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Synthesis and Spectrophotometric Study of Some New Azodyes Derived From 4,5-diphenylimidazole

Part I

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Abstract

This study involves the preparation of three azodyes 2-(sulfapyridineazo)- 4,5-diphenyl imidazole (M1) , 2-(2-arsonophenylazo)-4,5-diphenyl imidazole (M2) and 2-(sulfapyridineazo)- imidazole (M3) , they have been described by C.H.N. , I.R. and Visible spectroscopic techniques. The acid-base properties were studied at different pH values (0.65-12) , then the ionization and protonation constants were determined. The solvents effect were studied at different solvents polarities

Key Words : 4,5-diphenylimidazole , Azodyes , Ionization & Protonation constants and Spectral studies

تخليق ودراسة طيفية لبعض الصبغ الآزوية الجديدة المشتقة من ٤,٥- داي فنيل ايميدازول

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الخلاصة

في هذه الدراسه تم تخليق ثلاث صبغ ازويه جديده ٢- (سلفابايريدين ازو)-٤,٥-ثنائي فنيل ايميدازول (M1) و ٢-(٢- ارزونوفنيل ازو)-٤,٥- ثنائي فنيل ايميدازول (M2) و ٢- (سلفابايريدين ازو) ايميدازول (M3) . وتم تشخيصها بواسطة التحليل العنصري (CHN) وتقنية الاشعه تحت الحمراء وتقنية الأشعه المرئيه . وتم دراسة الصفات الحامضيه- القاعديه عند قيم مختلفه من الدوال الحامضيه (٠.٦٥ – ١٢) كما وتم حساب ثوابت البرتنه والتأين . ودرست تأثير مذيبات مختلفة القطبيه .

1- Introduction

The study of azo dyes with interesting physical and spectrophotometric properties have been active area of research . They are very important class of chemical compounds containing a heterocyclic moiety which have been attracted the attention of many researchers in the recent years[1]. They are highly colored and have been used as dyes and pigments for long years [2] .Synthetic azo dyes are among the most explored classes of organic compounds. Azo dyes are widely used in many practical applications such as photochromic materials, colorants, non-linear optics, sensors and indicators [3-6]. The azo dyes of heterocyclic compounds are regarded highly active towards most of the metal ions. They have great importance in chemical analysis because these compounds contain more than one active group[7-9]. This class of azo dyes being a (π-acidic) azo imine system (-N=N-C=N-) for this reason a number of these dyes were synthized and their abilities as chelating ligands [10,11]. Among the heterocyclic reagents 4,5-diphenyl imidazole and imidazole dyes are extensively used for the spectrophotometric extraction of metal ions [12-14]. The o-arsenlic acid is widely used for analytical reagents for the determination of metals like Arsenazo I and Arsenazo III , and also used of some azodyes reagents [15،16]. The study of electronic spectra in different polarities of solvents may be given changes wavelength or intensity or shape of the absorption bands due to the interaction effect between solute and solvent [17].

2- Experimental

Double distilled water, and all the reagents and solvents were of reagent-grad quality . Infrared spectra (

in KBr pellets) were recorded on IR Affinity-1shimadzu.Meltingpoint were determined on melting point apparatus . The dyes were recorded by using and element analysis (C.H.N.), they were carried out by perkin elemer 2400-11 element analysis . Visible absorption spactra were recorded by using LKB (Biochrom ultra space II-4050 UV./V.) spectrophotometer .The pH measurements were made with pH-Meter (Trans Instruments Professional Benchtop BP3001). Accutate balance E-Mette Weender (Land Strasse) 94-108.

2-1 Diazotization

0.005 mole of each aromatic amine sulfapyridine , o-Arsanic acid and sulfapyridine of weights 1.245 , 1.085 and 1.245 g. respectively were dissolved in 3ml concentrated hydrochloric acid , then 20 ml of distilled water to each salt forming .The solutions were cooled to 0 – 5 Co in ice-bath . 5 ml of sodium nitrite 0.4g. was then added drop wise with stirring continued to each solution to produce diazonium salt .

2-2 Preparation of dyes M1 - M3

0.005 mole of each 4,5-diphenyl imidazole , 4,5-diphenyl imidazole and imidazole of weights 1.1 , 1.1 and 0.34 g. respectively were dissolved in 50 ml alkaline ethanol . These solutions were added to the above diazonium salt solutions to forming sodium forms of the dyes M1 – M3 . The dyes solutions neutralized to the hydrogen forms by adding diluted hydrochloric acid by aid of pH paper . The precipitates were filtered off and twice recrystallized from 1:1ethanol : methanol mixture .

2-3 Solutions

- A stock solution of (1 x 10^{-3} M) of each M_1 , M_2 and M_3 dye was prepared by dissolving an accurately weighed amount of the compounds in the required volume of ethanol , more dilute solutions were obtained by accurate dilution.
- Universal (pH_{2-12}) and Acetate ($pH_{0.65-2}$) buffer solutions [18] were prepared

2-4 Procedure

- Acid – Base studies (15) : To study the effect of pH values on the absorption spectra on the dyes M1-M3 and to determine the protonation and ionization constants , a series of buffer solutions (acetate and universal) were prepared with different pH values (0.65– 12).,with concentrations of dyes are 4 x 10-5 M, the absorbance of these solutions was recorded at range of (350 – 660 nm.) using a cell of 1cm. length and buffer solution as a blank solution ,. By the aid of half height method the constants were calculated.

- For solvent effect studies, A series of solutions of dyes (M1-M3) were prepared of concentration of 4 x 10-5 M in Ethanol , H2O , Methanol , Ethyl Acetate , Acetone , Dimethylformamid (DMF) and Dimethyl sulfoxide (DMSO) . The absorbance of these solutions were recorded at range of (350 – 600 nm.) using cell of 1cm. length and using a solvent as a blank solution .

3- Results and Discussion

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

Table 1- Some Physical Properties and Elemental analysis data for synthesized dyes

Name	Chemical Formula	m.p. (°C)	Color	%C		%H		%N	
				Calc.	Found	Calc.	Found	Calc.	Found
M_1	$C_{26}H_{20}N_6O_2S$	163-165	Yellow	64.98	65.10	4.20	4.53	17.49	17.25
M_2	$C_{21}H_{17}AsN_4O_3$	191-194	Yellow	56.26	56.59	3.82	4.11	2.50	12.75
M_3	$C_{14}H_{12}N_6O_2S$	170°C	Yellow	51.21	51.53	3.68	3.92	25.59	25.81

IR Analysis :

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

Table (2)- The famous IR frequencies of important bands of azodyes M1 – M3

AzoDyes	ν (N-H)	ν (C=N)	ν (N=N)	ν (O=S=O)
M_1	3423mb	1631S	1496m	1392m &1138 s
M_2	3435mb	1635m	1446m	----------
M_3	3485mb	1631S	1463m	1390m & 1139 S

b = board , s= strong and m= med

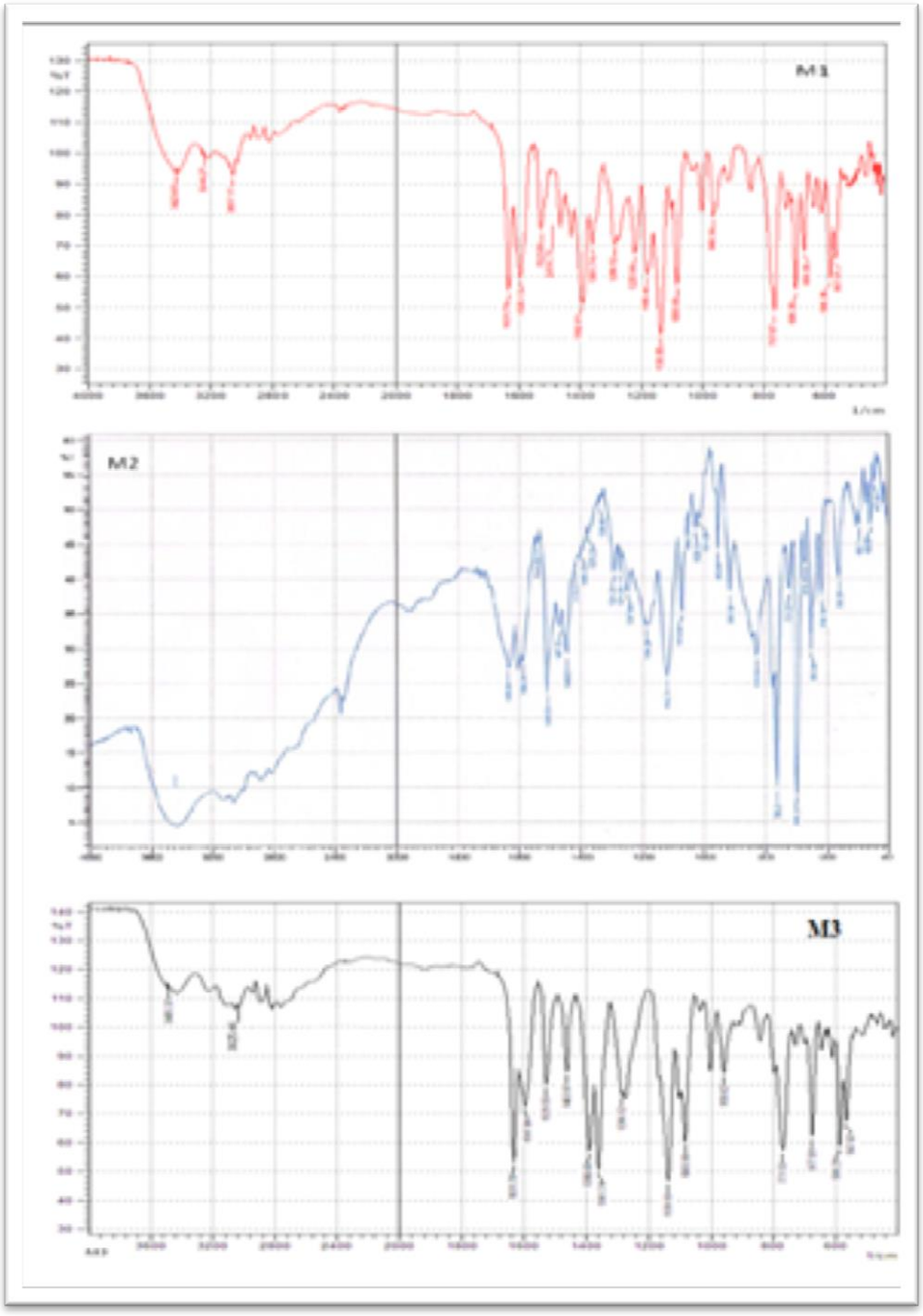
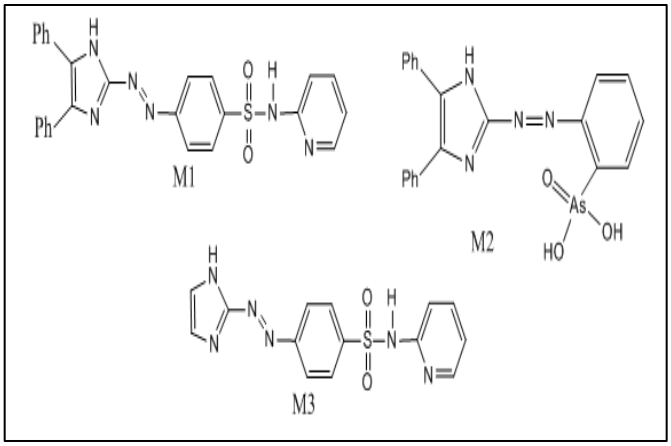


Fig.(1) – IR spectra of the azodyes M_1 – M_2

From IR analysis , Elemental analysis (CHN) and literatures and scientific previous researches , the chemical formula of azo dyes M1-M3 was suggested (schemes 1).



(schemes 1)

Acid- Base Properties

To see the effects of acidity and basicity 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 [19].The absorbance of dyes (of total concn.4x10-5 M) were measured in the range of (350 – 600 nm.) ,using buffer solution of such pH value as a blank solution. For M1(Fig.2), the spectra characterized by two maximum bands at 490 nm. in pH range (8 , 10,11 & 12) and at 440 nm. for the other pH range . The first which more intense bands due to ionized form (basic form , anionic form).And the second of pH range (< 7) related to protonation form (acidic form , cationic form).

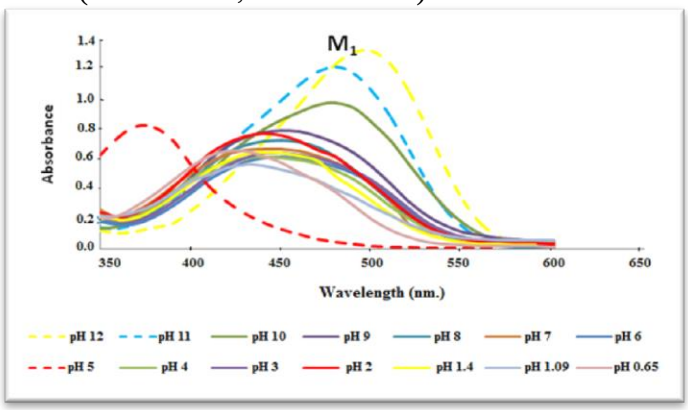


Fig.- 2: The electronic spectra of M1 at different pH values

For M2 (Fig, 3) , the spectra are also characterized by two maximum bands at 490 nm. in pH range (8 , 10,11 & 12) and at 440 nm. for the other pH range . The first which less intense bands at 380 nm. , due to ionized form (pH > 6), And the second of more intense at 360 nm. of pH range (< 7) related to protonation form.

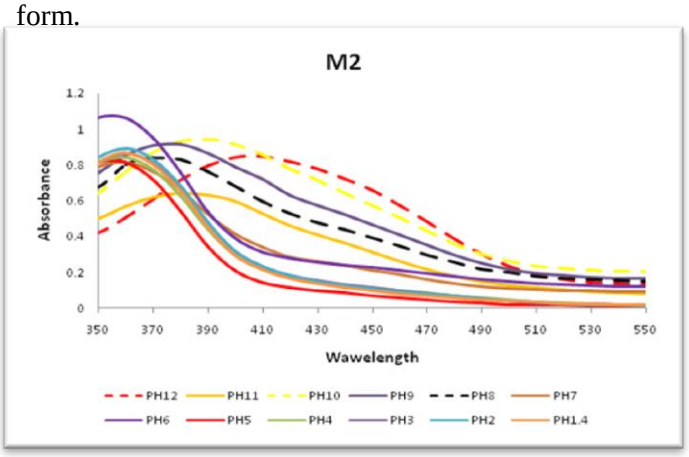


Fig.- 3 : The electronic spectra of M2 at different pH values

For M3 (Fig. 4) , at max. wavelength range (360-380 nm.) of acidic medium , this due to protonation . And the other wavelength max. in alkaline medium at 420 and 450 nm.

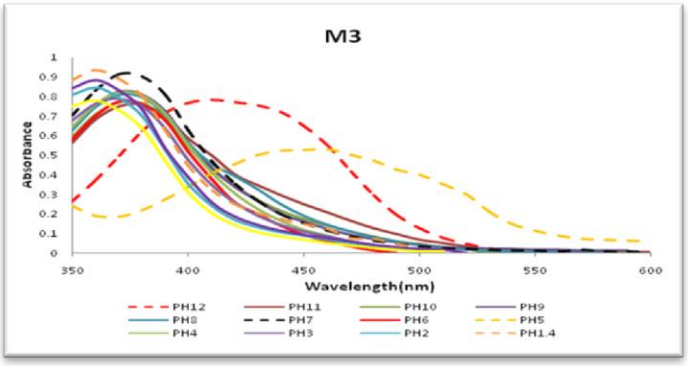


Fig.- 4: The electronic spectra of M3 at different pH values .

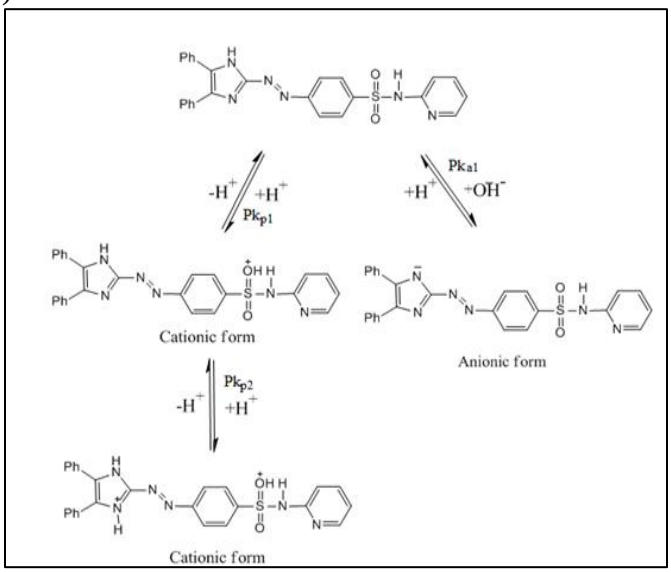
The ionization and protonation constants were calculated (Table 3) by the aid of Figs. (2-4), the absorbance – pH curves were plotted (Figs. 5-7).
From Absorbance – pH curve (Figs. 5-7 for M1 - M3) and by the aid of height method the pK values were obtained by the relation :

pK = pH (at A1/2) where

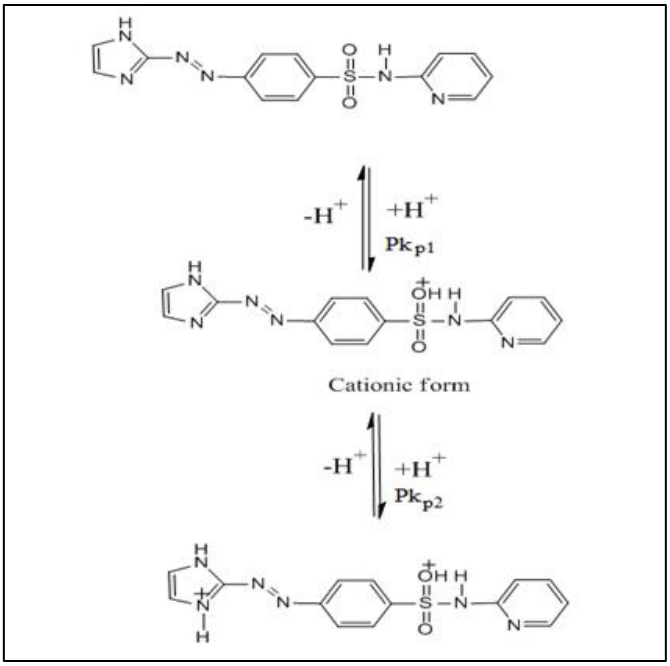
A1/2 = (AL+ Amin.) / 2

Where AL and Amin are limiting and minimum absorbances respectively

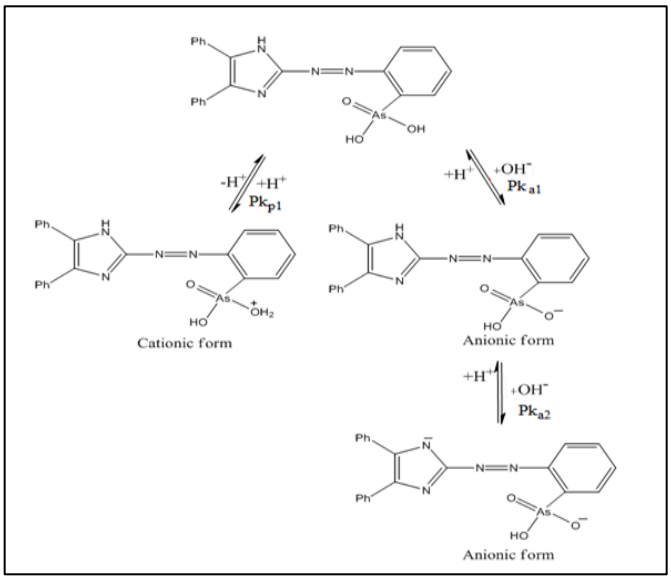
From Figs. 5-7 the mechanism of the ionization and protonation of each dye can be suggested (schemes 2-4)



(schemes 2)



(schemes 4)



(schemes 3)

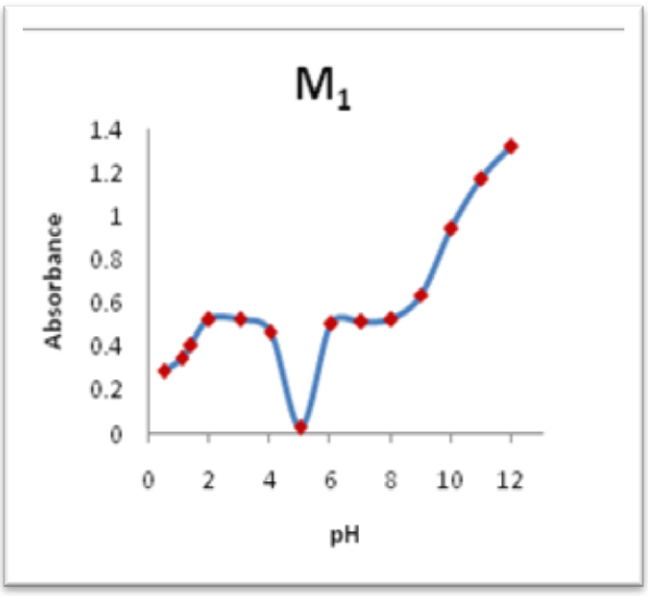


Fig.-5: pH – Absorbance curve for dye M_1

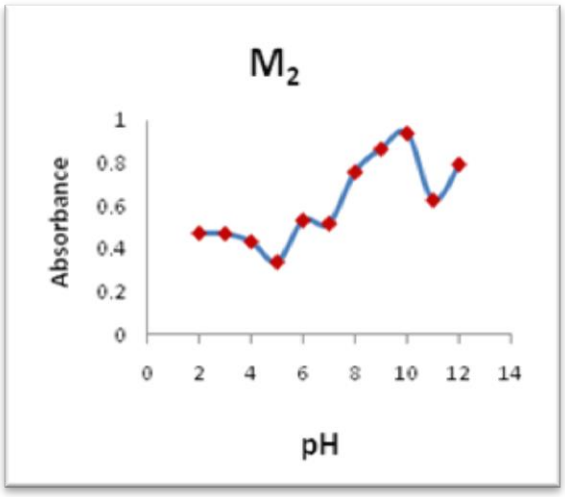


Fig.-6: pH – Absorbance curve for dye M_2

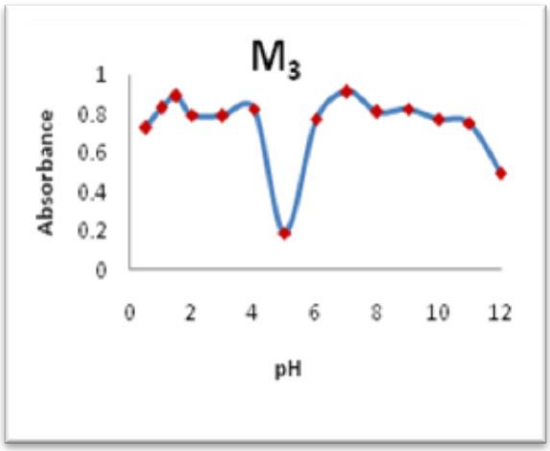


Fig.-7: pH-Absorbance curve for dye M3

Table-3 : The protonation (pK_p) and ionization (pK_a) constants of azodyes M_1-M_3

Dye	λ_{max} nm	$A_{1/2}$	pKp_1	$A_{1/2}$	pKp_2	$A_{1/2}$	pKa_1	$A_{1/2}$	Pka_2
M_1	490	0.4	1.4	0.27	5.6	0.91	10	------	------
M_2	380	0.44	5.5	------	------	0.69	7.8	0.71	11.6
M_3	370	0.81	0.9	0.48	5.7	------	------	------	------

Band assignments and solvent effects

Figs. (8-10) show the spectra of azodyes with strong bands λmax at 450 ,370 and 380 nm. for azodyes M1 , M2 and M3 respectively , at different solvents of different polarities (1,4-dioxane , Ethyl acetate , Acetone , Methanol , Ethanol , DMF , DMSO and Water).There are no any appearance shifts . The absorption spectra in various solvents are influenced by salvation and / or dielectric effects of solvents. To verify whether the band shift (Δν) is due to change in salvation energy or pure dielectric effects , the Gati and Szalay was used:

$$\Delta\nu = \{ (a-b) [(n2 -1) / (n2 + 1)] \} + b [(D-1) / (D + 1)]$$

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

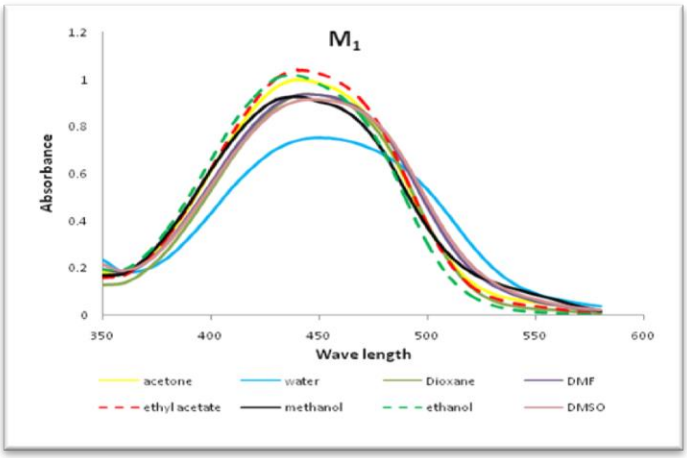


Fig.- 8: Absorption spectra of dye (M1) in various solvents

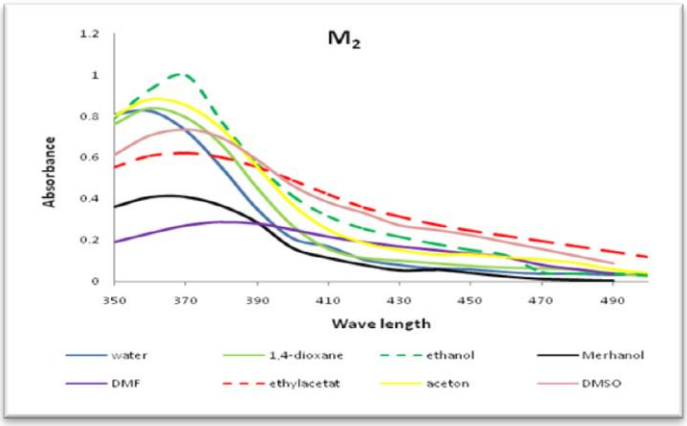


Fig.-9: Absorption spectra of dye (M2) in various solvents

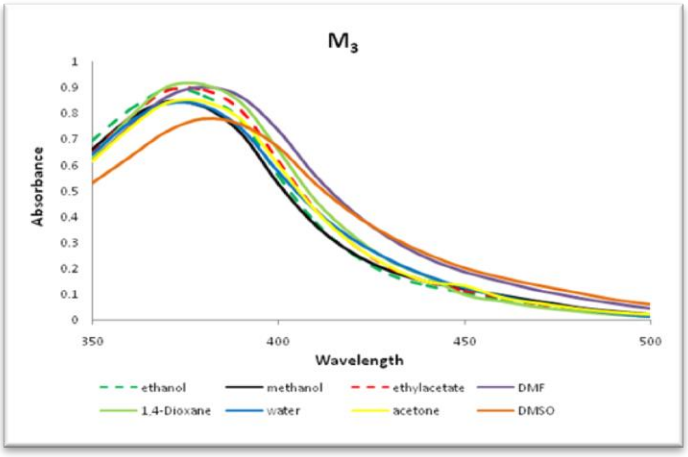


Fig.- 10: Absorption spectra of dye (M3) in various solvents

The plot of f (D) = [2(D-1) / (2D+1)]) against the λmax (Table 4) gives more or less linear relation with solvents of moderate polarities (Fig.11).This denotes that the dielectric constant of the medium is the main factor governing the band shift in such solvents .

Table-4: The dielectric constants , dielectric function f(D) of solvents and λmax of azodyes

No.	Solvent	D	f (D)	λ max		
				M1	M2	M3
1	1,4-dioxane	2.30	0.464	440	360	380
2	Ethyl Acetate	6.02	0.77	440	380	380
3	Acetone	21.00	0.930	440	360	380
4	Methanol	24.55	0.940	440	370	370
5	Ethanol	32.70	0.955	440	370	370
6	DMF	36.71	0.960	440	380	380
7	DMSO	46.68	0.968	450	370	380
8	H_2O	78.30	0.981	450	360	370

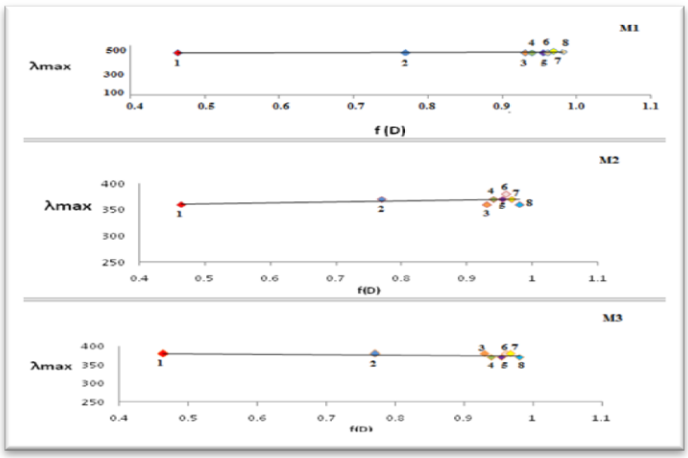


Fig.- 11: λmax With f(D) for (M1- M3) : Where ; 1=1,4-dioxane, 2= ethyl acetate, 3= acetone, 4= methanol, 5= ethanol, 6 = DMF, 7=DMS, 8= water

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