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

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Abstract

The aims of this investigation were the determination of stability constants of some dyes formed by reactions of imines with diazotized sulphanilic sodium salt at different pH values and temperatures . These stability constants were evaluated spectrophotometrically by reactions of donor imines in a forms of oxime or Schiff bases with sulphanilic sodium salt as an acceptor . This study led to a comparison between stability constants values of similar imines in a forms of syn or anti oximes or Schiff bases having substituents as OH , NH_2 , NO_2 and CH_3 groups on aromatic ring of primary amine parts of Schiff bases . Finally , results collected were interpreted and discussed in detail .

الخلاصة

يشتمل البحث على تعيين ثوابت استقرار الاصباغ المتكونة من تفاعلات الايمينات مع ملح الصوديوم لحامض السلفانليك المؤزوت في دوال حامضية ودرجات حرارية مختلفة . تضمن البحث استعمال الطريقة الطيفية في حساب ثوابت استقرار الاصباغ المتكونة من تفاعل الايمينات الواهبة للالكترونات والتي هي على اشكال اوكزيمات او قواعد شيف مع ملح الصوديوم لحامض السلفانليك المؤزوت المستقبل للالكترونات .

اهتمت الدراسة بمقارنة قيم ثوابت الاستقرار للايمينات المتشابهة والتي هي على شكل اوكزيمات سين وأنتي او قواعد شيف الحاوية على معوضات OH , NH_2 , CH_3 على الحلقات الاروماتية المكونة للامين الاولي في قواعـد شيف .

Introduction

During the last 28 years , a considerable interest had paid by the Chemist to the spectroscopical studies of imines by UV[1-3] , IR[4-5] , NMR[6] and mass[7] spectra beside other kinetic[8], thermodynamic[9], tautomerism[9] and dyes[10] studies .

The diazotization reaction as analytical method was used for the determination of compounds such as 4-aminoantipyrine[11] , sulphonamide[12] , aniline[13], napthylamine[14] and nitrazipam[15] .

In our laboratory , Azzouz etal[16-18] had studied the stability constants of some azo dyes formation between donor imines with sulphanilic sodium salt as an acceptor . These consecutive reactions included the determination of structures[16]

of imines by physical method the stoichiometry[17] and the stability constants[18] of the dyes mentioned . These publications led the authors to study of influence of pH with the type of oxime isomer[17] and surfactant[18] on the stability of the dyes . Experimentally , all these physical parameters mentioned were found to be effective in determining the values of stability constants .

This work describes the influence of different structures of imines on the stability constants values of a dyes . These imines are derived from the mother compound 2,4-dihydroxy benzaldehyde and are in a forms of syn or anti oxime or Schiff bases having substituents as OH^- , NH_2 and CH_3 on the aromatic rings of primary amine parts .

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°.

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

C= molar concentration of the dye

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

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

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 :-

1. Comparison of stability constant of aldehyde DHBAL with syn DHBO and anti DHBD .

At pH values 5.4 and 7.4 , the following arrangement was observed

$K_{syn\ DHBO} > K_{Anti\ DHBO} > K_{DHBAL}$

At pH value 9.2 , it was impossible to determine the stability constant values at all five temperature as in Table (1) , due to the tautomerism reaction[3] DHBAL and anti DHBO show some stability constant values and some temperatures which were difficulty compared .

2. Comparison of DHBAL with unsubstituted Schiff bases DHBA .

At pH 7.1 , Table (2) shows a higher stability constant values for unsubstituted Schiff bases DHBA when compared with DHBAL with exclusion of temperature 283K . This was due to the presence of two and one aromatic ring in DHBA and DHBAL respectively . Therefore , the donation[19] property of DHBA was greater than DHBAL and consequently accompanied by greater stability constants in DHBA according to donor acceptor mechanism of complex formation .

3. Comparison of DHBA with other Schiff bases .

This paragraph was divided in to Schiff bases that contain substituents OH , NH_2 , NO_2 and CH_3 at different positions on aromatic ring of primary amine part . Hence the following division are required :-

(a) Schiff bases that contain OH group on the amine part .

Form literature , it was known that OH group had values of σ_m = 0.121 , σ_p = -0.37 . This means that such group had acceptor and donor properties at meta and para positions respectively . The behavior of OH at ortho position had nearly a similar electronic effect to para . This was in addition to the steric effect and intramolecular hydrogen bond formation of OH at ortho position .

It was observed that stability constants values of DHBA as in Table (2) at pH values 5.4 , 7.1 and all temperatures had a greater values when compared with similar Schiff bases having OH group in ortho , meta and para position . The cause for the lower stability constant values of Schiff bases having OH group in meta position was due to the capability of such group to behave as an acceptor as seen above from σ_m value mentioned . Originally it was anticipated that Schiff bases DHB-p-hydroxyaniline having a higher stability constant value , due to the negative value of σ_p stated before . This was experimentally accompanied by increasing the electronic density around to donor site in Schiff base .

Actually , the reverse of such result was expected experimentally in these Schiff bases due to possibility of hydrogen bond formation in OH group and the planarity of Schiff bases . The planarity was studied[20] by comparing the molar extension coefficient Σ_{max} of Schiff bases containing OH group in ortho , meta and p-positions . Estimated Σ_{max} had a values of 2040 , 1770 and 450 in unit of $L.mol^{-1}.cm^{-1}$ in Schiff bases DHB-o-HA , DHB-m-HA and DHB-p-HA respectively . The first and second numbers had approximate values and near similar planarity . The

low Σ_{max} value for DHB-p-HA means that such molecule is less planar and accompanied by low value of stability constant . Schiff bases DHB-m-HA did not show any stability constant value at pH 5.4 and all temperatures , due to complete protonation[3] of nitrogen atom at such acidic medium . At pH 9.2 , the stability constants values for Schiff bases contain OH group show a variable results . It was believed that these hydroxylic Schiff bases undergo the enol keto tautomerism reaction before dye formation . The last is fully accepted to Schiff bases DHB-p-HA at temperature range (303-323) K as in Table (2) .

(b) Schiff bases that contain NH_2 group

Table (2) showed unstable dye formation at pH 5.4 and temperature 283k for Schiff bases DHBA , DHB-o-HA and DHB-p-AA. The complete protonation of Schiff bases was a good answered to such case .

In the meantime , these Schiff bases showed a stable dyes at temperature 293K with the following arrangement of stability constant as :

$K_{DHBA} > K_{DHB\text{-}OAA} > K_{DHB\text{-}P\text{-}AA}$

Also these amino Schiff bases showed a variable stability constant values at pH 7.1 and 0.2 which were difficulty compared .

(c) Schiff bases that contain CH_3 group

These Schiff bases showed a stable dyes at some temperatures and pH values . The stability constants values collected were increased in the following arrangement :-

$K_{DHB\text{-}m\text{-}MA} > K_{DHB\text{-}p\text{-}MA} > K_{DHB\text{-}o\text{-}MA}$

Methyl group as known[19] as a good donor when present at para and meta positions on the aromatic rings . At ortho position, such group exerts some steric effect. The last effect was responsible on increasing stability constant values of the dye . Maximum stability constant value of the dye DHBA was observed when compared with others substituted methyle DHBA at some temperatures and pH 5.4 and 7.1 with exclusion the temperature 323K at pH 7.1 . The planarity statement stated before might be effective in this case . $\sum_{max}$ estimated for ortho and para methylated DHBA had values of 1112 , 361 in unit $Liter.mole^{-1}.cm^{-1}$ respectively . The greater $\sum_{max}$ value of ortho substituent resulted to greater stability constant value . A reverse to such result was true at pH 9.2 . This means that DHBA had a lower stability constant values than the methylated DHBA at some temperatures . In otherwords , a lower probability for tautomerism process was occurred in methylated DHBA , resulted to increase stability constants value or the dye .

(d) Schiff bases that contain NO_2 group

In this study all ortho , meta and para substituted nitro DHBA showed unstable dyes formation . This was due to the strong electronic acceptor property of nitro group . The last was cleared from σp and σm values of +0.778 and +0.710 respectively .

The nitro group in substituted DHBA resulted to an electron deficiency around the donor site in nitro Schiff bases . Certainly , this attributed by decreasing the probability of dye formation .

This supported the dye formation by donor – acceptor mechanism[21] .

The failure determination of stability constants for substituted nitro DHBA dyes were in full agreement with DHB-m-HA at all temperatures and pH 5.4 . The σm for OH group had value +0.121 , which means that such group was electron acceptor .

The influence of OH , NH_2 and CH_3 substituents in DHBA on the stability constants of dyes formation was accomplished by the use of Hammett equation[19] at temperature 20C° , using the following equation :-

$$\text{Log } K / K_0 = \sigma p \qquad \ldots\ldots (1)$$

K = stability constant for substituted dye .
K_0 = stability constant for unsubstituted dye .
P = reaction constant (sensitivity)
σ = Sigma constant .

From equation(1) the plot of log K / K_0 versus σ showed a linear lines with negative slope . Typical plots were shown in Fig. 1 for the meta and para substituted DHBA and at different pH values . The negative values of slopes in Fig.1 , mean that dye formation was accelerated by donor electron groups in substituted DHBA . This was in full agreement[21] with dye or complex formation . Carful examination of linear plot in Fig. 1 showed an intercept for each line . This was in disagreement with theoretical study of linear plot . The answered to such abnormal result was due to the high stability of dyes formed by reaction of DHB-p-AA with diazotized sulphanilic sodium salt at different pH values . Actually DHB-p-AA contained an amino group , and by help of resonance , the negative charge spread over eight resonance forms as in Scheme (1) . This enhanced the negative charge and consequently the donor site in DHB-p-AA and resulted to a greater stability constant values of dye mentioned .

Conclusions

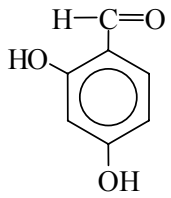
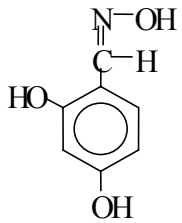
1. A spectrophotometric method was used in the determination of dyes formations by reactions of imines derived from the mother compound 2 , 4-dihydroxybenzaldehyde .

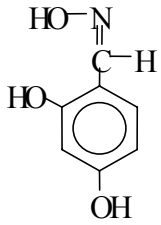
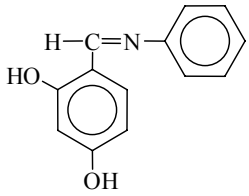
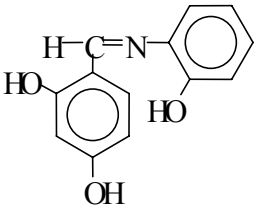
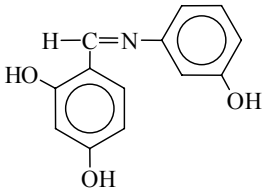
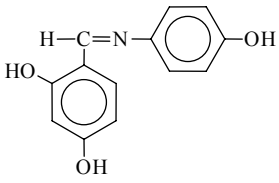
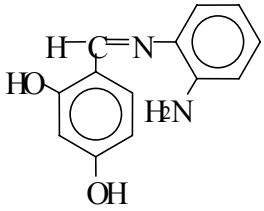
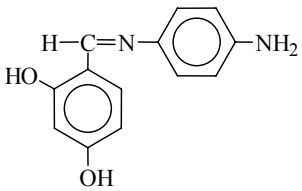
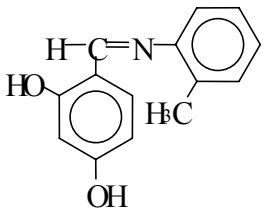
2. Imines under study were prepared by standard method and their chemical structures were confirmed[16] by the physical means , namely , UV , IR and melting points .

3. The stability constants for dye formation between imines under study and diazotized sulphanilic sodium salt were governed by the following factors :-

a- The chemical structure of imine
b- The temperature
c- The pH of the medium
d- Steric effect if available in imine
e- Planirity of imine

Tabel (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	-	
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	-	

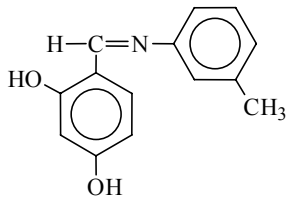
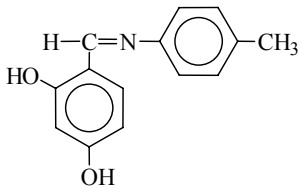
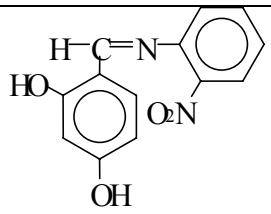
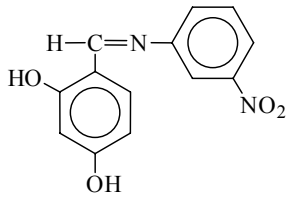
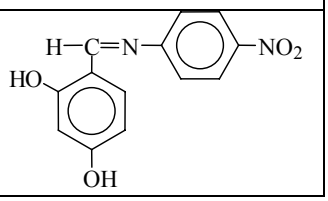
11	DHB-m-MA	2,4-dihydroxy benzylidene-m-methyl aniline	mild red	-	
12	DHB-p-MA	2,4-dihydroxy benzylidene-p-methyl aniline	red	-	
13	DHB-o-NA	2,4-dihydroxy benzylidene-o-nitro aniline	orange	-	
14	DHB-m-NA	2,4-dihydroxy benzylidene-m-nitro aniline	yellow	-	
15	DHB-p-NA	2,4-dihydroxy benzylidene-p-nitro aniline	yellow	-	

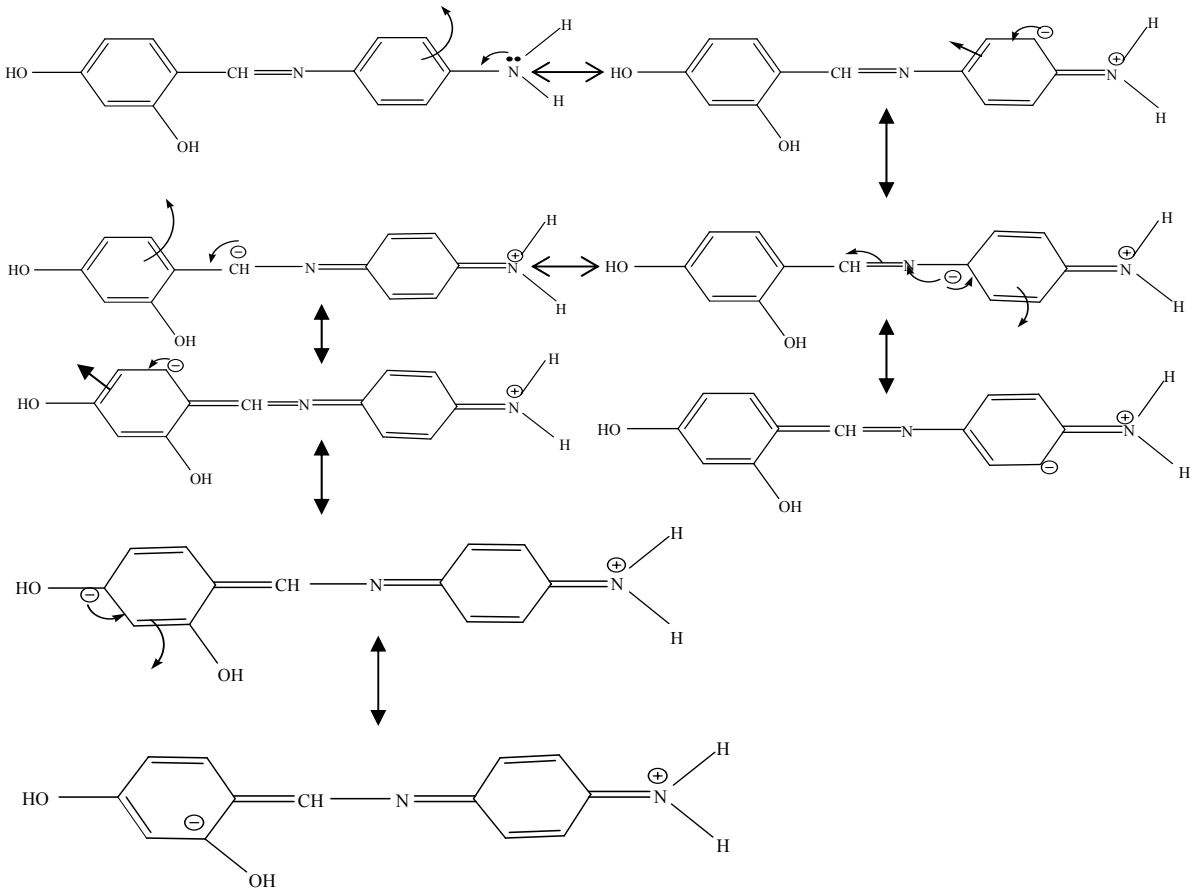
Table (2) : Stability constant values for the dyes at different pH and temperatures

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

			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
		5.4	323	0.221	0.310	0.28710	432458.0
			333	0.813	0.645	-	-
			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
		7.1	313	0.686	0.603	-	-
			323	0.672	0.593	-	-
			333	0.617	0.503	-	-
			283	0.644	0.594	-	-
2	**Syn DHBO**		293	0698	0.625	-	-
			303	0.715	0.485	-	-
			313	0.680	0.486	-	-
		9.2	323	0.687	0.581	-	-
			333	0.672	0.593	-	-
			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
		5.4	313	0.011	0.037	0.70270	30103.6
			323	0.011	0.009	-	-
			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
		7.1	313	0.028	0.054	0.48148	111834.3
			323	0.013	0.005	-	-
			283	0.054	0.070	0.22857	738281.3
3	Anti DHBO		293	0.055	0.075	0.26667	515625.0
			303	0.060	0.045	-	-
		9.2	313	0.058	0.033	-	-
			323	0.026	0.021	-	-
			283	0.044	0.042	-	-
			293	0.036	0.039	0.07692	7800000.0
			303	0.043	0.038	-	-
		5.4	313	0.036	0.032	-	-
			323	0.041	0.039	-	-
			283	0.054	0.041	-	-
			293	0.032	0.033	0.03030	52800000.0
			303	0.054	0.058	0.06897	9787500.0
		7.1	313	0.053	0.063	0.15873	1669500.0
			323	0.039	0.058	0.32759	313296.4
			283	0.054	0.069	0.21739	828000.0
4	DHBA		293	0.049	0.077	0.36364	240625.0
			303	0.028	0.063	0.55556	72000.0
		9.2	313	0.023	0.099	0.76768	19710.9
			323	0.011	0.119	0.90756	5611.3
			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
		5.4	313	0.091	0.185	0.50811	95263.7
			323	0.085	0.178	0.52247	87466.8
			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
5	DHB – o – HA	7.1	313	0.157	0.204	0.23039	724943.4
			323	0.225	0.326	0.30982	35923.6

		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
6	DHB – m – HA	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
		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
7	DHB – p – HA	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
			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	-	-
8	DHB – o – AA	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
		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	-	-	-
12	DHB – p - MA	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
		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	-	-



Scheme (1) :The influence of resonance in DHB-p-AA

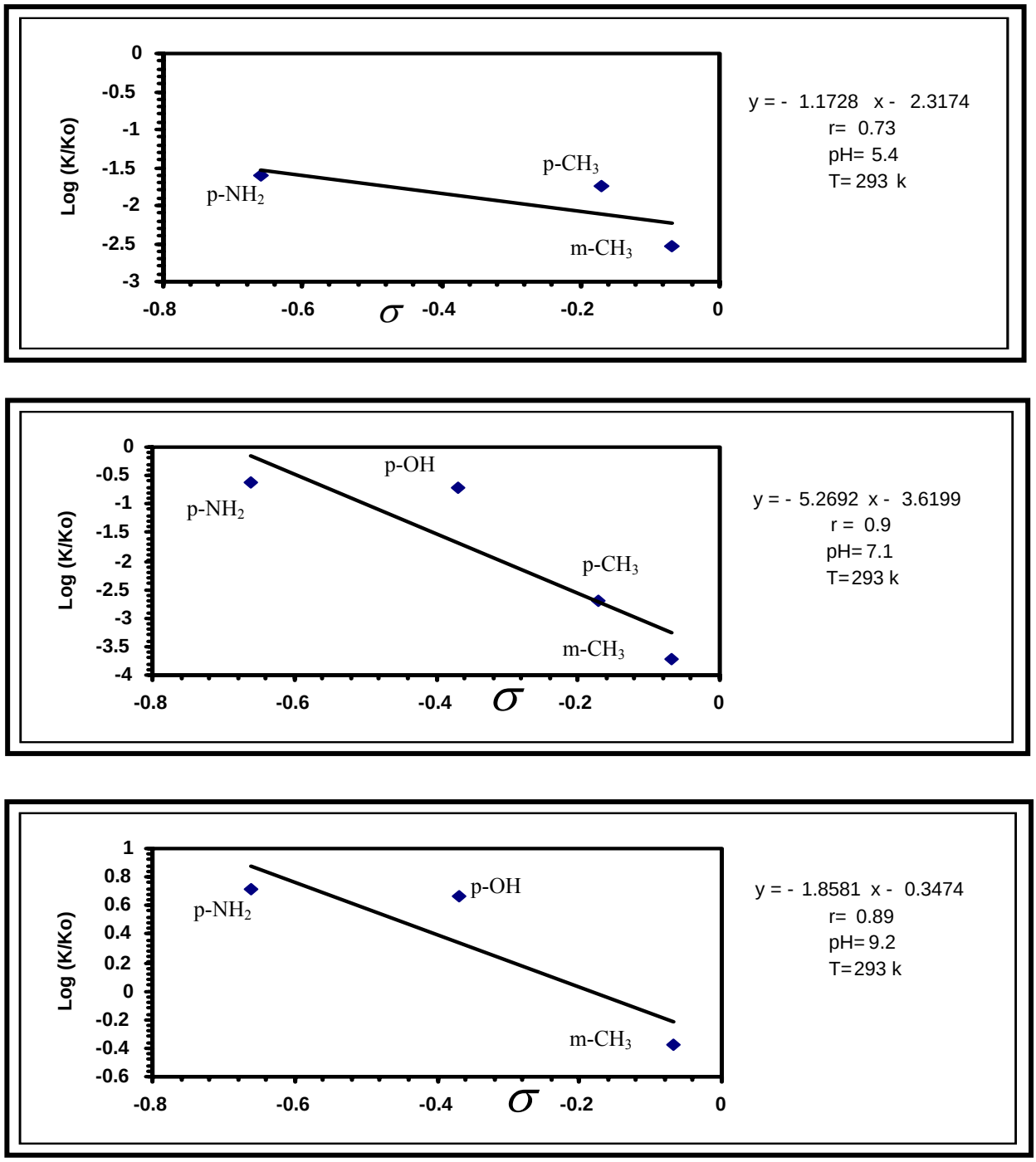


Fig. 1 : Relationship between log K / K_0 versus σ for dyes formed by reactions of m and p – substituted DHBA with donor .

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