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SYNTHESIS AND SPECTROPHOTOMETRIC STUDY OF SOME NEW AZO DYES DERIVED FROM PROCAINE

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ABSTRACT

This study involves the preparation of four azodyes 2-(Procaine azo) - imidazole (L4), 2-(Procaine azo) phenylephrine (L3), 2-(Procaine azo) oxindol (L1) and 2-(Procaine azo)-4,5-diphenyl imidazole(L2). They have been described by C.H.N., I.R. and Visible spectroscopic techniques. The acid-base properties were studied at different pH values (0.67-12), then the ionization and protonation constants were determined.

KEYWORDS

Procaine, Azodyes, Ionization and Protonation constants and Spectral studies.

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INTRODUCTION

The organic reagents with the widespread and characterized by multi-its use, because of the high stability and speed of preparation as it possesses many of which are sensitive and selective replay, making it the focus of attention of researchers^{1,2}, and where the form of azo dyes ratio ranging between (60% - 70%) of the total dyes^{3,4} have been prepared first type of azo dyes in 1862 AD by Marty dye Bismarck Brown called⁵ and can be set to azo be associated with several totals, including Aliphatic or aromatic and depending on this classified vehicles azo according associated with the parties to the totals azo group, and azo compounds

called aliphatic when two groups associated Aliphatic a relatively low prevalence of disintegration due to nitrogen and hydrocarbons^{6,7}. Kindly be groups associated with aromatic called compounds azo aromatic, as it is this type is the most important and widespread because of the emergence of the formulas resonance rings associated beside the azo group, and are classified as azo dyes aromatic into two types depending on the rings associated with the ends of azo group, compounds azo Heterocyclic which vehicles that are where groups linked to an aromatic homogeneous any do not contain atoms (C) such as loops (N, O, S) and where these episodes are not compensated characterized as reagents weak that the azo group is the only center for consistency with ions metallic⁸ and the simplest example of this type is azobenzene⁹. Azo compounds heterocyclic ring include compounds in which the azo group two, one of them be heterogeneous container (O, N, S) second episode either be homogeneous or heterogeneous, and features of these vehicles that molar high absorbance¹⁰ because it contains more than atom donor has the ability to grant her electron pair is Complicate to form complexes grapples with ions metallic¹¹ characterized by azo dyes stability and speed of interaction with ions metal has numerous uses, particularly in the field of analytical chemistry through use in the quantitative and qualitative assessment of the ions metallic¹². The azo compounds was as evidence acid - a base for her wealth of strong colors and clear vary depending on the installed making it more sensitive to acids and bases because they contain oxocromic groups and these groups acid (COOH, SO₃H, OH) are called azo dyes acidic either if it contains a base totals (NH₂, NRH, NR₂) are called azo dyes basal¹³, compounds azo many uses in medicine where is Plaulehrich founder of the first science Chemistry medicina Pharmaceutical Chemistry was his first work is to know the extent of biological effect of some compounds azo where reach antimalarials such as Trypanred¹⁴. The procaine of pharmaceutical compounds containing the secretary first group chemical composition of this compound (Figure No.1).

Santoni and his group¹⁵ determined of direct appreciation spectroscopy of procaine in the pharmaceutical when the wavelength of the greatest 290 nm and the applicability of the linearity (2-9) ppm were estimated procaine in the pharmaceutical interactions pairing where I am using 4-Amino-5-hydroxy naphthalene-2, 7-disulfoinic acid¹⁶ to estimate the waveform procaine at greatest length 530 nm and the applicability of the linearity (0.1-7) ppm. In another study used reagent 2,5-dimethoxy aniline waveform at greatest length 480 nm and the applicability of the linearity (0.2- 8) ppm and Molar absorption coefficient of $5.28 \times 10^4 \text{ M}^{-1} \text{ L cm}^{-1}$. In this study, four New Azo dyes preparation derived from the drug procaine and study spectrally.

EXPERIMENTAL

Materials

Double distilled water, solvents (for spectral use) and all chemicals of highest purity were used from different companies, Merck, Sigma, Fluka a procaine hydrochloric C₁₃H₂₁ClN₂O₂, imidazole C₃H₄N₂, and oxindole C₈H₇NO, phenylephrine hydrochloric HOC₆H₄CH (CH₂NHCH₃) OH HCl, banzal C₁₄H₁₀O₂, Hexamine C₆H₁₂N₄, ammonium acetate C₂H₇N₄, hydrochloric acid, sodium nitrite NaNO₂.

Apparatus

Visible absorption spectra were recorded by using PD-303 UV and Visible spectrophotometer, FT-IR-8400S spectrophotometer (Shimadzu) College of Education for Pure Science Basrah university, pH-meter (H.Jurgons Co. Beremen, L. Puls Munchen 15), Heraus CHN Pro apparatus, Petrochemical Institute (Iran), Bunchi B190K for melting point measurement, accurate balance E-Mette Weender (Land Strasse) 94-108.

Diazotization

0.005 mole of Metoclopramide of weight 1.680g. was dissolved in 1.8ml concentrated hydrochloric acid, then 10 ml of distilled water to each salt forming. The solutions were cooled to 0-5 Co in ice-bath. 5 ml of sodium nitrite 0.38g. was then added drop wise with stirring continued to each solution to produce diazonium salt.

Preparation of dyes L₁ – L₄

0.005 mole of each imidazole, phenylephrine, oxindole and 4,5-diphenyl imidazole, of weights 0.340, 1.018, 0.665 and 1.1 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 L₁ - L₄. 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 1:1 ethanol: methanol mixture.

Solutions

A stock solution of (1 x 10⁻³ M) of each L₁, L₂, L₃ and L₄ dyes were 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 (0.67-2) buffer solutions¹⁷ were prepared.

Procedure

Acid-Base studies¹⁸, to study the effect of pH values on the absorption spectra on the dyes (L₁-L₄) and to determine the protonation and ionization constants, a series of buffer solutions (acetate and universal) were prepared with different pH values (0.67-12) with concentrations of dyes are (0.2×10⁻⁴-1×10⁻⁴) M, the absorbance of these solutions was recorded at range of (310-580 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.

RESULTS AND DISCUSSION

Table No.1: C.H.N analysis of prepared dyes was illustrated in (Table No.1).

Table No.1: Elemental analysis data for synthesized dyes

S.No	N %		H %		C %		Chemical formal	simple
	Found	Calc	Found	Calc	Found	Calc		
1	14.29	14.73	6.82	6.31	66.52	66.33	C ₂₁ H ₂₄ N ₄ O ₃	L ₁
2	14.64	14.98	6.63	6.42	71.62	71.96	C ₂₈ H ₂₉ N ₅ O ₂	L ₂
3	13.32	13.52	7.86	7.24	64.12	63.78	C ₂₂ H ₃₀ N ₄ O ₄	L ₃
4	22.54	22.21	6.53	6.62	60.35	60.94	C ₁₆ H ₂₁ N ₅ O ₂	L ₄

IR Analysis

Table No.2: Shows the famous IR frequencies of important bands of functional groups frequencies as seen in Figure No.1.

Table No.2: The famous IR frequencies of important bands of azo dyes L₁-L₄

S.No	νN=N	νC=C	νC=N	νC=O	νH-N	νOH	Simple
1	1558.48m	1465.90m	---	1701.22s	3232.70m	3388.95bs	L ₁
2	1514.12m	1463.97m	1604.77s	1743.65m	3406.29w	---	L ₂
3	1581.63m	1468.97m	---	1720.71s	3471.27int	3271.27bs	L ₃
4	1508.33m	1460.11s	1604.77s	1712.79m	3402.42m	---	L ₄

b =bord s =strong m=med w=weak

Table No.3: The protonation (pK_p) and ionization (pK_a) constants of azodyes L₁-L₄

S.No	pK _{a1}	A _{1/2}	Pk _{p2}	A _{1/2}	Pk _{p1}	A _{1/2}	λ (nm)	Dyes
1	7.6	0.915	1.4	1.005	5.4	0.958	390	L ₁
2	8.8	0.575	1.6	0.445	6.4	0.516	450	L ₂
3	8.4	0.609	3.3	0.148	5.5	0.239	450	L ₃
4	9.5	1.189	2.2	1.169	5.6	1.163	370	L ₄

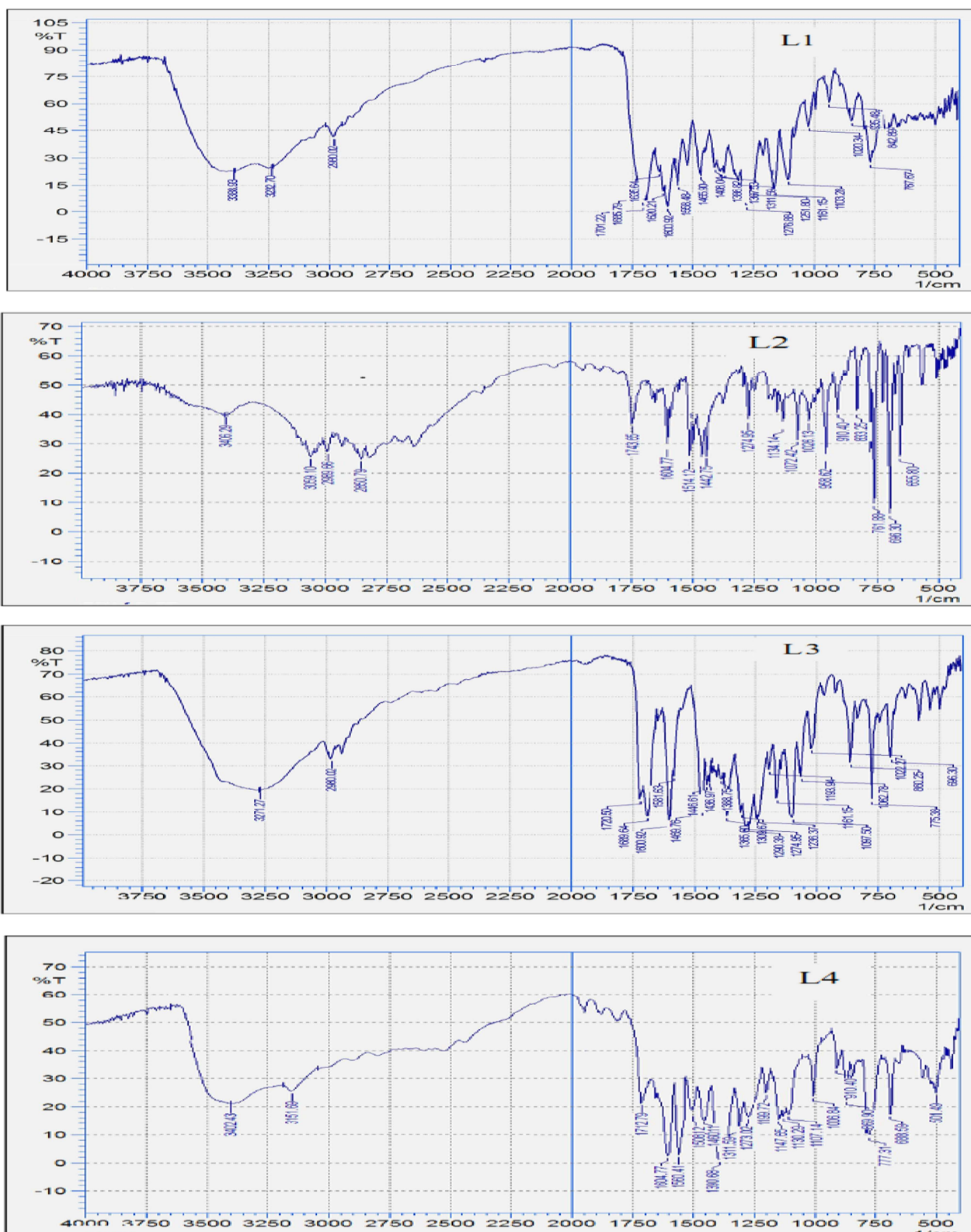
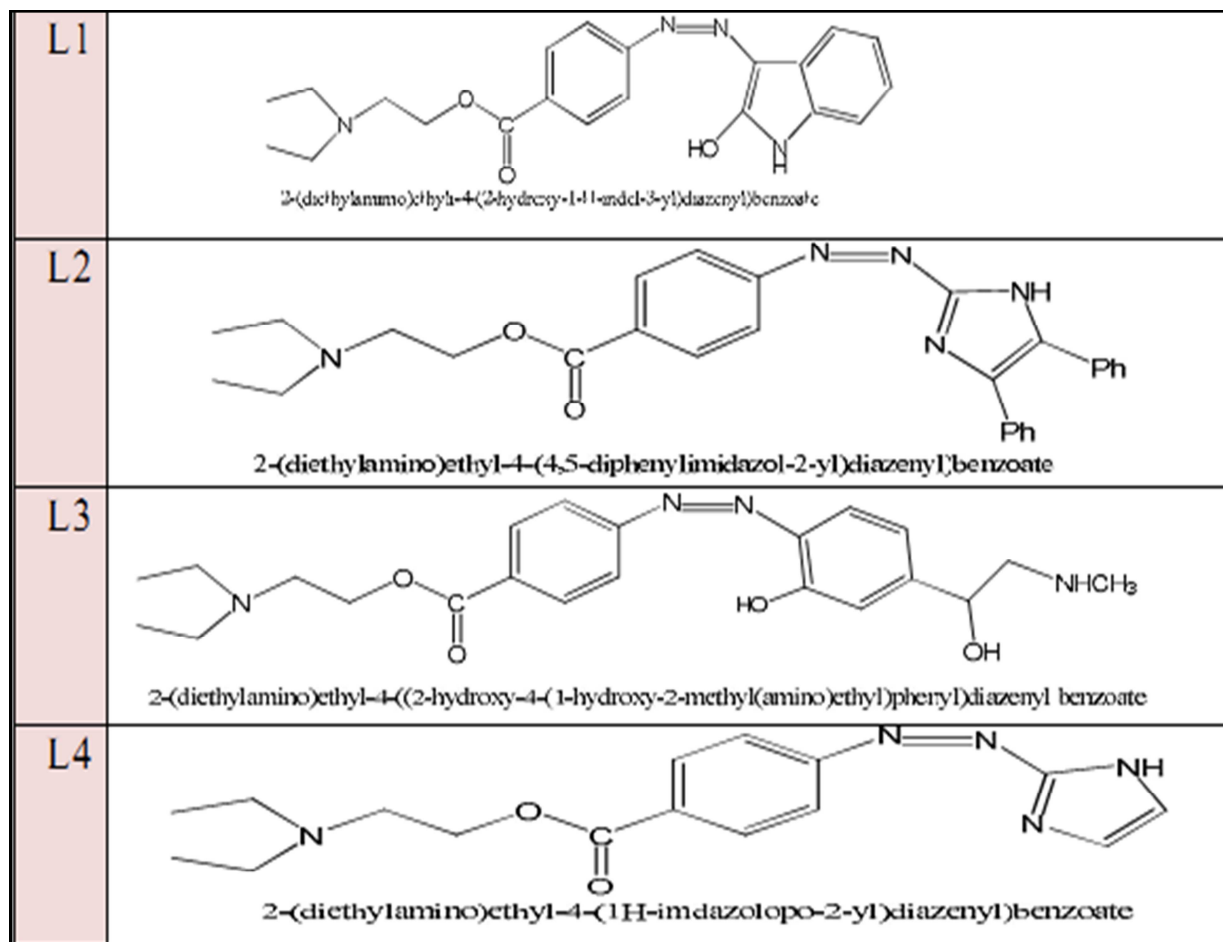


Figure No.1: IR spectra of the azodyes L₁–L₄

From IR analysis, Elemental analysis (CHN) and literatures and scientific previous researches, the chemical formula of azo dyes L₁-L₄ was suggested (Schemes No.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 [0.67-12] for each dye¹⁹. The absorbance with concentrations of dyes are (1×10^{-4} - 0.2×10^{-4}) M, the absorbance of these solutions was recorded at range of (310-580 nm), using buffer solution of

such pH value as a blank solution. For L₁ (Figure No.2), the spectra characterized by two wavelength maximum bands at 480nm in pH (12) and range (370-380 nm) for the other pH range. The first which a less intense bands due to ionized form (basic form, anionic form). And the second of pH range (< 12) related to protonation form (acidic form, cationic form).

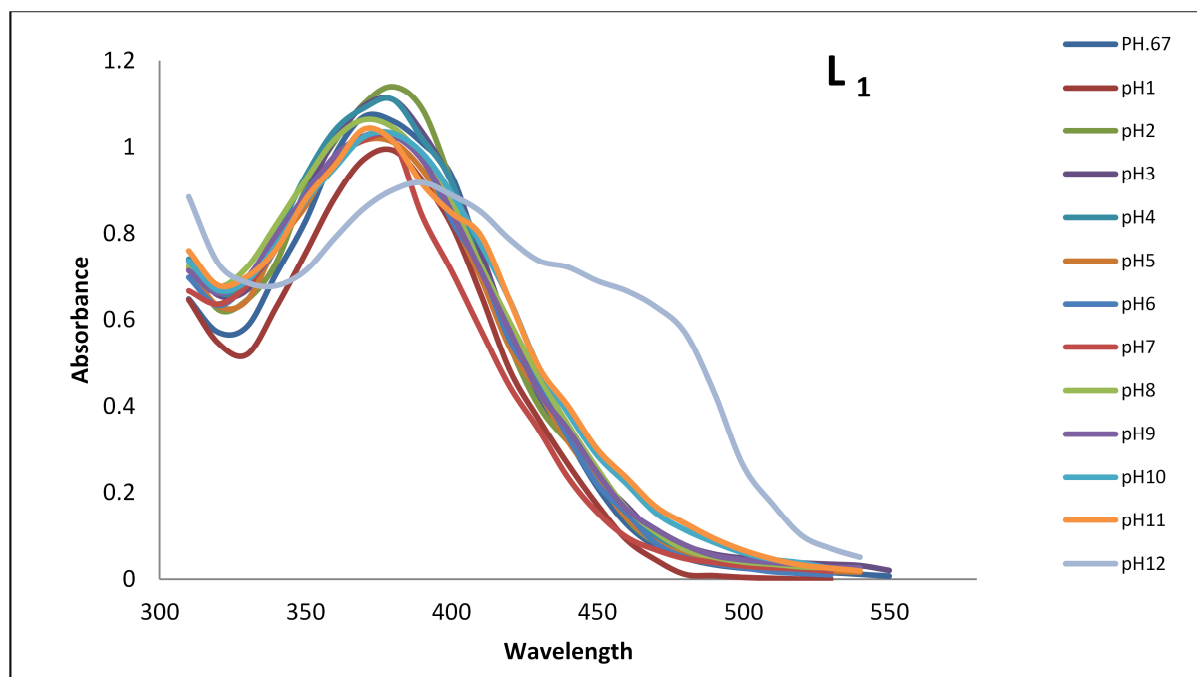


Figure No.2: The electronic spectra of L₁ at different pH values

For L₂ (Figure No.3), the spectra are also characterized by two maximum bands at 490 nm in pH range (9-12) and at 440 nm for the other pH range. The first which more intense bands at 490nm, due to ionized form (pH > 9), and the second of less intense at 440 nm of pH range (< 9) related to protonation form.

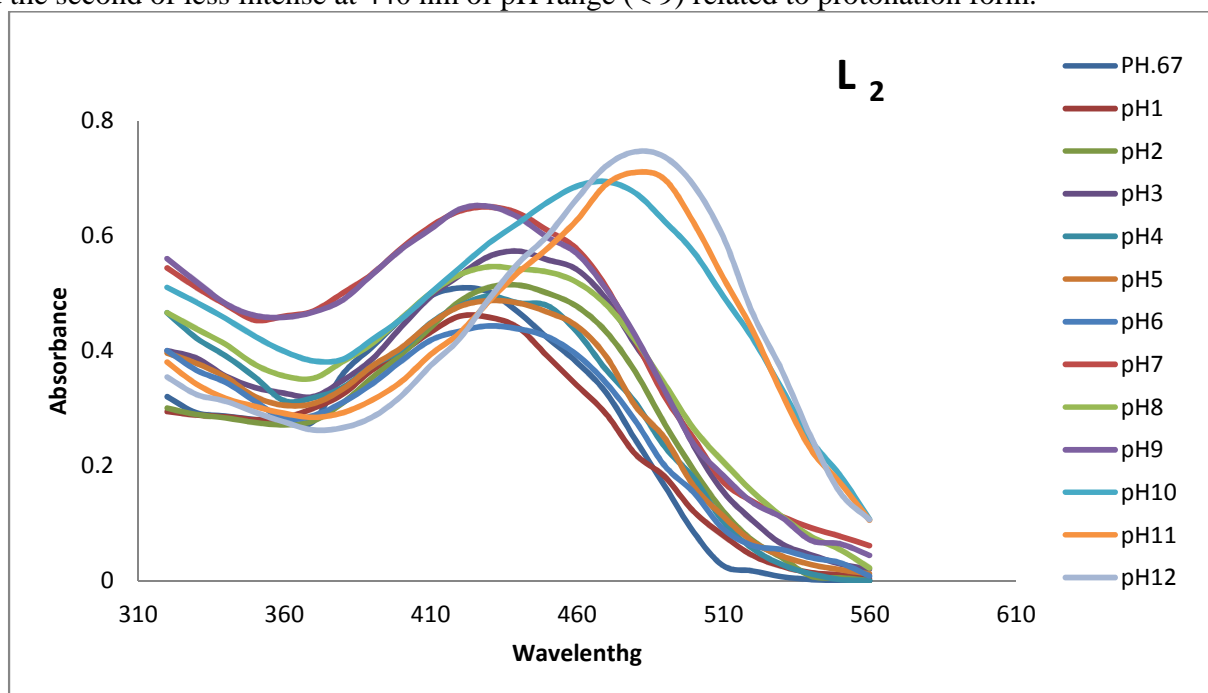


Figure No.3: The electronic spectra of L₂ at different pH values

For L_3 (Figure No.4), at max wavelength range (330-370nm) of acidic medium, this due to protonation. And the other wavelength max in alkaline medium at 470 nm.

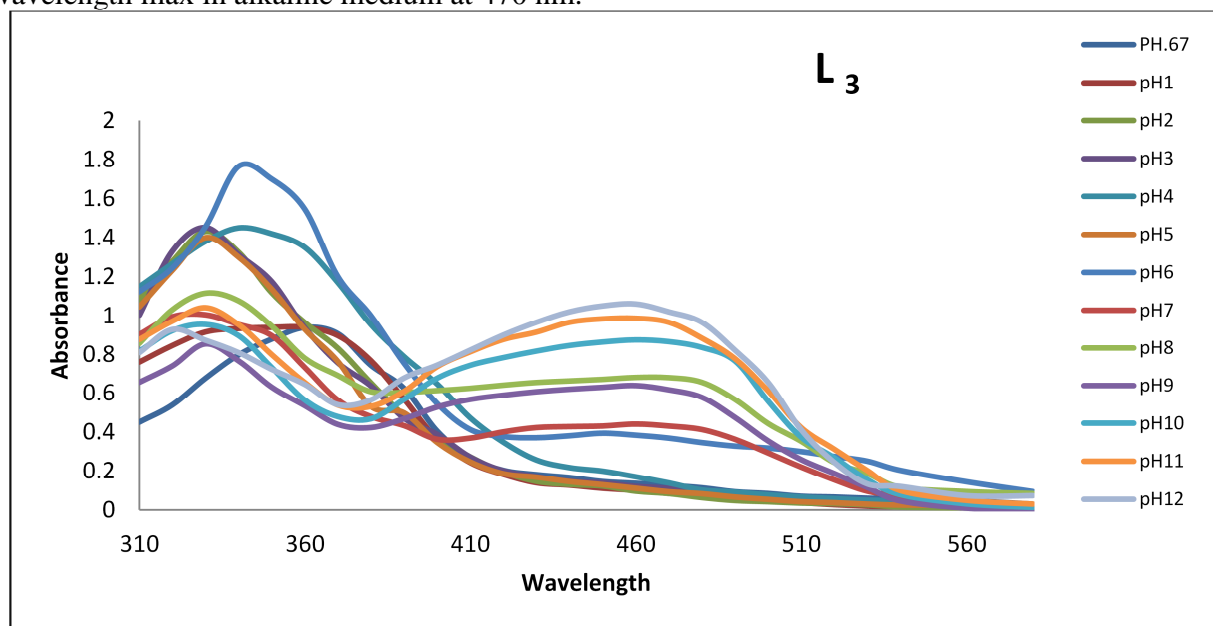


Figure No.4: The electronic spectra of L_3 at different pH values

For L_4 (Figure No.5), the spectra characterized by two wavelength maximum bands at 370 nm in pH range (4-12) and (350 nm) for the other pH range. The first which less intense bands due to ionized form (basic form, anionic form). And the second of pH range (< 4) related to protonation form (acidic form, cationic form).

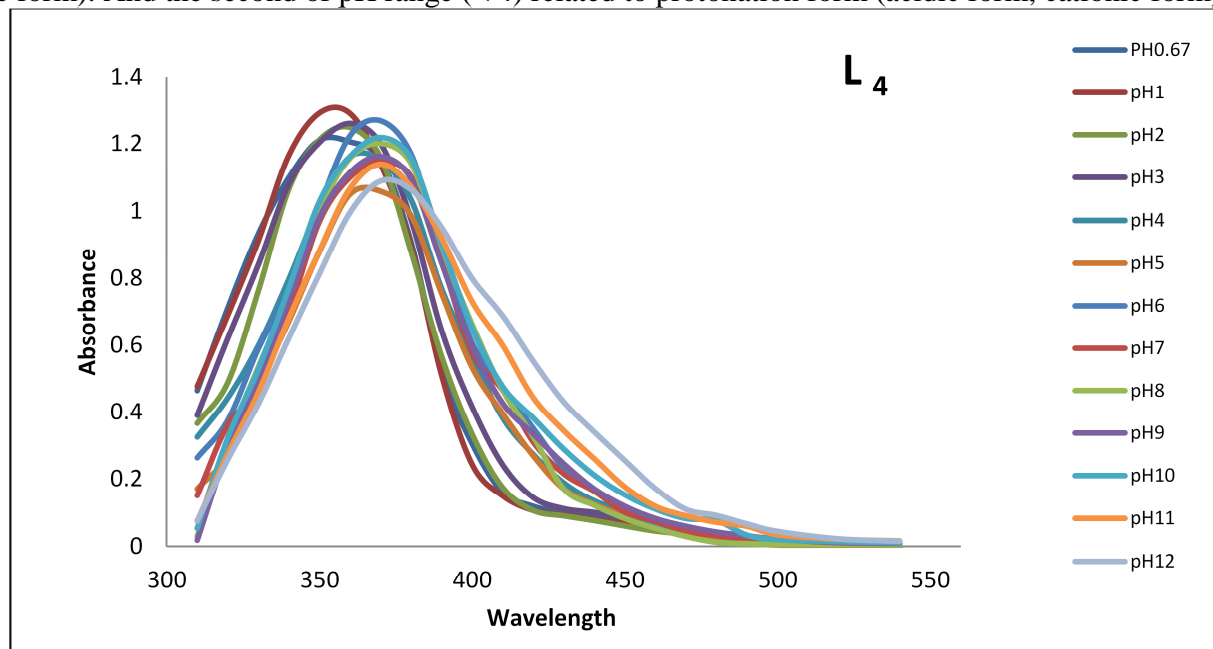


Figure No.5: The electronic spectra of L_3 at different pH values

The ionization and protonation constants were calculated (Table No.3) by the aid of Figures No.2-5, the absorbance - pH curves were plotted (Figure No.6). From Absorbance - pH curve (Figure No.6 for L₁ - L₄) and by the aid of height method the pK values were obtained by the relation²⁰:

$$pK = pH \text{ (at } A1/2 \text{)}$$

Where,

$$A1/2 = (AL + A_{min.}) / 2$$

Where AL and A_{min.} are limiting and minimum absorbance's respectively.

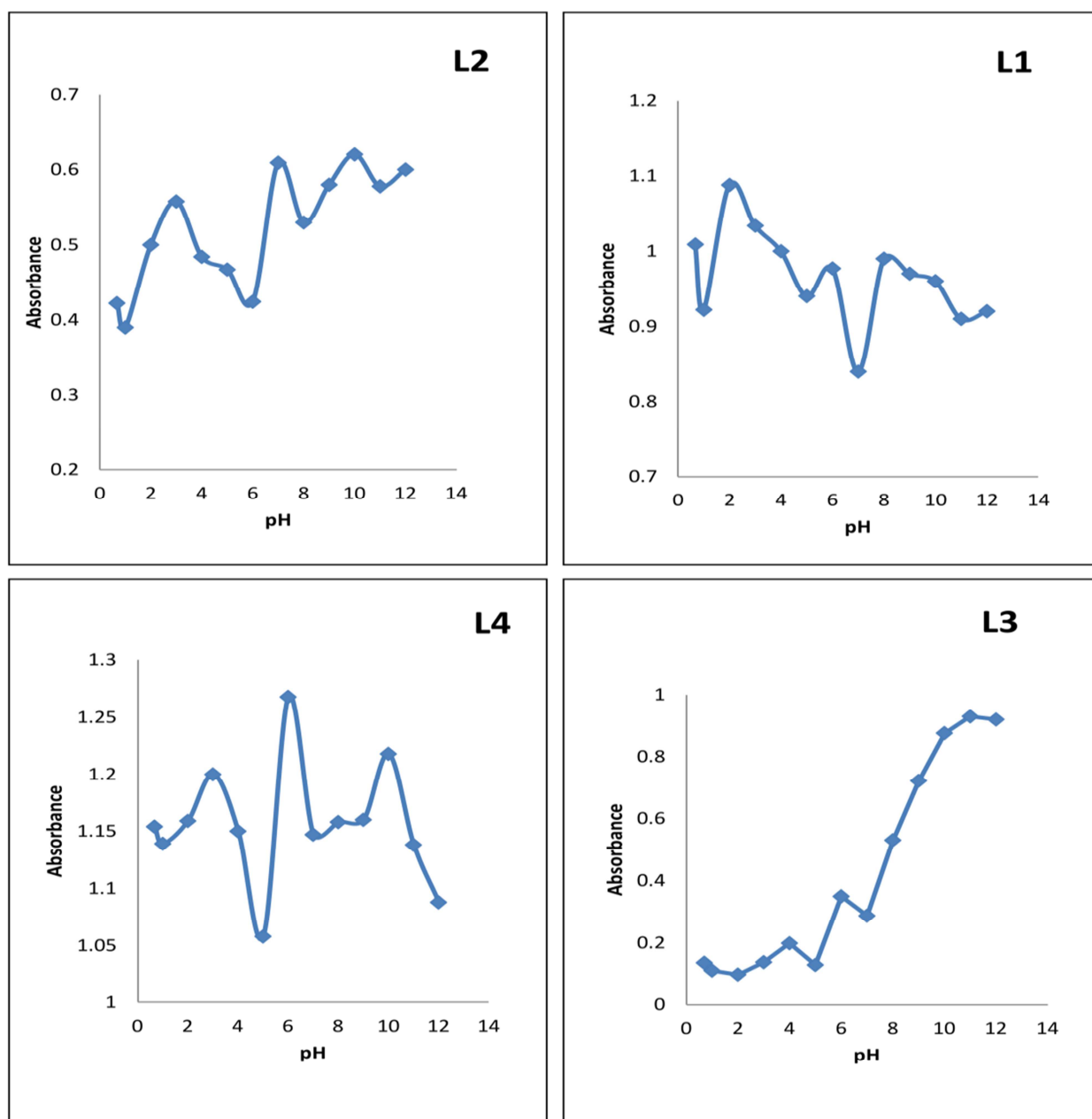
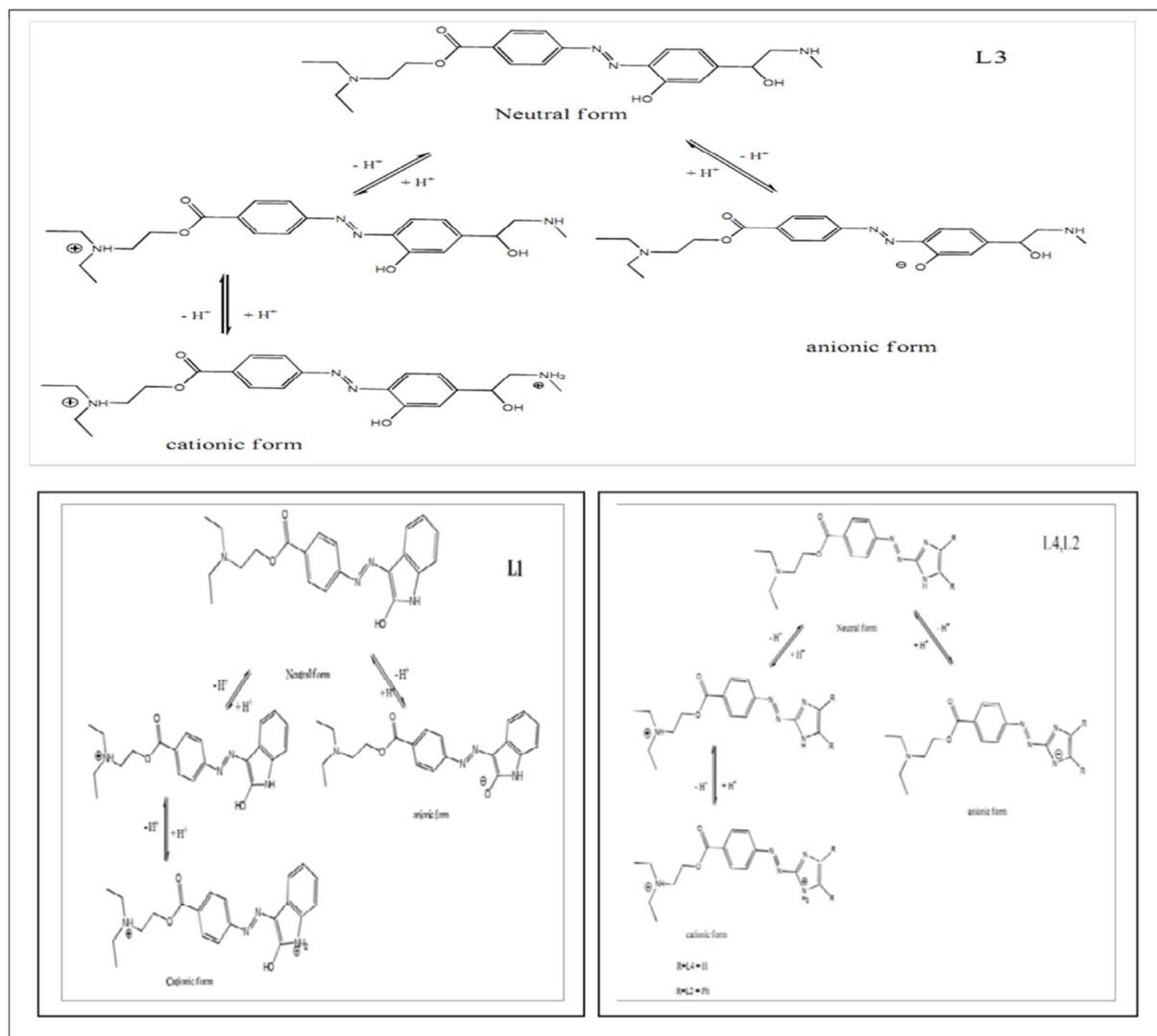


Figure No.6: pH – Absorbance curve for dyes L₁–L₄

From Figures No.6 the mechanism of the ionization and protonation of each dye can be suggested (Schemes No.2).



Schemes No.2

CONCLUSION

Were prepared and identification of four new compounds azo and studied in solutions of different pH and ionization constants account protonation.

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CONFLICT OF INTEREST

We declare that we have no conflict of interest.

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