Available online at: www.basra-science-journal.org

ISSN –1817 –2695

The Synthesis and The Spectrophotometric Study of Some New Azodyes Derived From 1-Hydroxy-2-naphthoic Acid and Sulfadiazine Derivatives

Asaad.A.A and Haider.A.A

Chemistry Dept. Education College. Basrah University

E.Mail:heider abdalsetr@ Yahoo.co

Received 9-9-2012, Accepted 26-12-2012

Abstract

This study involves the preparation of three azodyes derived from 1-hydroxy- 2-naphthoic acid and sulfadiazine derivatives. The characterization of Dyes 4-(sulfadiazineazo)-1-hydroxy-2-naphthoic acid (F_1) ,4-(sulfamerazineazo)-1-hydroxy2-naphthoic acid (F_2) and 4-(sulfamethazineazo)-1-hydroxy2-naphthoic acid (F_3) have been described by C.H.N. The I.R. and V. & UV. spectroscopic techniques were carried out . The acid-base properties were studied at different pH values and the dissociation and protonation constants of dyes were determined, as well as the solvents effect were studied at different solvents polarities

Key Words : Azodyes , Ionization & Protonation constants , Spectral studies , Isobestic point

1. Introduction

Recently , several studies have been published on the synthesis and spectral properties of azodyes [1-5]. This reflects their widely important applications in different field such as coloring fiber [1] , photo electronic applications [6] optical storage technology[7], sensitive chromogenic regent [8], sages detection [9] as well as their involvement in many biological reactions and in analytical chemistry [10]. Azo compounds are still a very important class of chemical compounds receiving much attention in scientific research due to their chromophoric properties[11] . These compounds have been commonly used in both industry and analytical chemistry[12] like acid-base indicator and metalochromic indicator ,and used as antipyretic reagents or as inhibitors from corrosion . The solvents of different polarities may be affected on the absorption spectra of π – conjugated compounds , exhibit $n \rightarrow \pi^*$ transition as well as $\pi \rightarrow \pi^*$ transition causing blue or red shifts . This work presents an investigation of electronic spectra of three azodyes involving sulfadiazine Dyes 4-(sulfadiazineazo)-1-hydroxy-2-naphthoic acid (F_1) ,4-(sulfamerazineazo)-1-hydroxy2-naphthoic acid (F_2) and 4-(sulfamethazineazo)-1-hydroxy2-naphthoic acid (F_3) . The characterization of the azo compounds has been performed by melting

point , I.R , C.H.N. Most of azodyes having acid – base properties with the presence of fixed isobestic points (which represent the number of equilibriums in such azodye) , for this reason they are used as acid – base indicators cause of their sensitivity toward acid and base substances .

2.Experimental

All the reagents and solvents were of reagent-grad quality . Infrared spectra (in K Br pellets) were recorded on FT.IR-8400S shimadzu . Melting point were determined on melting point apparatus . The dyes were recorded by using and element analysis (C.H.N.), they were carried out by perkin element 2400 element analysis . U.V.& V. absorption was recorded by using LKB (Biochrom ultra space II-4050 UV./V.) spectrophotometer .The pH measurements were made with pH-Meter (H .Jurgons Co. Bremen,L.Puls Munchen15)

2.1 Diazotization

Sulfadiazine [0.02245 gm ,0.001 mol] was dissolved in 50 ml of distilled water and 6 ml of concentrated hydrochloric acid was added, the solution was then cooled to 0 - 5 C^0 in ice-bath and maintained at this temperature. 5 ml of sodium nitrite (0.15 gm , 0.02 mol) was then added drop wise with stirring continued for 30 min to produce diazonium salt .

2.2 Preparation of 4-(sulfadiazine azo)-1-Hydroxy 2- Naphthoic acid (F_1)

The diazonium salt solution was added portion wise to the coupling with component solution prepared by dissolving (0.001 mol , 0.25 gm of 1-Hydroxy 2-naphthoic acid in l00 ml of alkaline solution). The mixture was stirred for farther 1 hrs of 0 C^0 and then the mixture was neutralized with dilute hydrochloric acid .The solid product was collected and recrystallized from ethanol .The purity of the dye is determined by thin layer chromatography (TLC). The yield reaction was of 84% and its color was red-Blood.The other dyes F_2 and F_3 were synthesized with the same manner.

3.Solutions

- A stock solution of (1 x 10^{-3} M) of each F_1,F_2 and F_3 dyes was prepared by dissolving an accurately weighed amount of the compounds in the required volume of ethanol , more dilute solution was obtained by accurate dilution. - Universal (pH_{2-12}) and Acetate (pH_{1-2}) buffer solutions [13] were prepared .

4. Procedure

- **For acid – base studies** and determination of ionization and protonation constants of the dye, a series of buffer solutions were prepared with different pH values (1.09 – 12), for each dye (F_1,F_2&F_3) concentration of (4 x 10^{-5} M) M via using buffer solutions , the absorbance of these solutions was recorded at range of (350 – 660 nm.) using acell of 1cm. length and buffer solution as a blank solution ,and by the aid of half height method the constants were calculated.

- **For solvent effect studies**, a series of solution of dyes (F_1,F_2&F_3) concentration of 4 x 10^{-5} M were prepared with Ethanol , H_2O , Ethyl Acetate , Dichloromethane(DCM) , Acetone , Dimethylformamid (DMF) and Benzene . The absorbance of these solutions were recorded at range of (350 – 650 nm.) using cell of 1cm. length by using a solvent as a blank solution .

5.Results and Discussion

Some of the physical the and chemical properties and C.H.N analysis of prepared dyes were illustrated in (Table 1) .

Table 1 Some Physical Properties and Elemental data for synthesized dyes

Name	Empirical formula	m.p. (^{o}C)	Color	Mol. Wt	%C		%H		%N	
					Calc.	Found	Calc.	Found	Calc.	Found
F_1	$C_{21}H_{15}N_5O_5S$	236	Red blood	449	56.17	56.90	3.36	3.75	15.59	15.09
F_2	$C_{22}H_{17}N_5O_5S$	232	Red blood	463	57.07	57.87	3.67	3.94	15.12	15.28
F_3	$S_{23}H_{19}N_5O_5S$	228	Red blood	477	57.91	57.67	3.98	3.62	14.68	14.98

IR Analysis :

Table (2) shows the famous IR frequencies of important bands of functional groups frequencies as seen in Figure 1 .

Table 2 The important IR- bands of the dyes

Dye	ν_{-OH}	$\nu_{C=O}$	$\nu_{C=C}$	$\nu_{N=N}$
F_1	3425b	1580 s	1540 m	1440 m
F_2	3420 b	1535 s	1535 m	1438m
F_3	3430 b	1510 s	1500 m	1450m

b = board s= strong m= med.

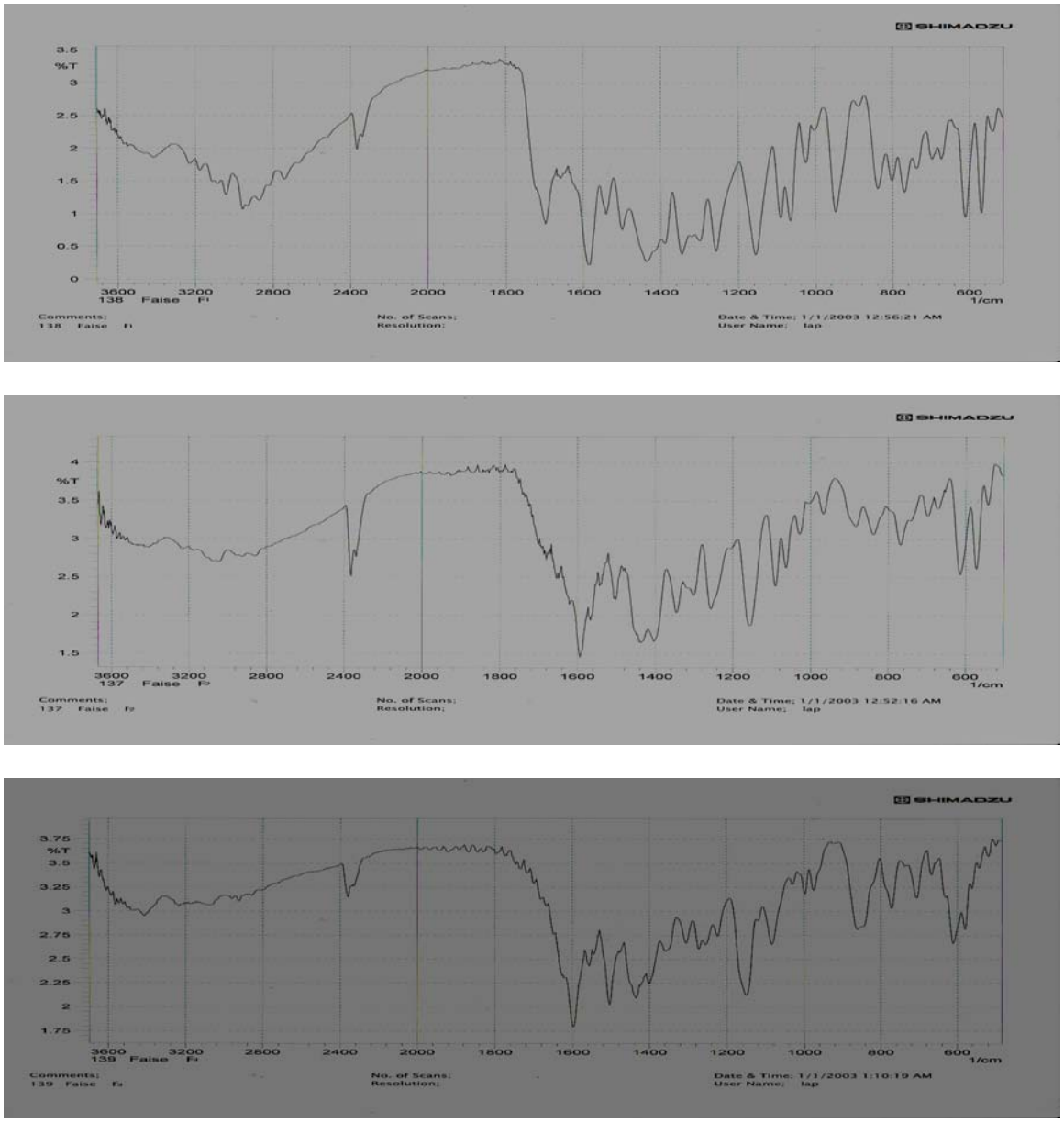


Figure 1 The IR – spectrum of the dyes F_1, F_2 & F_3

According to the above analysis (Tables 1 & 2), data show the dyes having this suggested chemical structure (scheme 1) :

X = H for F_1 .X= H,CH_3 for F_2 and X=CH_3 for F_3

Scheme 1 suggests molecular structure of dyes of F_1,F_2 and F_3.

Structure identification of F_1,F_2 and F_3 by IR spectra of azo dyes show two intense bands appearing at (1730 and 1725 cm^{-1}) these peaks are attributed to carbonyl group , a broad hydroxyl (-OH) peak observed with region 3200-3360 cm^{-1} the low frequency and the broadening of these bands attributed to these Dyes having a strong hydrogen bonding (O-H…….N) in the solid state [14-16] .The peak appearing in the region 1630-1625 cm^{-1} are attributed to ν(C=N) stretching

6.Acid- Base Properties

To see the effects of acidity and basesity of buffer solutions on the dyes , and to calculate the ionization and protonation constants, a series of acetate and universal buffer solutions were prepared at different pH values [0.65-12] for each dye [17].The absorbance of dyes ($4x10^{-5}$ M) measured in the range of (350 – 650 nm.) ,using buffer solution of such value as a blank solution. For F_1 (Fig, 2).The spectra characterized two maximum bands at 540 nm. in pH range (8 , 10,11 & 12) and at 410 nm.in other range of pH values. And no maximum band at pH values of 1.09 isobestic point at 450 nm. The first which more intense bands due to ionized form hydroxyl group (basic form , anionic form). The second are due to the absorption of the protonated form (acidic form , cationic form) liable to exist in acid medium.

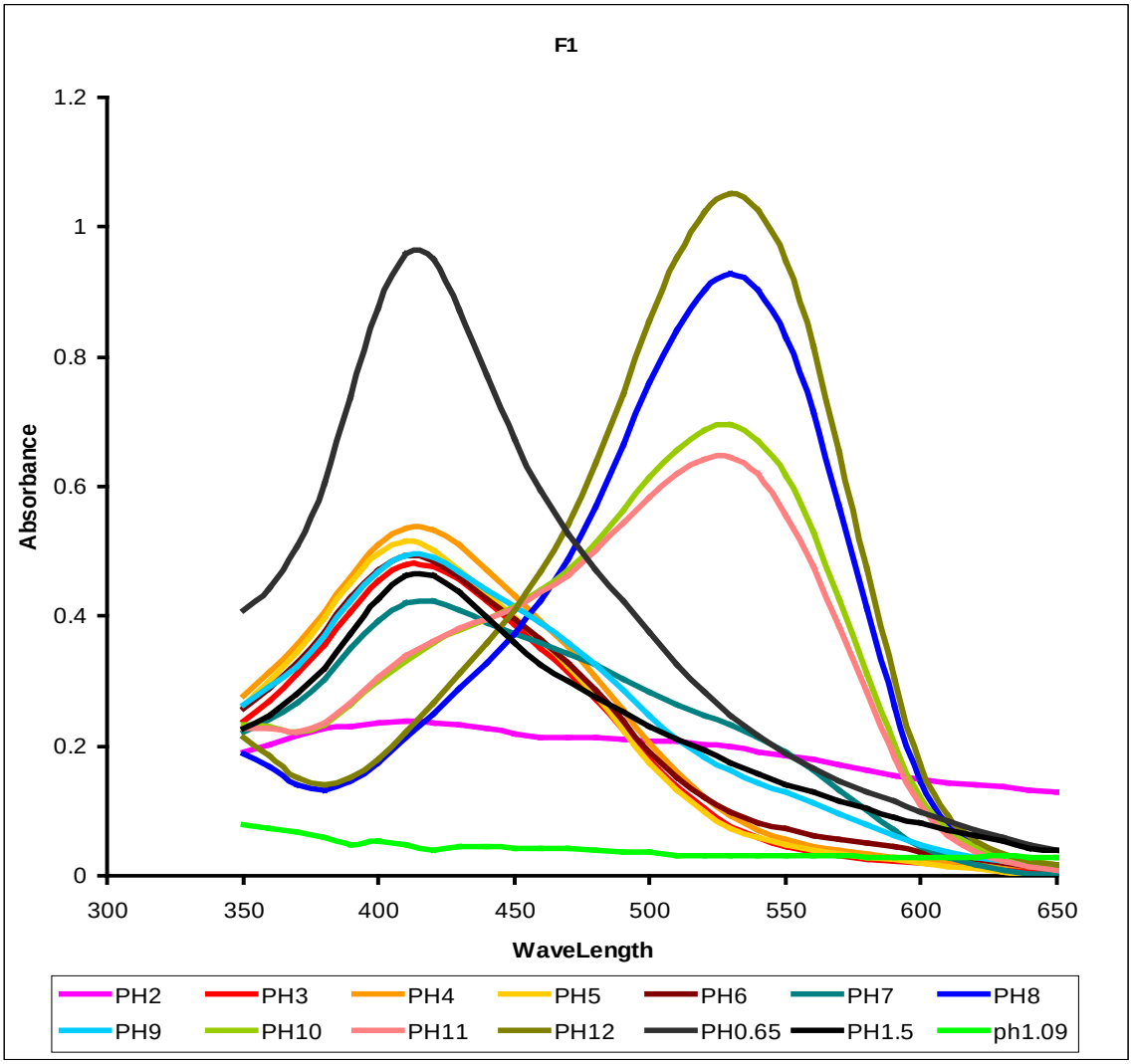


Figure 2 The electronic spectra of F_1 at different pH values .

For F_2 (Fig, 3).The spectra characterized two maximal bands at 540 nm. in pH range (8 , 10,11 & 12) and at 420 nm.in other range of pH values. And very weak band max at pH values of 1.09 & 2, with isobestic point at 460 nm. The first which are more intense bands due to ionized form of hydroxyl group (basic form , anionic form). The second due to the absorption of the protonated form (acidic form , cationic form) liable to exist in acid medium.

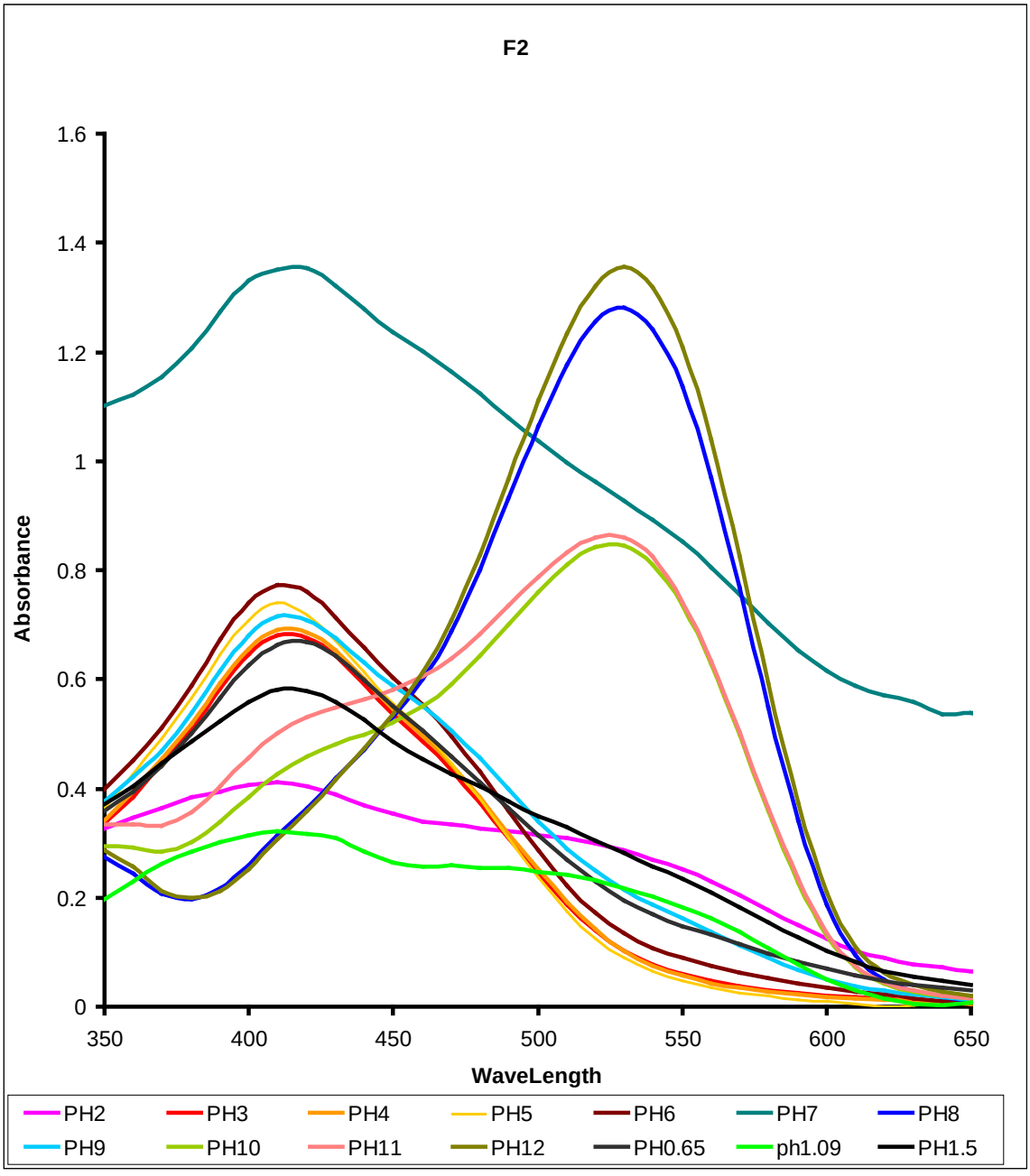


Figure 3 The electronic spectra of F_2 at different pH values .

For F_3 (Fig, 4).The spectra characterized two maximal bands at 540 nm. in pH range (8 , 10,11 & 12) and at 410 nm.in other range of pH values. And very weak band max at pH values of 1.09 & 2, with three isobestic points at 430 , 440

&460 nm. The first which more intense bands due to ionized form of hydroxyl group (basic form , anionic form). The second due to the absorption of the protonated form (acidic form , cationic form) liable to exist in acid medium.

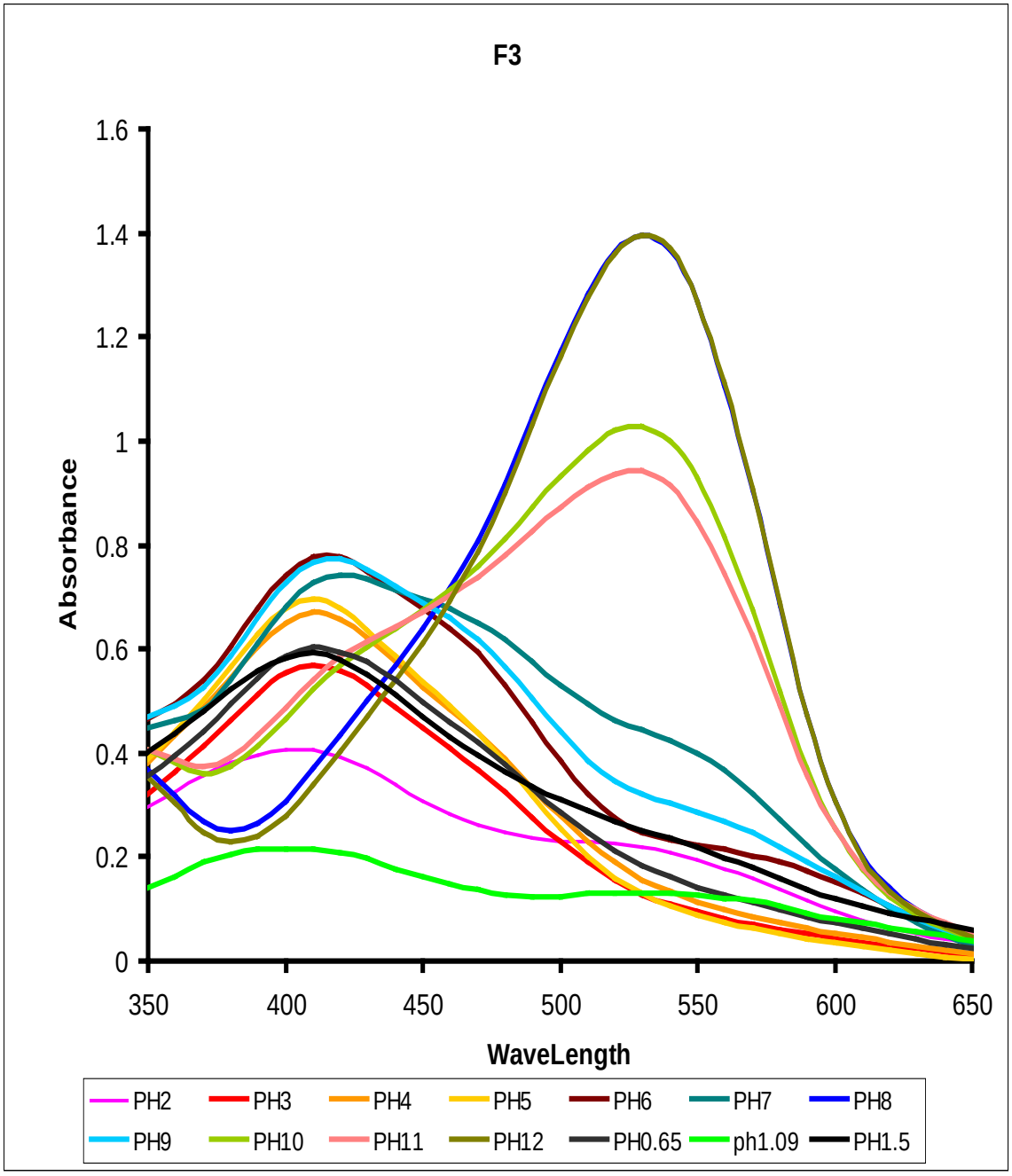
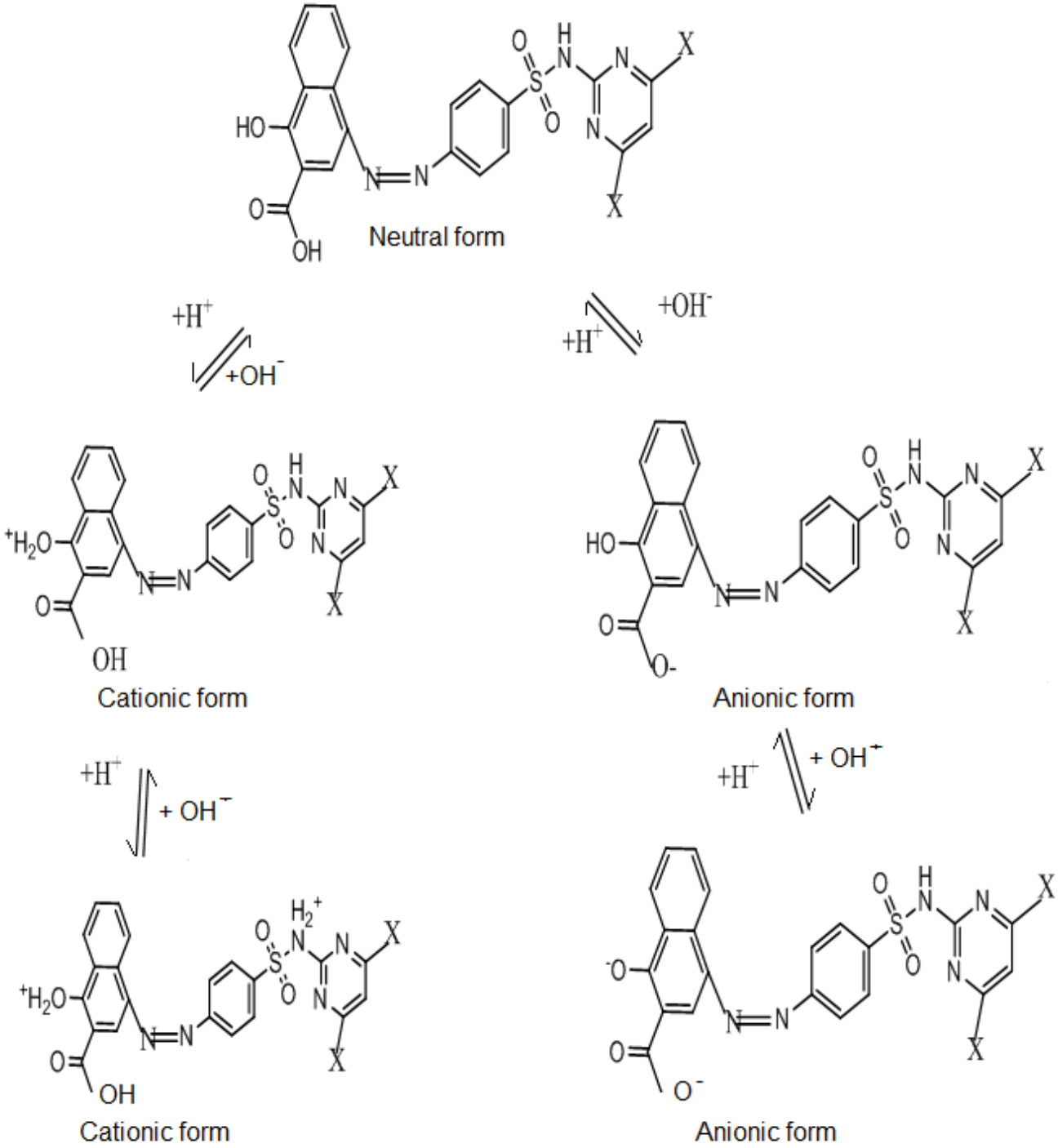
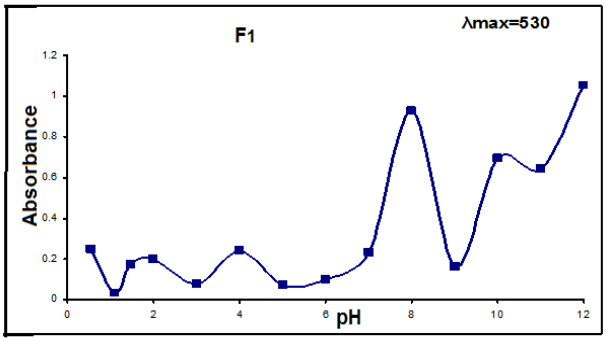


Figure 4 The electronic spectra of F_3 at different pH values .

The suggested mechanism of protonation and ionization was shown in scheme (2)



Scheme 2



Figuer 5 pH – A curve for F_1

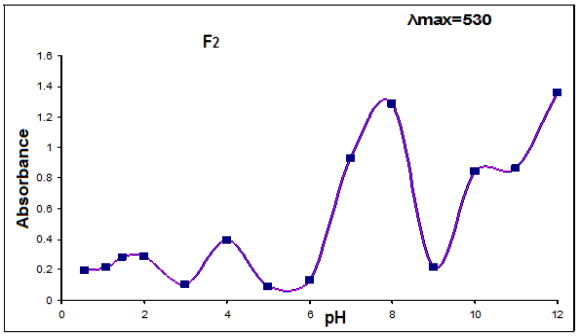


Figure 6 pH – A curve for F_2

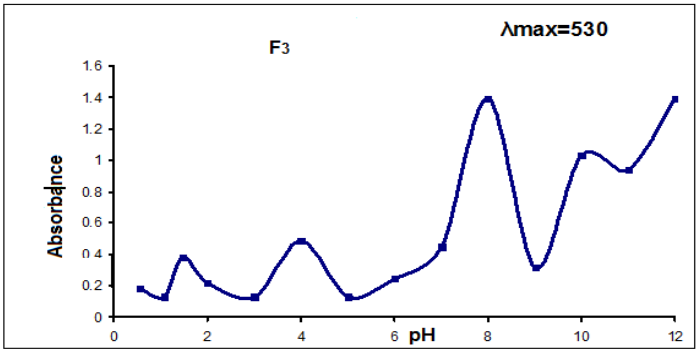


Figure 7 pH – A curve for F_3

From Absorbance – pH curve (Figs. 5-7 for F_1 , F_2 and F_3 respectively) and by the aid of height method , the pK values were obtained by the relation:

$$pK = pH \text{ (at } A_{1/2} \text{)} \quad \text{where} \quad A_{1/2} = (A_l + A_{min.}) / 2$$

Where A_l and A_{min} are limiting and minimum absorbances respectively

So the protonation (pK_p) and ionization (pK_a) constants were determined (Table 3) .

Table3 The Dissociation and protonation constants of dyes

Dye	λ (nm.)	$A_{1/2}$	pK_{P1}	$A_{1/2}$	pK_{P2}	$A_{1/2}$	pK_{a1}	$A_{1/2}$	pK_{a2}
F_1	530	0.41	1.4	0.69	3.6	0.57	7.6	0.42	9.7
F_2	530	0.25	1.3	0.24	3.5	0.2	7	0.52	9.8
F3	530	0.25	1.3	0.306	3.7	0.92	7.5	0.67	9.7

Where : pK_{p1} = protantion constant of –OH , pK_{P2} = protantion constant of-N , pK_{a1} = ionization constant of –COOH group and pK_{a2} = ionization constant of –OH group

7.Band assignments and solvent effects

Figs.(8 -10) : show the spectra of dyes with two bands,the first in the range of (350 – 430 nm.) in all solvents except for in Acetone and DMF , to the longer wavelength (red shift) with $\pi \rightarrow \pi^*$ transition (in the range of 480 - 500 nm.) (Table 4), because of the polarities of the ground state (G.S) and excited state (E.S) . Thus for the solvent of increasing polarity , the energy of the E.S (π^*) will decrease relatively to that of the G.S (π). The absorption spectra in various solvents are influenced by salvation and / or dielectric effects of solvents. To verify whether the band shift ($\Delta\nu$) is due to change in solvation energy or pure dielectric effects , the Gati and Szalay was used ;

$$\Delta\nu = \{ (a-b) [(n^2 -1) / (n^2 + 1)] \} + b [(D-1) / (D + 1)]$$

Where n and D are refractive index and dielectric constant of the medium , a and b are constants.

Table 4 λ_{max} and ε_{max}

symbol	Solvent	F1				F2				F3			
		$\pi \rightarrow \pi^*$ azo		$\pi \rightarrow \pi^*$ hydrazo		$\pi \rightarrow \pi^*$ azo		$\pi \rightarrow \pi^*$ hydrazo		$\pi \rightarrow \pi^*$ azo		$\pi \rightarrow \pi^*$ hydrazo	
		λ_{max}	ε_{max} x10^4	λ_{max}	ε_{max} x10^4	λ_{max}	ε_{max} x10^4	λ_{max}	ε_{max} x10^4	λ_{max}	ε_{max} x10^4	λ_{max}	ε_{max} x10^4
B	Benzene	410	0.91	-	-	400	1.83	-	-	410	1.82	-	-
T	Ethyl Acetate	430	1.43	-	-	420	2.03	-	-	420	2.21	-	-
M	DCM	410	1.85	-	-	410	1.70	-	-	400	1.98	-	-
A	Acetone	400	0.92	490	0.59	360	0.82	480	2.212	390	2.07	490	1.15
E	Ethanol	400	1.63	-	-	410	1.55	-	-	410	1.32	-	-
D	DMF	370	0.85	500	2.78	360	0.88	500	2.95	360	1.93	500	3.44
W	H_2O	420	1.25	-	-	420	1.76	-	-	410	1.51	-	-

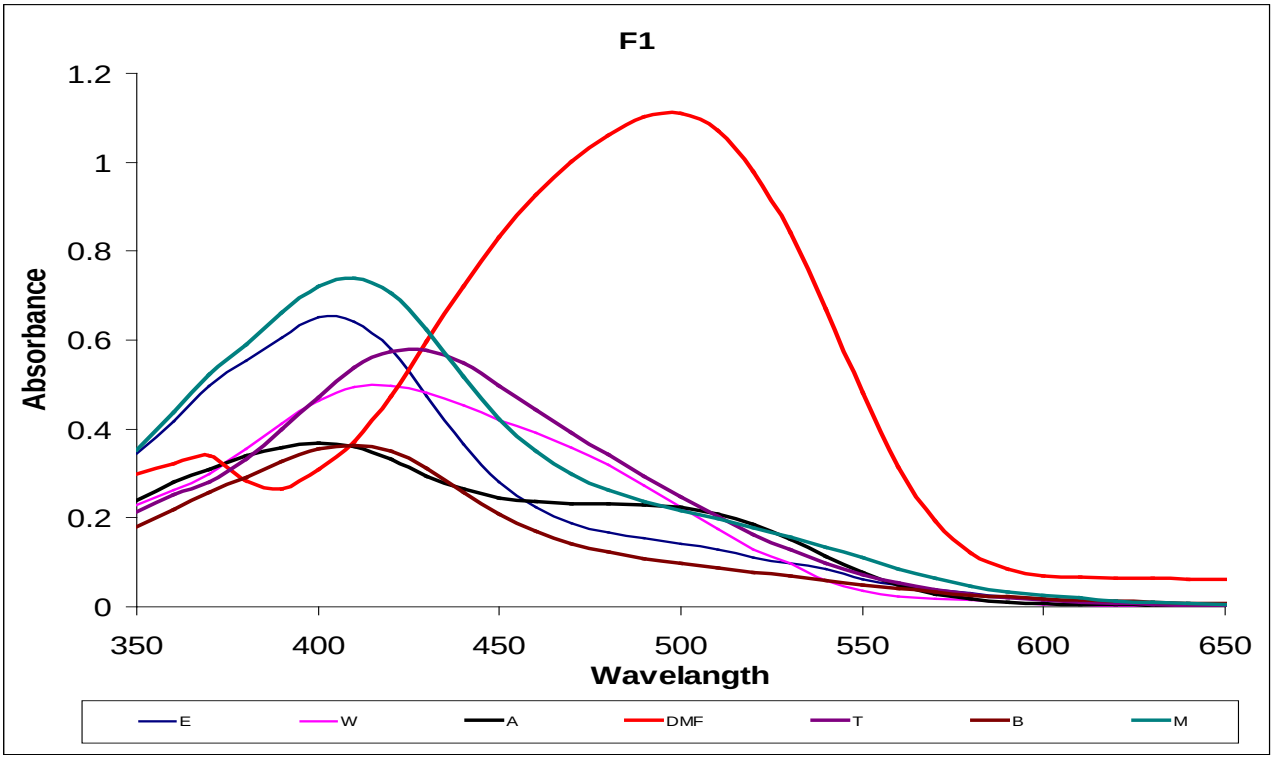


Figure 8 Absorption Spectra of dye (F_1) in Various Solvents

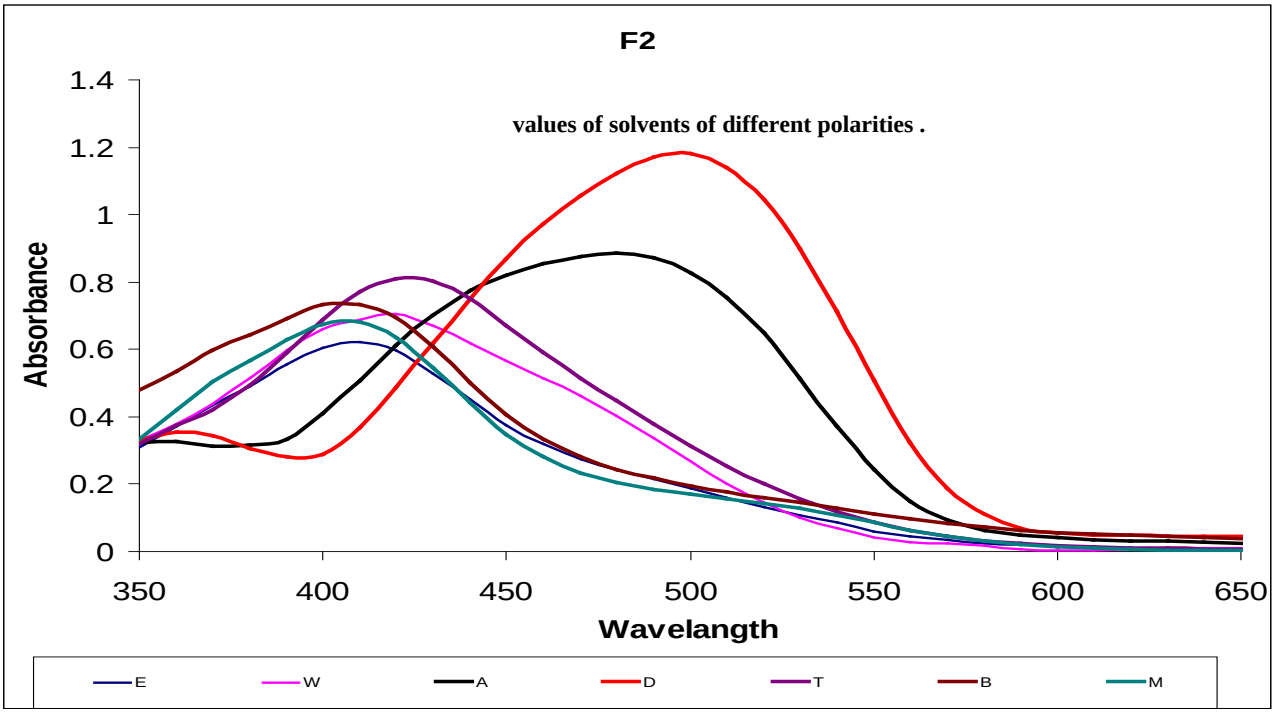


Figure 9 Absorption Spectra of dye (F_2) in Various Solvents

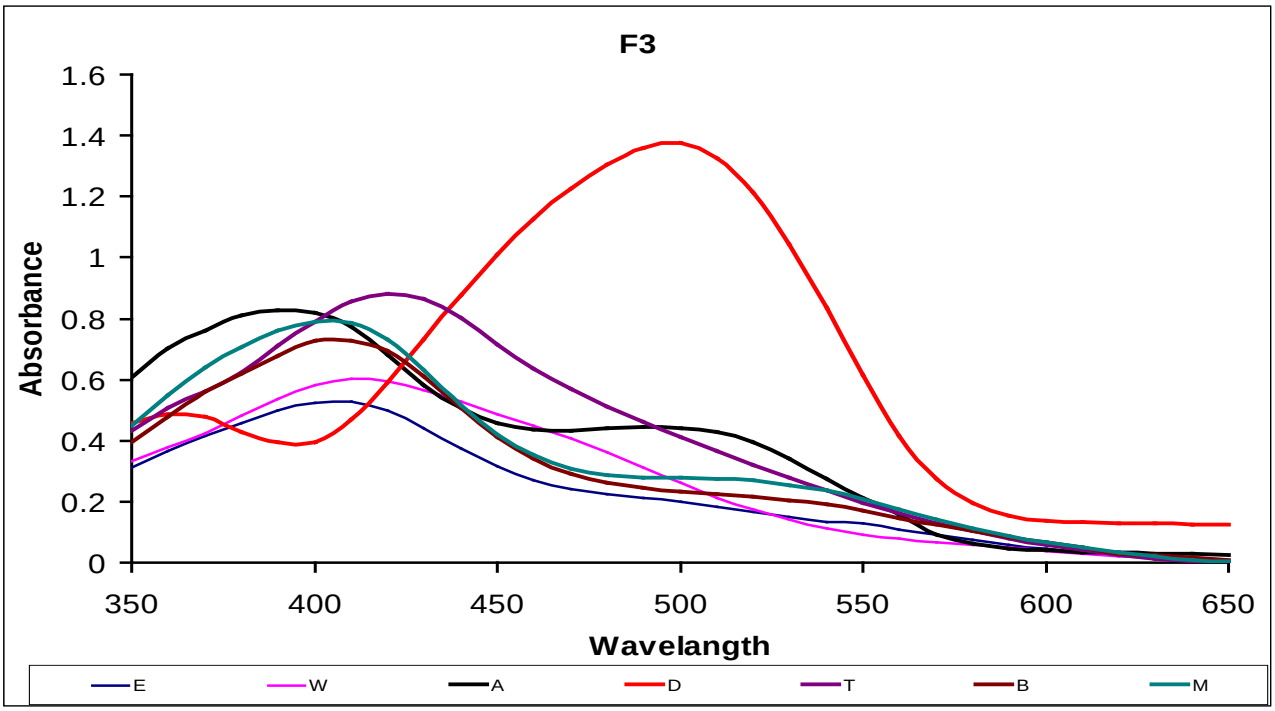


Figure 10 Absorption Spectra of dye (F_3) in Various Solvents .

The plot of f (D) = [2(D-1) / (2D+1)]) against the λ_{max} (Table 5) gives more or less linear relation with solvents of moderate polarities (Figs. 11-13) where D is th dielectric constant of the solvent. This denotes that the dielectric constant of the medium is the main factor governing the band shift in such solvents.

Table5 Dielectric Constant functions for solvents of different polarities F(D)

Symbol	Solvent	D	F(D)	λ_{max}		
				F_1	F_2	F_3
B	Benzene	2.3	0.464	410	400	410
T	Ethyl Acetate	6.02	0.771	430	420	420
M	DCM	8.93	0.841	410	410	400
A	Acetone	21.00	0.930	490	360	490
E	Ethanol	32.70	0.955	400	410	410
D	DMF	36.71	0.960	500	500	500
W	H_2O	78.30	0.981	420	420	410

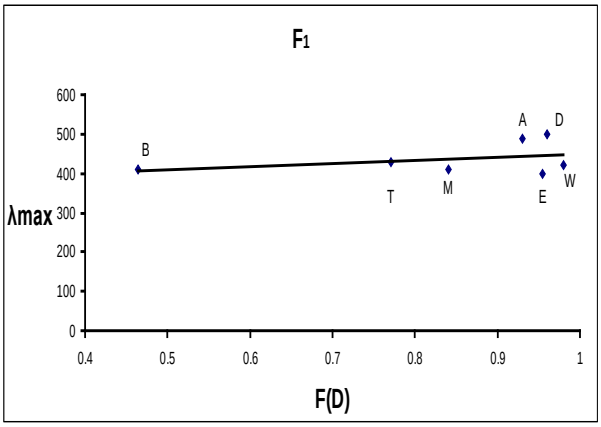


Figure 11 λ_{max} With F(D) For (F_1)

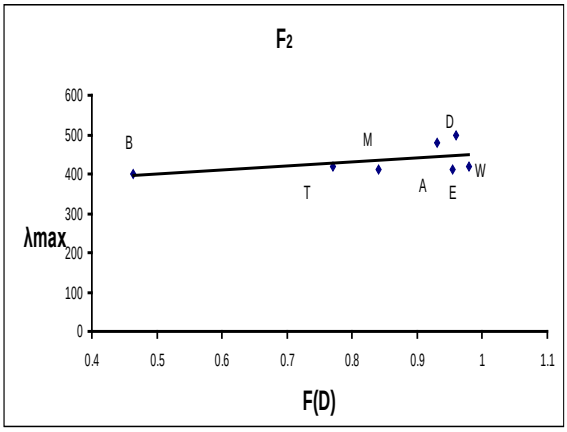


Figure 12 λ_{max} With F(D) For (F_2)

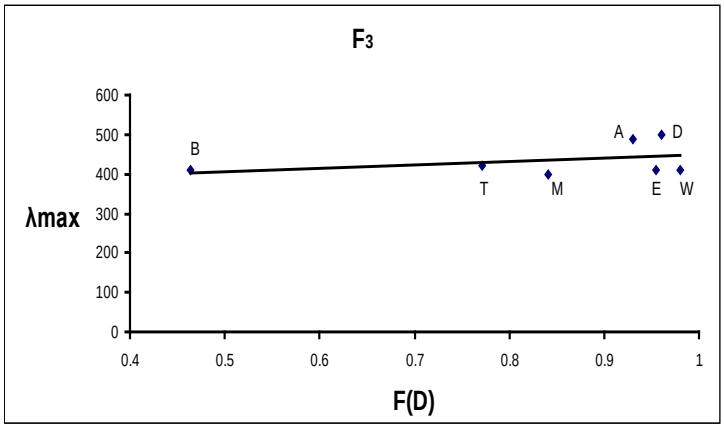


Figure 13 λ_{max} With F(D) for (F_3)

References

1. T.Hihara, Y.Okada and Z.Morita . *Dyes and pigments*, **73**, (2007), 141.
2. R. Skeltonm, F.Duboise and R.Zenobi, *Anal. Chem*, **72**, (2007), 707.
3. T.A.Fahad
4. R.H.Hamedaani, A.sakurai and M.sakakibara, *Dyes and pigment*, **72**, (2007), 157.
5. N.M.Rageb, N.M.lsmail and A.MK. El.dean, *Canadin J. of anal. Sici and spec*, **49**, (2004), 240.
6. G.R. Steter, J.O. Potolio, M.L.A.Campos and J.R.Romero, *J. Braz. Chem. Soc*, **17**, (2008), 660.
7. J.O. Oututu, D. D. Okoro and E.K. Ossai, *J. applied science*, **8**, (2008), 334.
8. S. Mallakpour, F. Rafieman, K. Faghihi, *Dyes and pigments* **74**, (2007), 713.
9. N. Di Csear and J.R. lakowicz, *Organic letter*, **3**, (2001), 3891.
10. H.B. Hassaib and S. A. Abdel,*Latif* , *spectrochim Acta*.
11. A. T .Peters, E. Chisowa, *Dyes Pigments*, **22**,(1993), 223-238.
12. M.Dakiky, I. Nemcova, *Dyes Pigments*, **44**,(2000**),**181-193.
13. J. A. Dean, " Lunges Handbook of Chemistry", *Mcgrawhill, ING. New York,* 15 Ed., **7. 55**, (1999).
14. B. Kiek and R. Grup, *Turk, J. chem*, **32**, (2008), 9.
15. M. S. Masoud and G. B. Muhamed, J.Korean. *chem. Soc*, **2**, (2002), 99.
16. S. Wang, S. shen and H.Xu, *Dyes and pigments*, **44**, (2000) ,195.
17. A.A.Ali. T.A. Fahad, L.A. Rusen and I.K. Mohamed. *J.Basrah Reseaecher (scicnce)* ,34, (2008), 48.

تحضير ودراسة مطيافية لبعض الاصباغ الازوية الجديدة المشتقة من 1- هيدروكسي -2 – خامض النفثويك و مشتقات السلفا دايزين

اسعد عبود علي و حيدر عبد الستار جايد اليوسف

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