

Synthesis And Spectral Properties Of Some New Derivatives Of 4-Aminoantipyrine Azo Dyes Part I

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الخلاصة

تضمنت هذه الدراسة تحضير ثلاث صبغات ازو جديدة هي ٤-امينوانتياپيرين مع كلاً من ٨-هيدروكسي كوينولين و ٢-ثايو حامض باربيتيوريك و حامض ٢- مثيل ثايو حامض الباربيتيوريك . وتم تشخيص هذه الصبغات الازويه بواسطة التحليل العنصري CHN وكذلك تقنية الاشعة تحت الحمراء والاشعة البنفسجية. كذلك تم دراسة الاطياف الالكترونية مثل الصفات الحامضية-القاعدية عند دوال حامضية (٦٥، ١٢٠) وميكانيكية البرتنه والتأين وتعيين النقاط الازوبستية كما وتم حساب ثوابت البرتنه والتأين . كما وتم دراسة الاطياف الالكترونية لمذبيات مخلفته القطبية

Abstract

This study involves the synthesis of three new azo dyes 4-aminoantipyrine with 8-hydroxyquinoline (L_1) , 2-thiobarbituric acid (L_2) and 2-methylthiobarbituric acid (L_3) . The characterization of dyes have been described by C.H.N. , I.R. and visible . spectroscopic techniques , the electronic spectra of these azo dyes were studied in term of acid-base properties at different pH values (0.65- 12) ,which includes establishing isobestic point , mechanism and determination of protonation and ionization constants of dyes. The effect of solvents of different polarities on the electronic spectra were also investigated.

Key Words: Azo Dye, Isobestic Points, Acid-Base Properties , Solvent Effects

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]. 4-aminoantipyrine and its complexes is a good analytical reagent in the medicine field [3]. In the other hand, 2- thiobarbituric acid is a good reagent for forming some of azo dyes e.g. with luminol and phenyl-4-cetic acid [4,5] . This reagent is also used for the determination of a lot of elements like silver ions [5]. Many of those dyes have additional uses , such as photometric reagents [6,7] and in coloring of gasoline [8]. 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[9]. This work involves the synthesis and characterization of new dyes, 5-(4-2 aminoantipyrineazo)-8-

hydroxyquinoline (L_1), 5-(4-aminoantipyrineazo)-2-thiobarbituric acid (L_2) and 5-(4-aminoantipyrineazo)-2-methyl thiobarbituric acid (L_3), followed by the study of solvent effect of different polarity, acid–base properties of different pH values and the determination of protonation and ionization constants of those dyes.

Experimental

Materials and Apparatus

Double distilled water , solvents (for spectra uses) and all the chemicals used were of commercial grade and were further purified by crystallization. UV-Vis. Absorption spectra were recorded by using PD-303 Spectrophotometer , IR. 8400s spectrophotometer (Shimadzu) ,pH meter (H. Jurgons Co. Beremmen, L. Puls Munchen 15) Heraus CHN Pro apparatus, Accutate balance E-Mette Weender (Land Strasse) 94-108.

Synthesis of azo dyes

The azo dyes reagents were prepared of dissolving 0.004 mole of 4-aminoantipyrine with 1.4 ml concentrated HCl , 20 ml distilled water ,then adding drop by drop solution of (0.304 g. sodium nitrite in 20 ml distilled water) to form diazonium salt at less than 5 °C temperature .Add alkaline solution 0.004 mole of 8-hydroxyquinoline (L_1) , 2- thiobarbituric acid (L_2) or 2-methylthiobarbituric acid (L_3) in 1.2% v./w. NaOH to the above diazonium salt . Then converting the prepared dye from sodium salt into hydrogen form by adding of dilute HCl . The dye was purified by recrystallization from methanol.

Solutions

- 1×10^{-3} M stock solution of azodye was prepared by dissolving accurate weight of each dye and complete the volume to 50 ml absolute ethanol
- 1000 ppm of nitrite solution , by dissolving 0.15g. of NaNO_2 in dilute. Water and complete to 100 ml
- 0.002 mole of each amine in 0.2 M HCl (complete to 50 ml)
- 0.002 mole of each coupler in 0.3 M NaOH (complete to 50 ml)
- Universal and acetate buffer solutions of pH(2-12) and pH 0.65-1.6 respectively [10].

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 (0.65 – 12) for total dye concentration 8×10^{-5} M via using universal buffer, the absorbance of these solutions

were recorded at range of (350 – 660 nm.) using cell of 1cm. length , by aid of half height method the protonation and ionization constants were calculated

- For solvent effect studies, a series of solution of dye at total concentration 6×10^{-5} M were prepared with , CH_2Cl_2 , DMF , DMSO , Etol and H_2O , the absorbance of these solutions were recorded at range of (350 – 580 nm.) using cell of 1cm. length

Results and Discussion

Elemental-Analysis

Table 1 shows the elemental analysis of prepared dyes, which give good results for the suggested dyes formula .

Table 1: C.H.N Analysis Of The Dyes

N%		H%		C%		Symbol
Found	Calculate	Found	Calculate	Found	Calculate	
19.46	19.49	4.88	4.77	66.74	66.84	L ₁
24.11	23.45	4.28	3.94	50.16	50.27	L ₂
23.15	22.57	3.97	4.33	52.11	51.60	L ₃

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 Dye

Frequency $\nu \text{ cm}^{-1}$			Groups
L ₃	L ₂	L ₁	
3550-3400	3550-3400	3500-3350	O-H&N-H
1680	1680	1650	C=O
1480	1455	1500	C=C
1600	1620	1547	C=N
1550	1540	1500	N=N--
1200	1180	-	C=S
1200	1180	1130	C-N

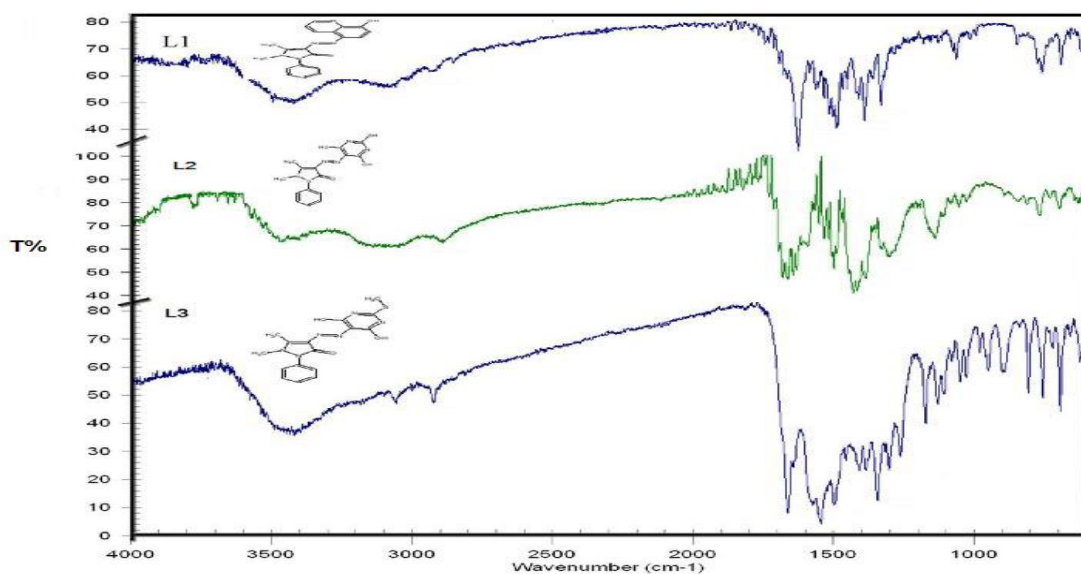
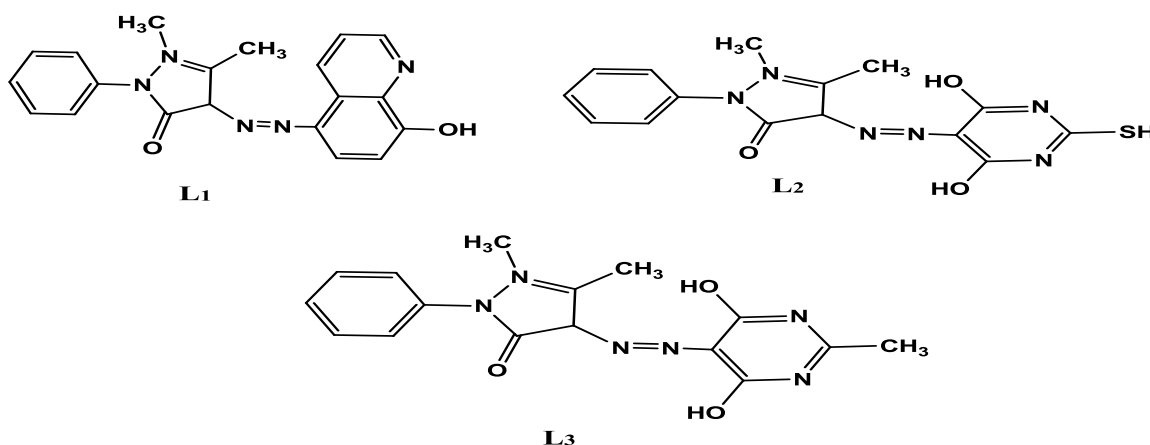


Fig. 1: The IR – Spectrum Of The Dyes (L)

According to the above analysis **Tables 1 and 2**, data show the dyes having this chemical structure (**Scheme 1**)



Scheme 1

Some of physical and chemical properties of dyes were illustrated in **Table 3**.

Table 3: Physical and chemical properties of the dyes

Dye	Empirical formula	M.Wt.	Color	°C M.P.
L ₁	C ₂₀ H ₁₇ N ₅ O ₂	359.4	Red	234-236
L ₂	C ₁₅ H ₁₄ N ₆ O ₃ S	358.4	Yellow	228-230
L ₃	C ₁₆ H ₁₆ N ₆ O ₃ S	372.4	Deep yellow	232-234

Acid-Base properties

The absorption spectra of 8×10^{-5} M solution of each dye in the range of wavelength (360-550 nm) of varying pH values (0.65 – 12) were represented graphically (**Figures 2-4**). The

spectra characterized two maximal bands , the first at 380nm.of each dye in the acidic medium due to the protonation of dye (cationic form) . The second high intense band at 470, (430 and 450) and (440 and 460) nm. for dyes L₁ , L₂ and L₃ respectively , in range the alkaline medium due to ionization of dye (anionic form).

The spectra show isobestic points at 430 ,410 and 410 nm. for dyes L₁ , L₂ and L₃ respectively

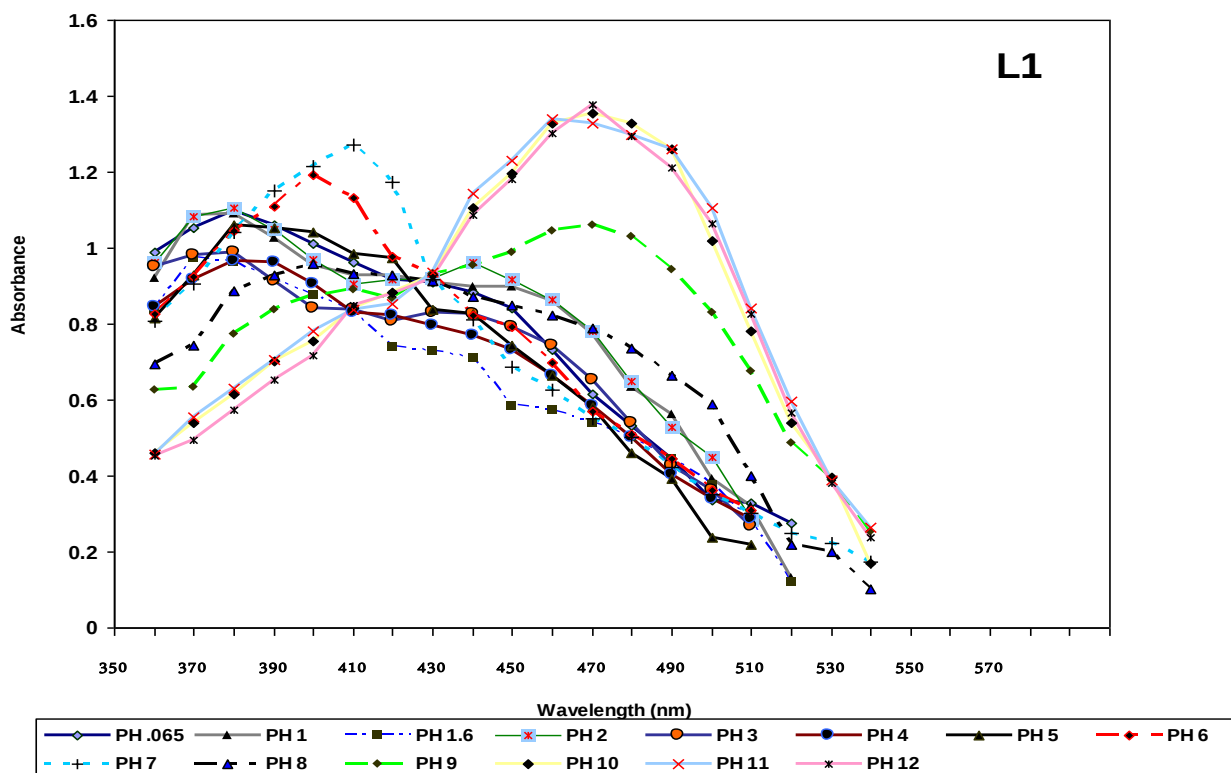


Fig. 2: Absorption Spectra Of L₁ At Different pH Values

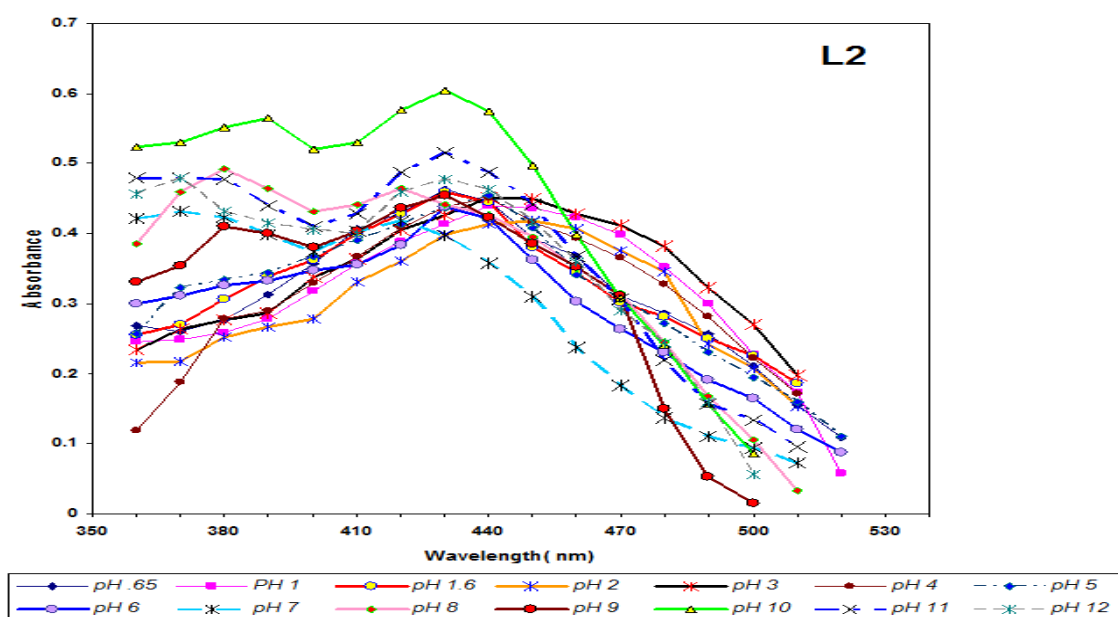


Fig. 3: Absorption Spectra Of L_2 At Different pH Values

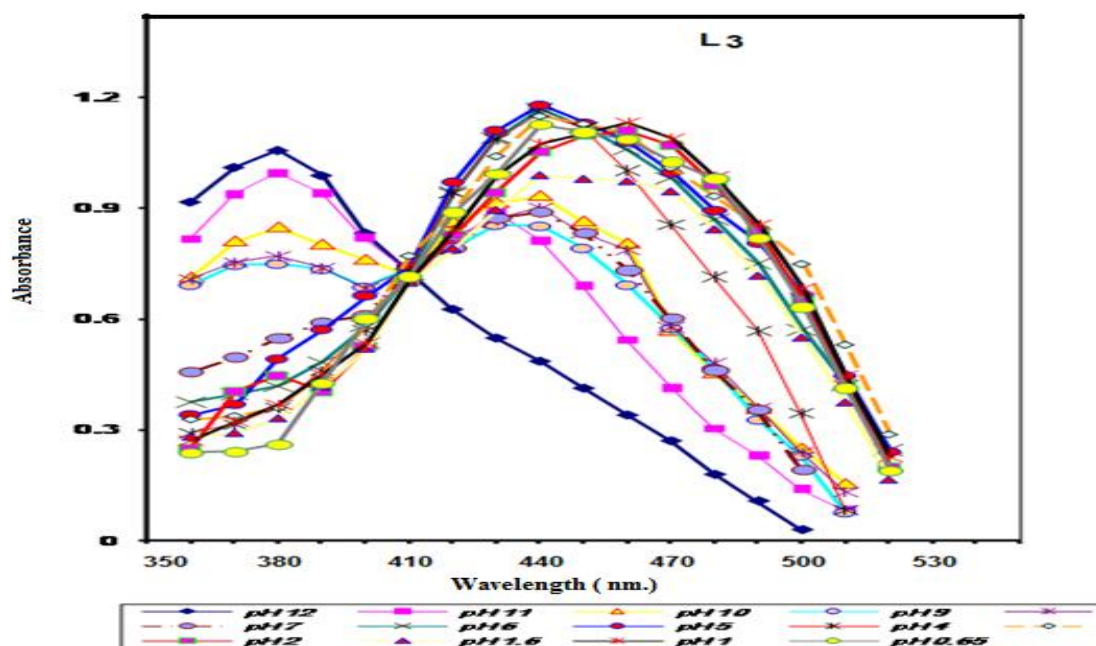
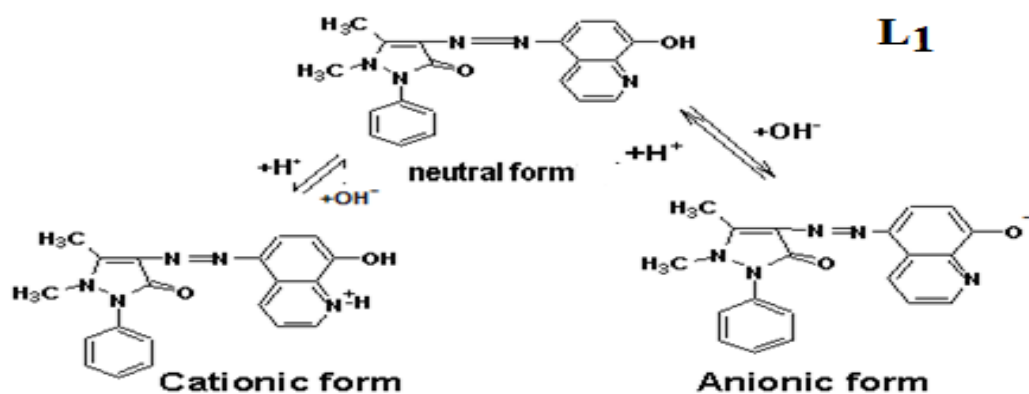
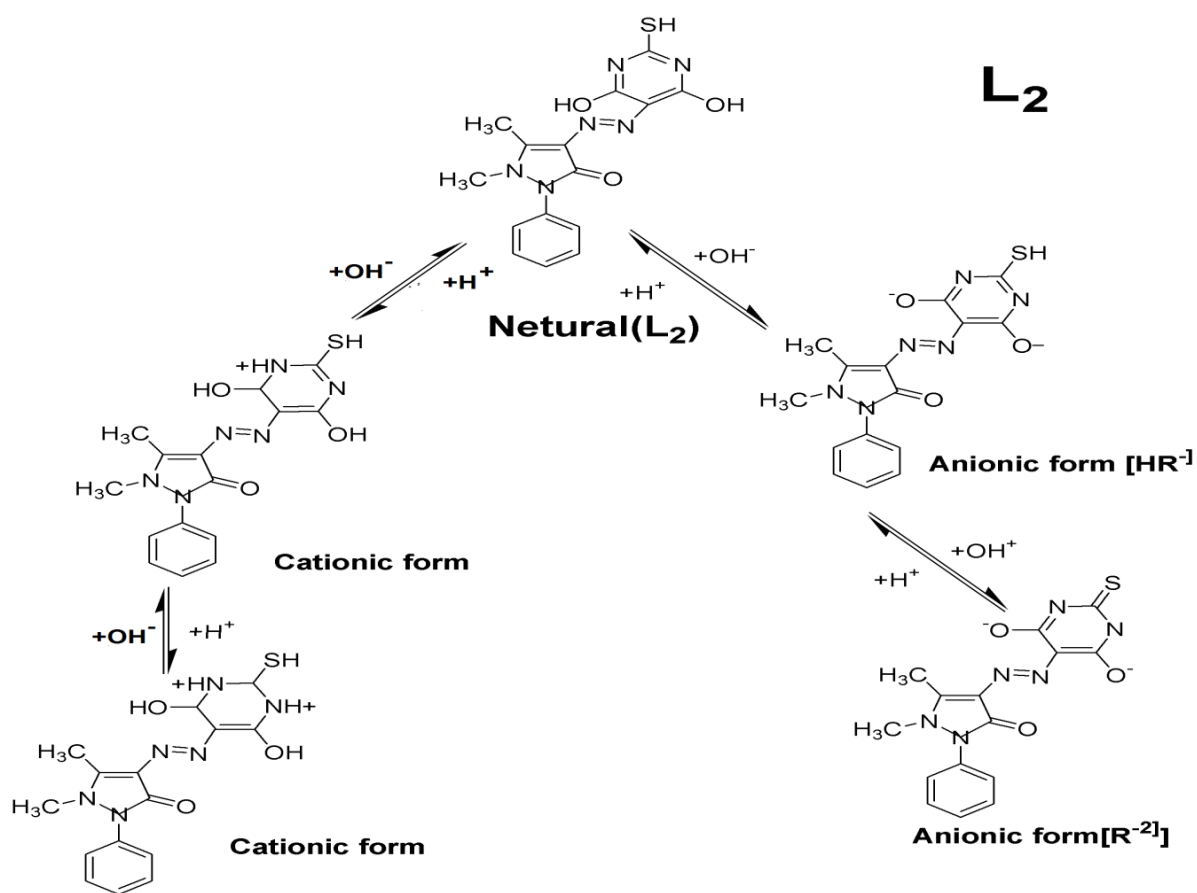


Fig. 4: Absorption Spectra Of L_3 At Different pH Values

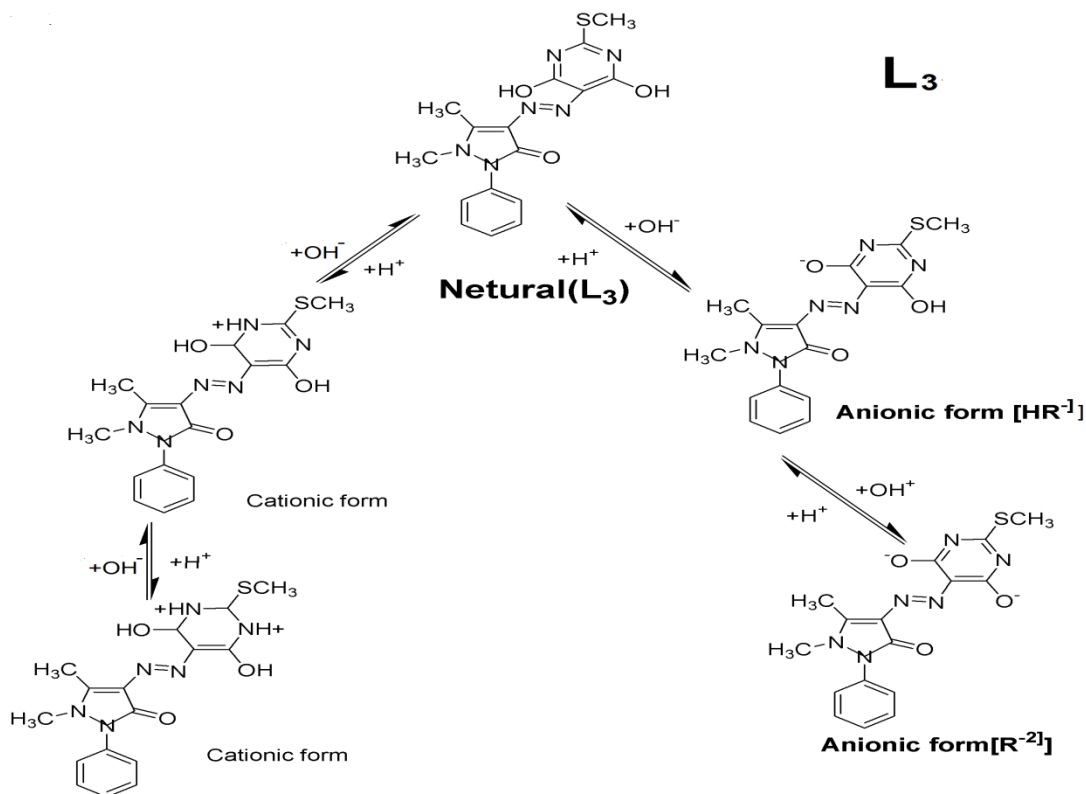
The suggested mechanism of protonation and ionization was shown in **Schemes 2-4**.



Scheme 2



Scheme 3



Scheme 4

From Absorbance – pH curve (Fig. 5) and by the aid of height method [11], the pK values were obtained by the relation :

$$\text{pK} = \text{pH} \text{ (at } A_{1/2} \text{)}$$

$$A_{1/2} = (A_1 + A_{\text{min.}}) / 2$$

Where A_1 and A_{min} are limiting and minimum absorbances respectively .

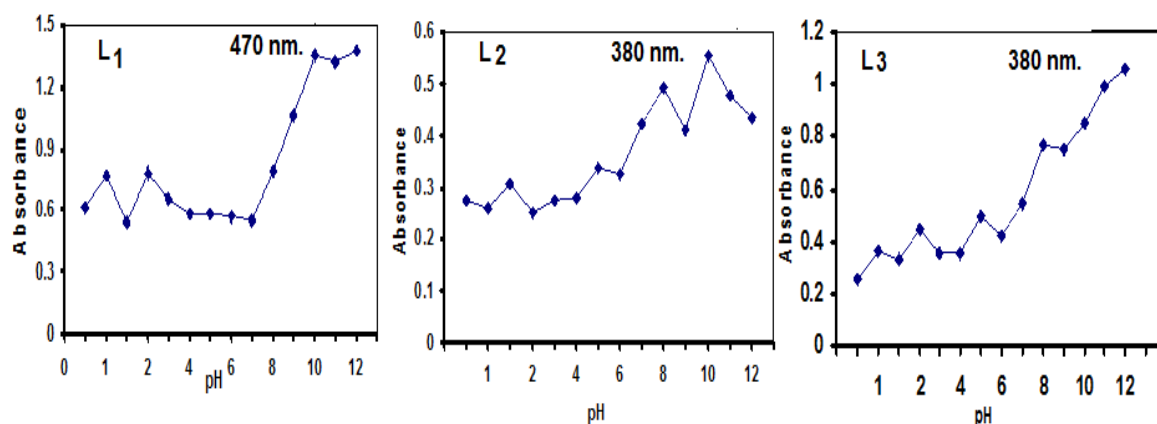


Fig. 5: The Absorbance – pH Curves Of Dyes

From above relations and **Figure 5** , so the protonation (pK_p) and ionization (pK_a) constants were calculated (**Table 4**) .

Table 4: The Protonation And Ionization Constants Of Dyes

pK_{a2}	pK_{a1}	pK_{p2}	pK_{p1}	$\lambda_{(max)}$ nm	Symbol
-	8.3	4.3	-	470	L_1
7.1	9.5	4.2	1.5	380	L_2
7.3	10	4.5	1.8	380	L_3

pK_{p1} is protonation constant for nitrogen atom

pK_{p2} is protonation constant for second nitrogen atom

pK_{a1} is ionization constant for hydroxyl group

pK_{a2} is the ionization constant for SH group

Solvents effect

Figure 6 shows the spectra of dyes at different solvents with λ_{max} in the range of (390-410nm.), (390-420 nm.) and (420-470 nm.) for dyes L_1 , L_2 and L_3 respectively. There is another weak bands at 500nm. (in ethanol) and 440 nm. (in DMSO) for L_1 and L_2 respectively. The absorption spectra in various solvents are influenced by solvation and / or dielectric effects of solvents.

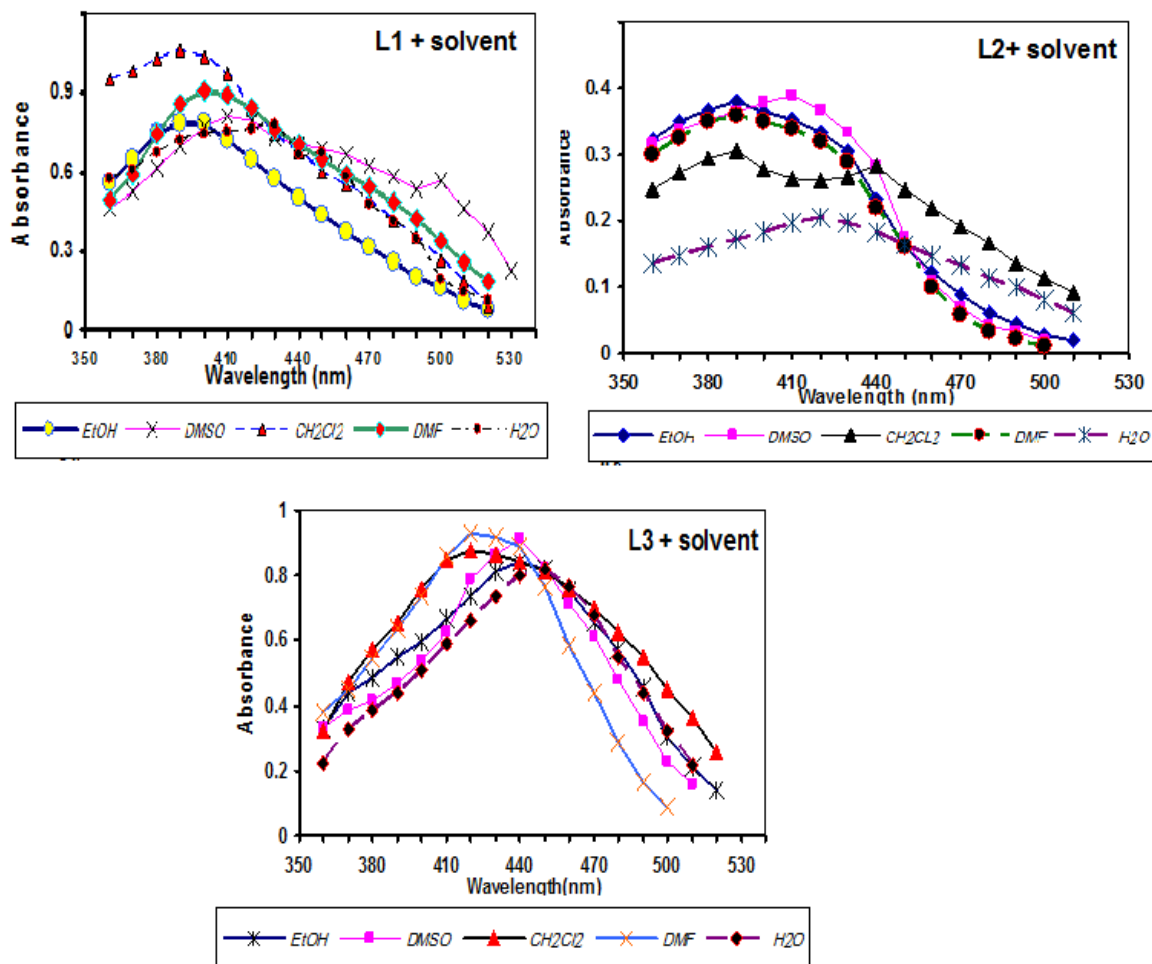


Fig. 6: Spectra Of Dyes At Different Solvents

To verify whether the band shift ($\Delta\nu$) is due to change in solvation energy or pure dielectric effects, the Gati and Szalay [12] was used;

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

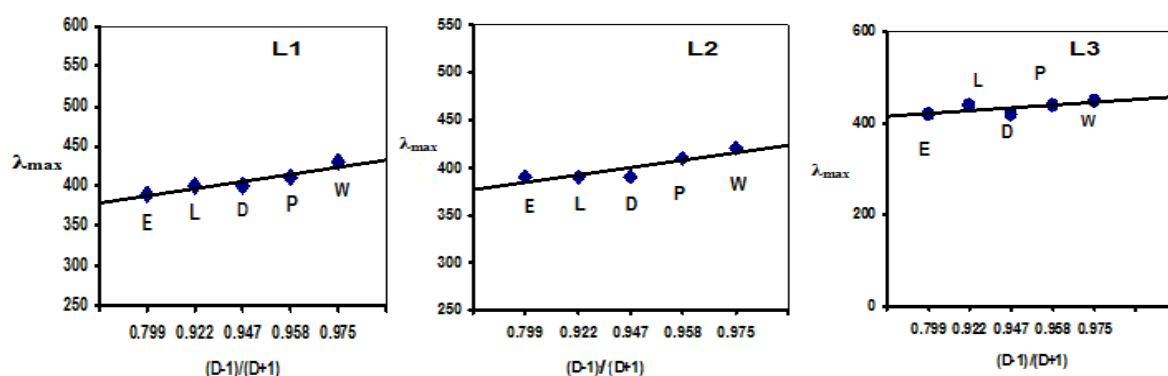
Where a and b are constants, n is refractive index.

Table 5 shows the functions $(D-1)/(D+1)$, $F(D)$ and $\phi(D)$ for every solvent. Where, D is dielectric constant of solvent, $F(D) = 2(D-1) / (2D+1)$ and $\phi(D) = (D-1)/(D+2)$.

Table 5: The Functions $(D-1)/(D+1)$, $F(D)$ And $\Phi(D)$ For Every Solvent.

$(D-1)/(D+1)$	$D)\Phi($	$F(D)$	D	Solvent	Symbol
0.799	0.726	0.841	8.93	CH ₂ Cl ₂	E
0.922	0.887	0.940	24.55	C ₂ H ₅ OH	L
0.947	0.923	0.960	36.71	DMF	D
0.958	0.938	0.968	46.68	DMSO	P
0.975	0.963	0.981	78.3	H ₂ O	W

It can be seen from **Figure 7**, the plot of $\lambda_{\max}$ vs. dielectric function of solvents , shows a linearity relationship that means the dielectric constant is the main factor covering the salvation .

**Fig. 7:** The Relation Between $\lambda_{\max}$ And Dielectric Function $(D-1)/(D+1)$ Of Dyes

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