sup>2</sup> = 0.979 Std. Error = 0.589 No of observation = 9	
30	TE	-8.835E <sup>-4</sup>
	NH <sub>2(M)</sub>	-21.778

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	$O_M$	-24.744
	(Constant) = -406.617 $R^2 = 0.982$ Std. Error = 0.524 No of observation = 9	
40	TE	$-2.532E^{-4}$
	$N_L$	-70.873
	Length of C=N	-70.432
	(Constant) = -23.652 $R^2 = 0.988$ Std. Error = 0.381 No of observation = 9	
50	TE	$-2.685E^{-4}$
	$N_L$	-64.025
	Dipole2	0.095
	(Constant) = -120.512 $R^2 = 0.993$ Std. Error = 0.289 No of observation = 9	
60	TE	$-2.799E^{-4}$
	$N_L$	-76.529
	Dipole2	0.134
	(Constant) = -127.607 $R^2 = 0.994$ Std. Error = 0.251 No of observation = 9	

**Table 14:** Comparison between experimental and calculated pKa at different temperatures

Temp. °C	Comp. No.	pka(ex)	pka(th)	*Res
20	1	5.5703	5.8674	-0.2971
	2	12.0071	12.2156	-0.2085
	3	12.6649	12.4645	0.2004
	4	6.0452	5.5432	0.5020
	5	5.0654	5.8284	-0.7630
	6	6.4392	5.8801	0.5591
	7	10.8390	10.9272	-0.0882
	8	12.0386	11.5402	0.4984
	9	11.0559	11.4590	-0.4031
30	1	4.9776	5.0109	-0.0333
	2	11.8881	11.8670	0.0211
	3	11.9403	11.9625	-0.0222
	4	5.9065	5.5703	0.3362
	5	5.1375	5.8926	-0.7551
	6	6.2557	5.8034	0.4523

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	7	10.4026	10.5605	-0.1579
	8	11.7211	11.1677	0.5534
	9	10.7043	11.0988	-0.3945
40	1	4.8493	4.8892	-0.0399
	2	11.3241	11.0804	0.2437
	3	11.1983	11.3389	-0.1406
	4	5.8529	5.6594	0.1935
	5	5.5875	6.0849	-0.4974
	6	6.1989	5.8659	0.3330
	7	10.0965	10.0594	0.0371
	8	11.2900	11.0069	0.2831
	9	10.3075	10.7200	-0.4125
50	1	4.5346	4.3265	0.2081
	2	10.8871	10.6473	0.2398
	3	10.7135	10.6250	0.0885
	4	5.7380	5.6862	0.0518
	5	5.6590	6.0976	-0.4386
	6	6.0704	5.9262	0.1442
	7	9.7394	9.9196	-0.1802
	8	11.0213	10.9130	0.1083
	9	9.9751	10.1970	-0.2219
60	1	4.1392	3.9836	0.1556
	2	10.4736	10.4732	0.0004
	3	10.6297	10.4116	0.2181
	4	5.6651	5.6340	0.0311
	5	5.7129	6.0900	-0.3771
	6	6.0387	5.8713	0.1674
	7	9.4293	9.5600	-0.1307
	8	10.9132	10.7829	0.1303
	9	9.6029	9.7980	-0.1951

\*Res= pKa(exp)-pKa(calc)

The results obtained from the MLRA was carried out at 20-60C° and by using ethanol as solvent in simulation to the experimental conditions are listed in table (13). These results were formulated as five linear equations at five different temperatures (eqs. 3-7) and used for the calculation of the theoretical pKa values [15-17]

$$pKa = -213.790 - 4.820 \times 10^{-4} \times TE - 25.951 \times N_L \text{ of } NH_2 - 21.932 \times O_L \text{ of } OH \dots (3)$$

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$$pKa_{at30C} = -406.617 - 8.835 \times 10^{-4} \times TE - 21.778 \times N_{Mof} NH_2 - 24.744 \times O_{Mof} OH \dots \dots (4)$$

$$pKa_{at40C} = -23.652 - 2.532 \times 10^{-4} \times TE - 70.373 \times N_L - 70.432 \times C = N \dots \dots (5)$$

$$pKa_{at50C} = -120.512 - 2.685 \times 10^{-4} \times TE - 64.025 \times N_L + 0.095 \times Dipol2 \dots \dots (6)$$

$$pKa_{at60C} = -127.607 - 2.799 \times 10^{-4} \times TE - 76.529 \times N_L + 0.134 \times Dipol2 \dots \dots (7)$$

The above equations (3-7) were employed to calculate the value of pKa at 20,30,40,50 and 60°C respectively. Comparison between calculated pKa with the experimental values are given in Table (14) and plotted in figure (2). This comparison showed good agreement between the experimental and calculated pKa; better correlation is indicated in terms of R<sup>2</sup> and SE.

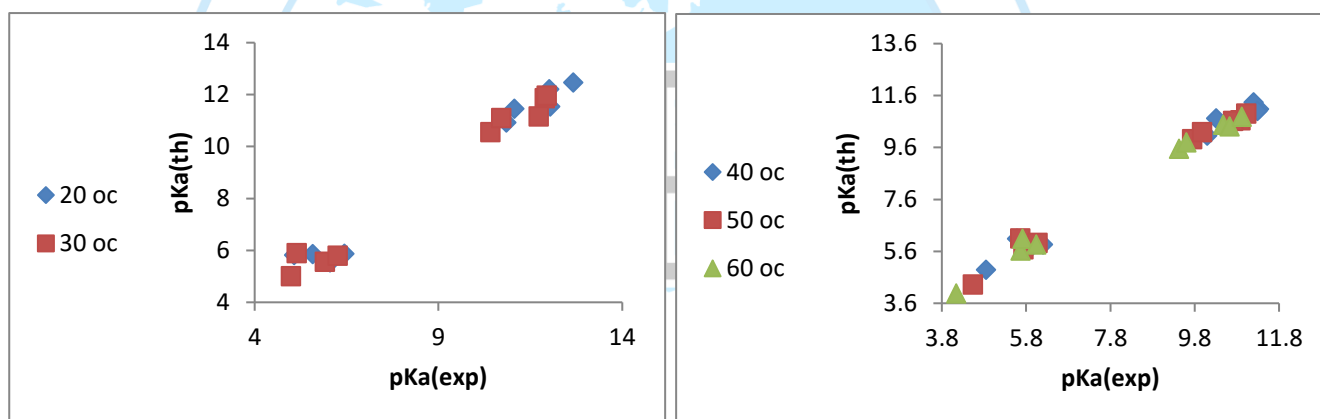


Figure (2): Relation between experimental [9] and calculated pKa values

Table (15): Variation of parameters with increasing temperature and improving the R<sup>2</sup> and SE.

T °C	Parameter	R <sup>2</sup>	SE
20	TE L <sub>NH2</sub> L <sub>OH</sub>	0.979	0.589
30	TE M <sub>NH2</sub> M <sub>OH</sub>	0.982	0.542
40	TE N <sub>L</sub> C=N	0.988	0.381
50	TE N <sub>L</sub> Dipol2	0.993	0.289
60	TE N <sub>L</sub> Dipol2	0.994	0.251

This improvement in the values of R<sup>2</sup> and SE from 20-60C° could be attributed to the freedom acquired by the molecules as a results of destruction of physical forces between solvent and



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considered Schiff bases, among the solvents molecules (C<sub>2</sub>H<sub>5</sub>OH) and among the studied molecules themselves. At 20 and 30°C the Lowding and Mullikan charge of N and O atoms in NH<sub>2</sub> and OH charges (L<sub>NH2</sub>, L<sub>OH</sub>, M<sub>NH2</sub>, M<sub>OH</sub>) with the TE were dominant. While at 40°C, the dependence on the charge decreased and the length of azo imine bond (C=N) started to appear in parameter which may be due to the increase of the charge movement across the two aromatic rings in the studied molecules. The increasing of temperature into 50 and 60. The correlation between the calculated and experimental pKa became more consistent, a new parameters appeared in the regression analysis (Dipol2) which is indicated to the increase of charge separation across the Schiff base collected for this study with increasing temperature due to breaking down of all physical forces. Separation of the charges leading to formation of dipoles on the rings. This is supported by the increase of R<sup>2</sup> to be more close to unity and raising the consistency between the experimental and calculated pKa values to less than 5%, of the accepted experimental error.

### Evaluation of thermodynamic functions

The thermodynamic functions are valuable parameters. Their study and estimation are very important since they give good indications about the favored direction of the ionization process of the Schiff bases and the type of forces controlling the ionization process due to the acquiring or releasing temperature throughout the ionization process and the order of studied system. In order to calculate, ΔG<sup>o</sup>, ΔH<sup>o</sup>, ΔS<sup>o</sup>. The values of ΔG<sup>o</sup> is estimated at equilibrium and when K is determined at various temperatures by equation(8) [15,16].

$$\Delta G^o = -nRT \ln K = nRT pKa \dots \dots \dots (8)$$

$$\text{since } pKa = -\ln K a \dots \dots \dots (9)$$

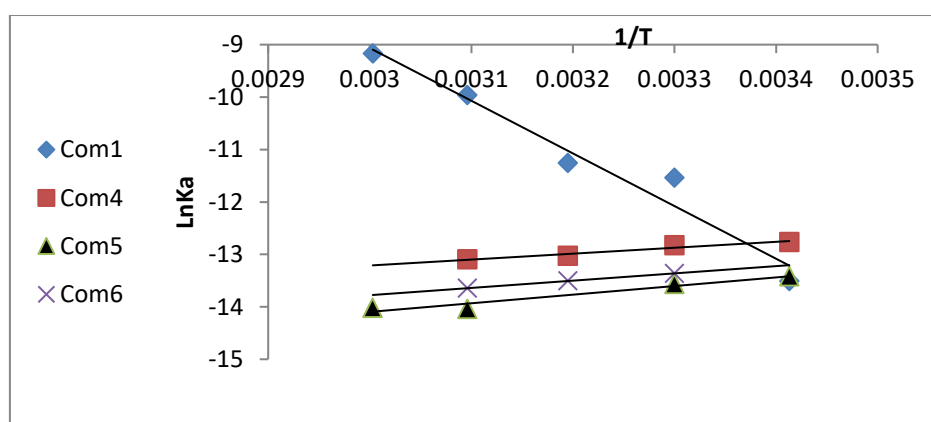
$$\ln K a = \frac{-\Delta G^o}{RT} \quad , \quad \Delta G^o = \Delta H^o - T\Delta S^o$$

$$\ln K a = \frac{-(\Delta H^o - T\Delta S^o)}{RT} = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} \dots \dots \dots (10)$$

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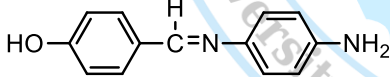
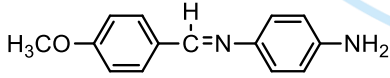
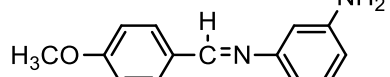

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According to Van't Hoff (Eq. 10) The plot of  $\ln K_a$  versus  $\frac{1}{T}$  should give straight line with slope equal to  $-\frac{\Delta H^\circ}{R}$  and intercept  $\frac{\Delta S^\circ}{R}$  (Fig. 3).



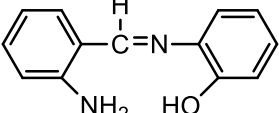
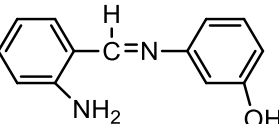
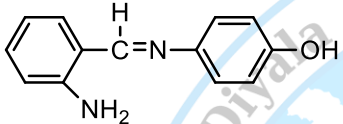
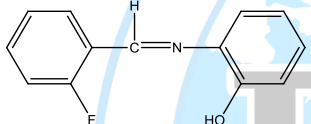
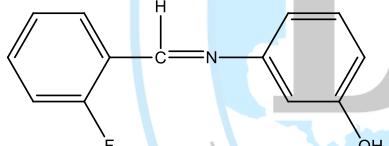
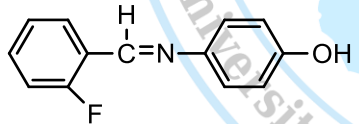
**Figure (3):** Application of Van't Hoff equation on the calculated  $K_a$  to estimate the thermodynamic functions theoretically.

**Table (16):** Thermodynamic functions determined theoretically

Comp	$\ln K_a$	T K°	$\Delta G(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta H(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta S(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$
	-13.5102	293	32.910	83.489	172.622
	-11.5380	303	29.065		179.615
	-11.2577	313	29.295		173.142
	-9.9621	323	26.752		175.656
	-9.1725	333	25.394		174.458
	-28.1274	293	68.518	88.211	67.212
	-27.3248	303	68.835		63.949
	-25.5135	313	66.393		69.707
	-24.5164	323	65.836		69.272
	-24.1155	333	66.765		64.403
	-28.7006	293	69.914	101.888	109.124
	-27.5448	303	69.389		107.257
	-26.1087	313	67.942		108.453
	-24.4649	323	65.698		112.042
	-23.9735	333	66.372		106.655
	-12.7636	293	31.092	-9.382	-138.138
	-12.8261	303	32.310		-137.601
	-13.0311	313	33.910		-138.316
	-13.0930	323	35.160		-137.902

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	-12.9728	333	35.915		-136.031
	-13.4204	293	32.692	-18.163	-168.108
	-13.5682	303	34.180		-166.581
	-14.0111	313	36.460		-166.371
	-14.0403	323	37.704		-165.089
	-14.0227	333	38.822		-162.401
	-13.5395	293	32.982	-11.519	-151.884
	-13.3628	303	33.662		-149.110
	-13.5068	313	35.148		-149.100
	-13.6455	323	36.643		-149.113
	-13.5191	333	37.428		-146.992
	-25.1608	293	61.291	63.230	6.617
	-24.3165	303	61.256		6.514
	-23.1626	313	60.275		9.440
	-22.8408	323	61.337		5.862
	-22.0128	333	60.943		6.867
	-26.5722	293	64.729	33.366	-107.042
	-25.7146	303	64.778		-103.671
	-25.3444	313	65.953		-104.111
	-25.1281	323	67.479		-105.613
	-24.8286	333	68.739		-106.225
	-26.3853	293	64.274	78.711	49.274
	-25.5559	303	64.378		47.304
	-24.6838	313	64.234		46.255
	-23.4795	323	63.052		48.481
	-22.5608	333	62.460		48.802

The results obtained for the calculation of the thermodynamic functions ( $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ ) theoretically are listed in table (16). The sign and values of the variation in the enthalpy  $\Delta H^\circ$  indicate that all compounds are endothermic indicated by the positive sign except (comp.No.4,5, and 6) which have negative sign representing exothermic reaction. This could be attributed to the inter and intra molecular hydrogen bonding which are assigned by the values of  $\Delta H^\circ$  (9-18) KJ.mol<sup>-1</sup>. Other compounds are endothermic and need additional heat to start the ionization process of the compounds under consideration. This is supported by non-spontaneous reaction (positive value of  $\Delta G^\circ$ ). The spontaneity increases ( $\Delta G^\circ$  became less) with increasing temperatures

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except for the (comps 4-6) in which the spontaneity decreases ( $\Delta G^\circ$  increasing as a positive values) with increasing temperature. Looking at the entropy values, the positive values indicating into the disorder of studied system except (comp 4,5,6 and 8) which pointing out to increasing the order of system indicated by the negative values of the  $\Delta S^\circ$  which may indicate to the increasing of order of the system considered. Values of  $\Delta H$  of comp (4,5,6 and 8KJ.mol<sup>-1</sup>)(less than 40KJ.mol<sup>-1</sup>) where as other compounds showed chemical bonds. The value of  $\Delta S^\circ$  of comp. 4,5,6 and 8 showed more ordered system indicated by negative values and the rest of the compounds showed increasing disorder indicated by the positive sign of  $\Delta S^\circ$  obtained [12,13].

### Conclusion

The above discussion so far showed very good consistency between the practical and theoretically calculated values conducted in this study. The strength of consistency between each two of the considered parameters are evaluated in terms of  $R^2$ . Simple regression analysis is used for estimation of this consistency. The relation between the calculated and experimental thermodynamic functions, pKa(calc) and pKa(exp), and  $\Delta G^\circ$ (exp) and  $\Delta G^\circ$ (calc) to the pKa(exp) values [9]. The results of these correlations are listed in Table (17).

**Table (17):** Simple regression analysis used to find relations between thermodynamic functions, pKa(calc) and pKa(exp), and  $\Delta G^\circ$ (exp)[9]

parameter	pKa(exp)	pKa(calc)	$\Delta G^\circ$ (exp)	$\Delta G^\circ$ (calc)
pKa(exp)	1.000			
pKa(calc)	0.993	1.000		
$\Delta G^\circ$ (exp)	0.886	0.877	1.000	
$\Delta G^\circ$ (calc)	0.982	0.989	0.883	1.000

Looking at table (17) shows good correlation between pKa(exp) and pKa(calc) ( $R=0.993$ ), the relation between  $\Delta G^\circ$  (calc) and pKa (calc) ( $R=0.989$ ), and between  $\Delta G^\circ$ (calc) and  $\Delta G^\circ$ (exp) (0.883). The  $\Delta G^\circ$ (calc) and  $\Delta G^\circ$ (exp) are in good agreement in their values and in the physical meaning.

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This method has proved so far to be applicable to such calculations and the DFT as a good choice for such applications.

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