حساب ثوابت تفكك حامضي و بعض بيانات الدينمة الحرارية لبعض قواعد شيف المشتقة من 4، 6-ثنائى مثيل 2-أمينو بيرميدين

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الخلاصة

تم في هذا البحث حساب ثوابت تفكك حامضي لعدد من قواعد شيف المشتقة من4، 6-ثنائي مثيل- أمينو بيرميدين فى محيط (50%) حجم /حجم دايوكسان/ ماء فى 0.003 (X=H,OH;Y=H,OH,OCH3; Z=H,OH حيث ان مولارى KCl) وفى ثلاث درجات حرارية مختلفة مجهاديا. وكذلك حسبت الطاقات الثرموداينميكية (ΔG^0 ، ΔH^0 ، ΔS^0 والعدد الموجى (سم $^{-1}$) لاهتزاز المطي لمجموعة الهيدروكسيل في طيف الاشعة pKaوتم التوصل لعلاقة خطية بين تحت الحمراء

Determination of pKa and Thermodynamic Data of Some Schiff Bases Derived From 4,6-Dimethyl 2-Amino Pyrimidine

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Abstract

Acid dissociation constants of some Schiff bases derived from 4, 6-dimethyl 2-amino pyrimidine of the type (1) in 50% V/V dioxane-water mixture in 0.003M KCl, at three different temperatures were determined potentiometrically. The thermodynamic energies were calculated and a good linear correlation was obtained between pKa and IR OH. Stretching frequencies.

Introduction

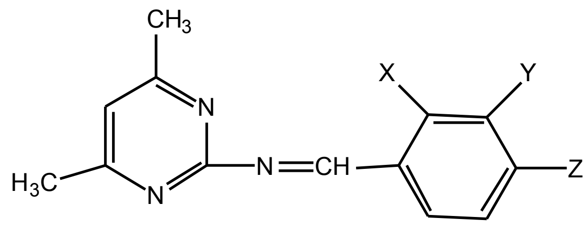
Schiff bases have recently received much attention because of their power chelation with traces of metal ions. The formation of hydrogen bonding adducts between 1-phenyl 2-aminopyrimidine and vanillin was done in ethyl alcohol at 1993(1). The pKa values (macroscopic acidity constant K_1 and K_2) of 1, 2-cyclopropanediammoniumdibromide (0.5M) were determined by potentiometric titration with KOH in carbon dioxide free water, special measures were taken to avoid errors due to cis-trans isomerization or decomposition during the titration([2).
The pKa values of pigments were determined by a three-parameter function derived from the Handerson-Hassellbach equation.

$$\Delta A = \frac{\Delta A_{max}}{1 + 10^{\,n(pKa - pH)}}$$

Where the parameters are ΔA and ΔA_{max}, the absorbance difference and the maximum absorbance difference, correspondingly, between the protonated and deprotonated states, (n) is the number of protons participating in the above transition, and pKa is the midpoint of transition(3).

Under the chromatographic conditions used in the determination of mixtures of carboxylic acids and selected inorganic anions by ion exclusion chromatography; the degree of ionization, of the solutes was determined by the acid dissociation constant (pKa) of the solutes(4). Also acid dissociation constant of some 2-methyl-N-(substituted phenyl)-4,5-dihydrofuran-3-carboxamides in 50% V/V dioxane-water mixture 0.003M KCl at three different temperatures were determined potentiometrically(5). The measurements of pK_1 and pK2 for two amino acids (proline and valine) at four different temperatures in the range 293.15-323.15K, were done conductimetrically in water and in glycerol-water mixtures with three different mole fractions of glycerol(6).

In the present study the dissociation constant of some Schiff bases derived from 4, 6-dimethyl2-amino pyrimidine was determined potentiometrically in 50% V/V dioxane-water (structure 1) at three different temperatures. ΔG°, ΔH° and ΔS° functions were also calculated.



Structure 1

Comp. No	X	Y	Z
A	H	OCH_3	OH
B	OH	H	OH
C	H	H	OH
D	OH	H	H
E	H	OH	OH
F	H	OH	H

Experimental

Schiff bases of the type (1) were synthesized by the following general procedure(7,8). Equimolar proportion of 4, 6-dimethyl 2-amino pyrimidine and the appropriate aldehyde were heated under reflux in absolute ethanol for 1 hour and the solid yield was recrystalised from absolute ethanol. Schiff bases, obtained, were found to give single spots on TLC and chractreized by their CHN analysis.

Potassium hydroxide (0.01M), carbonate free titrant was prepared from BDH (CVS).
An electronic pH–meter (model Kent) with a combined glass electrode was used to record the hydrogen ion concentration, in which the pH was maintained to±0.0.1unit.
The pH-meter was calibrated with buffers of pH 4.00 and 9.00 supplied from BDH.
The IR-spectra was recorded on a Pye-Unicam SP-300S infrared spectrometer, as KBr disk by using polystyrene film as a standard.
The following stock solutions were prepared and used:
0.02M solution of Schiff bases was prepared in dioxane-water v/v 50%.
0.1M potassium chloride was prepared by using deionized water.

The volumes of the various solutions were added in such amounts that the final concentration in the solution becomes 0.01M ligand and 0.003M KCl. The final volume was completed to 50ml of well-stirred, double wall cell, in which nitrogen was bubbled. Potassium hydroxide was added in small increments through microburette. Constant temperature was maintained with the help of HAAKE E_3 thermostat.

Results and Discussion

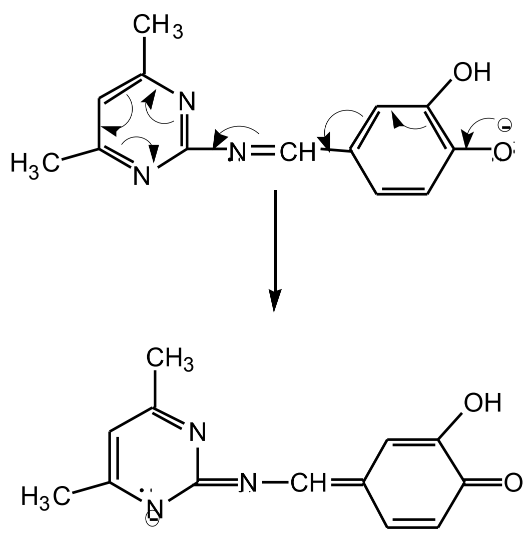
pKa determination

The calculation of the acid dissociation constants depends on the evaluation of the average number of associated with the reagent(9) $\tilde{n}_A$, using the equation used by Masoud, which was the protons determined at different pH΄s

$$\tilde{n}_A = Y - V_1 N^{\circ} / V_{\circ} C^{\circ} R$$

Where V_1 denotes the volume of alkali required to reach a given pH on the titration curve, $V_\circ$ is the initial volume of the ligand, N° is the alkali concentration, $C^\circ R$ is the total concentration of the reagent and Y is the number of displaceable hydrogen atoms in the reagent and the pKa values was obtained by point-wise calculation method(9,10). Table (1) summaries the pKa values obtained at three different temperatures. The data indicates that the compounds under investigation are different in acidic strength, due to the number and position of substitutents (especially compounds B & E) have lower values of pKa, which is attributed to the longer conjugation(11) (structure 2), which leads to stabilize the anion compounds and because all

atoms (except H) have an octet state. Also shows that as temperature of the medium increases, the pKa values decreases.



Structure (2) Compound (E)

IR spectra

The infrared data shown in Table (2), indicates that the band at 3600cm^{-1} due to free OH is absent and replaced by a band or bands at the range (3140-3320) cm^{-1}. This may be attributed to the hydrogen bonding (inter and intra).

Fig.(1) shows the correlation between the pKa with wave number (cm^{-1}) of OH stretching in IR spectra, and the best indication for the formation of Schiff bases is due to the formation of C=N bonding Table (2) with stretching vibrations (1630-1680)cm^{-1}(12,13).

Thermodynamic parameters

The change in free energy is related to the other parameters by the following equations:

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

$$\Delta G^\circ = -RT \ln Ka$$

From the above two equations

$$-RT \ln Ka = \Delta H^\circ - T\,\Delta S^\circ$$

$$-2.303\ RT \log Ka = \Delta H^\circ - T\Delta S^\circ$$

$$-\log Ka = \Delta H^\circ / 2.303\ RT - \Delta S^\circ / 2.303R$$

A plot of pKa vs.1/T does not deviate much from linearity Fig.(2). The slope of the line gives ΔH° value and the intercept gives $-\Delta S^{\circ}$ value. The thermodynamic parameters, calculated from these relations are reported in Table (3).

The positive values of ΔG° indicate that the dissociation process is non spontaneous which support that no weak acid of its own dissociates into ions.

$$LH \longrightarrow L^{-} + H^{+}$$

The higher degree of solvation of the negative ions than that of the undissociated molecule, causes the negative value of ΔS°,and more salvation means a system is more orderly fashion, which implies loss of entropy.

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Table (1): pKa values for the Schiff bases (A-F) at three different temperatures, ±0.1° C, in 50% V/V dioxane-water, 0.003M KCl

Compound No.	pKa ± 0.05 25° C	pKa ± 0.04 35°C	pKa ± 0.05 45° C
A	7.02	6.81	6.64
B	o.OH(7.9),P-OH(6.7)	7.69 , 6.56	7.46 , 6.43
C	7.05	6.85	6.63
D	6.85	6.70	6.54
E	m-OH(7.85),p-OH(6.5)	7.65 , 6.36	7.44 , 6.23
F	7.55	7.37	7.18

Where o=ortho, m=meta, p=para

Table (2): IR frequencies in cm^{-1} for the prepared Schiff bases

Compound No.	OH str.	C=N str.
A	3180	1635
B	3310 , 3140	1630
C	3190	1635
D	3160	1630
E	3320 , 3110	1645
F	3300	1640

Table (3): Thermodynamic parameter values (ΔG°, ΔH°, ΔS°) for hydroxyl group in the Schiff bases (A-F) in 50% V/V dioxane – water, 0.003M KCl at 25°C± 0.1

Compound No.	ΔG° KJ/mole	ΔH° KJ/mole	$-\Delta S$ J/mole.K°
A	40.06	34.48	18.72
B	45.08 , 38.23	39.93 , 24.50	17.28 , 46.07
C	40.23	38.11	7.11
D	39.09	28.13	36.78
E	44.79 , 37.09	37.21 , 24.50	25.43 , 42.25
F	43.08	33.55	31.98

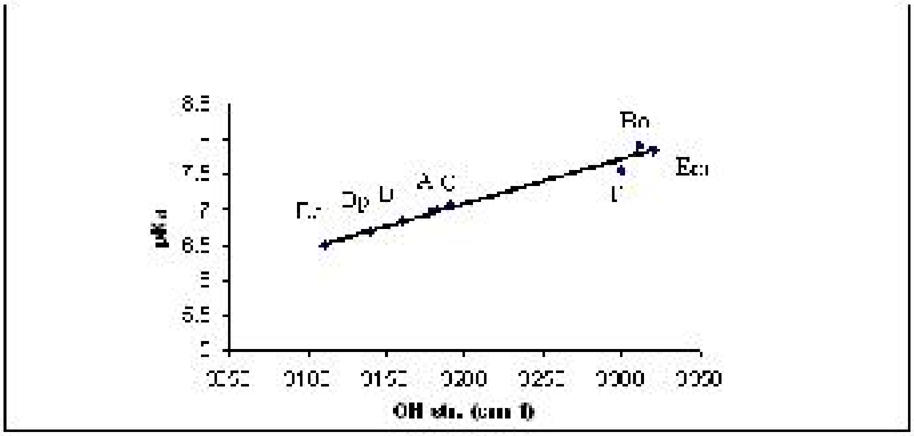

Fig. (1) Relation between pKa and OH stretching vibration frequency of Schiff bases (A-F). Where Ep,Bp represent the values for para hydroxyl group, while Bo and Em represent the values for ortho and meta hydroxy groups respectivel.y

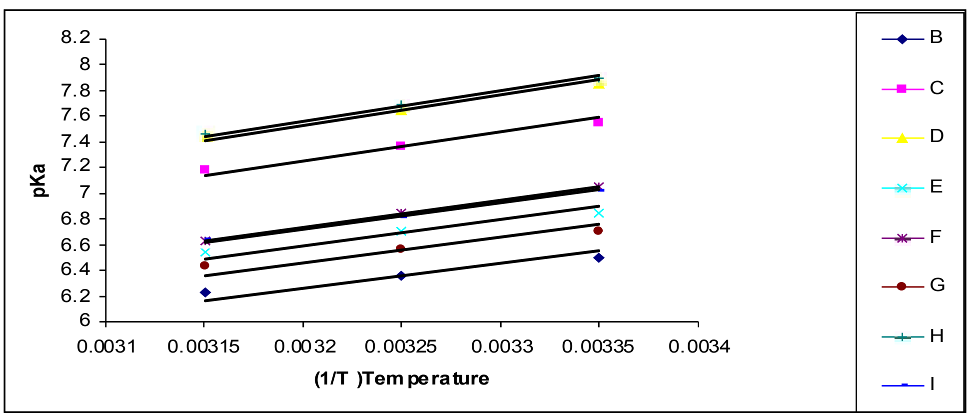

Fig. (2) Plot of pKa at 25^{o} C against 1/T of Schiff bases (A-F)