Synthesis and Spectral Properties of some new derivatives of Luminol azo dyes

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Abstract

The thesis involves two parts :

The first partincluded synthesis eight new Azodyes , derived of *Luminol* L_1 = *5-[(phthalyl hydrazide) azo]-6-amino indzole*, L_2 *2- [(phthaly hydrazide) azo] phenylephrine*, L_3 = *3-[(phthalyihydrazide)azo]-2-Hydroxy indole*. have been described by C.H.N. and Visible spectroscopic spectra , The functional groups were characterized by I.R. technique. Acid – Base properties were also studied spectrophotometrically , using buffer solutions of pH values of (0.67 – 12) in the visible region.

The second part of the study concern with the ability of azo dye (L_2) for forming complex with, Ni(II). From calibration curve of L_2 complex : Sandell sensitivity ($8.19x10^{-3}$) cm^{-2}, Detection limit 0.0674µg ml^{-1}, ,Standard devation 0.004432, Correlation coefficient 0.9965, molar absorbitivity 7169×10^{-4} $L.mol^{-1}.cm^{-1}$, specific absorbtivity 0.1221 $ml.g^{-1}.cm^{-1}$ and obeyness of Beer's law region was determined for complex, ppm , and up to 0-14 ppm.

الخلاصة

تناولت هذه الدراسة محورين :

المحور الأول

يتضمن تخليق ثلاث صبغات ازوية جديدة مشتقة من الليمينول

L_1 = 5- [(phthalyl hydrazide) azo]-6-amino indzole, $L_2$2- [(phthaly hydrazide) azo] phenylephrine, L_3 = 3-[(phthalyihydrazide)azo]-2-Hydroxy indole

ودرست هذه الصبغات طيفياً وتم تشخيصها باستخدام تقنية التحليل العنصري الدقيق (C.H.N) وتقنية الاشعة تحت الحمراء (FT. IR) وفي هذه التقنية بالتحديد تم تشخيص اهم المجاميع الفعالة الموجودة في الصبغات المحضرة

ودرس أيضا تأثير المذيبات العضوية مختلفة القطبية على أطياف الامتصاص المرئية والفوق البنفسجية وتأثيرها على قمم الانزياح ووجد ايضاً ان العلاقة بين دوال ثوابت العزل الكهربائي وقيم الأطوال الموجبة العظمى (λ_{max}) للمذيبات المستعملة تبقى خطية ما عدا(L_2) لوحظ انحرافاً عن العلاقة الخطية.

كما درست الخصائص الحامضية – القاعدية طيفياً في محاليل مختلفة الدالة الحامضية بمدى (12- 0.67) في المنطقة المرئية والفوق البنفسجية على قمم الامتصاص من خلال اطياف الامتصاص

<u>المحور الثاني</u>

يتضمن استخدام الصبغة الأزوية (L_2) في تكوين معقد مع ايون النيكل الثنائي. ووجد إن هناك انحرافا واضحاً في الطول الموجي الأعظم (λ_{max}) في المعقد كما هو في الصبغة (L_2) وكذلك تم حساب حساسية ساندل ($8.19x10^{-3}$) مايكروغرام .سم$^{-2}$ ومعامل الارتباط 0.9965 والامتصاص المولاري ($7169x10^{4}$) لترمول$^{-1}$سم$^{-1}$ ومدى انطباق قانون بير (0-14) جزء بالمليون والامتصاصية النوعية (0.1221) مل غم$^{-1}$سم$^{-1}$ والحد الكشف (0.0674) مايكروغرام مل$^{-}$

Introduction

Azo compounds are a category of alchemical compounds that are of continuing concern in scientific research[1].The investigation of azo dyes with intriguing spectrophotometric and physical properties have been active area of research diction.widely utilized in numerous practical applications, for example, colorants, photochromic materials, nonlinear optics, receiver and indicators [2].The structural features in organic compounds, that sometimes produce colour are N = O, C = C, N=N, aromatic rings, C = O and NO_2. Above all, the gatherings that constantly give colour are the azo (– N=N–) and nitroso (– N=O) while different gatherings really do as such in specific situations [3].Aromatic azo dyes are the biggest gathering of organic dyes to applications it in numerous regions of material and medication [4].The solvents of various polarities might be influenced on the assimilation of π–conjugated compound show n →π*transition just as π→π*transition causing blue or red shifts. They utilized as great reagents for spectrophotometric assurance of metal ions and the extraction [5-9].

Experimental

Materials and Apparatus

distilled water, Solvents (for spectra uses),UV-Vis. Absorption spectra were recorded by utilizing 721 noticeable spectrophotometer, pH meter (Microproceor PH Meter), IR. FT_IR BRUKER,CHN Pro apparatus, Accurate balance ABS 120-4Electronic Balance, All absorbance measurements were conducted onusing 1 cm matched glass cells,College of science Kufa university,for melting point measurement use Electro thermal 9300,use pg Instruments AA 500 Spectrophotometer for Flame Atomic Absorption.

Synthesis of azo dyes

The azo dyes reagents were prepared of dissolving 0.005 moleof5-Amino-2,3-dihydro-1,4-phthalazinedione with 1.8 ml concentrated HCl, , 5 ml distilled water ,then adding drop by drop solution of (0.38 g. sodium nitrite in 5 ml distilled water) to form diazonium salt at less than *5 C temperature . Add alkaline solution 0.005 mole of 5- [(phthalyl hydrazide) azo]-6-amino indzole (L_1) ,2- [(phthaly hydrazide) azo] phenyl `` phrine (L_2) ,3-[(phthalyihydrazide)azo]-2-Hydroxy indole (L_3). NaOH to the above diazonium salt .At that point changing over the readied dye from sodium salt into hydrogen structure by adding of dilute HCl .The dye was cleaned by recrystallization from methanol.

Solutions

1. 1 x 10^{-3}supplies resolution of azo dye ready by dissolving exact load of each dye and complete the volume to 50 ml absolute ethanol
2. 2. 1000 ppm of nitrite sol , by dissolving 0.38g. of NaNO2 in weaken. Water and complete to 100 ml
3. 0.005 mole of each amine in 1.8 M HCl (complete to 5 ml)0.005 mole of each coupler in 1.5 M NaOH (complete to 10 ml) Universal and acetate buffer solutions of pH(2-12) and pH 0.67-5.2 respectively [10].

Procedure

1. a arrangement of cushion arrangements were set up with various pH esteems (0.67 – 12) for all out dye focus 1 x 10-4 M through utilizing universal buffer, the absorbance of these arrangements were recorded at scope of (300 – 600

nm.) utilizing cell of 1cm. length . For corrosive – base investigations and assurance of ionization and protonation constants of the dye.

2. prepared a series of solution of dye at total concentration 1×10^{-4}Mwith , DMF , DMSO , Ethanol ,Methanol,1,4-dioxane and H_2O , It has been recorded in the absorption of these solutions range (300-600 nm).For solvent effect studies

Results and Discussion

Elemental-Analysis

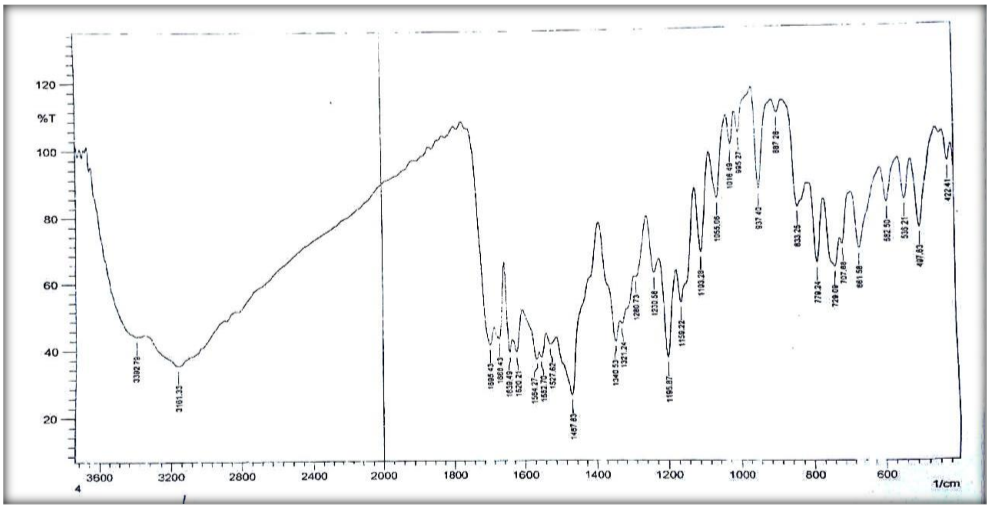
the elemental analysis of prepared dyesshowed in Table 1, Which gives good results for the formula proposed dyes

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

	C%		H%		N%	
	Calculated	Found	Calculated	Found	Calculated	Found
L_1	56.068	55.87	3.450	3.78	30.522	30.07
L_2	57.453	58.04	4.822	4.33	19.712	20.01
L_3	59.805	59.02	3.450	3.52	21.801	20.87

IR Analysis

Table 2 shows the infrared frequencies for large groups of useful aggregate frequencies as shown in Figure 1



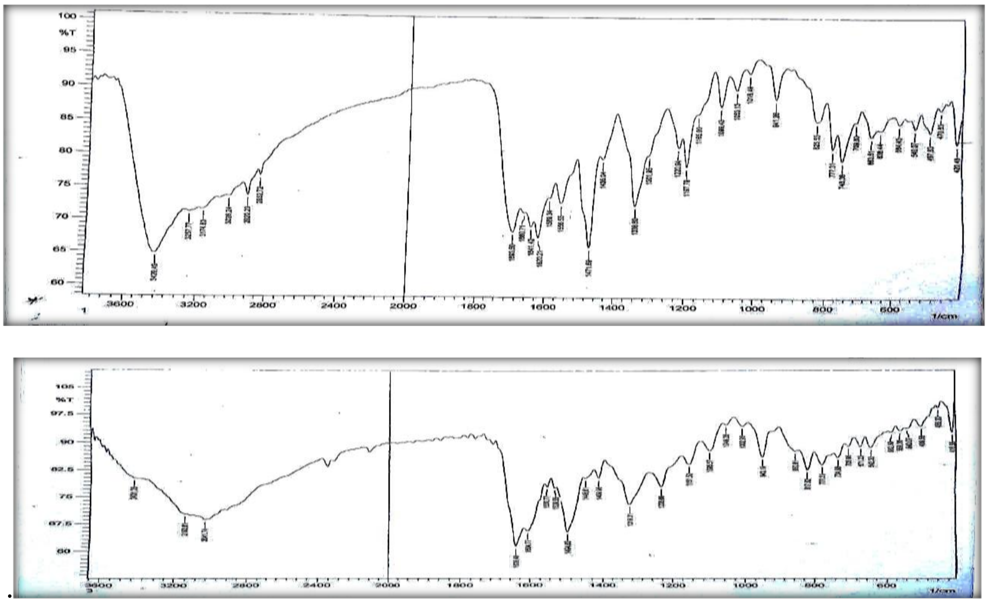
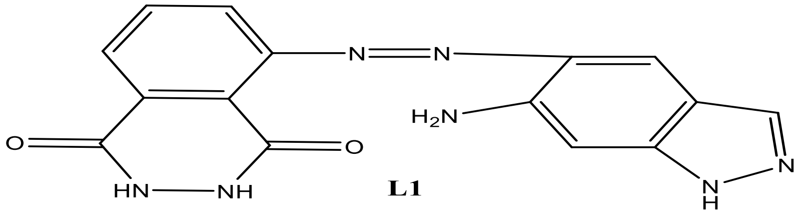


Fig. 1: The IR – Spectrum Of The Dyes (L_1-L_2-L_3)

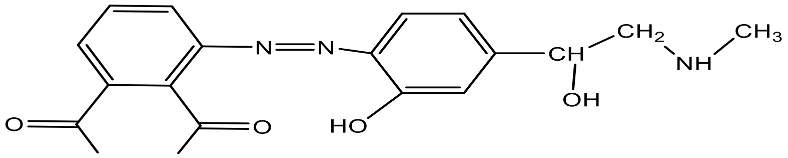
Table 2 shows the infrared frequencies for large groups of useful aggregate frequencies

Frequency vcm^{-1}			**Groups**
L_3	**L_2**	**L_1**	
		3161.31	NH_2
3153.61s.b	3257.77 m		O-H
3431.38.	3429.43 S b	3392.79	N-H
1639.48 S	1693.50 S	1695.3S	C=O
---		1639.49	C=N
1550.77m	1556.55 m	1552.70w	N=N
1494.83 S	1471.69 s	1467.83 S	C=C
1228.88 s	1197.79m	1195.87 S	C-N
W=Weak	M=Medium	S=Strong	b=broad

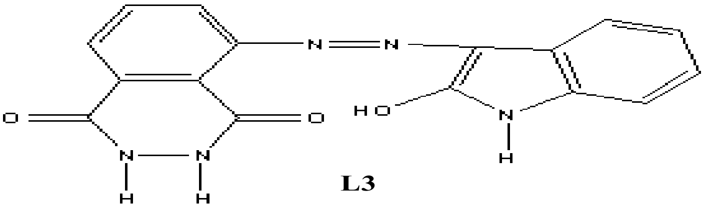
According to the above analysis Tables 1 and 2, information show the dyes have this chemical composition (Scheme 1)



L1



L2



L3

It was clarified some physical and chemical properties of the pigments in Table 3.

Table 3: Physical and chemical properties of the dyes

Dye	Empirical formula	M.Wt.	Color	^{o}C M.P.
L_1	$C_{15}H_{11}N_7O_2$	321.306	Yellowish orange	266-267
L_2	$C_{17}H_{17}N_5O_4$	355.366	Orange	120-130
L_3	$C_{16}H_{11}N_5O_3$	321.306	Yellow	110-112

Acid-Base properties

in the range of wavelength (300-600 nm) of varying pH values (0.67 – 12) were represented graphically (Figures 2-4)Absorption spectra of 1 x 10-4 m solution per dye .Featuring two spectra of the top bands, the first at (360-380) nm. of each dye in the acidic medium due to the protonation of dye (cationic form) . The second high intense band at (480,410) nm. for dyes , $L_2$and L_3 respectively in dyeL_1 The second weak intense band at 520nm the alkaline medium due to ionization of dye (anionic form) The spectra show isobestic points at (410,350,440) nm. for dye L_1 , (420,390,350) nm. for dye L_2 ,(460,390,380) nm. for dye L_3

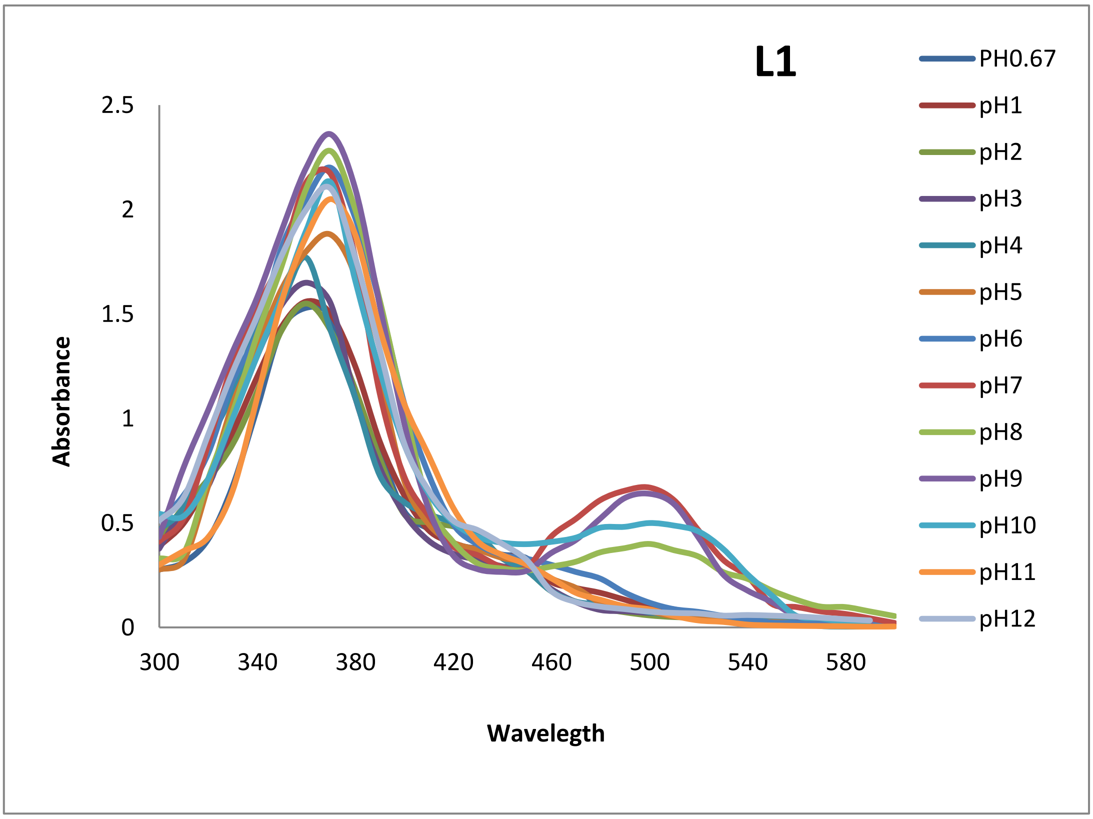


Fig. 2: Absorption Spectra Of L_1 At Different pH Values

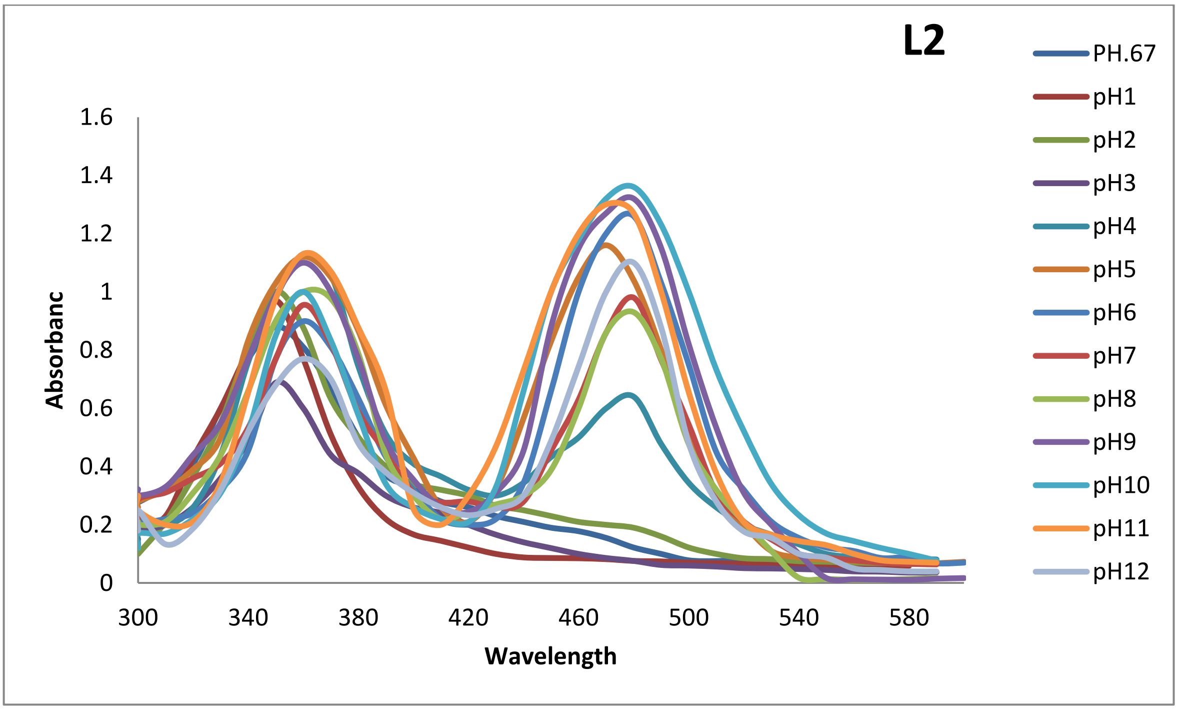


Fig. 3: Absorption Spectra Of L_2 At Different pH Values

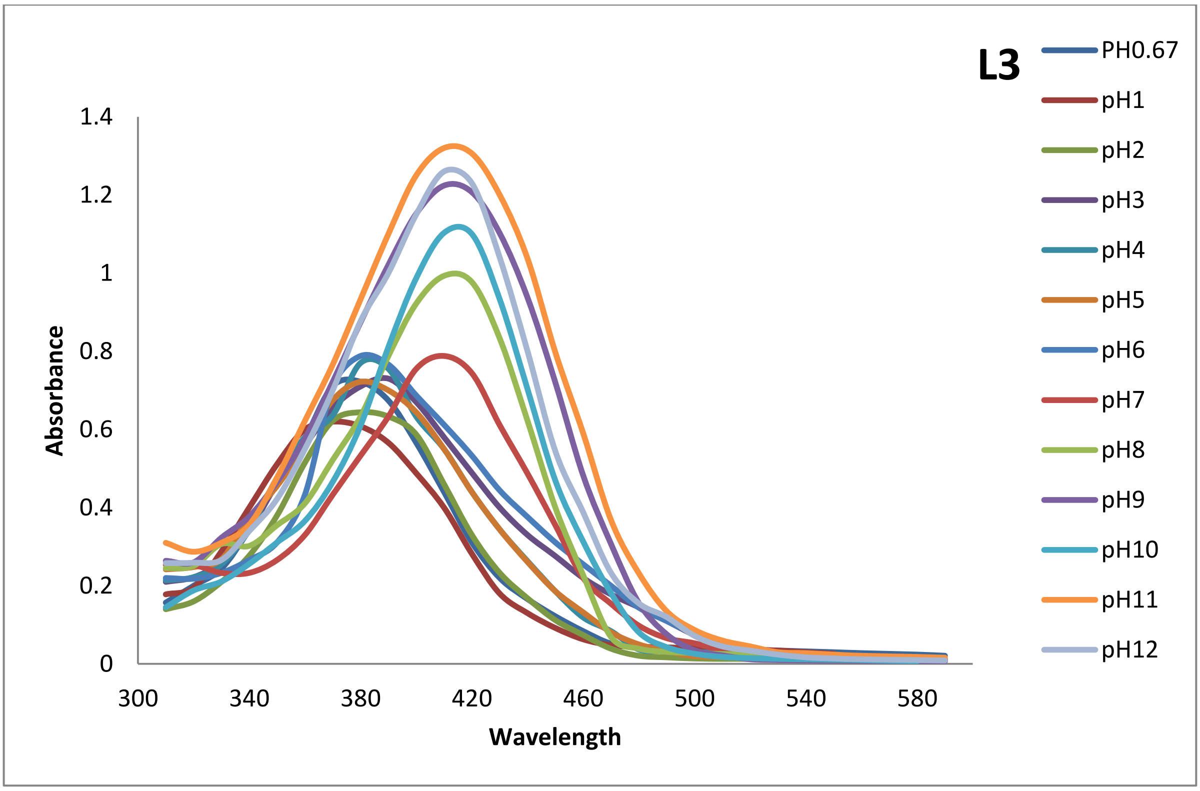
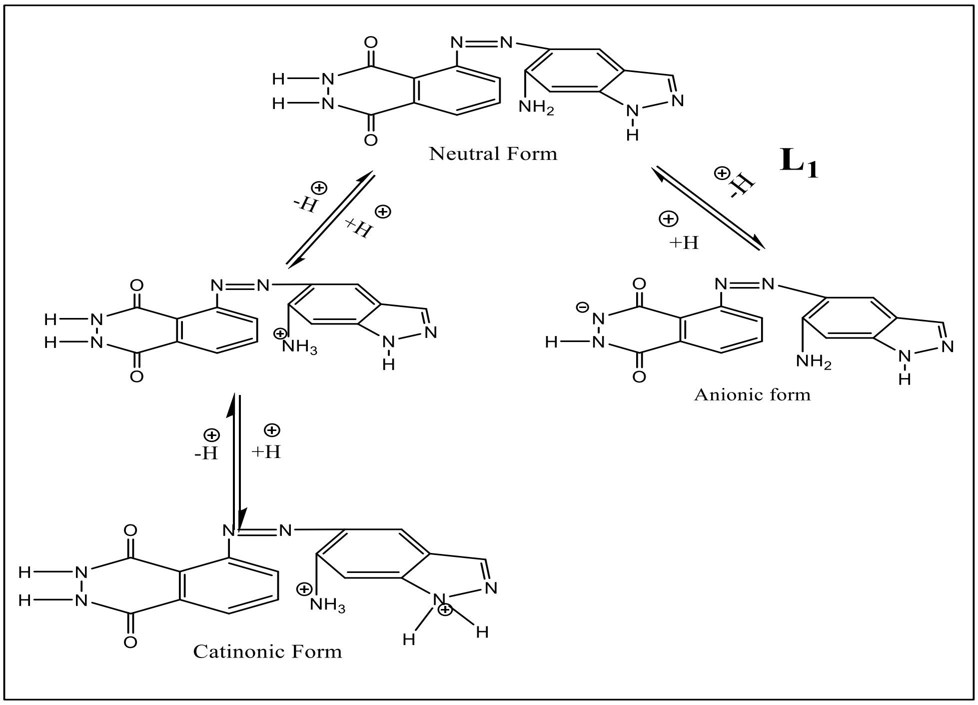
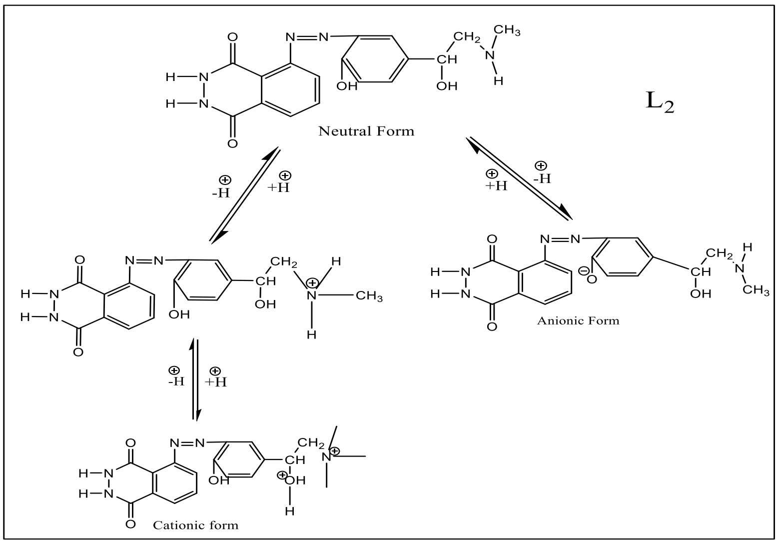


Fig. 4: Absorption Spectra Of L_3 At Different pH Values

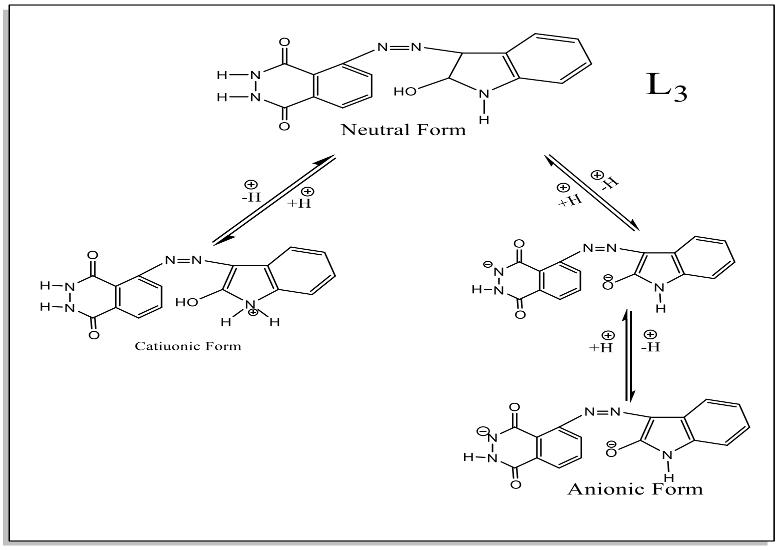
It has been proposed mechanism for ionization and ionization in the charts 2-4



Scheme 2

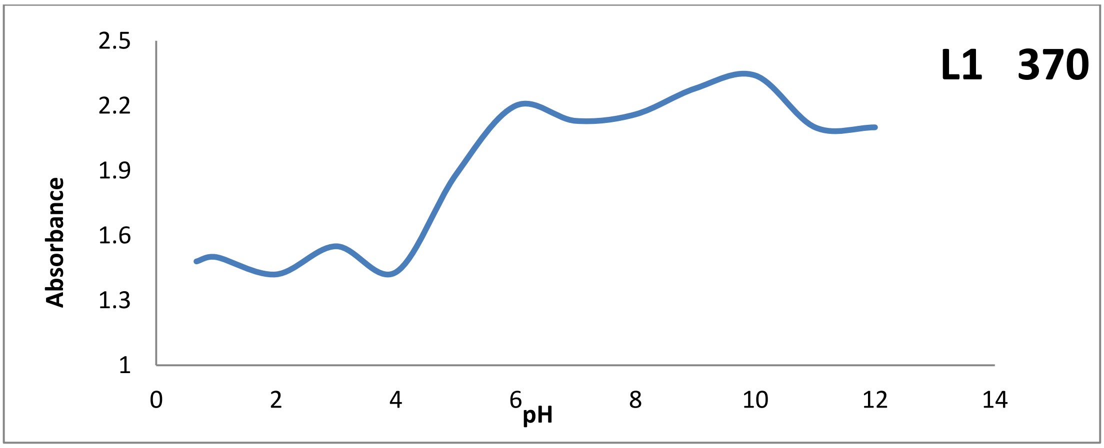


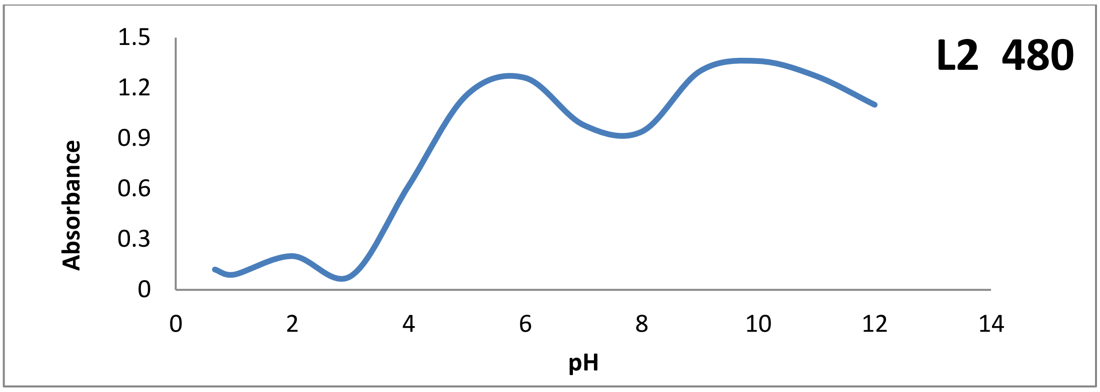
Scheme 3



Scheme 4

Where Al and Amin and the minimum absorbance are determined respectively, the pK values are obtained by relationship: pK = pH (at A1 / 2) A1 / 2 = (Al + Amin.) / 2, from the absorption curve - pH (Figure 5)) With the help of elevation method [11], .





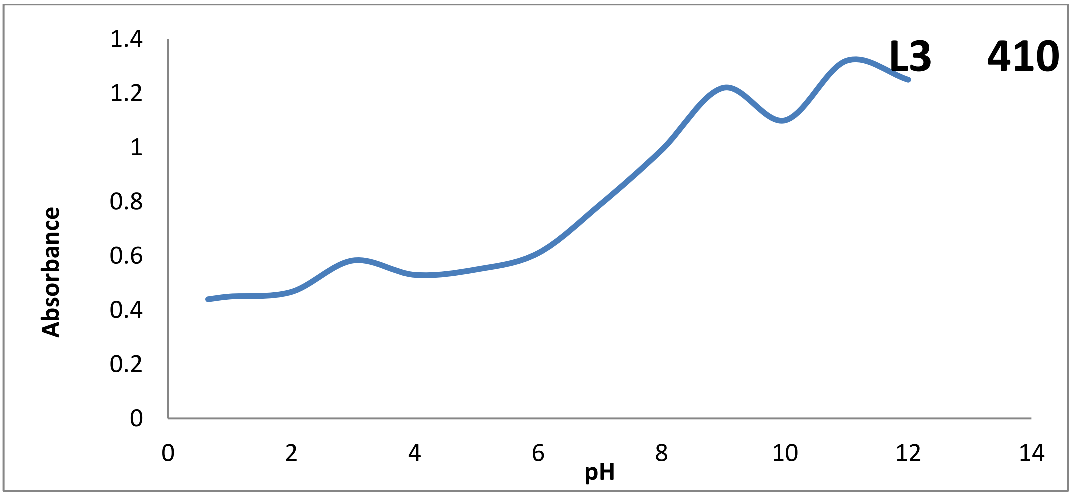


Fig. 5: The Absorbance – pH Curves Of Dyes

From above relations and Figure 5 , the protonation (pKp) and ionization (pKa) constants were calculated (Table 4) .

Table 4: The Protonation And Ionization Constants Of Dyes

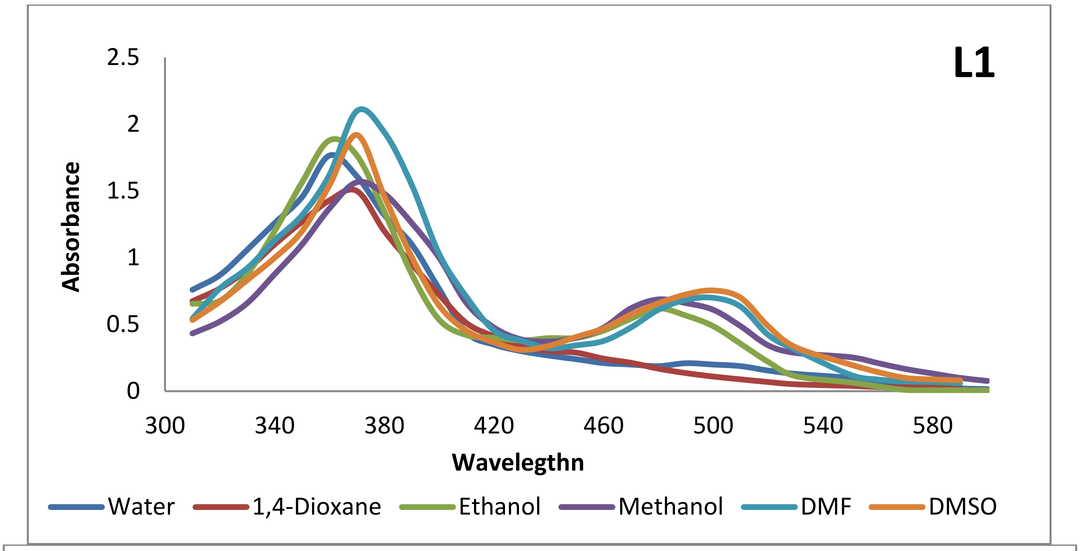
pK_{a2}	$A_{1/2}$	pK_{a1}	$A_{1/2}$	Pk_{P2}	$A_{1/2}$	Pk_{P1}	$A_{1/2}$	λ (nm)	Dyes
		8.8	2.25	2.4	1.485	4.9	1.815	370	L_1
		8.6	1.17	1.5	0.14	4.1	0.671	480	L_2
10.5	1.12	7.8	0.885			2.4	0.521	410	L_3

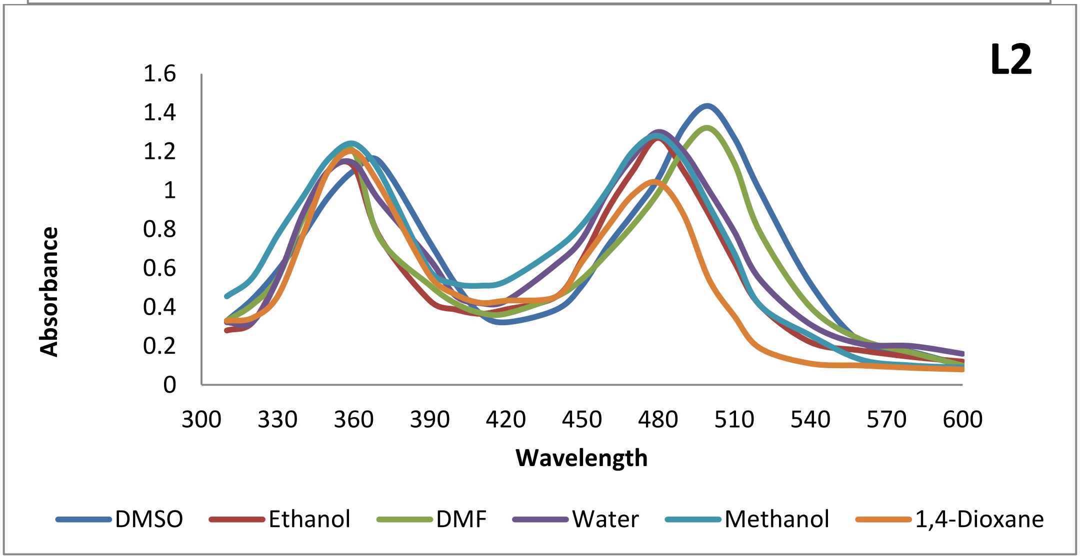
1-pKp1 is protonation constant for amine atom in phenylephrine,oxindole and indzole

2-pKp2 is protonation constant for second amine atom in indzolen and hydroxyl alcoholic group in phenylephrine
3-pKa1 is ionization constant for hydroxyl group in phenylephrine,oxindole for amid group in luminol
4-pKa2 is the ionization constant for amid group in luminol

Solvents effect

Figure 6 shows the spectra of dyes at different solvents with λmax in the range of (300-600nm).





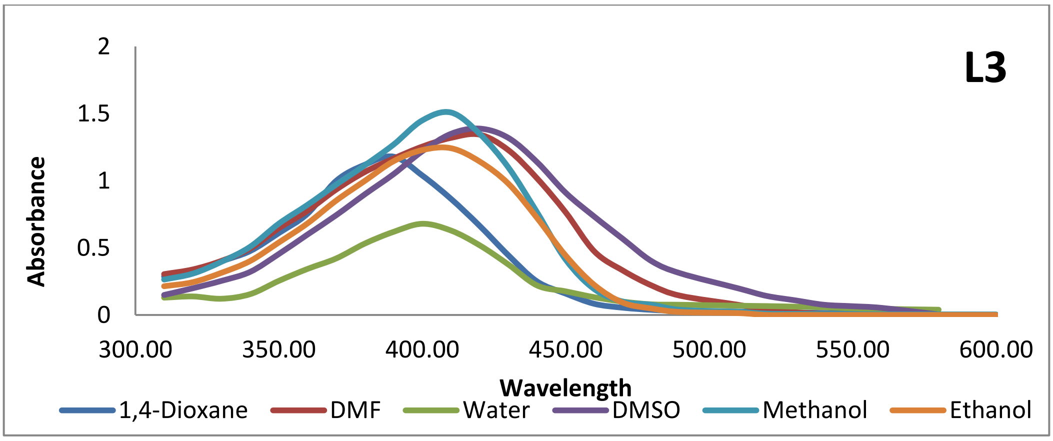


Fig. 6: Spectra Of Dyes At Different Solvents

The Gati and Szalay [12] was used ,To check if the range shift (Δν) is due to a change in salvation energy or purely insulating effects.

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

Wherever a and b are constants, n is the refractive index.

Table 5 shows the functions (D-1)/(D+1) , F(D) and ϕ(D) for every solevent. D is dielectric constant of solvent , $F(D)= 2(D-1) / (2D+1)$ and $\phi(D) = (D-1)/(D+2)$ [13-14]

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

D)θ(	F(D)	(D-1)/(D+1)	D	Solvent
0.884	0.92	0.920	24	Ethanol
0.915	0.956	0.942	33.6	Methanol
0.922	0.959	0.946	36.7	DMF
0.938	0.968	0.958	46.67	DMSO
0.962	0.98	0.975	78.3	Water
0.302	0.464	0.393	2.30	1,4-Dioxane

It can be seen from Figure 7, the plot of λmax vs. dielectric function of solvents , shows a linearity relationship that means the dielectric constant is the main factor covering the salvation for deys $L_1$and L_3.the dey L_2notesdeviation of relationship in high polar solventsonwater,DMSO and DMF

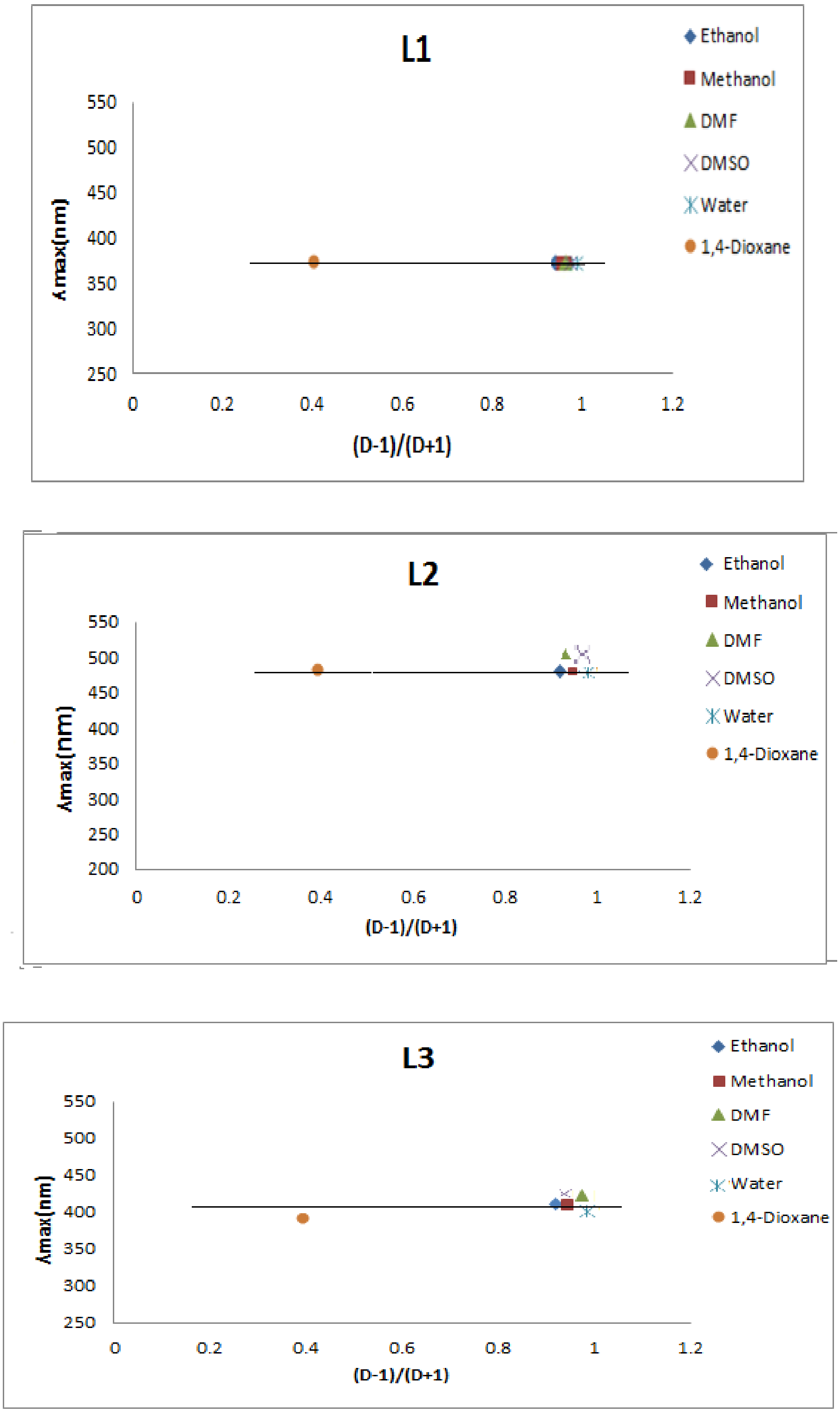


Fig. 7: The Relation Between λ_{max} And Dielectric Function (D-1) / (D + 1) Of Dyes

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