Synthesis and Spectroanalytical Studies of a New Azodye Derived From 2-Amino-6-ethoxybenzothiazole and 4-Chloro-3,5-dimethylphenol   and its Complexes With Fe (III) Ion

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Abstract

This study involves the synthesis of new azodye, derived from 2-Amino-6-ethoxybenzothiazole and 4-Chloro-3,5-dimethylphenol . The characterization of dye has been described by C.H.N. The TG , IR and Visible. spectroscopic techniques .The acid-base properties were studied at different pH values . The ionization and protonation constants of dye were determined. Solvents effects were also studied at different solvents polarities . The optimum conditions of this formation of complex with Fe(III) were investigated . The analytical applications of this azodye , were studied like; using it as acid-base indicator , and for the determination of nitrite ions .

Introduction

Most of azodyes are weak acids or weak bases of very important class of chemical compounds containing a heterocyclic moieties which have attracted the attention of many researchers in recent years [1]. They have high soluble in common solvents and highly colored (from yellow to blue , due to conjugated π system) . They used as dyes and pigments for long years [2] due to their stable adsorption on surface cotton or wool textiles. 2-Amino-6-ethoxybenzothiazole azo dyes with dicarboximidoethyl-sulphonephthyl group are useful as dyes for hydrophobic textiles materials [3]   , furthermore they have been studied widely for their excellent thermal and optical properties in applications. Recently azo metal chelate have also attracted on attention due to their interesting electronic and geometric features [4].They were used as good reagents for the extraction and spectrophotometric determination of metal ions [5-9] . Most of azodyes have acid – base properties with presence of a fixed isobestic points (which represent the number of equilibriums in such azodye) , for this reason they are used as acid – base indicators [10-12] for their sensitivity toward acid and base substances . Some of them can be used as metallochromic indicator , antipyretic reagents and inhibitors corrosion. The solvents of different polarities may be affected on the absorption spectra of π – conjugated compounds , exhibit n → π^* transition as well as $\pi \rightarrow \pi^*$ transition causing blue or red shifts. The present work involves the synthesis of new azodye derived from 2-Amino-6- ethoxybenzothiazole and 4-Chloro-3,5-dimethylphenol . Spectrophotometric studied on the dye were carried out like acid-base properties at different pH values , solvent effect of polar and non-polar solvents , the ability of using it as acid – base indicator and its complex with iron (III).

Experimental

Double distilled water , solvents (for spectral use) and all chemicals of highest purity were used .

Apparatus and materials

Visible absorption spectra were recorded by using PD-303 UV.,V. spectrophotometer , FT-IR-8400S spectrophotometer (Shimadzw) College of 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. and TG analysis at Polymer & Petrochemical Institute-Thermal Analysis (Iran) METER (STAR SW 10).

Synthesis of azodye reagent

The azodye reagent (**L**) (M.Wt. = 362) was prepared by coupling 0.02 mole of diazonium salt of 2-amino-6-ethoxybenzothiazole (M.wt.194.3) with alkaline solution of 0.02 mole of 4-chloro-3,5-dimethylphenol (M.wt. 156.6) at 0° C ,then converting the prepared dye from sodium salt into hydrogen form by aid of dil. HCl . The dye was purified by recrystallization from aqueous methanol . The purity of the prepared dye was checked via thin layer chromatography and melting point .

Solutions

- 1 x 10^{-2} M stock solution of azodye was prepared by dissolving 0.1810 g. and complete the volume to 50 ml absolute ethanol .
- 1000 ppm of nitrite solution , by dissolving 0.15g. of $NaNO_2$ in dil. Water and complete to 100 ml .
- 0.002 mole of 2-amino-6-ethoxybenzothiazole in 0.2 M HCl (complete to 50 ml)
- 0.002 mole of 4-chloro-3,5-dimethylphenol in 0.3 M NaOH (complete to 50 ml)

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-1 x 10^{-2} M stock solution of nitrate salts of Zn(II),Co(II),Cu(II),Sm(III),Fe(III) and V(III) ions

- Universal (pH_{2-12}) and Acetate ($pH_{1,1.4}$) buffer solutions [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 (2 – 12) for dye concentration 1.4 x 10^{-3} 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 constants were calculated.

- For acid – base titrations, visual and spectral titrations for HCl vs. NaOH were done in concentration range of azodye 0.8 – 1.6 x 10^{-3} M at λ_{max} the absorbance values were measured at wavelength of (350-580 nm.) .

- For solvent effect studies, a series of solutions of azodye concentration 1.4 x 10^{-3} M were prepared with Acetone , Chloroform , Cyclohexane , 1,4-Dioxane , DMF , DMSO , Ethanol , Methanol , THF and Water , the absorbance of these solutions were recorded at range of (350 – 580 nm.) using cell of 1cm. length .

- For nitrite determination, a series of solutions of (100 – 800 ppm) nitrite , add 1 ml of (0.002 mole solution of 2-Amino-6-ethoxybenzothiazole in 0.2 M HCl) ,to 1ml of (0.002 mole solution of 4-Chloro-3,5-dimethylphenol in 0.3 M NaOH) then complete to a volume of 5 ml with distilled water and measure the absorbance at λ_{max} (420nm.) of each solution using mixture of amine and nitrite as blank solution.

– For complex formation, the absorbance of series solutions of 0.001M of each dye and metal ions (Zn(II),Co(II),Cu(II),Sm(III),Fe(III) and V(III)) were measured at wavelength range of 360 – 530 nm.

Results and Discussion

Some of physical and chemical properties of prepared dye were illustrated in Table(1) . The R_f value indicates the similarity of affinity of dye to eluant as a result of its containing hydroxyl group.
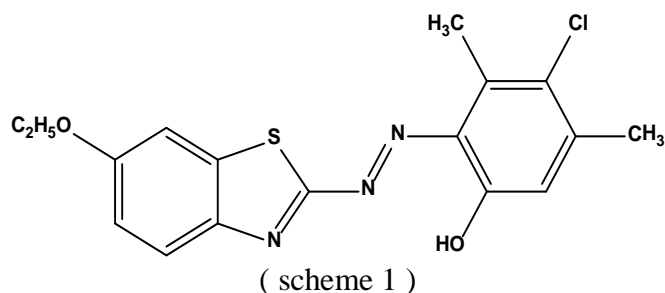
Identification of the prepared dye

Elemental-Analysis

Table (2) shows the elemental analysis of prepared dye, which gives good results for the suggested dye formula .
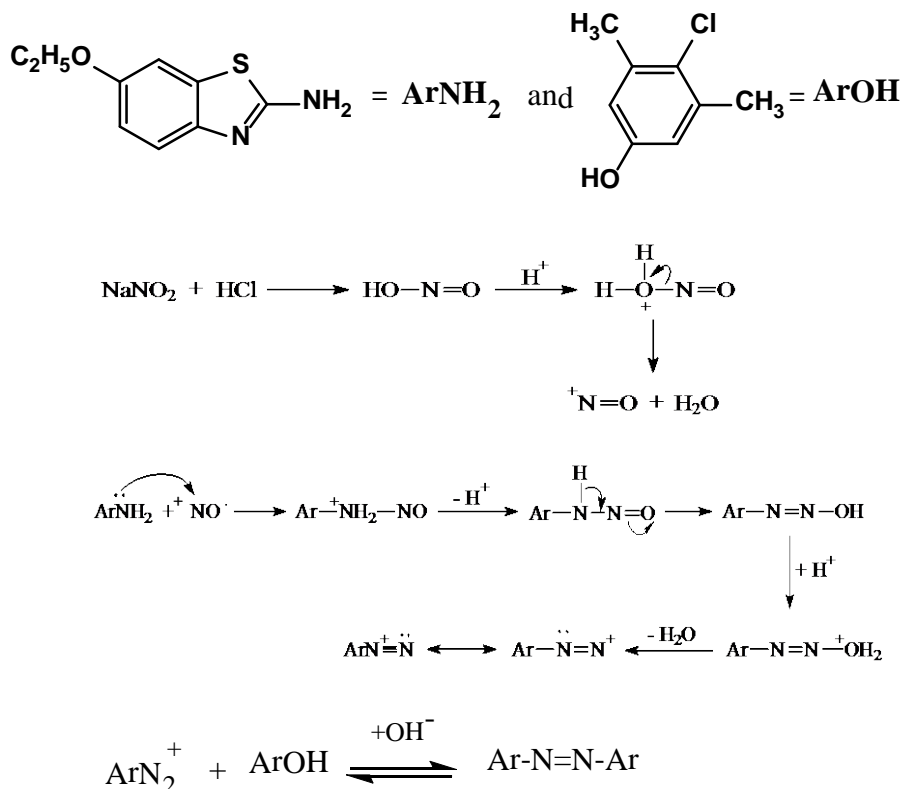
IR Analysis

Table (3) shows the famous IR frequencies of important bands of functional groups frequencies as seen in Fig. (1) .
According to the above analysis (Tables 2 & 3), data show the dye having this chemical structure (scheme 1) :

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(scheme 1)

The mechanism coupling reaction is :

$$NaNO_2 + HCl \longrightarrow HO-N=O \xrightarrow{H^+} H-\overset{H}{\underset{+}{O}}-N=O$$

$$\downarrow$$

$$^+N=O + H_2O$$

$$ArNH_2 + ^+NO^- \longrightarrow Ar-^+NH_2-NO \xrightarrow{-H^+} Ar-\overset{H}{N}-N=O \longrightarrow Ar-N=N-OH$$

$$\downarrow +H^+$$

$$Ar\overset{+}{N}=\overset{..}{N} \longleftrightarrow Ar-\overset{..}{N}=N^+ \xleftarrow{-H_2O} Ar-N=N-^+OH_2$$

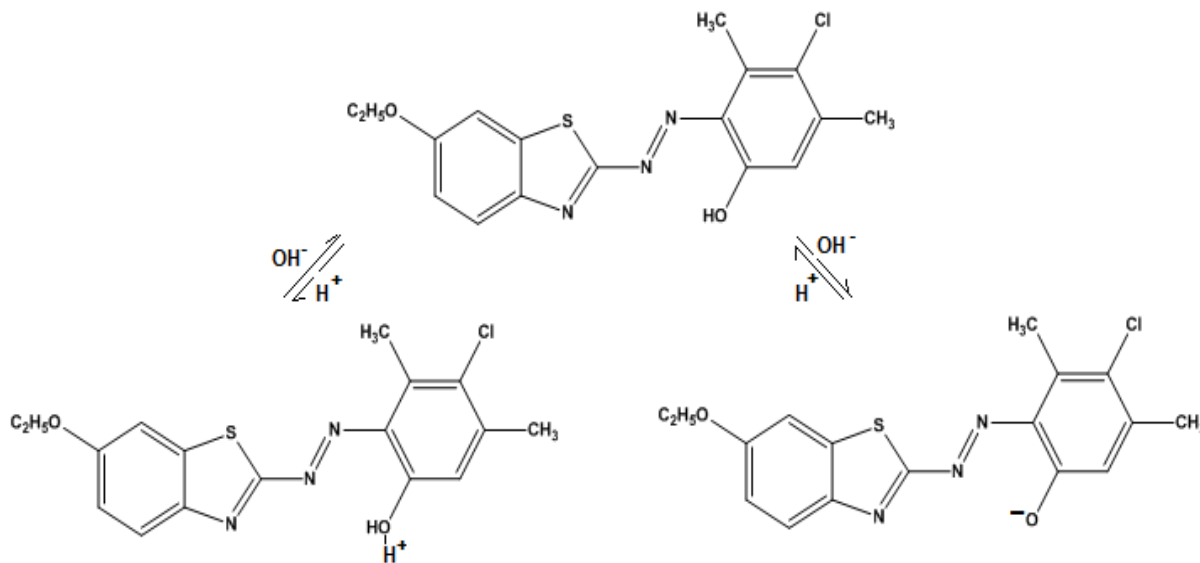$$ArN_2^+ + ArOH \underset{}{\overset{+OH^-}{\rightleftharpoons}} Ar-N=N-Ar$$

Thermal analysis

From Fig.(2) , it was found that dye is stable up to 150 ^oC , and about 95% losing in weight and converted to gases (like CO_2 .CO and nitrogen and sulpher oxides) , remaining only a few of carbon .

Acid-Base properties

The absorption spectra of 1.4×10^{-3} M solution of dye of varying pH values (2– 12) were represented graphically (Fig. 3) . The spectra characterized two maximal bands at 410 nm. in pH range (2 - 7) and 510 nm. in range of (9 – 12). The first due to the absorption of the protonated form of   hydroxyl group (acidic form , cationic form) liable to exist in acid medium and the second is more intense bands due to ionized form of hydroxyl group (basic form , anionic form) except for at pH 8 value there are two bands at 420 and 510 nm. (Fig.3) . The spectra were characterized by the presence of common isobestic point at 450 nm. due to the ionization of dye in acidic and basic medium .
The suggested mechanism of protonation and ionization was shown in scheme (2)

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(scheme 2)

From Absorbance – pH curve (Fig. 4) and by the aid of height method the pK values were obtained by the relation :

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

$A_{1/2} = (A_l + A_{min.}) / 2$

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

So the protonation (pK_p) and ionization (pK_a) constants were found to be 4.11 and 8.23 respectively .

Band assignments and solvent effects

Fig. (5) shows the spectra of dye with strong bands λ_{max} in the range of (415 – 430nm.) for all solvents. THF. It was found a very weak broad bands at λ_{max} at 480 except for DMSO and Water at 500 and 520 nm. respectively. The band moves to shorter wavelength (blue shift) due to $n \rightarrow \pi^{*}$ transition while to the longer wavelength (red shift) with $\pi \rightarrow \pi^{*}$ transition (in the range of 460 to 585 nm.) , because of the polarities of the ground state (G.S) and excited state (E.S) . Thus for solvent of increasing polarity , the energy of the E.S (π^{*}) will decrease relative to the that of the G.S (π) whereas with blue shift the non bonding electrons having affinity to hydrogen bonding more than bonding with π electrons, so the n energy level will decrease more than π^{*} decreasing and the $n \rightarrow \pi^{*}$ transition energy be more in the presence of polar solvent [13] . The absorption spectra in various solvents are influenced by salvation and / or dielectric effects of solvents. To verify whether the band shift (Δv) is due to change in salvation energy or pure dielectric effects , the Gati and Szalay was used ;

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

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

The plot of f (D) = [2(D-1) / (2D+1)]) against the λ_{max} (Table 4) gives more or less linear relation with solvents of moderate polarities (Fig. 6) 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.

Applications of the azodye

1- As indicator

Strong acid (HCl) with Strong base (NaOH)

HCl and NaOH were standardized visually by recommended procedure [14] ,they found to be 0.098 and 0.097 M respectively .

Visual titrations

Table (5) shows that the best conc. of dye which gives small relative error is in the range of (0.2 – 1.0 x 10^{-3} M) with sharp color change from red (acid medium) to yellow (base medium) at end point.

Spectrophotometric titrations

It was found from spectrophotometric titration of HCl with NaOH a sharp change   in absorbances at end point region (Fig. 7). At concentration range of (0.8 –1.6 x10^{-3} M) of dye , it was found the concentration of NaOH equal to 0.0961 M with relative error of - 0.93 (at 0.8 x 10^{-3} M) . From above results , it was seen that the dye is successfully used as indicator.

2- Determination of nitrite

At λ_{max} = 420 nm. of orange color of the dye, the calibration curve (Beer's law) at varying concentrations of nitrite (50 – 800 ppm) vs. absorbanes was done (Fig. 8) , and from Beer s law Sandel Sensitivity (S) , Molar Absorptivity (ε_{max}) , Specific Absorptivity (a) and Correlation Coefficient (r) were determined (Table 6) . It
was found also Limit of beer s law of 700 ppm. and the value of standard deviation of six measurement (S.D) of 0.0032 .

3-Fe(III)-L complex formation

Fig.(9) shows the electronic spectra of the solutions of 0.001M of each dye and metal ions (Zn(II),Co(II),Cu(II),Sm(III),Fe(III) and V(III)), at wavelength range of 360 – 530 nm. It was shown all studied metal ions dose not form a complex with dye (L) expect for Fe(III) which form,(that means they are not interfering with Fe(III)-L complex) .

pH effect on the Fe(III)-L complex

From Fig.(10),shows the pH effect on the formation of Fe(III)-L complex at different pH values (1 – 12) in wavelength range (250 – 310 nm.). It was found that pH_{12} is the suitable pH value for forming the complex because it gives highest absorbance .

So the λ_{max} (at pH_{12}) of the dye and Fe(III)-L complex are 280 nm. and 300 nm. respectively (Fig. 11) using the dye with pH_{12} as blank solution .

It was found from Fig.(11) shift in wavelength λ_{max} (Red shift) from 280 to 300 nm. due to forming of complex

Time effect on the stability of Fe(III)-L complex

It was found from Fig. (12) the absorbances are constant up to 90 min. that means the complex is of highest stability , the absorbance decreases slowly with time increased .

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Table (1) Physical and Chemical properties of the dye

Empirical formula	M.Wt.	Color	% Yield	^{o}C M.P.
$C_{17}H_{16}ClN_3O_2S$	362	Orange	85	115.4

Table (2) : C.H.N analysis of the dye

C %		H %		N %	
Calculated	Found	Calculated	Found	Calculated	Found
56.35	56.92	4.42	4.34	11.60	11.49

Table (3) : The important IR- bands of the dye

Groups	ν cm^{-1}	Groups	ν cm^{-1}	Groups	ν cm^{-1}
N=N	1465.9s	C=C	1412w	C-O	1170s
OH	3319.5sb	C-N	1026.1m	C=N	1587.4s
N-H	3300.2w	C-Cl	638.5s	C-H	2964.6

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Table (4) : The f (D) and λ$_{max}$ values of using solvents if different polarities

Solvent	D	f (D)	λ$_{max}$ (nm.)
Ethanol	24.55	0.940	420
Acetone	21	0.930	420
Chloroform	4.81	0.718	420
water	80	0.981	420
Cyclohexane	2.02	0.405	420
Methanol	33	0.955	420
1,4-Dioxane	2.3	0.464	420
THF	7.5	0.813	420
DMSO	46.7	0.968	420
DMF	38	0.961	420

Table (5) : The effect of concentration of dye

[D] , M	[NaOH] , M	Relative error %
0.2×10^{-3}	0.092	- 5.15
0.4×10^{-3}	0.094	- 3.03
0.6×10^{-3}	0.096	- 1.03
0.8×10^{-3}	0.098	1.03
1.0×10^{-3}	0.098	1.03

Table (6): were determined from Beers law.

S μg. / cm^{-2}	ε l.mol^{-1}.cm^{-1}	a ml.g^{-1}.cm^{-1}	r	S.D	Limit of beer s law (ppm)
0.0191	2400	0.0522	0.9986	0.0032	700
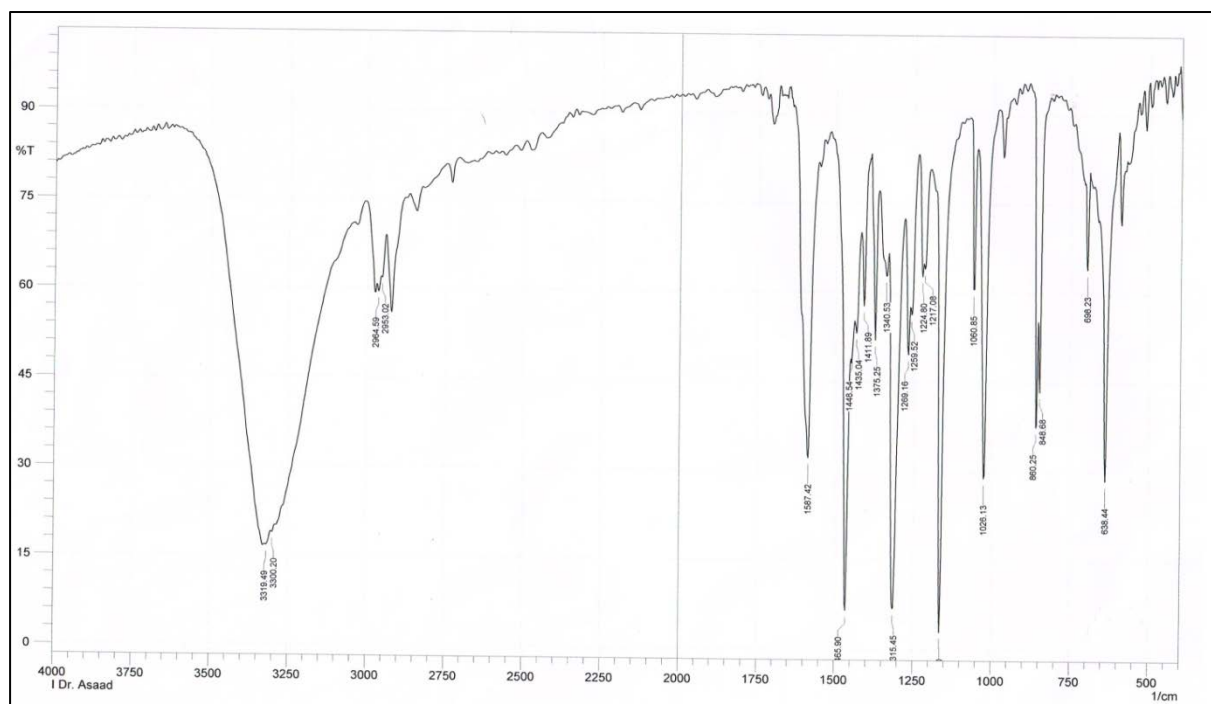
Fig. (1) : The IR – spectrum of the dye (L)

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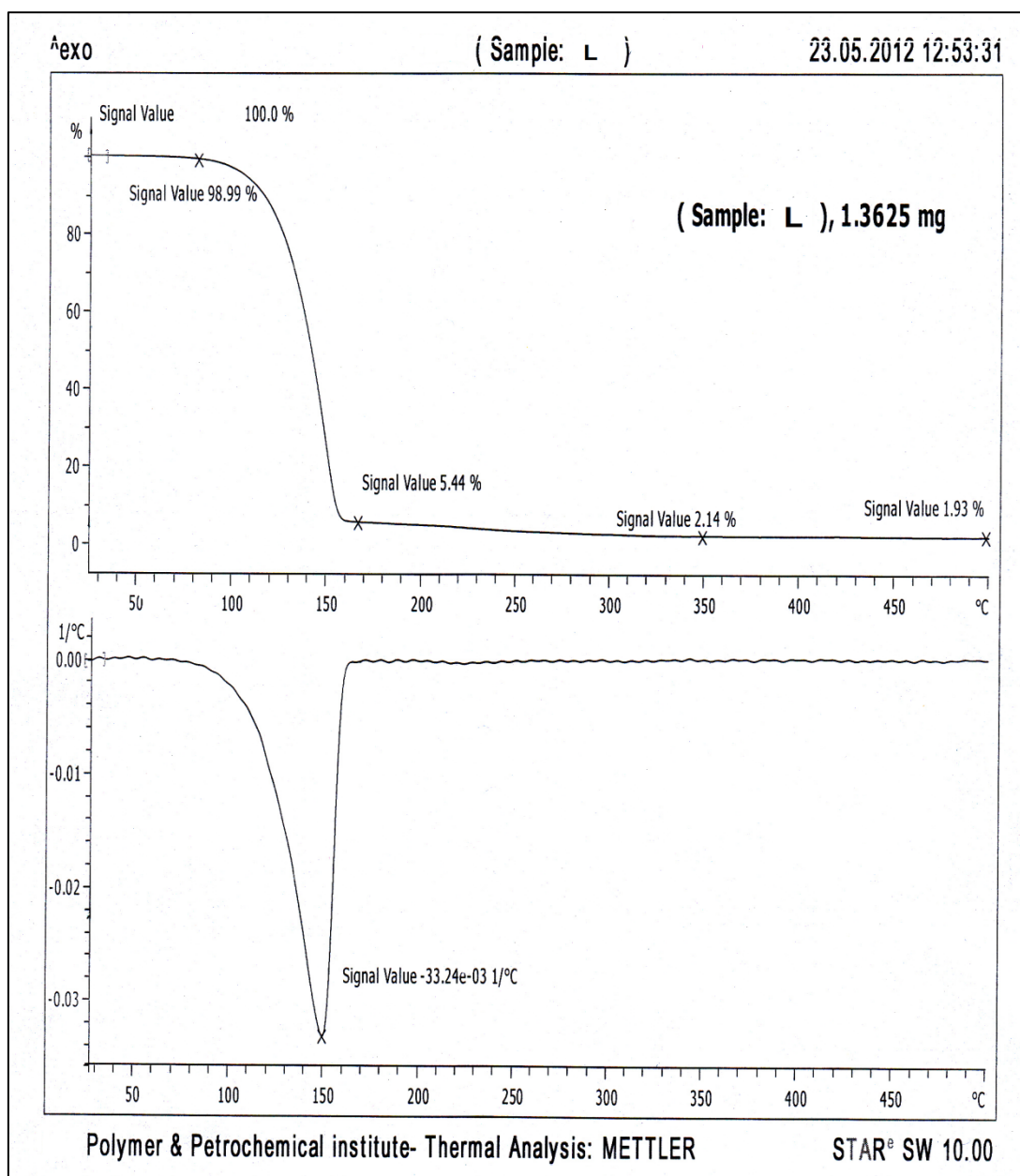
Fig.(2) : The TG analysis of the dye

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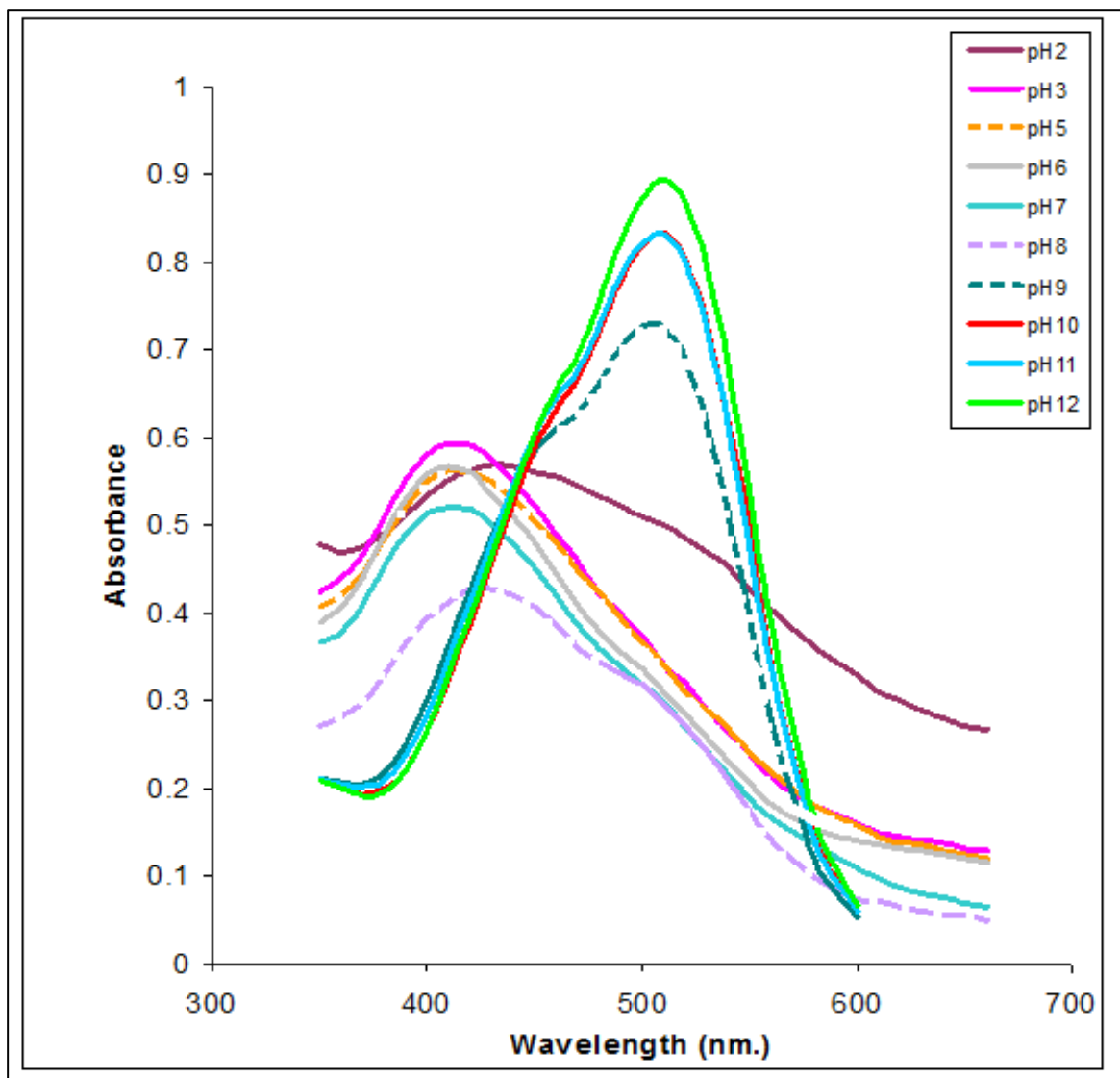
Fig. (3) : Spectra of dye at different pH values
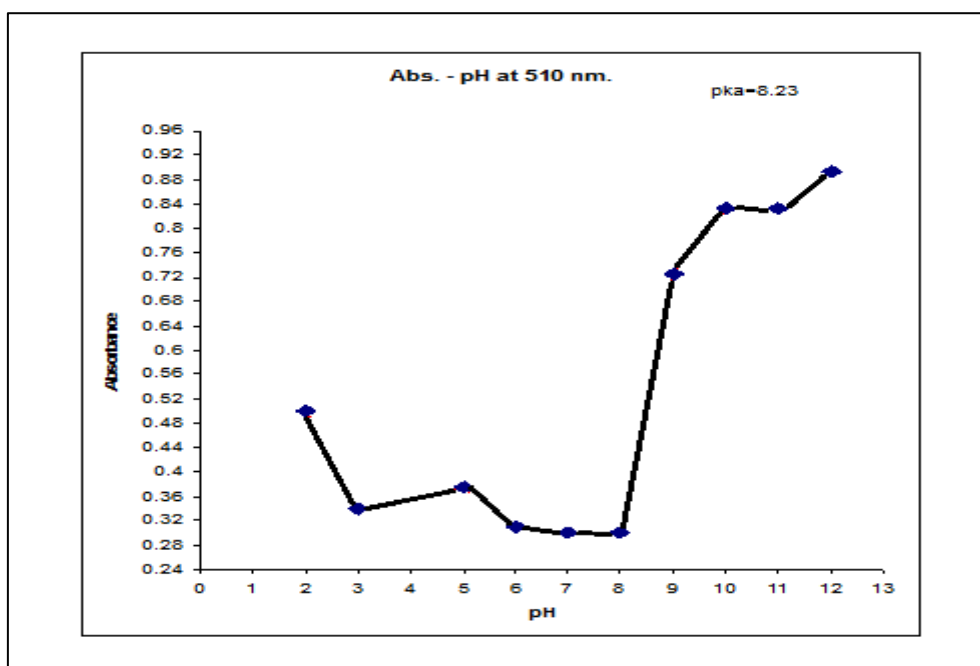
Fig. (4) : Absorbance – pH curve of dye at λ_{max} = 510 nm.
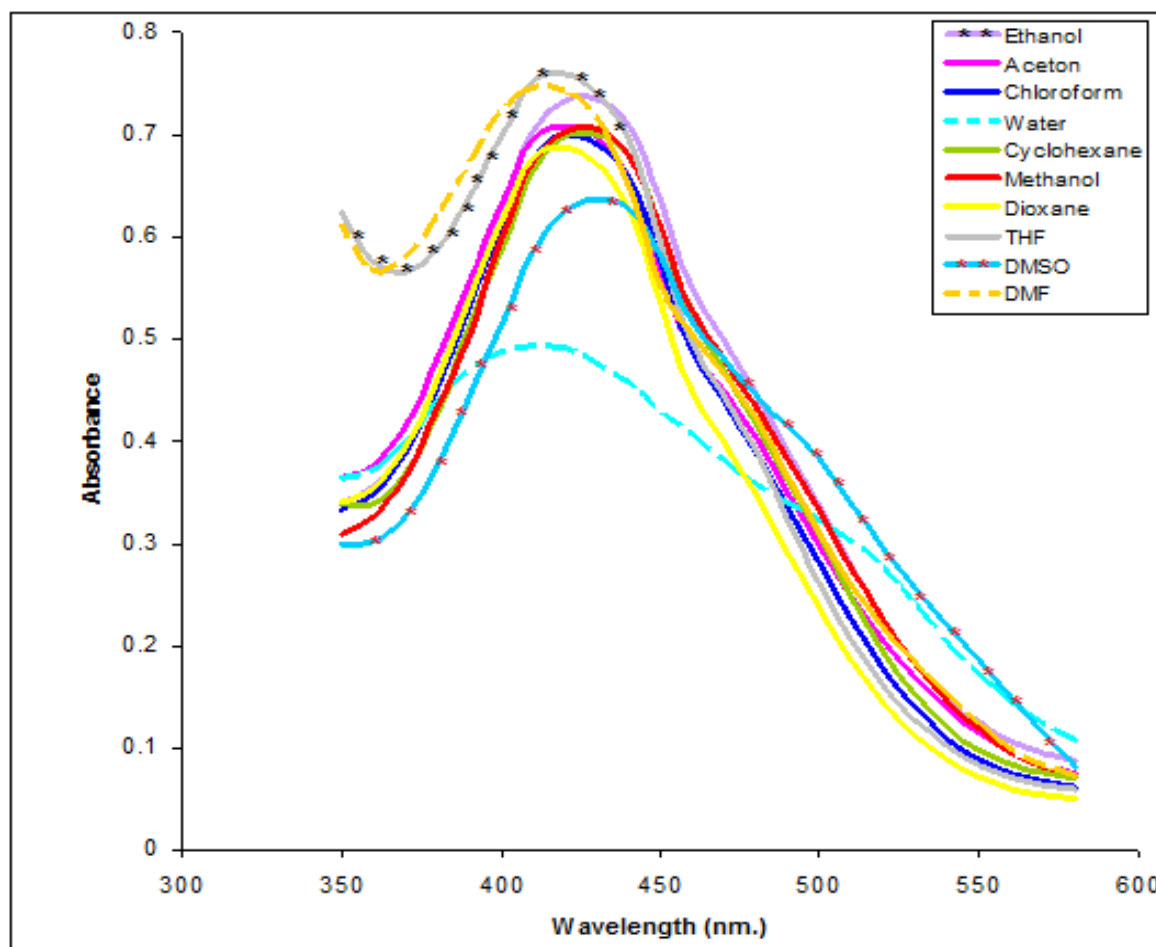
Fig. (5) : The spectra of the dye at different solvents

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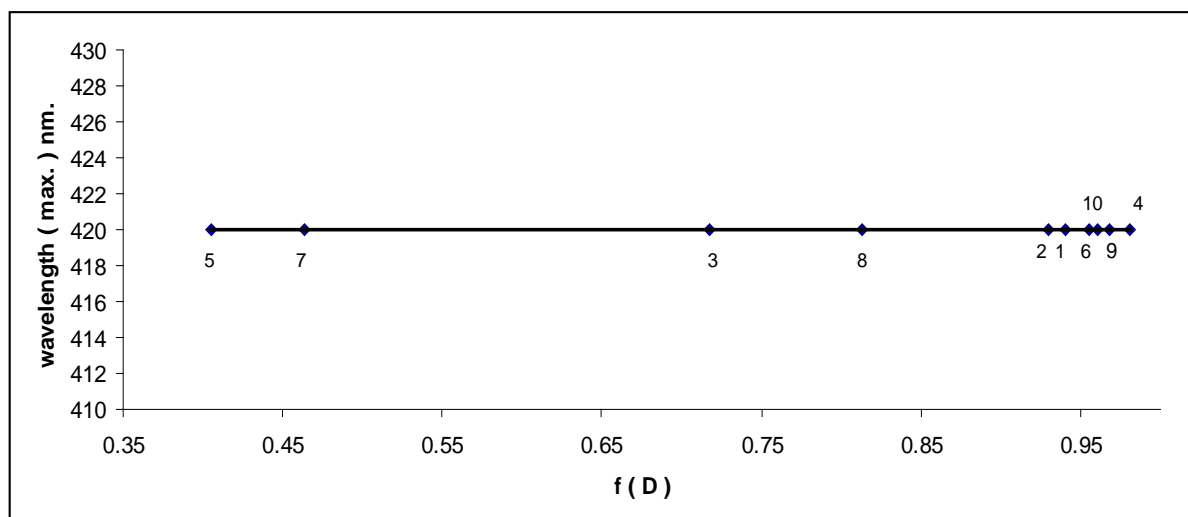
Fig. (6) : plot of λ_{max} against the function f (D) , where : 1= ethanol, 2 = acetone, 3 = chloroform, 4 = water, 5 = cyclohexane, 6 = methanol, 7= 1,4-dioxane, 8= THF, 9 = DMSO and 10= DMF.
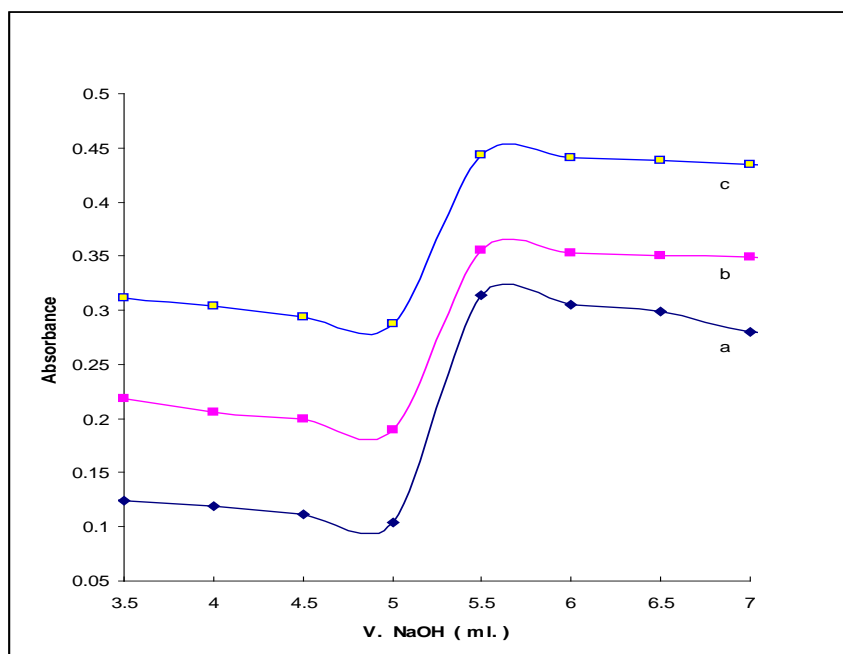

Fig. (7) : spectrophotometric titration curves of concentrations of dye : a = 0.8 x 10^{-3}, b = 1.2 x 10^{-3} and c = 1.6 x 10^{-3} M

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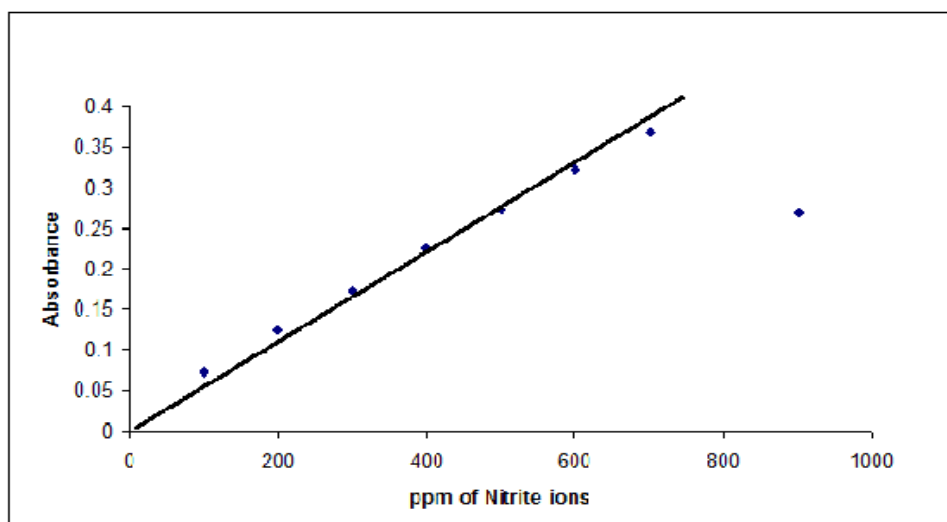
Fig.(8) : The calibration curve of nitrite ion
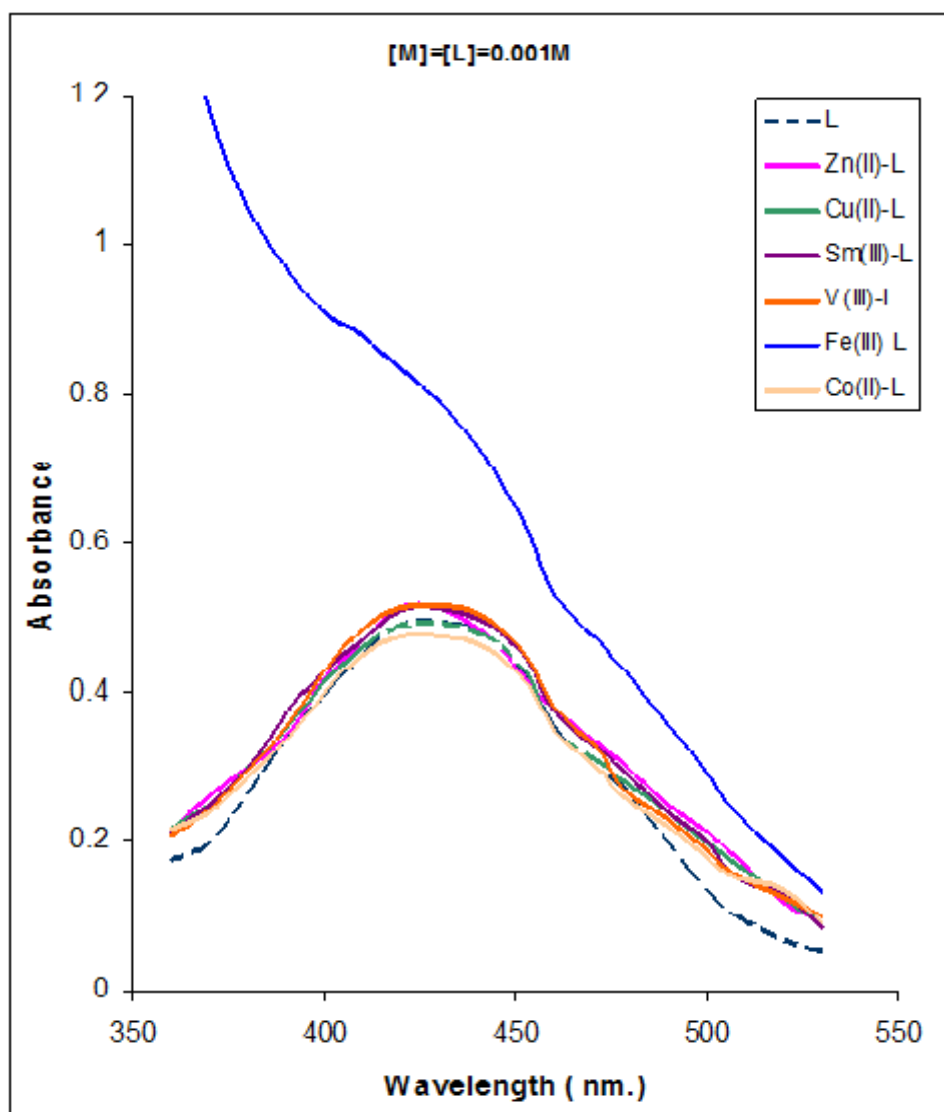
Fig. (9) : The electronic spectra of dye complex

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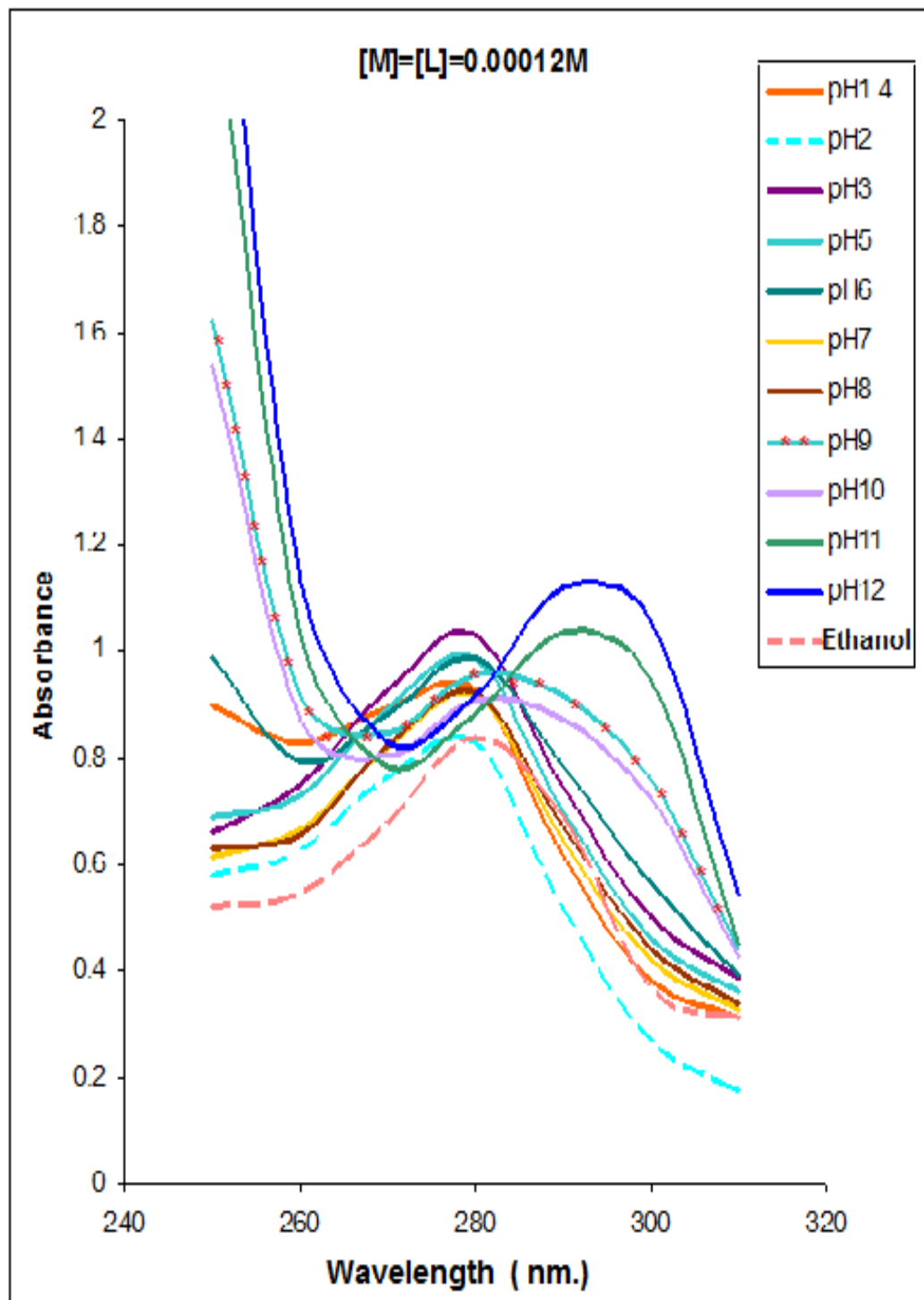
Fig.(10): The pH effect on the electronic spectra of Fe(III)-L complex

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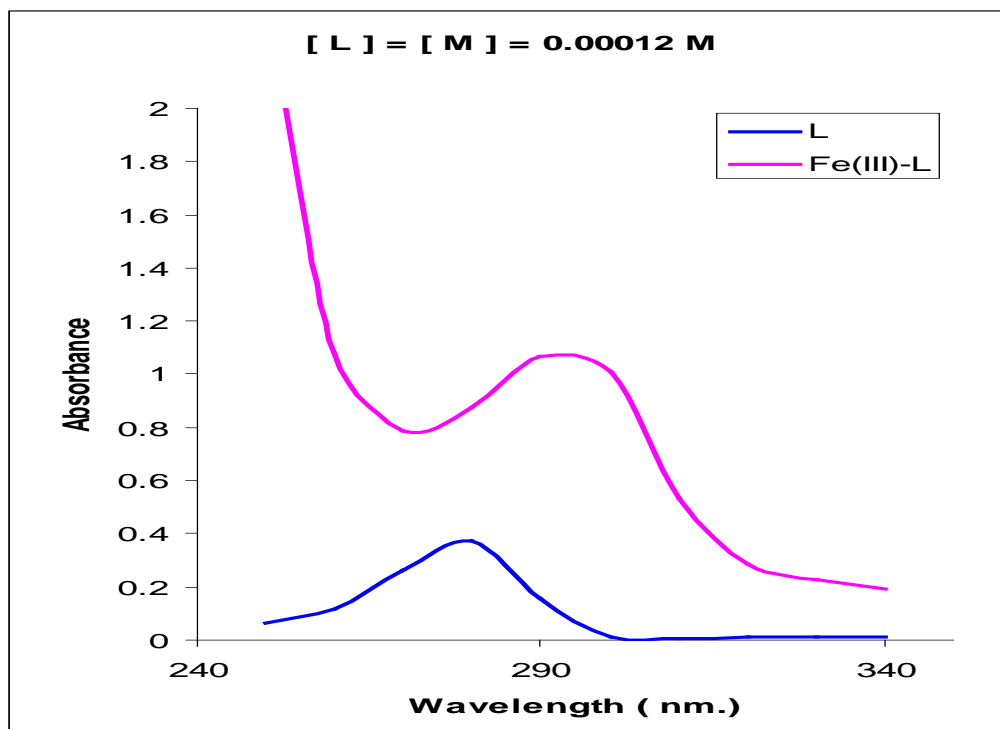
[L] = [M] = 0.00012 M

at pH$_{12}$ Fig. (11) : the electronic spectra of dye and its complex
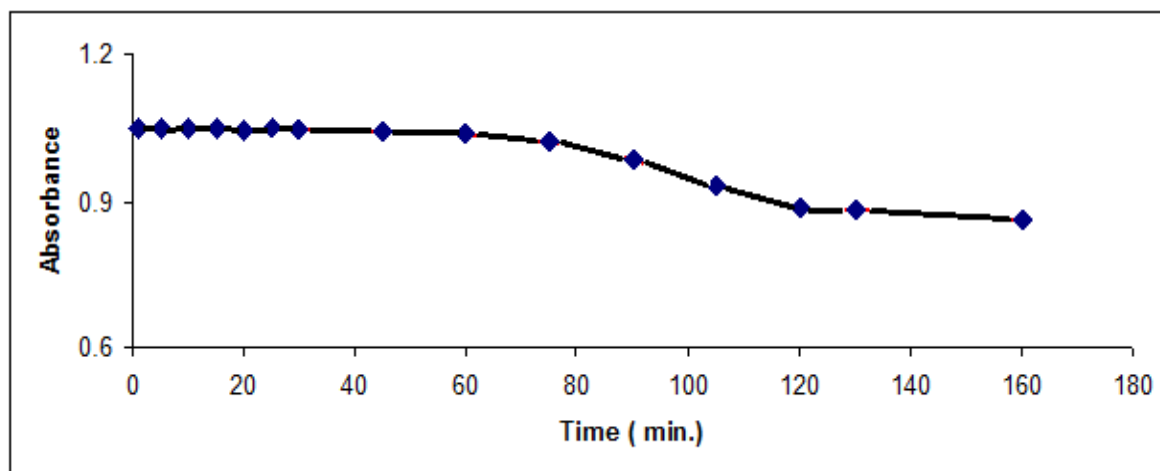
Fig. (12) : Time effect on the stability formation complex at λ_{max} (at pH$_{12}$) ,
[L] = [Fe^{3+}] = 0.00012 M

تخليق ودراسات طيفيه ـ تحليليه لصبغه ازويه جديده مشتقة من 2- امينو-6- ايثوكسي بنزوثايوزول و 4- كلورو-3,5-داي مثيل فينول ومعقدها مع ايون الحديد الثلاثي

اسعد عبود علي

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الخلاصة

هذه الدراسه تتضمن تخليق لصبغه ازويه جديده مشتقه من 2- امينو-6-ايثوكسي بنزوثايوزول و 4- كلورو-3,5-داي مثيل فينول . تشخيص هذه الصبغه تمت بواسطة التحليل العنصري الدقيق و التحليل الحراري و تقنية مطيافية اشعة تحت الحمراء و الاشعه المرئيه . كما ودرست الصفات الحامضيه ـ القاعديه وتاثير قيمة الاس الهيدروجيني وتعيين ثوابت البرتنه والتاين لها . وتم ايضا دراسة تاثير المذيبات مختلفة القطبيه . وثبتت الظروف المثلى لتكوين معقد هذه الصبغه مع الحديد الثلاثي .ودرست تطبيقات هذه الصبغه مثلا باستخدامها كدليل حامضي ـ قاعديوتقدير ايونات النتريت .

الكلمات المفتاحية : آزودات ، ثوابت ايون الهيدروجين الموجب والتاين ،دراسات طيفية