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Influence of temperatures on the stability constants values for some dyes formed by reactions of donors imines and the diazotized sulphanilic sodium salt

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ABSTRACT

In this work, a numbers of dyes were prepared by reactions of donor imines derived from mother aldehyde as 2,4-dihydroxy benzaldehyde with diazotized sulphanilic sodium salt as an acceptor. These imines were oximes in a forms of syn and anti forms beside Schiff bases hading a substituents on the primary amines part of the molecules as OH, NH_2, CH_3 and NO_2. A spectrophotometric method was used for the investigation of stability constants values of dyes mentioned at pH values of 5.1, 7.1 and 9.2 at temperature range (283–323)K. The thermodynamic parameters of dyes formations, namely $\Delta G°$, $\Delta H°$ and $\Delta S°$ were determined, discussed and interpreted.

INTRODUCTION

During the 28 years ago a considerable interest had paid by the chemists to the spectroscopical studies of imines by UV[1-3], IR[4,5], NMR[6] and mass[7] spectra, beside other kinetic[8], stability constants of charge transfer complexes[9] and tautomerisum of dyes[10] studies. These were for their applications[11-15] in many fields, e.g, biological, inorganic and analytical chemistry.

Azzouz et al[16-21] had studied the influence of temperatures on various physical topics as pKa of acids[16], tautomerisum[17] of imines, association between phenols with benzyl mono benzylidene aniline[18] or ortho methoxy – benzylidene -p- amino aniline[19] kinetic of re arrangement of aldoximes[20] and stability constants of dyes[21]. The authors in these studies concluded that the temperature was a main factor influencing any of the physical constants mentioned.

The present investigation was extension of the last study. It deals with influence of temperature range between (283-323)K on the stability constants of dyes formations from reactions of imines derived from 2,4-dihydroxybenzaldehyde with diazotized sodium sulphanilic salt at pH 5.1, 7.1 and 9.2. The thermodynamic parameters of dyes formations were calculated and discussed. A suitable interpretation for $\Delta G°$, $\Delta H°$ and $\Delta S°$ parameters were given.

EXPERIMENTAL

All chemicals used throughout this work were supplied by Fluka origin. The synthesis of imines in a forms of Schiff bases or syn and anti oximes[12] are followed, by using a similar procedures. Products are obtained by reactions of 2,4 dihydroxy- benzaldehyde with an appropriate primary amines, purified by recrystallization in ethanol, dried and collected. The chemical structures of these imines are identified and confirmed by

using physical method such as m.p·s, UV and IR spectra as cited in our previous communication[16].

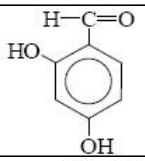
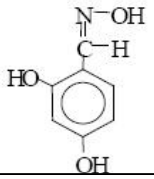
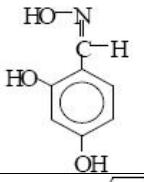
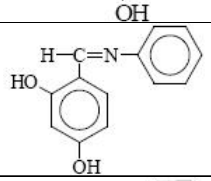
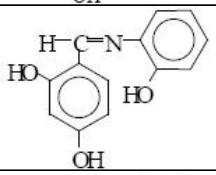
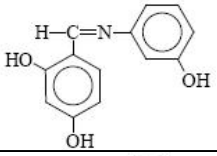
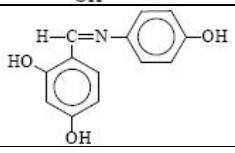
Preparation of solutions

1 2×10^{-3}M reagent of diazonium salt as derived from sulphanilic sodium salt was prepared by a standard method[17]. Then after it was diluted to 10^{-3}M by distilled water.
2 0.1M Na_2CO_3 and 2N HCl as basic and acidic solutions respectively, were prepared by a standard method. These solutions were used to obtain the pH values of 5.4, 7.1 and 9.2 during dye stability constant study. Na_2CO_3 is elected among other bases, due to its capability to give a maximum absorbance value of yellow dye.

Instrumentation

1 A computerized double beam uv_visible Shimadzu, 1601 spectro-photometer, matched silica cell of dimensions $1\times1\times3cm^3$ are used. All absorbance measurements were performed versus blank.
2 Single beam Cecil CE 1011/1000 spectrophotometer.
3 pH measurements were achieved by using pw 9400 pH meter (Philips).
4 Water bath L200 (Memmert) was used to regulate the temperature of dye solutions, whenever is required in a range between 20-60C°.

TABLE 1 : Symbol, nomenclature and some physical constants of imines.

Comp. No.	Symbol of 2,4- Comp. derivatives	Nomenclature	Colour	m.p. (°C)	Structure
1	DHBAL	2,4-dihydroxy benzaldehyde	pink	134-136	
2	Syn DHBO	Syn-2,4-dihydroxy benzaldoxime	milky	188-190	
3	Anti DHBO	Anti-2,4-dihydroxy benzaldoxime	colourless	110-112	
4	DHBA	2,4-dihydroxy benzylidene aniline	Deep red	-	
5	DHB-o-HA	2,4-dihydroxy benzylidene-o-hydroxy aniline	red	-	
6	DHB-m-HA	2,4-dihydroxy benzylidene-m-hydroxy aniline	Mild red	-	
7	DHB-p-HA	2,4-dihydroxy benzylidene-p-hydroxy aniline	red	-	

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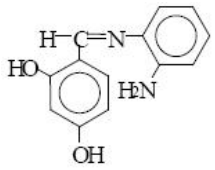
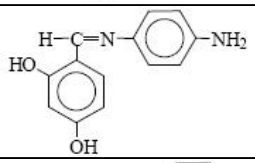
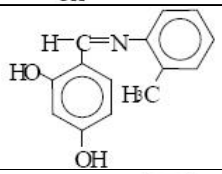
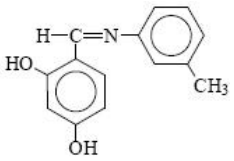
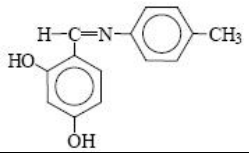
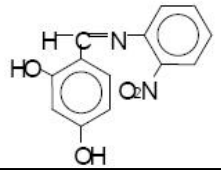
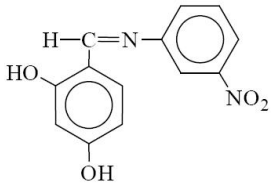
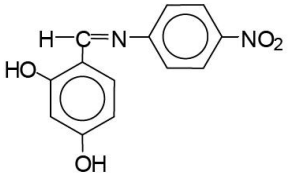
Comp. No.	Symbol of 2,4- Comp. derivatives	Nomenclature	Colour	m.p. (°C)	Structure
8	DHB-o-AA	2,4-dihydroxy benzylidene-o-amino aniline	sandy	-	
9	DHB-p-AA	2,4-dihydroxy benzylidene-p-amino aniline	red	-	
10	DHB-o-MA	2,4-dihydroxy benzylidene-o-methyl aniline	red	-	
11	DHB-m-MA	2,4-dihydroxy benzylidene-m-methyl aniline	Mild red	-	
12	DHB-p-MA	2,4-dihydroxy benzylidene-p-methyl aniline	red	-	
13	DHB-o-NA	2,4-dihydroxy benzylidene-o-nitro aniline	orange	-	
14	DHB-m-NA	2,4-dihydroxy benzylidene-m-nitro aniline	yellow	-	
15	DHB-p-NA	2,4-dihydroxy benzylidene-p-nitro aniline	yellow	-	

RESULTS AND DISCUSSION

The stability constant value K of the dye product DA is formed by the reaction of donor-acceptor mechanism[16] is evaluated from the following reaction:-

$$D + A \rightleftharpoons DA$$

where D and A are imine donor and the diazonium salt molecule acceptor respectively. DA is the dye product.

The value of stability constant K is evaluated[17] experimentally from equation 1 of the form:

$$K = \frac{1-\alpha}{\alpha^2 C} \quad (1)$$

C = molar concentration of the dye; α = degree of dissociation of the dye as defined in equation 2

$$\alpha = \frac{E_m - E_s}{E_m} \quad (2)$$

E_s = Absorbance of the dye at 1:1 stoichiometric ratio; E_m = Absorbance of the dye at optimal conditions

The stability constants of a dyes formation between donor imines and sulphanilic sodium salt were studied spectrophotometrically. Their stability constant values were determined at fixed pH and temperature as shown in TABLE 2. The pH were selected at values 5.4, 7.2 and 9.2. Similarly, the temperature were varied in a range (283-323)K. In order interpret the stability constant values clearly the following division of results were thought necessary.

The stability constants for a dyes formations from reactions of imines derived from 2,4-dihydroxy benzaldehyde in a forms of synor anti oximes and Schiff bases with diazotized sodium sulphanilic salt at different temperatures were listed in TABLE 1. The variation of stability constants values with temperatures encourage the workers to evaluate the thermodynamic parameters of dye formation namely ΔG°, ΔH° and ΔS°. The heat of dye formation ΔH° was calculated[24] from the integrated form of vant Hoff equation of the forms:-

$$\ln K = \text{constant} - \Delta H^\circ / RT \quad (3)$$

K = Stability constant of dye; ΔH° = Enthalphy of dye formation; T = Absolute temperature.

From equation 3 ΔH° was calculated from the plot of lnK versus T^{-1}. A straight lines were obtained for all dyes under study with correlation coefficient range (0.9572-1.0). Typical plots were shown in Figure 1-4 for imines DHBAL, anti DHBO, DHBA and DHB-o-HA at pH values of 5.1, 7.1 and 9.2.

In general, TABLE 1 showed that equilibrium constants of dyes formation were decreased by an increase of temperatures. ΔH° were calculated for any dye at different temperatures. The negative signs of ΔH° values means that dyes formations were happened with an exothermic process. ΔH° calculated and collected had a range value (207451.4-238835.5)J.mole^{-1}. Also ΔG° values for the dyes mentioned had calculated[24] from equation of the form:-

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

The negative signs of ΔG° shown in TABLE 1 mean that dyes formations were happened in a spontaneous

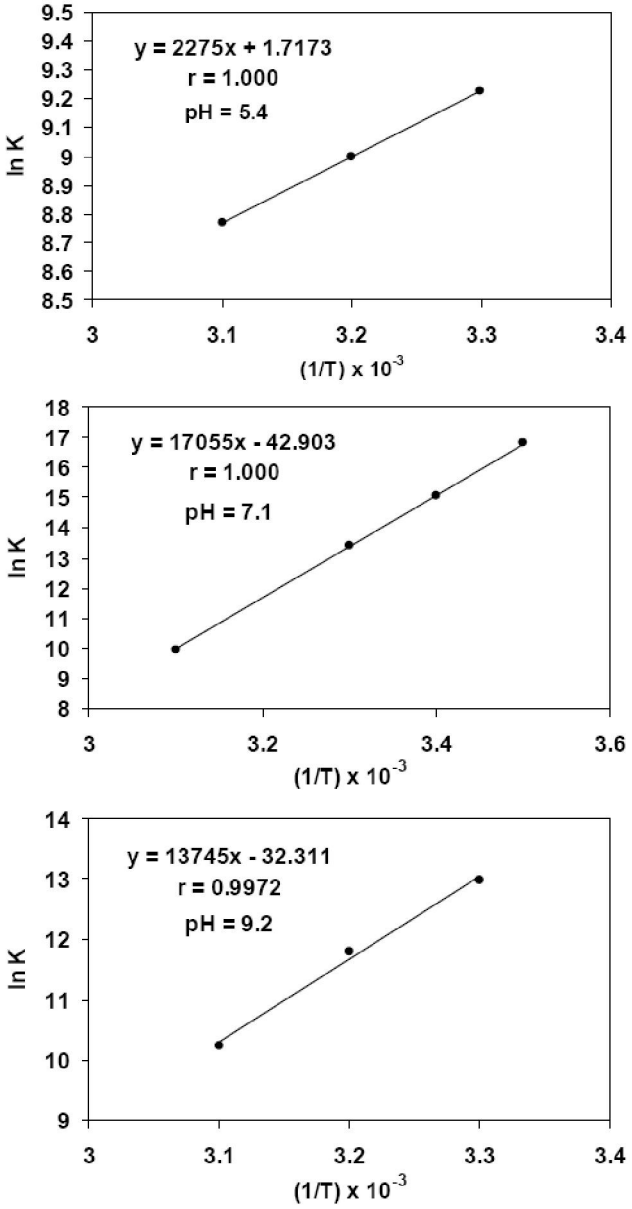


Figure 1 : Influence of temperature on azo dye formed by reactions of DHBAL with diazotized sulphanlic sodium salt at different pH values

process. ΔG° values collected in TABLE 1 were depended on the values of stability constants.

Finally, the ΔS° values for the dyes formations were calculated from Gibbs equation of the form:-

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ, \quad \Delta S^\circ = S_2 - S_1$$

where S_2 = Entropy of dye product; S_1 = Entropy of dye reactant.

Theoretically speaking ΔS° was expected of negative signs. These were in full agreement with many dyes listed in TABLE 1. The other few rest values of dyes as in TABLE 1 had a positive values of ΔS° which were in

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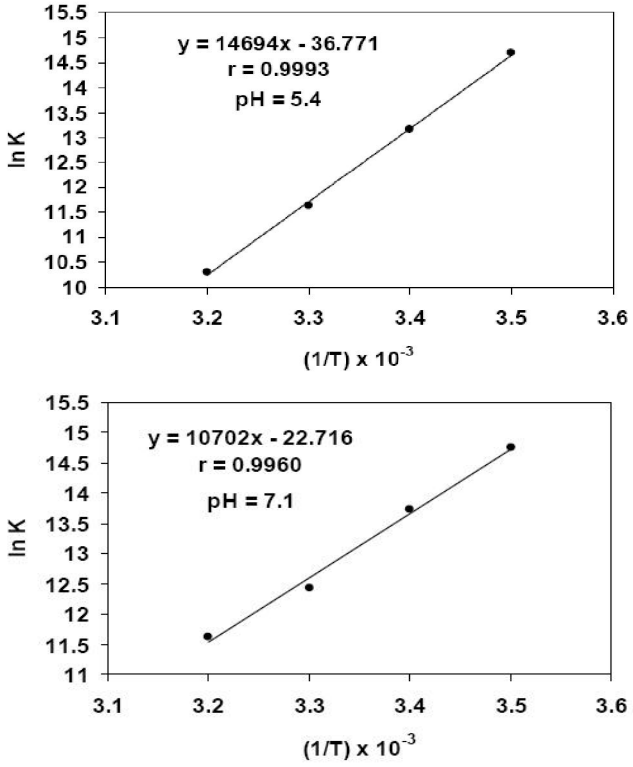

Figure 2 : Influence of temperature on azo dye formed by reactions of AntiDHBO with diazotized sulphanlic sodium salt at different pH values

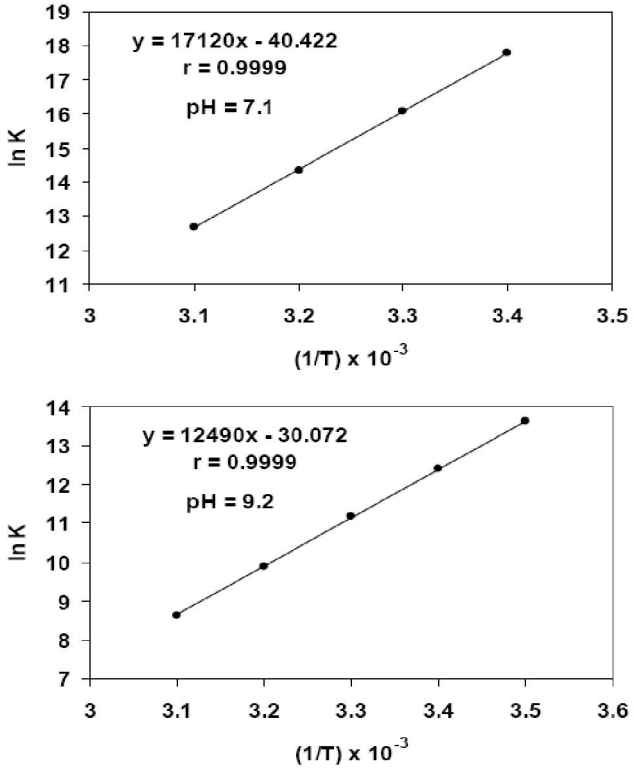

Figure 3 : Influence of temperature on azo dye formed by reactions of DHBA with diazotized sulphanlic sodium salt at different pH values

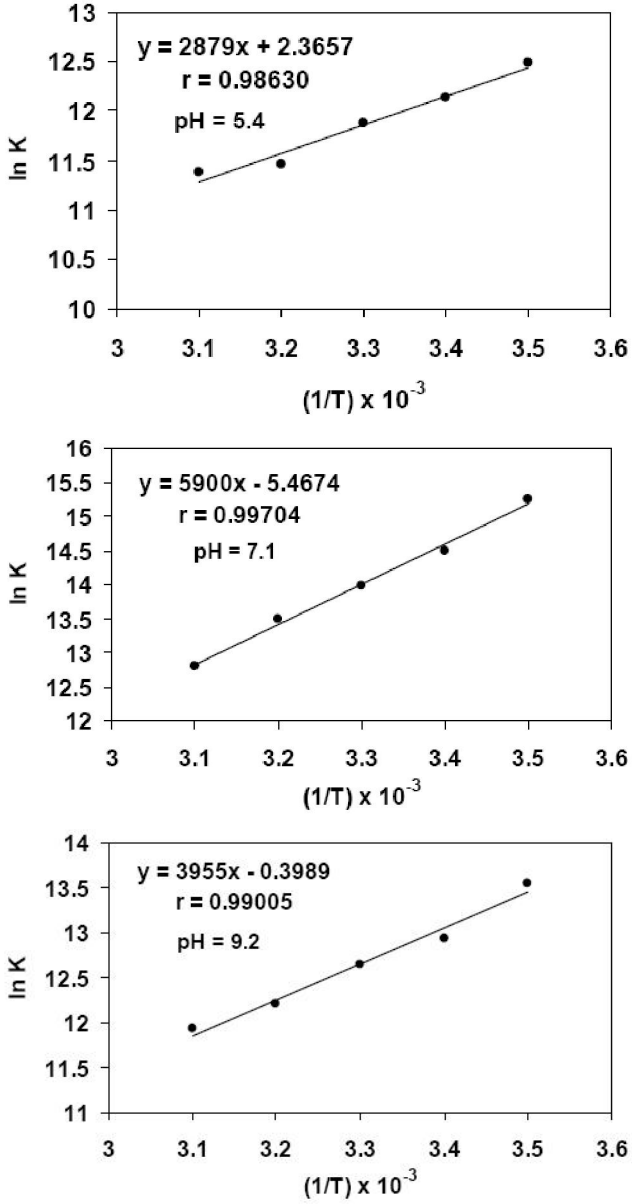

Figure 4 : Influence of temperature on azo dye formed by reactions of DHB-o-HA with diazotized sulphanlic sodium salt at different pH values

disagreement with other theoretical prediction. The cause for the last could be explained by the greater strength of hydrogen bonding in reactants imines under study as compared with dye products. Moreover, the hydrogen bond energies of the last were expected to varies with temperatures. In other words, the hydrogen bonding stated in dyes reactions were effective and change $\Delta S°$ to a positive values.

The missing values of K, $\Delta G°$ and $\Delta S°$ as in TABLE 1 mean that these values of dyes at any temperature were undetermined experimentally or a failure formation

TABLE 2 : Influence of temperature and thermodynamic parameters of azo dyes formations at different pH values

Comp. No	Symbol of 2,4– Comp. Derivatives	pH	T (K)	lnK	ΔG (J. mo1^{-1})	$\Delta \bar{G}$ (J. mo1^{-1})	ΔH (J. mo1^{-1})	$\bar{\Delta H}$ (J. mo1^{-1})	ΔS (J. mo1^{-1}. K^{-1})	$\bar{\Delta S}$ (J. mo1^{-1}. K^{-1})
			283	-	-		-		-	
			293	-	-		-		-	
		5.4	303	9.225	-23240.1	-23400.7	-18913.9	-18931.7	+14.27789	+14.27775
			313	8.997	-23412.1		-18943.2		+14.27764	
			323	8.770	-23549.8		-18938.1		+14.27771	
			283	16.798	-39523.5		-140468.4		-356.69576	
			293	15.061	-36687.9		-141199.7		-356.69556	
1	DHBAL	7.1	303	13.400	-34699.7	-34416.8	-141834.2	-141367.8	-353.57921	-355.91655
			313	-	-		-		-	
			323	9.964	-26756.2		-141968.9		-356.69567	
			283	-	-		-		-	
			293	-	-		-		-	
		9.2	303	12.989	-32720.7	-30300.6	-114116.7	-114382.9	-268.63366	-268.63365
			313	11.791	-30682.4		-114764.7		-268.63355	
			323	10.240	-27498.6		-114267.3		-268.63375	
			283	16.477	-38767.9		-75063.2		-128.25194	
			293	15.520	-37807.4		-75385.2		-128.25188	
		5.4	303	14.557	-36672.3	-36606.1	-75532.6	-75466.4	-128.25182	-128.25182
			313	13.424	-34933.6		-75076.4		-128.25176	
			323	12.977	-34849.4		-76274.7		-128.25170	
			333	-	-		-		-	
2	SynDHBO		283	17.089	-40207.3		-172687.6		-468.12827	
			293	16.085	-39183.0		-176344.5		-468.12799	
		7.1	303	12.874	-32430.2	-37273.5	-174273.1	-174435.1	-468.12838	-468.12821
			313	-	-		-		-	
			323	-	-		-		-	
			333	-	-		-		-	
		9.2	283 -333	-	-	-	-	-	-	-
			283	14.707	-34602.3		-121119.4		-305.71413	
			293	13.153	-32041.1		-121615.3		-305.71399	
		5.4	303	11.644	-29333.9	-30703.3	-121965.2	-121806.1	-305.71386	-305.71401
			313	10.312	-26835.8		-122524.3		-305.71406	
			323	-	-		-		-	
			283	14.754	-34713.6		-88161.2		-188.86078	
			293	13.739	-33468.4		-88804.6		-188.86075	
3	AntiDHBO	7.1	303	12.424	-31298.1	-32432.8	-88522.9	-88713.3	-188.86073	-188.86082
			313	11.625	-30250.9		-89364.4		-188.86102	
			323	-	-		-		-	
			283	13.512	-31792.1		-		-	
			293	13.153	-32041.1		-		-	
		9.2	303	-	-	-31916.6	-	-	-	-
			313	-	-		-		-	
			323	-	-		-		-	

Comp. No	Symbol of 2,4– Comp. Derivatives	pH	T (K)	lnK	ΔG (J. mo1^{-1})	$\bar{\Delta G}$ (J. mo1^{-1})	ΔH (J. mo1^{-1})	$\bar{\Delta H}$ (J. mo1^{-1})	ΔS (J. mo1^{-1}. K^{-1})	$\bar{\Delta S}$ (J. mo1^{-1}. K^{-1})
			283	-	-		-		-	
			293	15.870	-38658.5		-		-	
		5.4	303	-	-	-38658.5	-	-	-	-
			313	-	-		-		-	
			323	-	-		-		-	
			283	-	-		-		-	
			293	17.782	-43317.0		-141054.3		-333.57440	
4	DHBA	7.1	303	16.097	-40549.7	-38784.0	-141622.7	-141524.9	-333.57426	-333.57435
			313	14.328	-37285.6		-141694.4		-333.57444	
			323	12.655	-33983.8		-141728.3		-333.57430	
			283	13.627	-32061.9		-102817.2		-250.01873	
			293	12.391	-30184.5		-103439.9		-250.01843	
		9.2	303	11.184	-28175.2	-27867.5	-103930.8	-103623.1	-250.01848	-250.01855
			313	9.889	-25733.8		-103989.6		-250.01853	
			323	8.633	-23182.0		-103938.0		-250.01858	
			283	12.484	-29371.9		-23805.8		+19.66820	
			293	12.133	-29554.7		-23791.9		+19.66826	
		5.4	303	11.872	-29907.4	-29845.0	-23947.9	-23885.5	+19.66832	+19.66831
			313	11.464	-29833.6		-23677.4		+19.66837	
			323	11.379	-30557.5		-24204.6		+19.66842	
			283	15.242	-35862.6		-48726.6		-45.45795	
			293	14.496	-35313.1		-48631.7		-45.45597	
5	DHB-o-HA	7.1	303	13.988	-35237.2	-35176.2	-49010.4	-48949.4	-45.45611	-45.45633
			313	13.494	-35114.8		-49342.5		-45.45591	
			323	12.793	-34353.4		-49035.6		-45.45573	
			283	13.547	-31873.9		-32812.5		-3.31661	
			293	12.931	-31499.5		-32471.3		3.31672	
		9.2	303	12.646	-31855.8	-31807.3	-32860.7	-32812.2	-3.31650	-3.31657
			313	12.208	-31768.1		-32806.2		-3.31661	
			323	11.931	-32039.2		33110.4		-3.31641	
			283	-	-		-		-	
			293	-	-		-		-	
		5.4	303	-	-	-	-	-	-	-
			313	-	-		-		-	
			323	-	-		-		-	
			283	13.904	-32713.1		-27438.7		+18.63746	
			293	13.734	-33457.2		-27996.4		+18.63754	
6	DHB-m-HA	7.1	303	13.266	-33417.4	-33445.3	-27770.3	-27738.1	+18.63729	+18.63743
			313	12.741	-33155.7		-27322.2		+18.63738	
			323	12.729	-34183.0		-28163.1		+18.63746	
			283	17.720	-41691.5		-95586.2		-190.44064	
			293	16.924	-41227.1		-97026.1		-190.44027	
		9.2	303	15.771	-39729.6	-39109.2	-97433.1	-96812.6	-190.44059	-190.44053
			313	14.495	-37718.9		-97326.8		-190.44058	
			323	13.100	-35178.7		-96691.0		-190.44056	

Comp. No	Symbol of 2,4– Comp. Derivatives	pH	T (K)	lnK	ΔG (J. mo1^{-1})	$\Delta \bar{G}$ (J. mo1^{-1})	ΔH (J. mo1^{-1})	$\bar{\Delta H}$ (J. mo1^{-1})	ΔS (J. mo1^{-1}. K^{-1})	$\bar{\Delta S}$ (J. mo1^{-1}. K^{-1})
			283	13.988	-32911.3		-		-	
			293	13.376	-32584.6		-		-	
		5.4	303	-	-	-32748.0	-	-	-	-
			313	-	-		-		-	
			323	-	-		-		-	
			283	17.782	-41838.6		-119523.1		-274.50353	
			293	16.123	-39297.7		-119727.2		-274.50341	
7	DHB-p-HA	7.1	303	14.883	-37492.5	-39542.9	-120667.0	-119972.4	-274.50330	-274.50341
			313	-	-		-		-	
			323	-	-		-		-	
			283	14.811	-34849.1		-		-	
			293	13.935	33944.7		-		-	
		9.2	303	-	-	-34396.9	-	-	-	-
			313	-	-		-		-	
			323	-	-		-		-	
			283	-	-		-		-	
			293	15.423	-37569.1		-		-	
		5.4	303	15.320	-38592.2	-38080.7	-	-	-	-
			313	-	-		-		-	
			323	-	-		-		-	
			283	14.430	-33950.9		-38550.7		-1625371	
			293	13.871	-33789.7		-38552.1		-16.25393	
8	DHB-o-AA	7.1	303	13.305	-33516.4	-33711.0	-38441.3	-38635.9	-16.25380	-16.25386
			313	12.847	-33430.5		-38518.0		-16.25399	
			323	12.612	-33867.3		-39117.3		16.25387	
			283	-	-		-		-	
			293	16.908	-41188.6		-166747.4		-428.52833	
		9.2	303	14.707	-37047.7	-35025.8	-166891.9	-167012.7	-428.52871	-428.52849
			313	12.467	-32443.6		-166573.0		-428.52844	
			323	10.957	-29423.3		-167838.0		-428.52848	
			283	-	-		-		-	
			293	12.169	-29644.7		-		-	
		5.4	303	-	-	-29644.7	-	-	-	-
			313	-	-		-		-	
			323	-	-		-		-	
			283	18.923	-44523.9		-206198.4		-571.28799	
			293	16.333	-39785.9		-207173.3		517.28806	
9	DHB-p-AA	7.1	303	13.816	-34803.2	-37207.5	-207903.6	-207451.4	571.28845	-571.28817
			313	11.420	-29717.1		-208530.3		571.28818	
			323	-	-		-		-	
			283	-	-		-		-	
			293	14.092	-34173.7		-31407.6		+9.44061	
		9.2	303	13.577	-34201.4	-35499.7	-31340.9	-31443.7	+9.44059	+9.44059
			313	13.272	-34537.5		-31582.6		+9.44058	
			323	-	-		-		-	

Comp. No	Symbol of 2,4– Comp. Derivatives	pH	T (K)	lnK	ΔG (J. mo1^{-1})	$\bar{\Delta G}$ (J. mo1^{-1})	ΔH (J. mo1^{-1})	$\bar{\Delta H}$ (J. mo1^{-1})	ΔS (J. mo1^{-1}. K^{-1})	$\bar{\Delta S}$ (J. mo1^{-1}. K^{-1})
			283	15.043	-35394.7		-37271.2		-6.63074	
			293	14.558	-35462.0		-37404.7		-6.63038	
		5.4	303	14.121	-35572.1	-35499.7	-37581.1	-37508.7	-6.63036	-6.63043
			313	13.651	-35524.7		-37600.0		-6.63035	
			323	13.236	-35544.8		-37686.4		-6.63034	
			283	15.199	-35760.5		-45249.3		-33.52933	
			293	14.658	-35707.0		-45531.2		-33.52969	
10	DHB-o-MA	7.1	303	14.037	-35362.1	-35396.6	-45521.6	-45556.0	33.52970	-33.52950
			313	13.521	-35184.5		-45679.2		-33.52939	
			323	13.022	-34968.9		-45798.9		-33.52941	
			283	15.049	-35407.4		-30122.9		+18.67315	
			293	14.682	-35766.4		-30295.1		+18.67338	
		9.2	303	14.357	-36167.9	-36023.1	-30509.9	-30365.1	+18.6327	+18.67321
			313	13. 944	-36285.2		-30440.5		+18.67316	
			323	13.588	-36488.5		-30457.1		+18.67307	
			283	10.377	-24414.7		-		-	
			293	10.009	-24381.6		-		-	
		5.4	303	-	-	-24398.2	-	-	-	-
			313	-	-		-		-	
			323	-	-		-		-	
			283	12.612	-29673.2		-		-	
			293	9.182	-22367.8		-		-	
11	DHB-m-MA	7.1	303	-	-	-26020.5	-	-	-	-
			313	-	-		-		-	
			323	-	-		-		-	
			283	-	-		-		-	
			293	11.513	-28045.5		-		-	
		9.2	303	9.393	-23661.5	-25853.5	-	-	-	-
			313	-	-		-		-	
			323	-	-		-		-	
			283	12.183	-28665.3		-27055.3		+5.68905	
			293	11.850	-28866.2		-27199.2		+5.68942	
		5.4	303	11.528	-29341.1	-28978.1	-27317.2	-27254.3	+5.68944	+5.68930
			313	11.195	-29132.3		-27351.6		+5.68914	
			323	10.868	-29185.7		-27348.0		+5.68947	
			283	11.738	-27618.6		-15844.0		+41.60636	
			293	11.541	-28112.7		-15921.9		+41.60683	
12	DHB-p-MA	7.1	303	11.362	-28623.3	-28569.4	-16016.5	-15962.6	+41.60660	+41.60660
			313	11.161	-29043.0		-16020.1		+41.60671	
			323	10.966	-29449.5		-16010.6		+41.60650	
			283	14.177	-34753.4		-70942.8		-127.87774	
			293	13.911	-33887.2		-71355.4		-127.87782	
		9.2	303	13.048	-32870.8	-33837.1	-71617.7	-71305.3	-127.87756	+127.87771
			313	-	-		-		-	
			323	-	-		-		-	

of dyes at some temperatures under study.

Finally, the change in structures of imines under study resulted to a different values of thermodynamic parameters and were in full agreement with several studies[9,25,26].

REFERENCES

[1] A.S.P.Azzouz, A.B.N.Al-Dabagh; Nat.J.Chem., **32**, 677 **(2008)**.
[2] A.A.Saeed, A.W.Sultan, S.A.Selman, N.A.Abood; Can.J.Spectros., **28**, 104 **(1983)**.
[3] A.S.P.Azzouz, A.N.Obed Agha; Physical Chem.An Indian J., **2(3)**, 15 **(2007)**.
[4] A.S.P.Azzouz, A.A.Rahman, A.G.Taki; J.Edu.Sci., **15(2)**, 1 **(2003)**.
[5] A.A.Saeed, N.A.Abood, N.A.Al-Mosoudi, G.T.Matti; Can.J.Spectros., **30**, 142 **(1985)**.
[6] Ed.S.Patai; 'The Chemistry of Carbon Nitrogen Double Bond', John Wiley, New York, 149-180.
[7] A.S.P.Azzouz; Spectros.Letter, **28**, 1 **(1995)**.
[8] A.S.P.Azzouz, K.A.Abdullah, Kh.I.Al-Niemi; Microchem.J., **43**, 54 **(1991)**.
[9] A.S.P.Azzouz; Z.Phys.Chem., **216**, 1 **(2002)**.
[10] A.S.P.Azzouz, A.N.Obed Agha; Nat.J.Chem., **30**, 251 **(2008)**.
[11] Z.Cimerman, S.Miljanic, N.Galic; Croatica Chemica Acta, **73(1)**, 81-95 **(2000)**.
[12] P.Singh, R.L.Goel, B.P.Singh; J.Indian Chem.Soc., **52**, 958 **(1975)**.
[13] B.F.Perry, A.E.Beezer, R.J.Miles, B.W.Smith, J.Miller, M.G.Nascinento; Microbois, **45**, 181 **(1988)**.
[14] A.Elmail, M.Kabak, Y.Elerman; J.Mol.Struct., **477**, 151 **(2000)**.
[15] P.R.Patel, B.T.Thaker, S.Zele; Indian J.Chem., **38(A)**, 563 **(1999)**.
[16] A.S.P.Azzouz, M.M.Saeed, K.I.Al-Niemi; Nat.J. Chem., **25**, 38 **(2007)**.
[17] A.S.P.Azzouz, A.B.N.Al-Dabagh; Nat.J.Chem., **26**, 295 **(2007)**.
[18] A.S.P.Azzouz; Z.Phys.Chem., **216**, 1053 **(2002)**.
[19] A.S.P.Azzouz, S.S.Othman, A.N.Al-Dabagh; Nat.J.Chem., **36**, 782 **(2009)**.
[20] A.S.P.Azzouz, K.A.Abdullah, Kh.I.Al-Niemi; Mutah J.Res.and Stud., **10**, 77 **(1995)**.
[21] A.S.P.Azzouz, A.N.Obed Agha; Nat.J.Chem., **30**, 251 **(2008)**.
[22] A.S.P.Azzouz, M.M.Al-Niemi; J.Edu.Sci., **21(1)**, 1 **(2009)**.
[23] A.S.P.Azzouz, M.M.Al-Niemi; Tikrit J.Pure Sci., **13(3)**, 118 **(2008)**.
[24] J.Hine; Physical Organic Chem., 2nd Edition, Hill Book Company, London, 33 **(1962)**.
[25] A.S.P.Azzouz, A.N.O.Agha; J.Edu.Sci., **17**, 10 **(2005)**.
[26] A.S.P.Azzouz; Mutah J.Res.and Stud., **8**, 93 **(1993)**.