The influence of pH on the stability constants values of dyes formed by reaction of imines with diazotized sulphanilic sodium salt.

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Abstract

The main object of the study , is the determination of stability constants of some azo dyes formed by the reactions of donor imines with diazotized sulphanilic sodium salt as an acceptor , using the spectophotometric method. These stability constants are evaluated under pH values of 5.4 , 7.1 and 9.2 respectively and at five different temperatures. At pH of 5.4, some experiments are proved the formation of unstable dyes and the failure evaluation of some of their values. They are attributed to the partial or complete protonation of donor imines and the formation of phenoxonium or nitrilium ions or both of them. Other donor imines form a stable dyes at pH 7.1. The last shows a maximum stability constant values for the dyes , due to the presence of imine in the enolic form. Conversely , a minimum stability constant value for the dye is obtained at pH 9.2 , due to the tautomeric conversion of enol form to keto form in imine.

الخلاصة

الهدف الرئيسي للدراسة هو تقدير ثوابت استقرار بعض اصباغ الازو المتكونة بتفاعلات الايمينـات الواهبة للالكترونات مع ملح الصوديوم للحامض السلفانليك المؤزوت ، بأسـتعمال الطريقـة الفوتومتريـة . حسبت ثوابت الاستقرار تحت قيم دوال حامضية pH تبلغ 5.4 ، 7.1 ، 9.2 على الترتيـب وفـي خمـسة درجات حرارية مختلفة . بدالة حامضية 5.4 ، اثبتت بعض التجارب تكوين اصباغ غير مستقرة مما ادى الى فشل حساب ثوابت استقرارها . اعزيت مثل هذه النتيجة الى البرتنة الجزئية او الكليـة للايمينـات الواهبـة وتكوين ايونات الفينوكزونيوم والنتريليوم فيها . اما الايمينات الاخرى فأنها كونت اصـباغ مـستقرة بدالـة حامضية 7.1 . الدالة الاخيرة اعطت قيم ثوابت استقرار قصوى للاصباغ بسبب تواجـد الايمينـات بالهيئـة الاينولية . وعكس ذلك وبدالة حامضية 9.2 كانت قيم ثوابت الاستقرار للاصباغ بالحد الادنى ، بسبب تفاعل توتومرية تحول الهيئة الاينولية الى الهيئة الكيتونية في الايمين .

Introduction

During the last few years , a considerable importance had been paid to the spectroscopical studies of imines dy UV[1-2] IR[3] , N.M.R[4] and mass[5] spectra , beside other kinetic[6] and thermodynamic[7] studies.

In the last years , some workers had used the diazotization reaction as analytical method for the determination of compounds such as 4-aminoantipyrine[8] , aniline[9] and 1-napthylamine[10]. These works led to a conclusion that the diazotiztion method is simple , precise and sensitive for determination of trace amounts of samples mentioned.

Azzouz[11] had studied the influence of surfactant and solvents on the stability constant value of some azo dyes formed by the reaction between oximes and the diazotized sulphanilic sodium salt. This led to concluded that , stability constant value of the dye is highly varied by these two physical parameters.

The present investigation deals with the influence of pH and the temperature on the values of stability constants of the dyes formed by reactions of donor imines with an acceptor , namely the diazotized sulphanilic sodium salt. This will open a subsequent future works for some physical or analytical studies on imines mentioned.

Experimental

All chemicals are used throughout this work is 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 communciation[13].

Preparation of solutions:

1. 2×10^{-3}M reagent of diazonium salt as derived from sulphanilic sodium salt was prepared by a standard method[14]. 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 , are prepared by a standard method[15]. These solutions are 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[14] for yellow the 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 are performed versus blank.
2. Single beam Cecil CE 1011/1000 spectrophotometer.
3. pH measurements are achieved by using pw 9400 pH meter (Philips).
4. Water bath L200 (Memmert) is used to regulate the temperature of dye solutions , whenever is required in a range between 20-60C°.

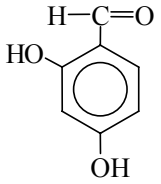
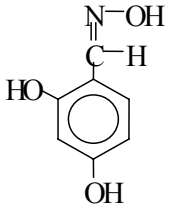
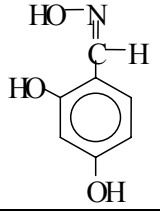
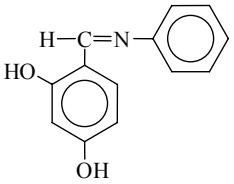
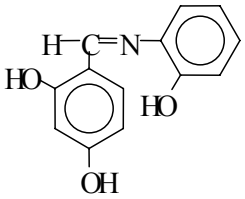
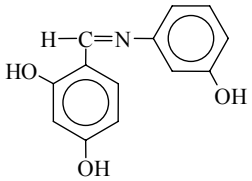
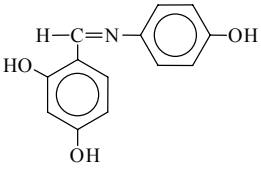
Results and discussion

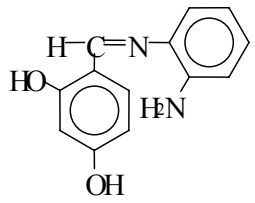
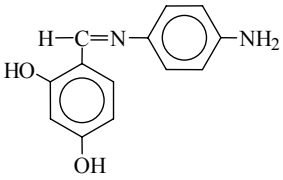
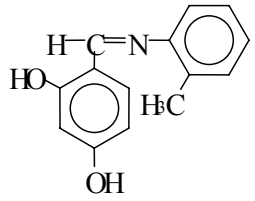
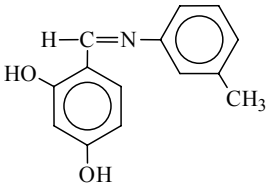
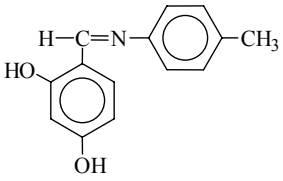
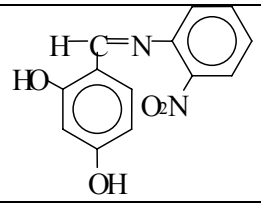
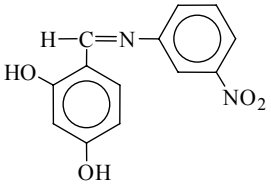
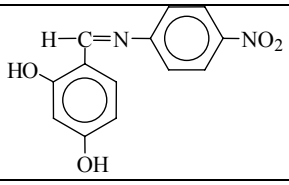
Table (1) shows nomenclature , symbol and other physical constants of imines under investigations.

Earlier work[13] in this laboratory deals with spectrophotometric study of optimal conditions of azo dye formation by reaction of imines under study with a diazotized sulphanilic sodium salt. This includes several experimental parameters , such as excess reagent , volume of 0.1M Na_2CO_3 to obtain the pH values of 5.4 , 7.1 and 9.2 , order of addition ,

development time , stability period and optimal wavelengths of the dyes. Then after a 1:1 stoichiometric ratio for the dyes are obtained by a mole ratio method[11].

Tabel (1) Symbol , nomenclature and some physical constants of Imines.

Comp. No.	Symbol of 2,4- Comp. Derivatives	Nomenclature	Colour	m.p. (^{o}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	-	

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	-	

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

C= molar concentration of the dye

α = degree of dissociation of the dye as defined in equation (2)

Table (2) optimal conditions for azo dyes formed by reactions of imines with diazotized sulphanilic sodium salt at 20C°

Symbol of 2,4- comp. Derivatives	pH	Order of addition	λ (nm)	Development time (min.)	Stability Period (min.)
Syn DHBO	**5.4**	0.2ml Na_2C0_3 + 0.2ml (Syn DHBO) + 0.8 Reagent	440	25	10
	7.1	0.2ml(Syn DHBO) + 0.5ml Na_2CO_3 + 0.8ml Reagent	424	25	20
	9.2	0.8ml Reagent + 0.2ml (Syn DHBO) + 0.9ml Na_2CO_3	428	5	55
Anti DHBO	**5.4**	0.05ml Na_2CO_3 + 0.2ml (Anti DHBO) + 0.8ml Reagent	483	0	35
	7.1	0.8ml Reagent + 0.2 (Anti DHBO) + 0.15ml Na_2CO_3	465	0	40
	9.2	0.2ml (Anti DHBO) + 0.3ml Na_2CO_3 + 0.8ml Reagent	470	0	20
DHBA	**5.4**	0.1ml $Na_2 C0_3$ + 0.2ml (DHBA) + 0.5ml Reagent	438	10	15
	7.1	0.2ml Na_2CO_3 + 0.5ml Reagent + 0.2ml (DHBA)	430	15	15
	9.2	0.5ml Reagent + 0.2ml (DHBA) + 0.35ml Na_2Co_3	414	10	55
DHB –o– HA	**5.4**	0.1ml Na_2CO_3 + 0.2ml (DHB –o– HA) + 0.6ml Reagent	437	2	33
	7.1	0.25ml Na_2CO_3 + 0.2ml (DHB–o– HA) + 0.6ml Reagent	422	0	15
	9.2	0.4ml Na_2CO_3 + 0.2ml (DHB–o– HA) + 0.6ml Reagent	412	0	65
DHB–m– HA	**5.4**	0.4ml Reagent + 0.03ml Na_2CO_3 + 0.2ml (DHB –m– HA)	443	20	35
	7.1	0.2ml (DHB–m–HA) + 0.08ml Na_2CO_3 + 0.4ml Reagent	436	45	25
	9.2	0.2ml (DHB –m– HA) + 0.4ml Reagent + 0.15ml Na_2CO_3	437	0	95
DHB–p–HA	**5.4**	0.2ml (DHB–p–HA) + 0.025ml Na_2CO_3 + 0.3ml Reagent	441	25	35
	7.1	0.075ml Na_2CO_3 + 0.2ml (DHB –p– HA) + 0.3ml Reagent	442	10	65
	9.2	0.2ml (DHB –p– HA) + 0.1ml Na_2CO_3 + 0.3ml Reagent	435	0	35
DHB–o-AA	**5.4**	0.1ml Na_2CO_3 + 0.2ml (DHB–o– AA) + 0.8ml Reagent	427	0	70
	7.1	0.2ml (DHB –o– AA) + 0.8ml Reagent + 0.25ml Na_2CO_3	430	65	15
	9.2	0.2ml (DHB–o– AA) + 0.8ml Reagent + 0.5ml Na_2CO_3	425	45	45
DHB–p–AA	**5.4**	0.09ml Na_2CO_3 + 0.2ml (DHB–p– AA) + 0.5ml Reagent	430	5	15
	7.1	0.2ml Na_2CO_3 + 0.2ml (DHB–p– AA) + 0.5ml Reagent	427	5	15
	9.2	0.5ml Reagent + 0.35ml Na_2CO_3 + 0.2ml (DHB–p– AA)	425	30	65
DHB–o– MA	**5.4**	0.2ml (DHB –o– MA) + 0.16ml Na_2CO_3 + 0.9ml Reagent	427	40	20
	7.1	0.9ml Reagent + 0.35ml Na_2CO_3 + 0.2ml (DHB–o– MA)	422	15	20
	9.2	0.2ml (DHB–o– MA) + 0.9ml Reagent + 0.6ml Na_2CO_3	416	15	80
DHB–m– MA	**5.4**	0.2ml (DHB–m– MA) + 0.8ml Reagent + 0.16ml Na_2CO_3	425	35	20
	7.1	0.8ml Reagent + 0.325ml Na_2CO_3 + 0.2ml (DHB–m– MA)	410	35	15
	9.2	0.5ml Na_2CO_3 + 0.8ml Reagent + 0.2ml (DHB–m– MA)	420	20	15
DHB–p– MA	**5.4**	0.2ml (DHB–p– MA) + 0.8ml Reagent + 0.16ml Na_2CO_3	430	10	30
	7.1	0.8ml Reagent + 0.325ml Na_2CO_3 + 0.2ml (DHB–p– MA)	413	25	20
	9.2	0.55ml Na_2CO_3 + 0.8ml Reagent + 0.2ml (DHB–p– MA)	422	35	15

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

E_s = Absorbance of the dye at 1:1 stoichiometric ratio

E_m = Absorbance of the dye at optimal conditions

Table (2) shows the optimal conditions for azo dyes products included here in this investigation at 20C°.

Table (3) Stability constant values for the dyes at different pH and temperatures

Comp. No.	Symbol of 2,4-Comp. Derivatives	pH	T (K)	E_s	E_m	α	K (l. mol^{-1})
1	DHBAL	5.4	283	0.157	0.031	-	-
			293	0.155	0.043	-	-
			303	0.018	0.122	0.85246	10151.6
			313	0.015	0.121	0.87603	8076.7
			323	0.012	0.116	0.89655	6434.9
		7.1	283	0.155	0.163	0.04908	19738281.3
			293	0.157	0.177	0.11299	3473625.0
			303	0.019	0.025	0.24000	659722.2
			313	0.039	0.005	-	-
			323	0.009	0.037	0.75676	21237.3
		9.2	283	0.161	0.079	-	-
			293	0.153	0.045	-	-
			303	0.005	0.007	0.28571	437500.0
			313	0.006	0.011	0.45455	132000.0
			323	0.004	0.014	0.71429	28000.0
2	Syn DHBO	5.4	283	0.230	0.244	0.05738	14316326.5
			293	0.240	0.264	0.09091	5500000.0
			303	0.234	0.273	0.14286	2100000.0
			313	0.228	0.299	0.23746	676175.4
			323	0.221	0.310	0.28710	432458.0
			333	0.813	0.645	-	-
		7.1	283	0.607	0.634	0.04259	26394924.6
			293	0.577	0.620	0.06936	9673877.8
			303	0.687	0.981	0.29969	398853.2
			313	0.686	0.603	-	-
			323	0.672	0.593	-	-
			333	0.617	0.503	-	-
		9.2	283	0.644	0.594	-	-
			293	0698	0.625	-	-
			303	0.715	0.485	-	-
			313	0.680	0.486	-	-
			323	0.687	0.581	-	-
			333	0.672	0.593	-	-

		5.4	283	0.013	0.015	0.13333	2437500.0
			293	0.011	0.015	0.26667	515625.0
			303	0.012	0.023	0.47826	114049.6
			313	0.011	0.037	0.70270	30103.6
			323	0.011	0.009	-	-
		7.1	283	0.020	0.023	0.13043	2555555.6
			293	0.023	0.029	0.20690	926388.9
			303	0.025	0.039	0.35897	248724.5
			313	0.028	0.054	0.48148	111834.3
			323	0.013	0.005	-	-
3	Anti DHBO	9.2	283	0.054	0.070	0.22857	738281.3
			293	0.055	0.075	0.26667	515625.0
			303	0.060	0.045	-	-
			313	0.058	0.033	-	-
			323	0.026	0.021	-	-
		5.4	283	0.044	0.042	-	-
			293	0.036	0.039	0.07692	7800000.0
			303	0.043	0.038	-	-
			313	0.036	0.032	-	-
			323	0.041	0.039	-	-
		7.1	283	0.054	0.041	-	-
			293	0.032	0.033	0.03030	52800000.0
			303	0.054	0.058	0.06897	9787500.0
			313	0.053	0.063	0.15873	1669500.0
			323	0.039	0.058	0.32759	313296.4
4	DHBA	9.2	283	0.054	0.069	0.21739	828000.0
			293	0.049	0.077	0.36364	240625.0
			303	0.028	0.063	0.55556	72000.0
			313	0.023	0.099	0.76768	19710.9
			323	0.011	0.119	0.90756	5611.3
		5.4	283	0.137	0.211	0.35071	263942.7
			293	0.088	0.147	0.40136	185808.7
			303	0.086	0.154	0.44156	143209.3
			313	0.091	0.185	0.50811	95263.7
			323	0.085	0.178	0.52247	87466.8
		7.1	283	0.216	0.241	0.10373	4164480.0
			293	0.209	0.245	0.14694	1975501.5
			303	0.220	0.270	0.18519	1188000.0
			313	0.157	0.204	0.23039	724943.4
			323	0.225	0.326	0.30982	35923.6
5	DHB – o – HA	9.2	283	0.148	0.191	0.22513	76413.2
			293	0.145	0.205	0.29268	412847.2
			303	0.149	0.222	0.32883	310358.4
			313	0.136	0.223	0.39014	200343.5
			323	0.130	0.229	0.43231	151872.3

		5.4	283	0.185	0.145	-	-
			293	0.176	0.159	-	-
			303	0.101	0.055	-	-
			313	0.112	0.064	-	-
			323	0.123	0.093	-	-
		7.1	283	0.126	0.156	0.19231	1092000.0
			293	0.130	0.164	0.20732	922145..3
			303	0.132	0.177	0.25424	576888.9
			313	0.121	0.177	0.31638	341470.0
			323	0.118	0.173	0.31792	337421.5
6	DHB – m – HA	9.2	283	0.062	0.064	0.03125	49600000.0
			293	0.062	0.065	0.04615	22388888.9
			303	0.057	0.062	0.08065	7068000.0
			313	0.058	0.068	0.14706	1972000.0
			323	0.056	0.077	0.27273	488888.9
		5.4	283	0.022	0.027	0.18519	1188000.0
			293	0.025	0.033	0.24242	644531.3
			303	0.033	0.032	-	-
			313	0.040	0.018	-	-
			323	0.044	0.015	-	-
		7.1	283	0.064	0.066	0.03030	52800000.0
			293	0.055	0.059	0.06780	10140625.0
			303	0.050	0.057	0.12281	2908163.3
7	DHB – p – HA		313	0.052	0.042	-	-
			323	0.053	0.045	-	-
		9.2	283	0.055	0.063	0.12698	2707031.3
			293	0.047	0.058	0.18966	1126446.3
			303	0.048	0.044	-	-
			313	0.052	0.037	-	-
			323	0.059	0.031	-	-
		5.4	283	0.030	0.029	-	-
			293	0.019	0.021	0.09524	4987500.0
			303	0.027	0.030	0.10000	4500000.0
			313	-	0.017	-	-
			323	0.022	0.018	-	-
		7.1	283	0.028	0.033	0.15152	1848000.0
			293	0.033	0.041	0.19512	1057031.3
			303	0.024	0.032	0.25000	600000.0
			313	0.023	0.033	0.30303	379500.0
			323	0.028	0.042	0.33333	300000.0
8	DHB – o – AA	9.2	283	0.032	0.007	-	-
			293	0.041	0.043	0.04651	22037500.0
			303	0.026	0.030	0.13333	2437500.0
			313	0.022	0.034	0.35294	259722.2
			323	0.015	0.037	0.59460	57334.7

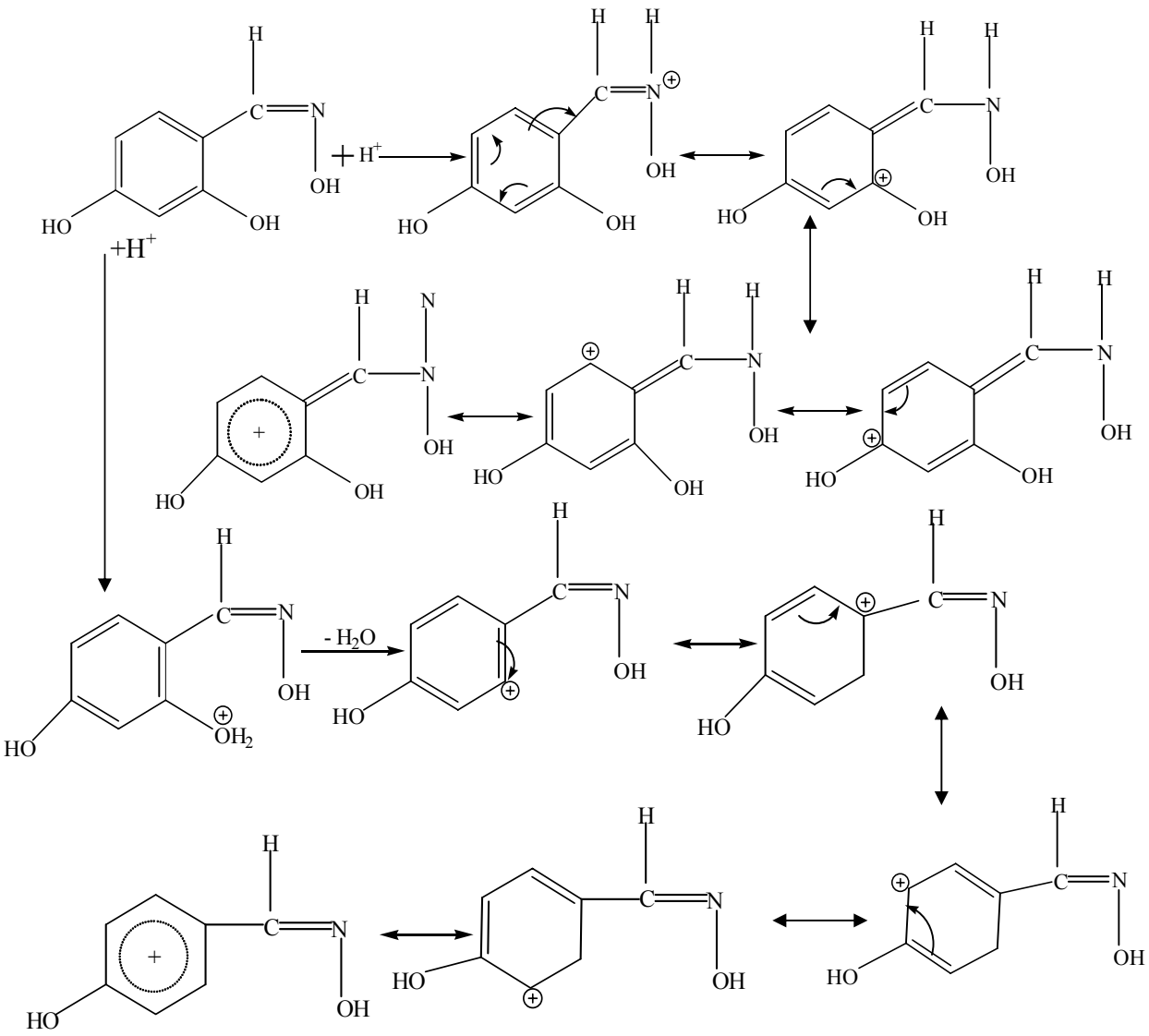
9	DHB – p – AA	5.4	283	0.052	0.041	-	-
			293	0.029	0.048	0.39583	192797.8
			303	0.050	0.017	-	-
			313	0.045	0.028	-	-
			323	0.054	0.005	-	-
		7.1	283	0.057	0.058	0.01724	165300000.0
			293	0.061	0.065	0.06154	12390625.0
			303	0.048	0.060	0.20000	1000000.0
			313	0.031	0.064	0.51563	91092.8
			323	0.052	0.043	-	-
		9.2	283	0.044	0.019	-	-
			293	0.063	0.077	0.18182	1237500.0
			303	0.063	0.081	0.22222	787500.0
			313	0.053	0.071	0.25352	580709.9
			323	0.035	0.033	-	-
10	DHB – o – MA	5.4	283	0.070	0.079	0.11392	3413580.3
			293	0.072	0.084	0.14286	2100000.0
			303	0.071	0.086	0.17442	1356888.9
			313	0.073	0.093	0.21505	848625.0
			323	0.075	0.101	0.25743	560281.1
		7.1	283	0.076	0.085	0.10588	3987654.3
			293	0.076	0.088	0.13636	2322222.2
			303	0.104	0.127	0.18110	1248393.2
			313	0.078	0.101	0.22772	744612.5
			323	0.079	0.110	0.28182	452133.2
		9.2	283	0.078	0.088	0.11364	3432000.0
			293	0.077	0.3089	0.13483	2379513.9
			303	0.070	0.083	0.15663	1718934.9
			313	0.073	0.090	0.18889	1136678.2
			323	0.081	0.104	0.22115	796219.3
11	DHB – m - MA	5.4	283	0.004	0.013	0.69231	32098.8
			293	0.004	0.016	0.75000	22222.2
			303	0.012	0.011	-	-
			313	0.009	0.003	-	-
			323	0.017	0.010	-	-
		7.1	283	0.002	0.003	0.33333	300000.0
			293	0.001	0.007	0.85714	9722.2
			303	0.002	0.001	-	-
			313	0.003	0.001	-	-
			323	0.005	-	-	-
		9.2	283	0.002	0.001	-	-
			293	0.002	0.004	0.50000	100000.0
			303	0.001	0.006	0.83333	12000.0
			313	0.004	0.002	-	-
			323	0.003	-	-	-

		5.4	283	0.117	0.193	0.39378	195472.7
			293	0.096	0.173	0.44509	140057.4
			303	0.099	0.197	0.49746	101535.8
			313	0.083	0.186	0.55376	72759.0
			323	0.080	0.205	0.60976	52480.0
		7.1	283	0.116	0.216	0.46296	125280.0
			293	0.110	0.218	0.49541	102794.9
			303	0.122	0.257	0.52529	86019.2
			313	0.096	0.218	0.55963	70303.7
			323	0.092	0.226	0.59292	57897.1
12	DHB – p - MA	9.2	283	0.074	0.085	0.12941	2599173.6
			293	0.097	0.120	0.19167	1100189.0
			303	0.088	0.122	0.27869	464359.9
			313	0.085	0.072	-	-
			323	0.090	0.044	-	-

In order to simplify the interpretation of the results as shown in Table(3) , the following divisions are thought necessary :-

1- At pH 5.4

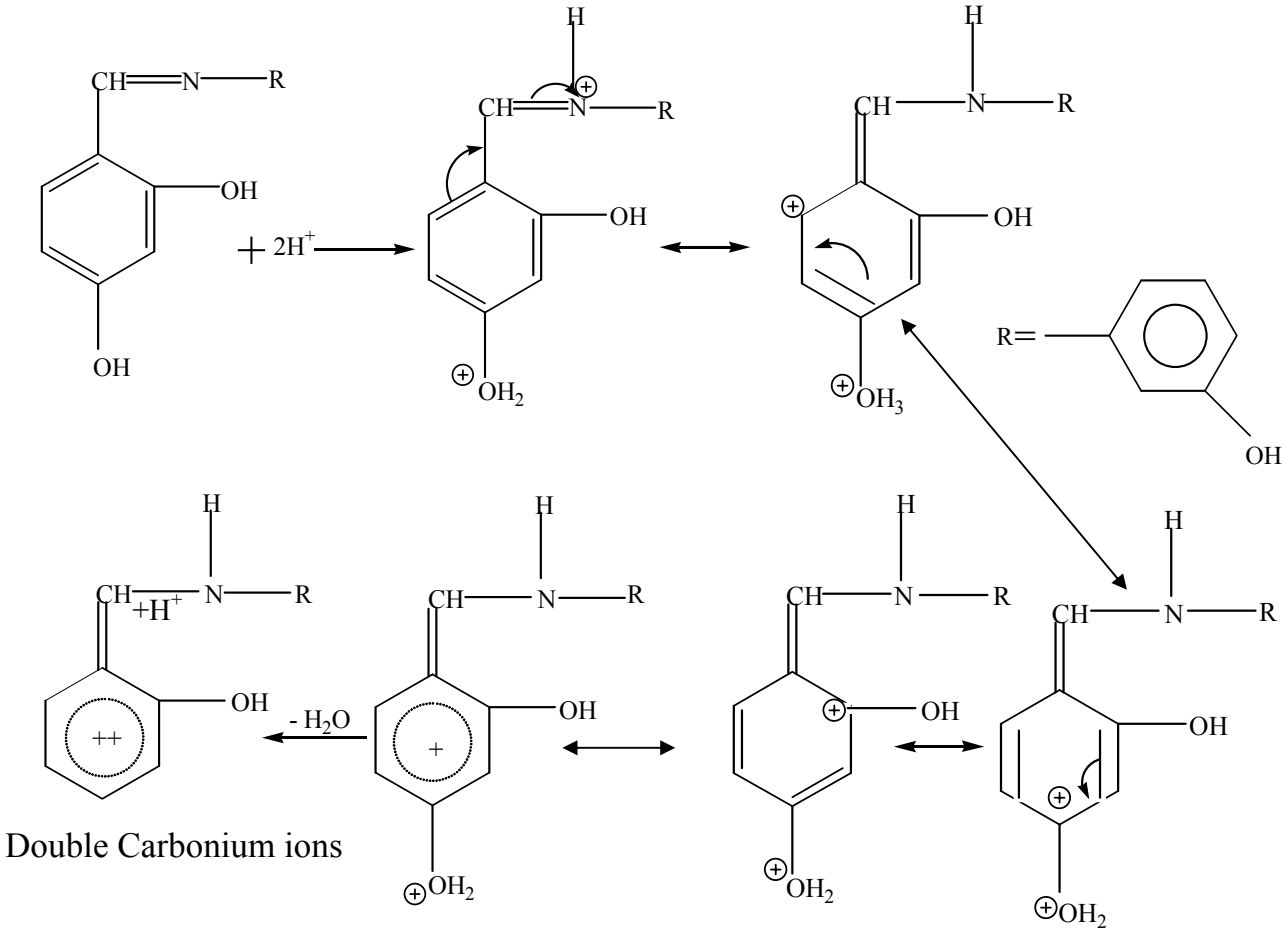
Table (3) shows a different five values of stability constants for imines (2,5,10,12). This means that their dyes are stable at five different temperatures. Other imines numbers 1,3,4,7,8,9 and 11 gave 1-4 values of stability constants , as interpreted by their partial protonation , before their dyes formation at a temperature mentioned . The partial protonation just mentioned is expected at acidic pH and results to the formation of nitrilium or phenoxonium ion as shows in scheme (1).



Scheme (1) Nitrilium and phenoxonium ions formed in anti- DHBO

Actually positive nitrilium or phenoxonium ions formed in scheme (1) are unable to react with a positive azo group formed from sulphanilic sodium salt , because by their ruplusion forces. The last lead to the formation of unstable dye product at some temperatures , depending on the chemical structures of imines.

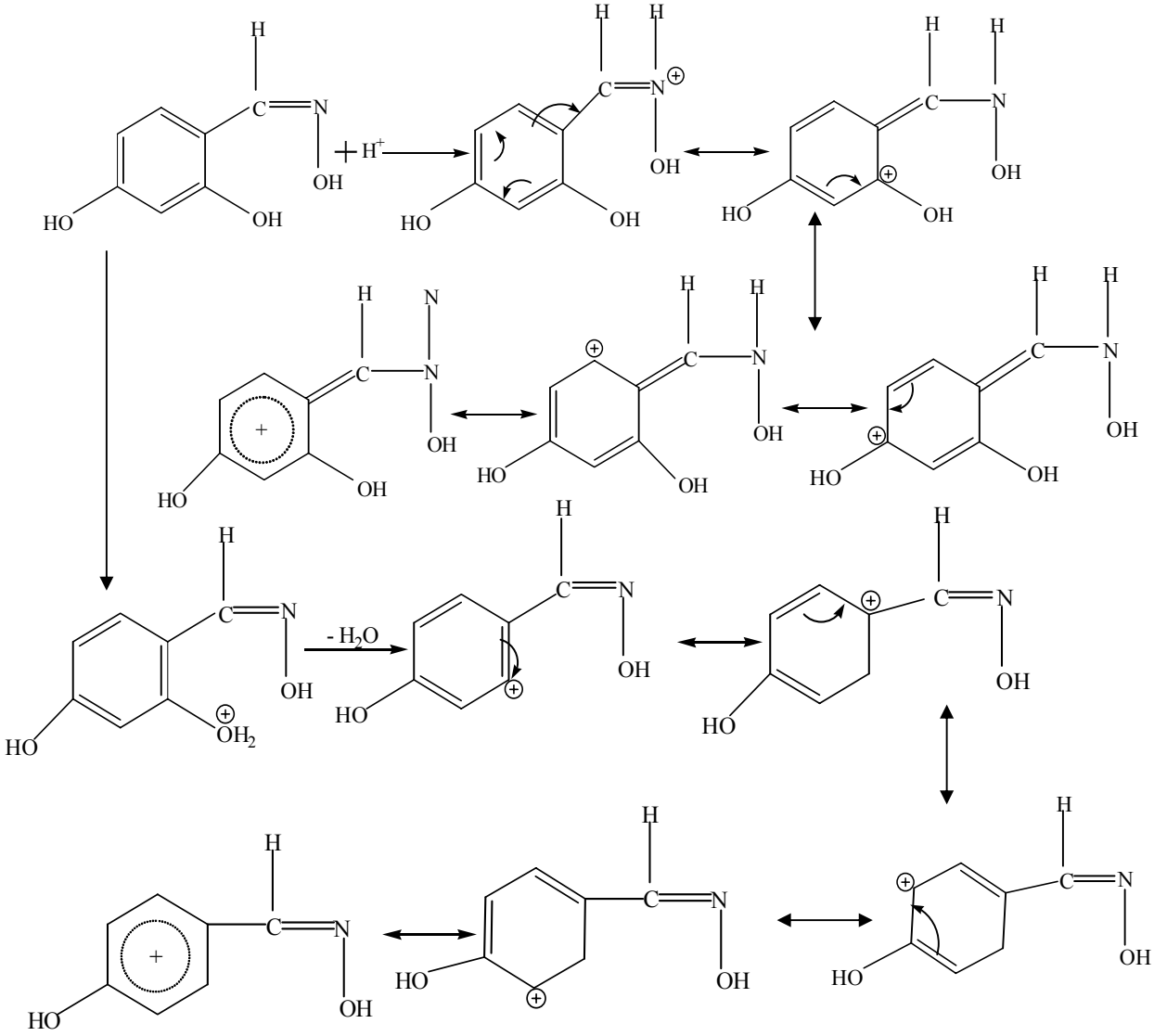
Imine (6) as symbolized DHB-m-HA shows unstable dye product at five different temperatures range between (283-323)K, due to the a complete protonation process of such imine , resulted to the formation of double[6] positive carbonium ions on the aromatic ring as shown in scheme (2).



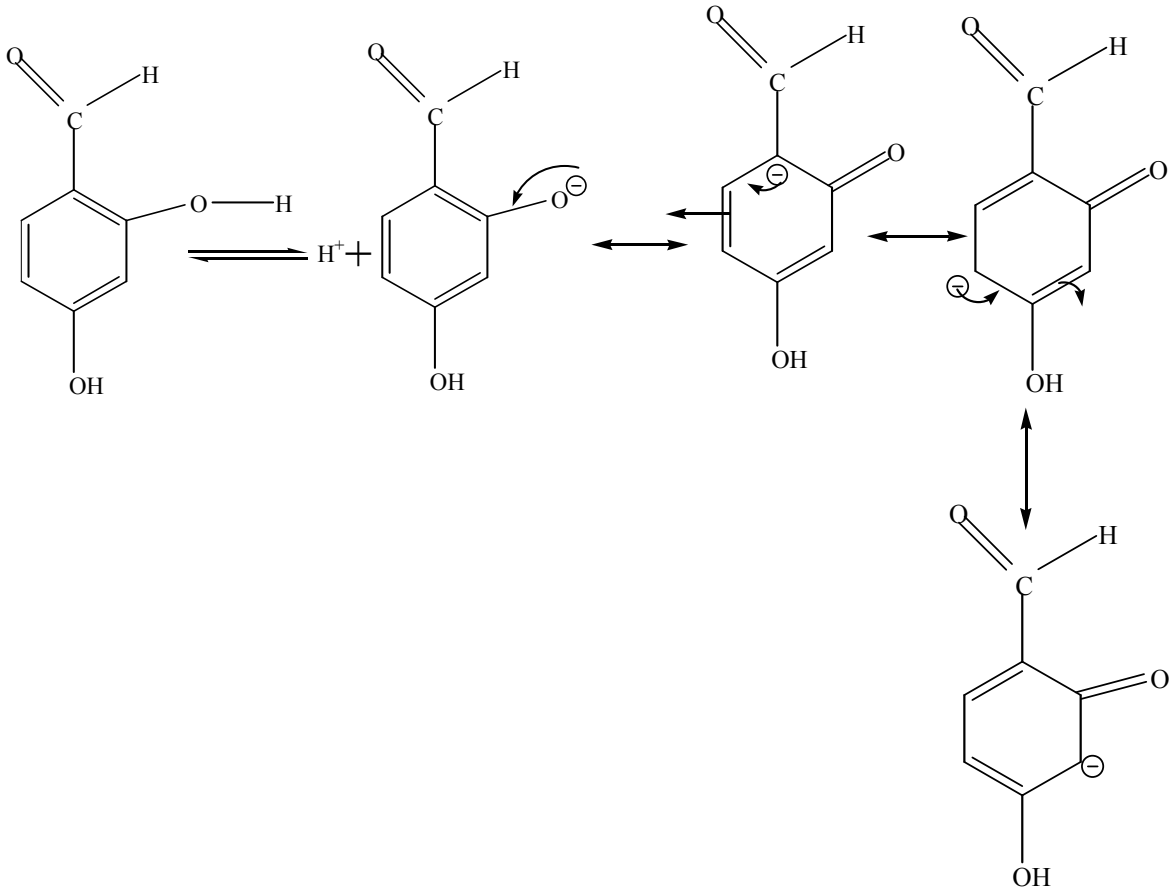
Scheme (2) A double positive ions formed in Schiff base (6).

The carbonium and phenoxonium ions in Schiff base (6) just mention are strongly repulsed by the positive azo group in sodium sulphanilic acid , leading to the unstable dye product at five different temperatures as shown in Table (3) .

2- At pH 7.1, originally it is anticipated that imines under investigation are exist as equilibrium tautomeric mixture of enol and keto forms , with greater extent[17] of enol form. Table (3) shows that imines numbers (1-7 , 9-10) are able to form a stable azo dyes with a maximum stability constant value when compared to other values observed at this pH , taking into consideration a fixed temperature of measurement. The reason for the last are the following :-



A- All imines under invstigation have an intermolecular hydrogen bonding as confirmed from the IR measurements shown in our earlier study[13]. This hydrogen bonding had proved in other studies to increase the stability and acidity of oximes[18] or the stability[4,7] of salicylidene aniline Schiff base. Hence such imines are easily ionized and its



Scheme (3) Resonance numbers in DHBAL

phenoxide ion is stabilized by resonance , typical example is shown in scheme (3) in DHBAL.

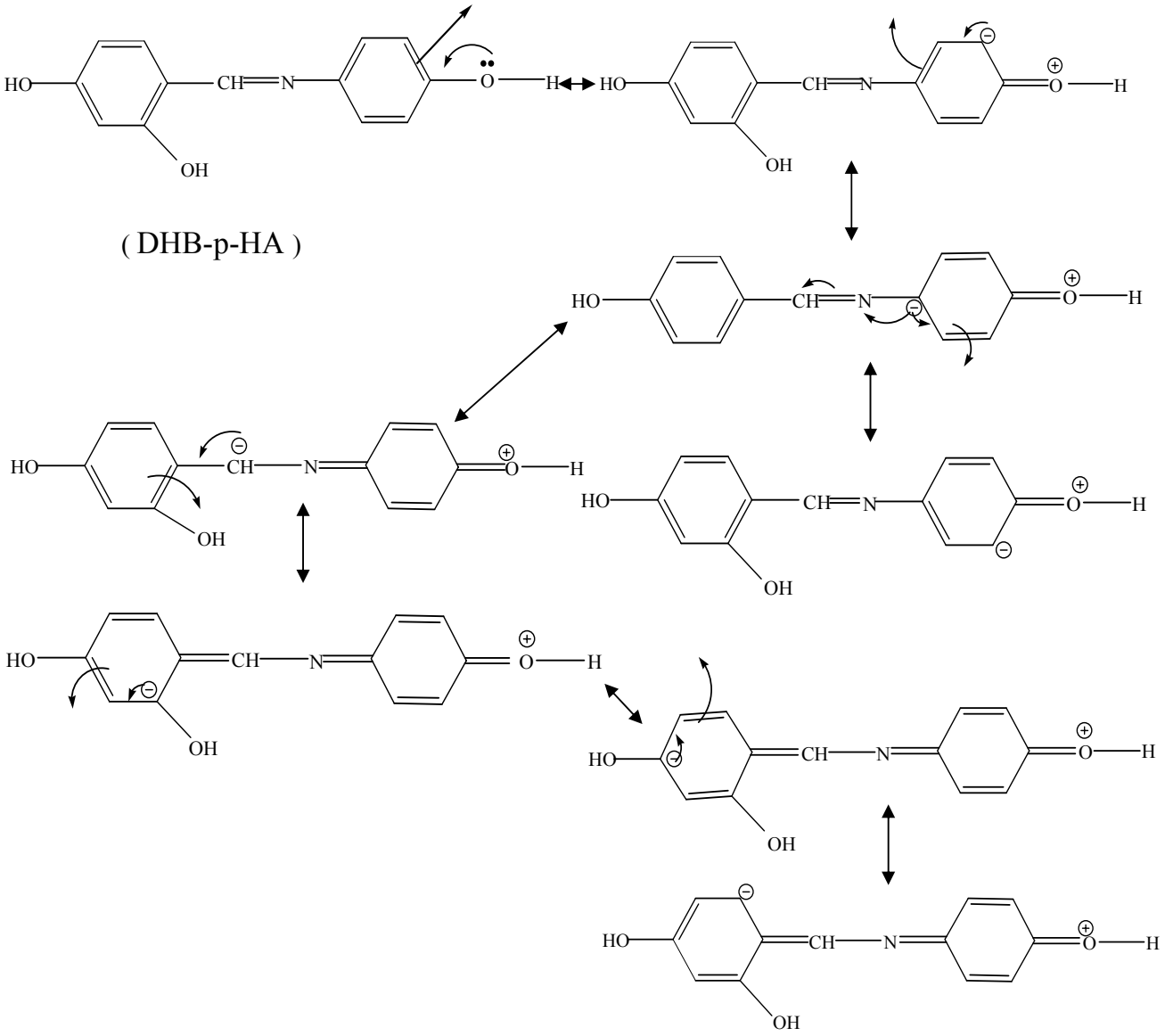
Scheme (3) shows a three resonance number for DHBAL of negative centers at ortho , meta and para positions with respect to phenolic group adjacent to the aldehyde group. This explains the favour[14] position of interring the positive azo group during a dye formation at para position and to a lesser extent at ortho position with respect to the two phenolic groups at the aldehyde ring. It explains the reason of obtaining a maximum[14] value of stability constant for the dye.

B- Actually , all imines under study are observed to be highly soluble in water. Their resistance toward melting , lead to the impossible determination of their usually melting points , especially for imines (4-15) as in Table (1). These observations lead the authors to assist the presence of imines mentioned in a zwitter[19-20] ions forms. The last contains a phenoxide ion and will stabilized by resonance as seen in the previous paragraph. Again this explains the maximum stability value of stability constant for the dye.

Imines 6,8,11 and 12 show an anomalous low values of stability constants at some temperatures. This is highly expected due to the variation of strength of hydrogen bonding , especially at some elevated temperatures.

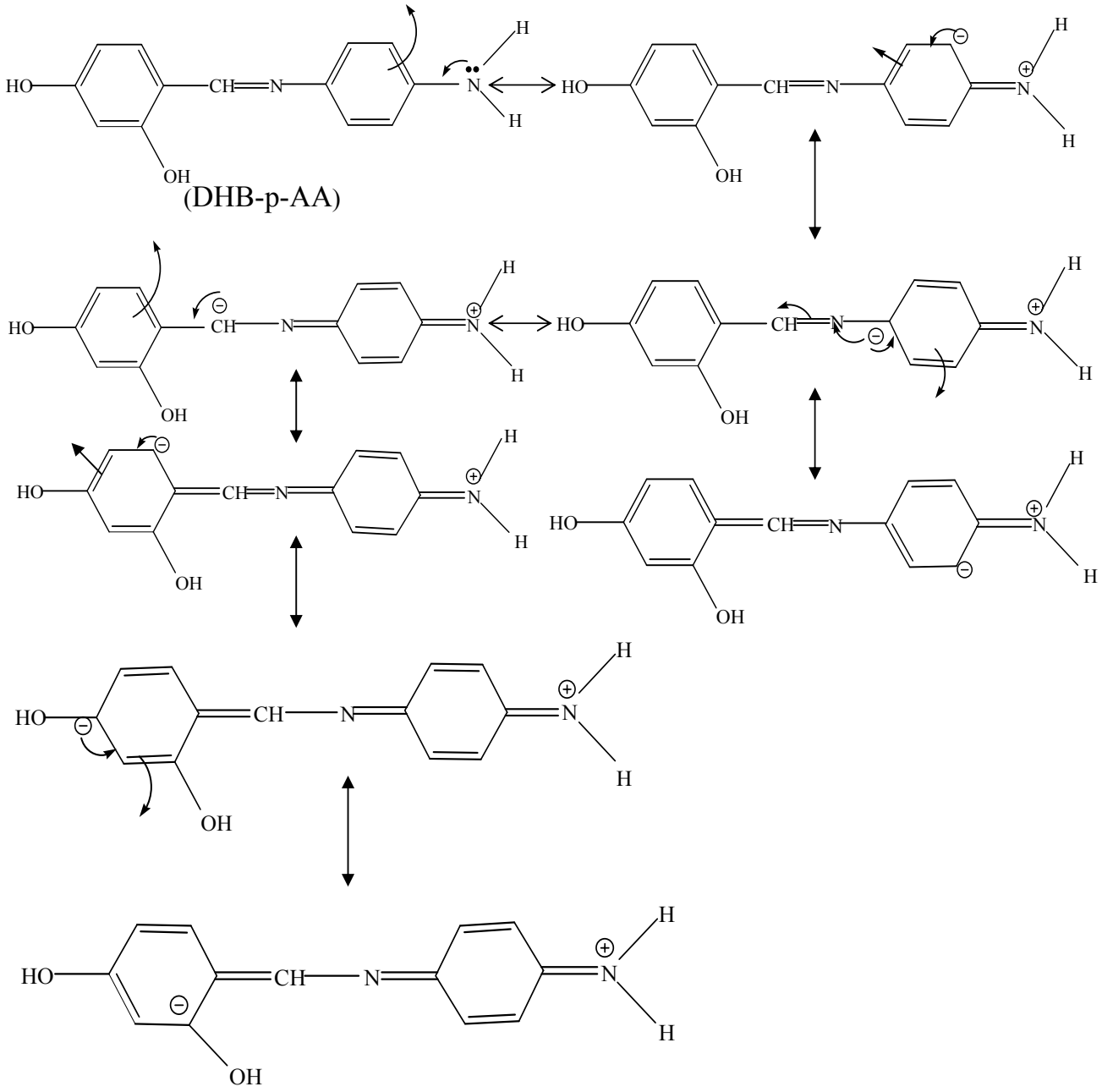
The stability constant values of the dyes DHB-p-HA and DHB-p-AA are greater than the syn and anti DHBO at

a condition of constant temperature. This is explained by the fact that the first two molecules contain a donating OH and NH_2 groups and an additional aromatic ring comes form their primary amines during synthesis as compared with DHBO. Hence the negative charges produced on DHB-p-HA and DHB-p-AA are stabilized by a greater resonance number shown in schemes (4-6).

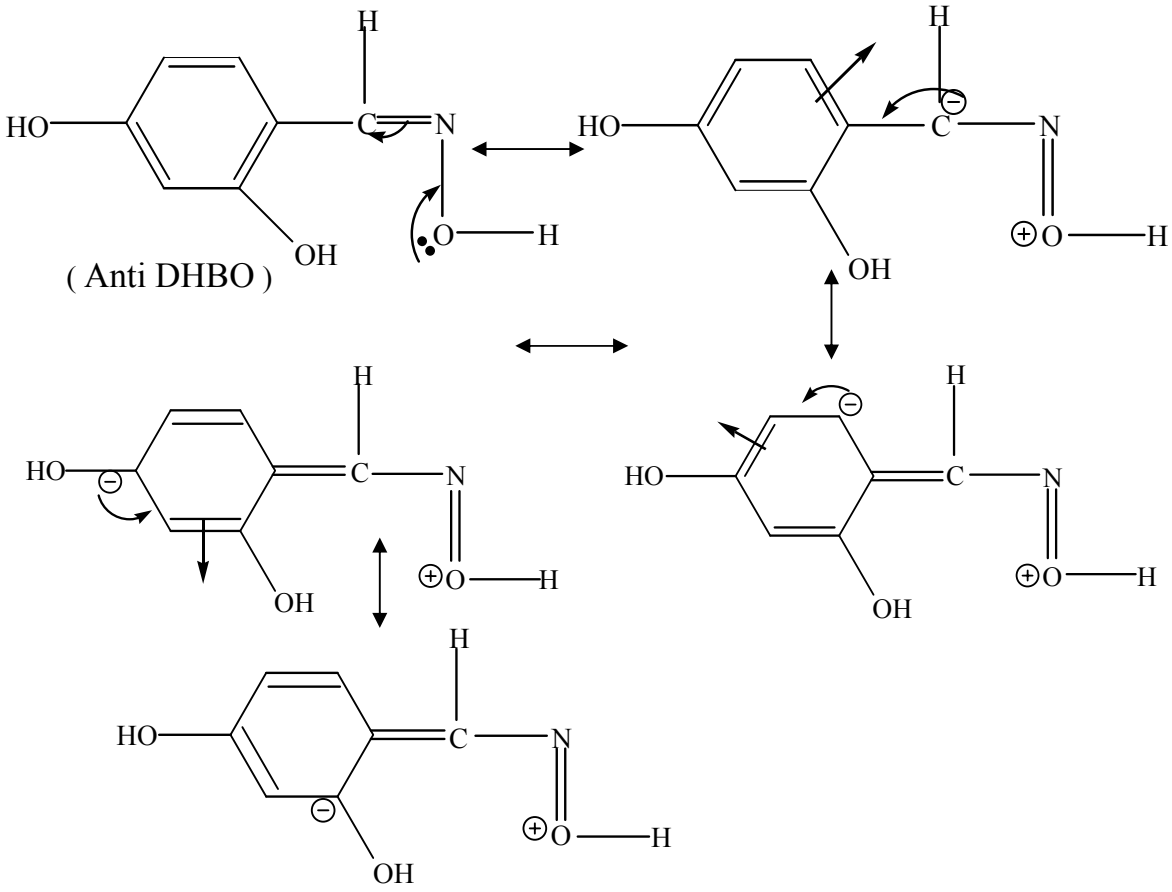


(DHB-p-HA)

Scheme (4): Resonance numbers in DHB-p-HA



Scheme (5): Resonance numbers in DHB-p-AA



Scheme (6): **Resonance numbers in (Anti DHBO)**

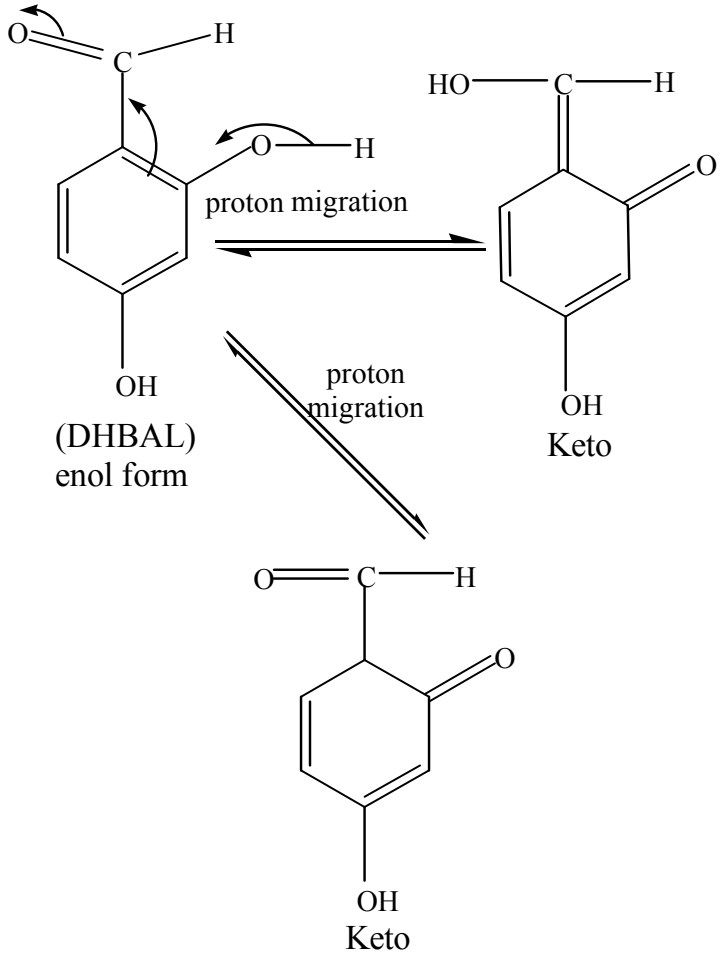
Imines DHB-p-HA , DHB-p-AA and anti or syn DHBO show eight , eight and five resonance numbers respectively. This means a greater stability for their negative ions are produced by resonance effect in these imines , or the negative charges of their ions are spreaded over a large areas , when compared to imine syn or anti DHBO. This explains the greater stability constant values in previous molecules by donor- acceptor mechanism[16] of a dye formation.

3- At pH 9.2

Table (3) shows the impossible determination of the stability constants values for a dye formed from imine 2 at a range of temperatures (283-333)K. Similarly imines 1,3,7,8,9,11,12 show some values of stability constants at some temperatures during the study. The reason for the failure determination of the stability constant values of last imines just mentioned is to the probability of conversion[21] of enol forms of phenol group present in these imines to their keto form by prototropic tautomerism reactions. This is accompanied by the destruction of aromatic systems in these imines and reduce the electronic density at position of attachment of azo group as shown before in this study. The stated tautomerism reactions are in agreement with tautomerism reactions as in conversion of oxime[11] to nitroso at

pH=9 during a dye formation of syn 2-hydroxy-1-naphtaldoxime with the same azo group of sulphanilic sodium salt or the conversion of enol in Schiff base benzylidene-2-hydroxyaniline[21] at pH=8 to its keto form when it reacts with last reagent mentioned , forming a dye product.

Prototropic tautomerism reactions occur in DHBAL , is Clearfield in scheme (7)



Scheme (7) Prototropic tautomerism reaction at basic medium for DHBAL .

Conclusions

1. The optimal condition for a dye product formed by the reaction of imines under investigation with azo group derived form sodium sulphanilic acid are evaluated spectrophotometrically with stoichiometric ratio of 1:1. This is in agreement with a previous dye study[11] on 2-hydroxy-1-naphthaldoxime and other with the same azo group.
2. The values of stability constant for the dye montioned are depend on the structure of imine , the pH of the medium and the ambient temperature , during a study.
3. At pH 5.4, some experiment prove the formation of unstable dye and the failure evaluation of stability

constants values. The last are attributed to the partial or complete protonation of donor imines and the formation[6] of phenoxonium or nitrilium ions or both of them.

4. At pH 7.1 , a maximum[11] stability constant value of any dye is observed , due to the presence of imine in the enolic form. Conversely , a minimum stability constant value is obtained for the dye at pH 9.2 due to tautomeric conversion of enol form in imine to its ketonic form.
5. At pH 9.2 , the syn DHBO , is tautomised to keto imine , nitroso , and keto eneamine tautomers. Similarly DHB-p-HA give keto imine , keto eneimine and keto enamine tautomers under the same condition.
6. Stability constant values of any dye at pH =9.2 is less than its analogue at pH=7.1 taking into consideration the same temperature of measurement. This is due to the prototropic tautomerism reaction occur in their imines , and are accompanied to the destruction of aromatic aldehyde ring.
7. It was observed that Schiff bases (13-15) contain a nitrogroups in ortho , meta and p-positions are unable to give a stable dyes , at five different temperatures under study. This is for the presence of powerful electronic withdrawing NO_2 group in these molecules , which reduce electronic densities in these molecules. The last decrease the probability of attachment of such molecules with positive azo group , leading to unstable dyes according to donor-acceptor mechanism[16] of dye formation.

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