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SYNTHESIS NOVEL LIGENDS DERIVED FROM SULFADRUGS AND CHROMOTROPIC ACID AND THEIR COMPLEXES WITH OXOVANADIUM (IV)

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ABSTRACT

Three novel azo dyes ligands (L_1, L_2 and L_3) derived from sulfanilamide, sulfamethaxazole and sulfadiazine with chromotrpic acid, were synthesized. Characterization of these dyes have been done on the basis of elemental analysis, FT-IR. The work involves a study of acid – base properties of ldyes (as ligand) at different pH values. The ionization and protonation constants were also calculated. The complexes of L_1 – L_3 with Oxovanadium (IV) were studied and prepared. These complexes have been concluded after fixing the optimum conditions (The effects of time, pH and sequence of addition). The spectra of the complexes solutions have been studied for a range of concentrations which Lambert – Beer s law were obeyed. The stoichiometry of the complexes has been found to be 1:2 (metal : ligand). The overall stability constants were determined by the corresponding solutions method. The ligand were screened for their antimicrobial activity.

KEY WORD: Azo compounds; Sulfa Drugs, Oxovanadium (IV) complexes, Spectroscopy and Biological activity.

INTRODUCTION

Azo compounds are a very important class of chemical compounds receiving attention in scientific research. They are highly colored and have been used as dyes and pigments for a long time. Furthermore, they have been studied widely because of their excellent thermal and optical properties in applications such as optical recording medium, toner, ink-jet printing, and oil-soluble lightfast dyes. Recently, azo metal chelates have also attracted increasing attention due to their interesting electronic and geometrical features in connection with their application for molecular memory storage, nonlinear optical elements and printing systems.[1] Azo derivatives complex combinations have been widely used as dyes for synthetic polyamide supports and as pigments.[2] azo derivatives and their metal complexes are very important pigments for synthetic leather and vinyl polymers. On the other hand, azo compounds are known to be involved in a number of biological reactions, such as inhibition of DNA, RNA, and protein synthesis, nitrogen fixation, and carcinogenesis.[3,4] Furthermore metal–azo complex dyes are used in the recording layer of DVD-R (Digital Versatile Disc-Recordable) discs . In comparison with the dyes themselves, metal–azo dyes are more light stable, allow for easier control of the wavelength by selection of the appropriate substituent groups and have good thermal stability.[5,6] Because of the good thermal stability of azo compounds and the ease with which the absorption band may be tuned by varying the substituent, one of the many applications of azo compounds is in optical data storage.[7,8] The sulfoderivatives azo dyes were studied, for example with 1-Hydroxy-2- naphthoic acid[9] Synthesis of a series of novel azo-sulfa drugs as 5-imino-3-methyl-1-phenyl-δ^2-pyrazolin-4-dithiocarbamy-azo dyes are described.[10] azo-sulfa drugs of piperidino-, morpholino-, mono-, and bis-piperazino-N-dithiocarbamyl-azo dyes are synthesiezed.[11] Some new azo sulfa drugs 3-cyano-4,6-diphenyl-1-[4-(*N*-substituted)sulfamyl]phenylazo-2-pyridinone dyes and 3-cyano-4,6-diphenyl-1-[4-(*N*-substituted)sulfamyl]phenylazo-2-pyridinethione dyes were synthesized.[12] azo dyes with high chemotherapeutic properties azo dyes were prepared for studies, by the diazotization of sulfa drugs and related amines.[13]

Chromotropic acid is a good reagent for forming azodyes indicatores like arseazo I and aresazo III.[14] Chromotropic acid is is used for preparing p-x-phenylazo chromotropic acid (X= Cl , NO_2, and I).[15]

Coordination of vanadium has acquired renewed interest since the discovery of vanadium in organisms such as certain ascidians and amanita mushrooms and as a constituent of the cofactors in vanadate-dependent haloperoxidases and vanadium itroginase.[16] The potential of vanadium (V) complexes as antiamoebic agents has thus far only been marginally explored.[17] Oxovanadium (IV) complexes of 1-(2-pyridylazo)-2-naphthol (PAN) and 4-(2-pyridylazo) resorcinol (PAR) have been prepared.[18] A novel series of oxovanadium(IV) monomeric and polymeric complexes with 5-(4′ derivatives phenylazo)-8-hydroxy-7-quinolinecarboxaldehyde were prepared.[19]

The present work aimed chiefly to throw more light on the synthesis and characterization a novel three azo dyes (ligands L_1, L_2 and L_3) derived from sulfanilamide, sulfamethaxazole and sulfadiazine with chromotrpic acid. Study acid – base properties of ligands at different pH values. The coordination behavior of these azo compounds towards VO (1V) ion. is reported using different analytical tools.

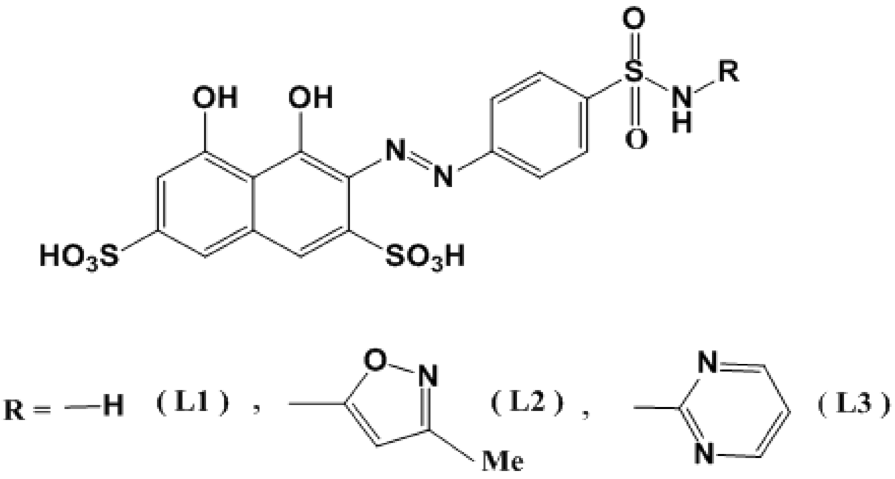
EXPERIMENTAL

All the reagents and solvents were of reagent-grad quality, The progress of reaction was monitored by TLC using silica gel coated plate sand spots were visualized under UV radiation. Infrared spectra (in K Br pellets) were recorded on FT.IR-8400S shimadzu, Melting points were determined on melting point apparatus , Element analysis (C.H.N.) were carried out by Perkin element 2400 clement analysis and UV/V is absorption spectra studies of the dyes were recorded using Perkin Elmer Lampda EZ 210 UV/V Spectrophotometer. The pH measurements were made with pH-Meter (H. Jurgons Co. Bremen,L.Puls Munchen15).

Synthesis azodyes ligands[20]

azodyes ligands (sulfanilamide azo chromtropic acid L_1; sulfamethaxazole azo chromtropic acid L_2 and sulfadiazen azo chromtropic acid L_3 **),** were prepared by dissolving 0.004 mole of (sulfanilamaide or sulfamethaxazole or sulfadiazen) with 1.4 ml concentrated HCl and 20 ml distilled water then adding drop by drop with stirring solution of (0.304 g. sodium nitrite in 20 ml distilled water) to form diazonium salt at - 5 ^{o}C temperature. The alkaline solution of 0.004 mole of chromtropic acid in (1.2% w/v. NaOH) was added to the above diazonium salt. Then convert the prepared dye from sodium form into hydrogen form by adding of dilute HCl (keep pH value between 6.5 – 7.5). Filter the precipitate of dyes formed, and purify the dye by recrystallization from methanol and dried at 50.0C in an oven to give azodyes.

By the aid of CHN and IR, the suggested molecular structures of azo compounds were shown in Scheme -1.



Scheme -1

To calculate the ionization and protonation constants for hydroxyl and nitrogen groups, a series of acetate and universal buffer solutions were prepared with different pH values [0.5-12] for each azodyes ligands.[21]

Synthesis of the vanadyl complexes

Vanadyl azodyes complexes were prepared in a similar manner as described.[22] Thus, $VO(Ac)_2$ (0.004 mol) was added to a hot solution of the ligand (0.008 mol) in dichloromethane (70 ml) containing a few drops of triethylamine and the resulting mixture was refluxed for 1 h. A yellow precipitate separated, which was collected by filtration,washed with dichloromethane and diethyl ether, and recrystallized from ethanol /chloroform (1:3 v/v).

RESULTS AND DISCUSSION

The analytical and physical data of the ligands and vanadyl complexes are presented in Table 1. Elemental analysis and continues variation method of the complexes indicate the stoichiometry to be 1 : 2 (metal : ligand).

Table 1: Analytical and physical data of ligand and metal complexes.

Comp	Molecular formula	M.Wt	Color	M.P °C	Elemental Analysis Found (Calc.)			Cond. S cm2 mol^{-1}
					%C	%H	%N	
L_1	$C_{16}H_{13}N_3O_{10}S_3$	503	Orange	283	38.69 (38.17)	2.20 (2.60)	8.81 (8.35)	-
L_2	$C_{20}H_{16}N_4O_{11}S_3$	584	Red	275	41.75 (41.09)	.25 (2.76)	10.15 (9.58)	-

L_3	$C_{20}H_{15}N_5O_{10}S_3$	581	Dark - red	290	41.69 2.27 12.59 (41.31) (2.60) (12.04)	-
C_1	$C_{32}H_{24}N_6O_{21}S_6V$	071	Violet	>300	35.31 2.11 31.11 (35.85) (2.24) (31.37)	24.3
C_2	$C_{40}H_{30}N_8O_{23}S_6V$	1233	Violet	>300	39.04 2.32 30.01 (38.93) (2.43) (29.85)	20.4
C_3	$C_{40}H_{28}N_{10}O_{21}S_6V$	1227	Violet	>300	38.98 2.20 27.55 (39.12) (2.28) (27.38)	6.5

Where C_1 , C_2 & C_3 are L_1-VO^{2+} , L_2-VO^{2+} & L_3-VO^{2+} respectively

As mentioned, the ligands have different coordinating sites. The IR has proven to be, in this particular case, a suitable technique to give enough information to elucidate the way of bonding of the ligands. Thus a detailed interpretation of IR spectra of these and the effect of binding of oxovanadium (IV) ions on the vibration frequencies of the free ligands (Table 2).

Table -2: The I.R spectral data of (KBr disk)

	ν(OH)	*ν*(N=N)	*ν*(O-H)	υ(C = C)	*ν*(V=O)	υ(M–O)	υ (M-N)
L_1	3448 Sh	1436w	1349S	1506 w	970	-------	--------
L_2	3448 Sh	1461w	1343S	1496 s		--------	---------
L_3	3448 Sh	1436w	1347S	1498 s		------	--------
C_1	3500	1425w	---		970	532w	500
C_2	3510	1413w	---		977	560w	470
C_3	3510	1405w	------		970	548w	468

Sh = sharp, m = medium, br = broad, s = small, w = wea

The IR spectral analysis of compounds are in good arrangement (Fig.1) with the synthesis compounds, it show intense bands appearing at (1461-1434 cm^{-1}) these peaks are attributed to (-N=N-) group,abroad hydroxyl peak observed with region 3448 cm-1 the low frequency and these broading have a strong hydrogen bonding (O-H-----N) in solid state.[23] The presence of a sharp band at 11496-1502 cm^{-1} due to to the υ(C-C) (ring) vibrations,) (S=O str.asym.appear at 1264 -1274 cm^{-1}**.** The bands at 755 cm^{-1} for(N-H wag.). The peak appearing in the region 1325-1344 cm^{-1} are attributed to ν(C-N) stretching vibration The band belonging to ν(N-H) stretching vibration is not observed probably due to overlapping with the broad hydroxy peak .The other characteristic peaks of compounds are given in Table (2). These data are in agreement with those previously reported for similar compound.[24,25]

IR spectrum of complexes of oxovanadium (IV)

IR spectrum shows band at 1684 cm^{-1} *ν*(N=N) this has shifted to lower frequency region (10-48 cm^{-1}) in the complexes indicating the participation of azo group in chelation. Another important ligand band, occurring at about 1349 cm−1 due to phenolic-OH, has been found absent in complexes. This indicates the deprotonation of phenolic-OH on coordination with metal. A band at 1202 cm^{-1} due to phenolic C–O shifts to higher side (+10 cm^{-1}) in the complexes. The appearance of broad bands at 3355 and 3385 cm^{-1} in the spectra of complexes has been assigned to associate water molecules.[26] A medium intensity band at 655 cm−1 in complex is assignable to rocking mode due to water molecule. Some new bands of weaker intensity at (532-560 cm^{-1}) and (468-500 cm^{-1}), in the complexes, give inferences about *v*(M–O) and *v*(M–N) bonding. The characteristic band at 972-977 cm^{-1} has been assigned to *v*(V=O) vibrations .

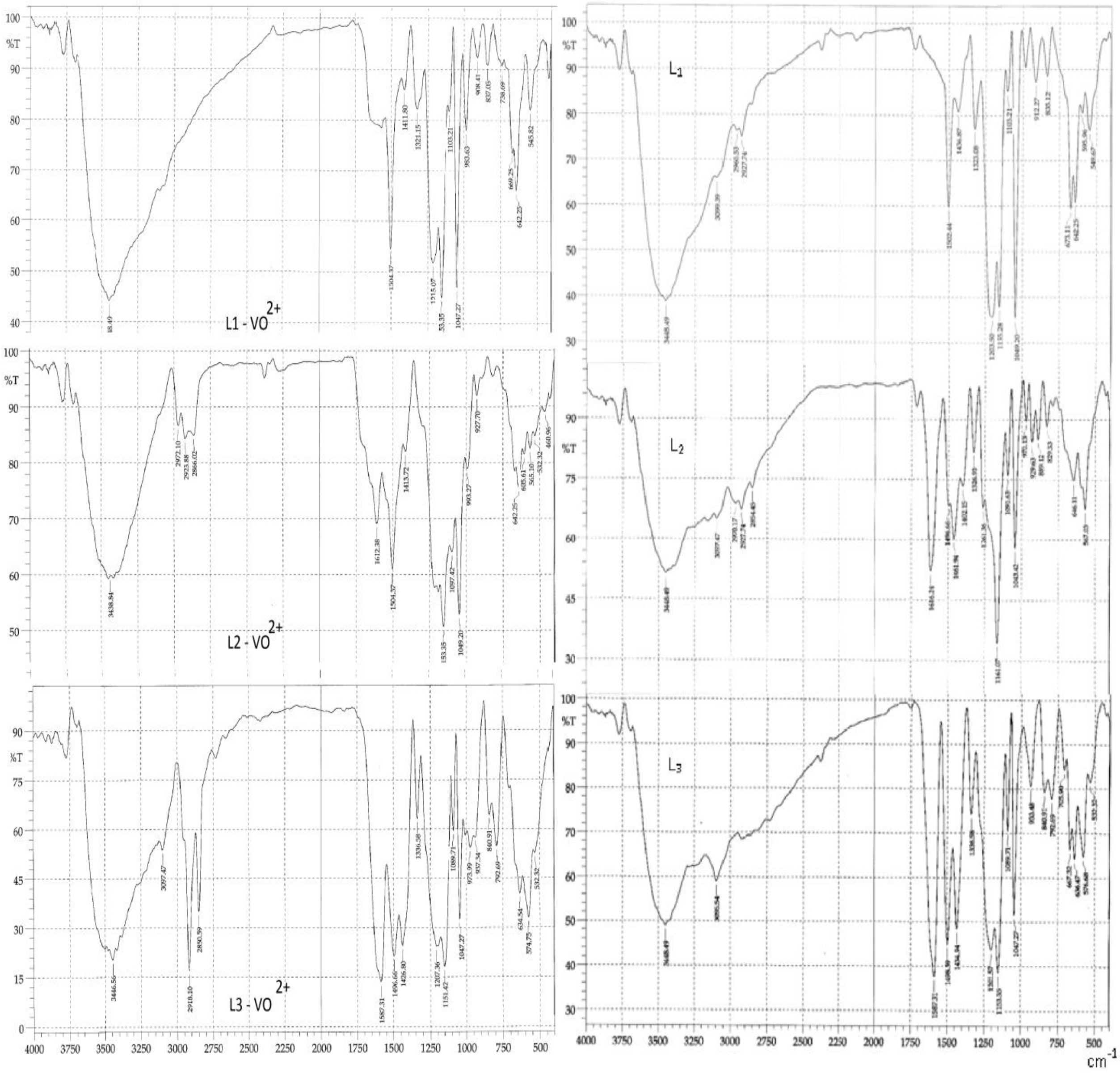


Fig.-1: IR spectra for dyes $L_1 – L_3$

Acid-Base properties and electronic spectra of dyes

The absorption spectra of 8 x 10^{-5} M solutions of dyes of varying pH values (0.7 – 12) (By using acetate and universal buffer solutions[14] were represented graphically (Figs. 2-4). The spectra of L_1 azo dye characterized two maximal bands at 370 nm. and 530 nm. in pH range (0.7 - 7) and one at 520 nm. in pH range (7-12).The spectra characterized by three isobestic points at 400, 460 and 550 nm. The spectra of L_2 azo dye characterized two maximal bands at 380 nm. and 520 nm. in pH range (0.7 - 7) and one at 510 nm. in pH range (7-12).The spectra characterized by three isobestic points at 400, 450 and 530 nm. The spectra of L_3 azo dye characterized two maximal bands at 385 nm. and 525 nm. in pH range (0.7 – 1.5) and one at 525 nm. in pH range (1.5-12). The spectra characterized by three isobestic points at 425 , 485 and 565 nm. The absorption bands due various electronic transitions liable to occur within the molecules due to $n \rightarrow \pi^*$ electronic and $\pi \rightarrow \pi^*$ transitions of N=N- group and the whole electronic system of the dyes compounds influenced by inter-molcular charge transfer character.[27]

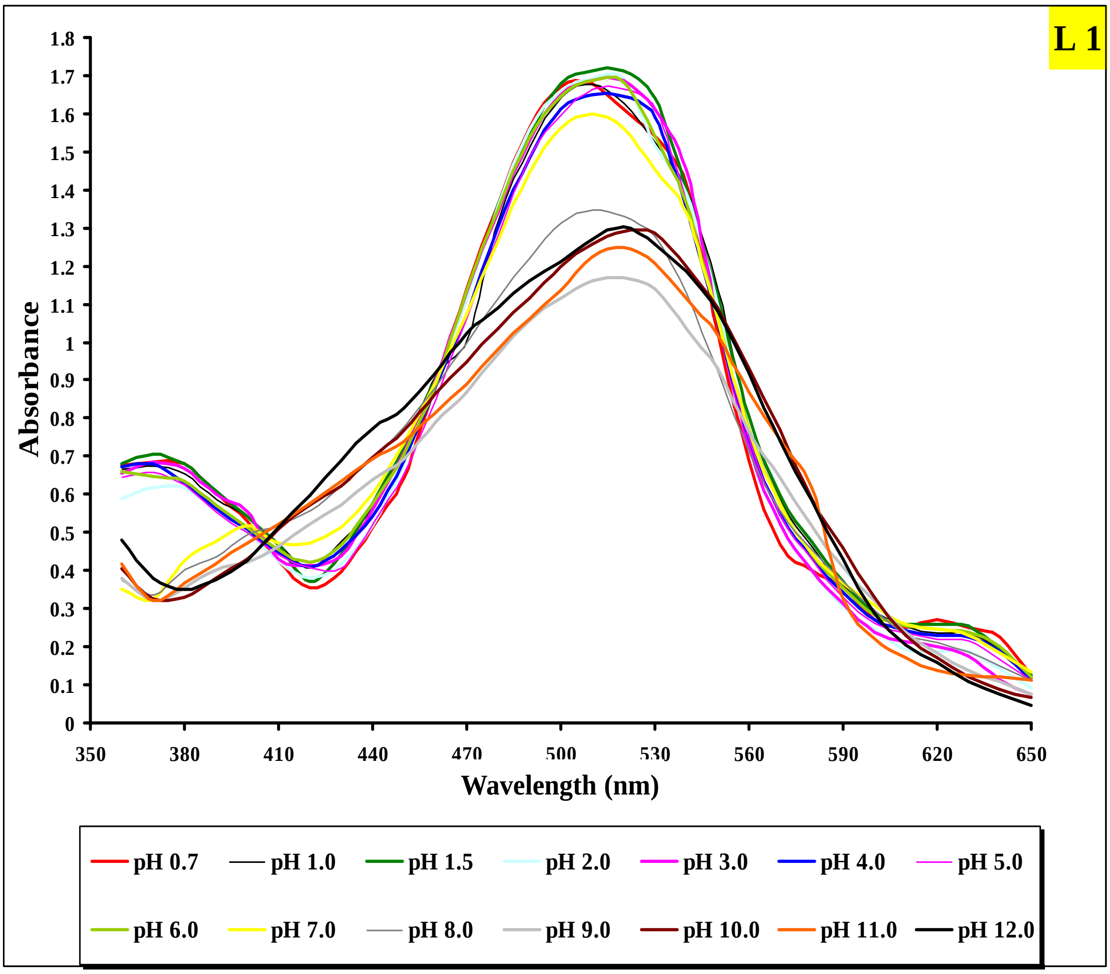


Fig.2- Electronic spectra for L_1 at different pH values

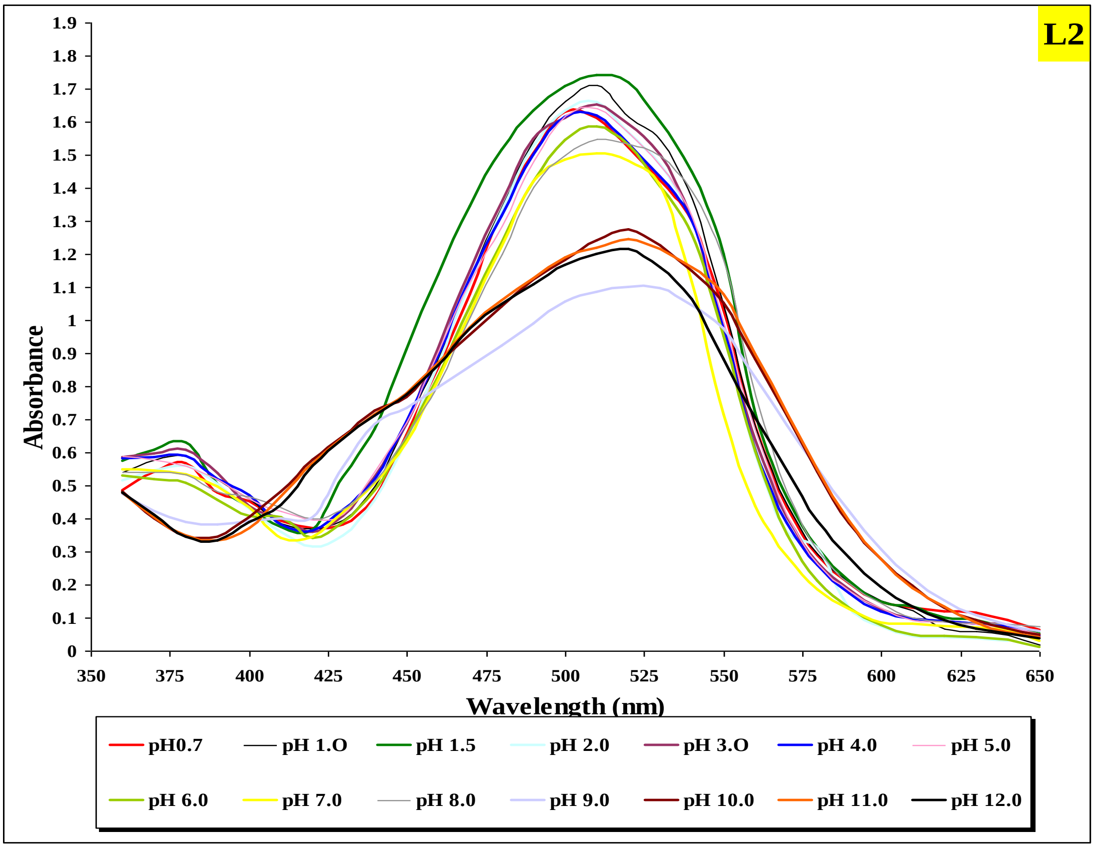


Fig.3- Electronic spectra for L_2 at different pH values

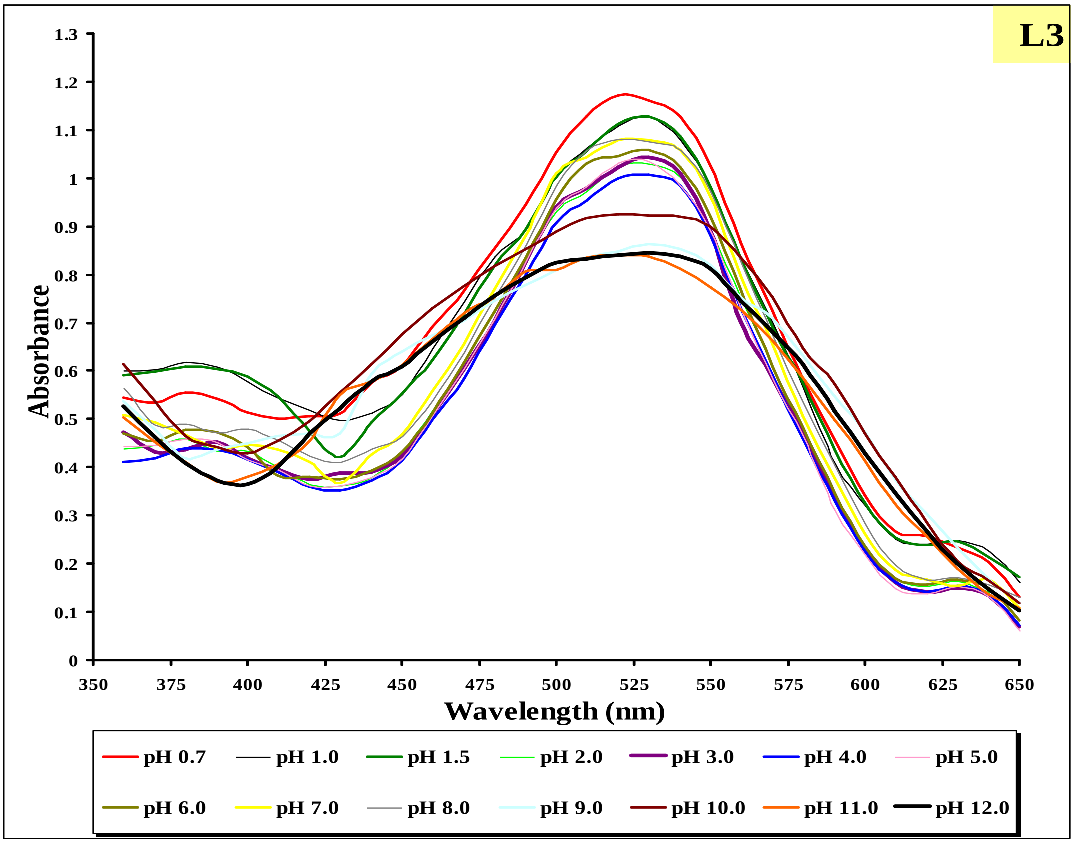


Fig.4- Electronic spectra for L_3 at different pH values

Ionization and protonation constants of compounds

By aid of Figs. (2 - 4) , the relation between absorbance and pH values of L_1 - L_3 at λ_{max} of each dye were plotted (Fig. 5) . The protonation and ionization constants (pK_p and pK_a) of dyes were determined from their spectral behavior in buffer solution of varying pH. From the absorbance - pH curves , the pK_a and pK_p values were determined by using of half height method.[21]

$pK = pH$ (at $A_{1/2}$) where $A_{1/2}$ = ($A_l + A_{min.}$) / 2

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

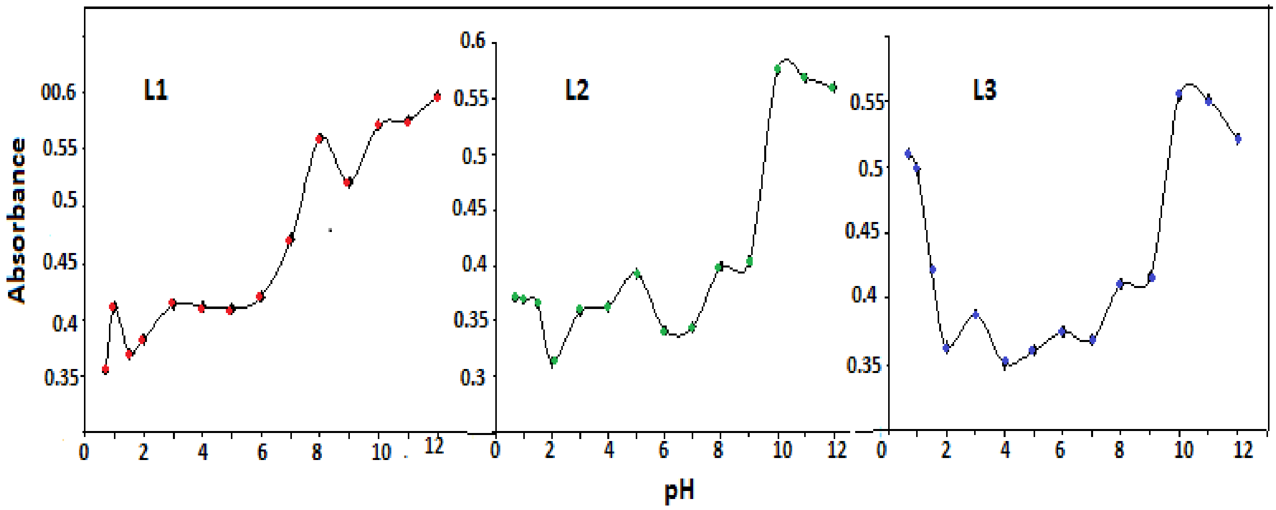


Fig.(5)-Absorbance-pH curves for L_1 –L3

From above relations and Fig. (5) so the protonation (pK_p) and ionization (pK_a) constants were calculated (table 3).

Table-3: The ionization and protonation constants of azodyes ligands

	λ_{max} (nm)	pk_{p1}	pk_{p2}	pk_{a1}	pk_{a2}
L_1	420	2.4	-	7.4	9.5
L_2	420	2.5	4.5	7.5	9.5
L_3	440	2.5	5	7.5	9.5

pKp_1 is protantion constant of first N (in –NHR group)

pKp_2 is protantion constant of second –N- (inside the ring)

pKa_1 & pKa_2 are first & second ionization constant of – OH groups of Chromotropic Acid

Complex formation studies

The complexes of oxovanadium (IV) ions with L_1 – L_3 solutions were always performed (C_1-C_3) respectively. These complexes were identified optimum conditions for the composition of these complexes (time, pH and sequence of addition effects). The interaction of the oxovanadium (IV) ion with the dye manifest itself in the absorption spectra by the appearance of a peak in the range (530 and 520 nm) for ($C_1 – C_3$) respectively . A great red shift in the visible region was detected in the complex solutions spectra with respect to that of the free dye. The shift in the (λ_{max}) gave a good indication for complex formation. (Fig.-6).

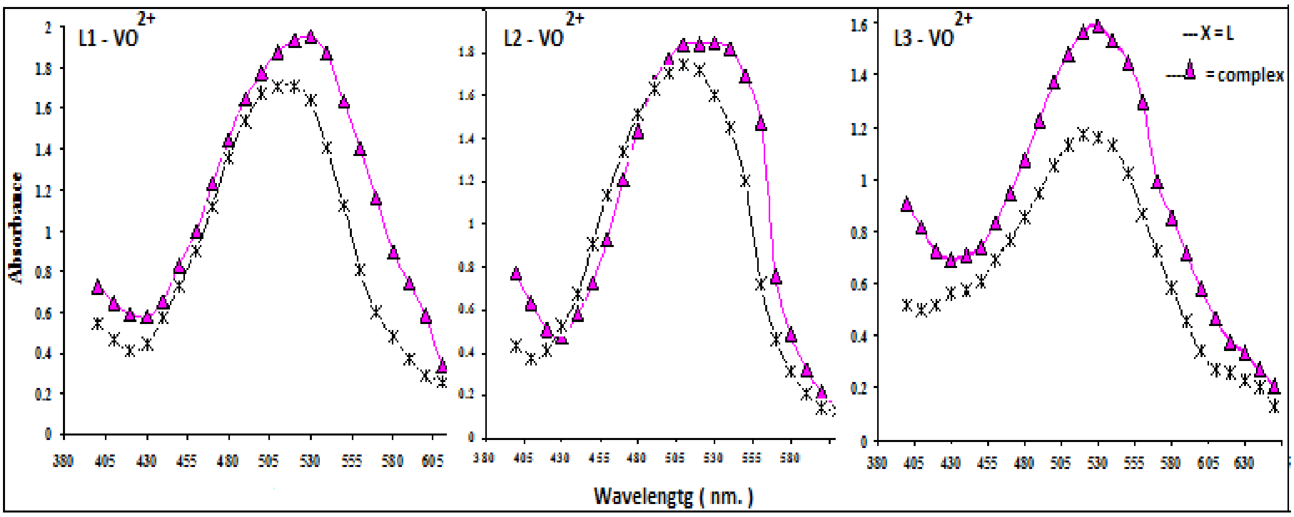


Fig. -6: The electronic spectra of L_1 and their complexes .(VO^{2+}] = [L] = 8 x 10^{-5} M)

The optimum conditions for complexes formation

Time effect

It was found from Fig. (7) the absorbances are constant from 15 min up to 48 hrs. that means the complex is of high stability.

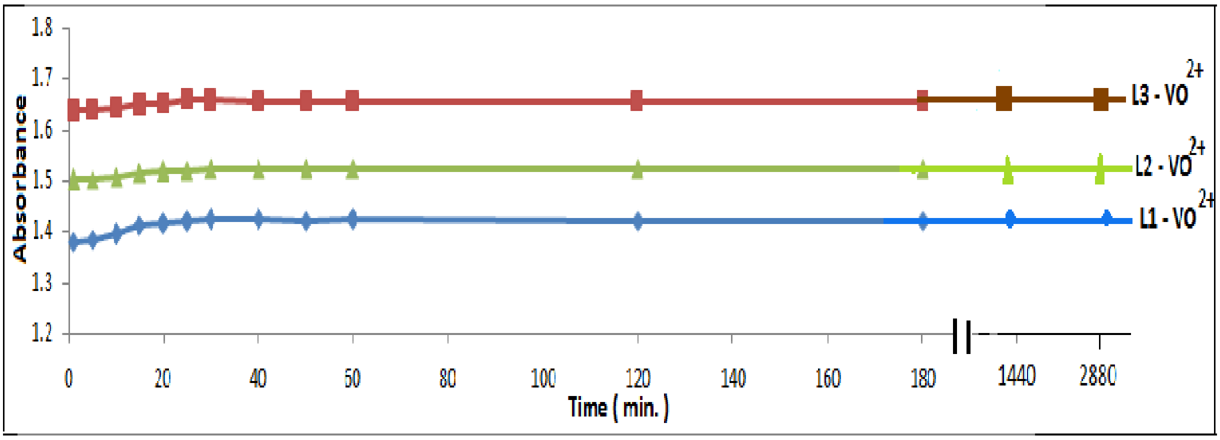


Fig.-7: Effect of time on the absorbance of azo dyes complexes ($C_1 – C_3$) at λ_{max} of each complex (VO^{2+}] = [L] = 8 x 10^{-5} M)

pH effect

The influence of pH values on the absorbance of complexes $C_1 – C_3$ was studied at different pH values (Fig-8) by using of acetate and universal buffer solutions (pH 0.7-13) . It was found that the highest absorbance at using methanol alcohol with respect L_1- VO^{2+} and ethanol alcohol for two complexes L_2- VO^{2+} and L_3- VO^{2+}. This is because of complete dissolving complexes in alcohol medium.

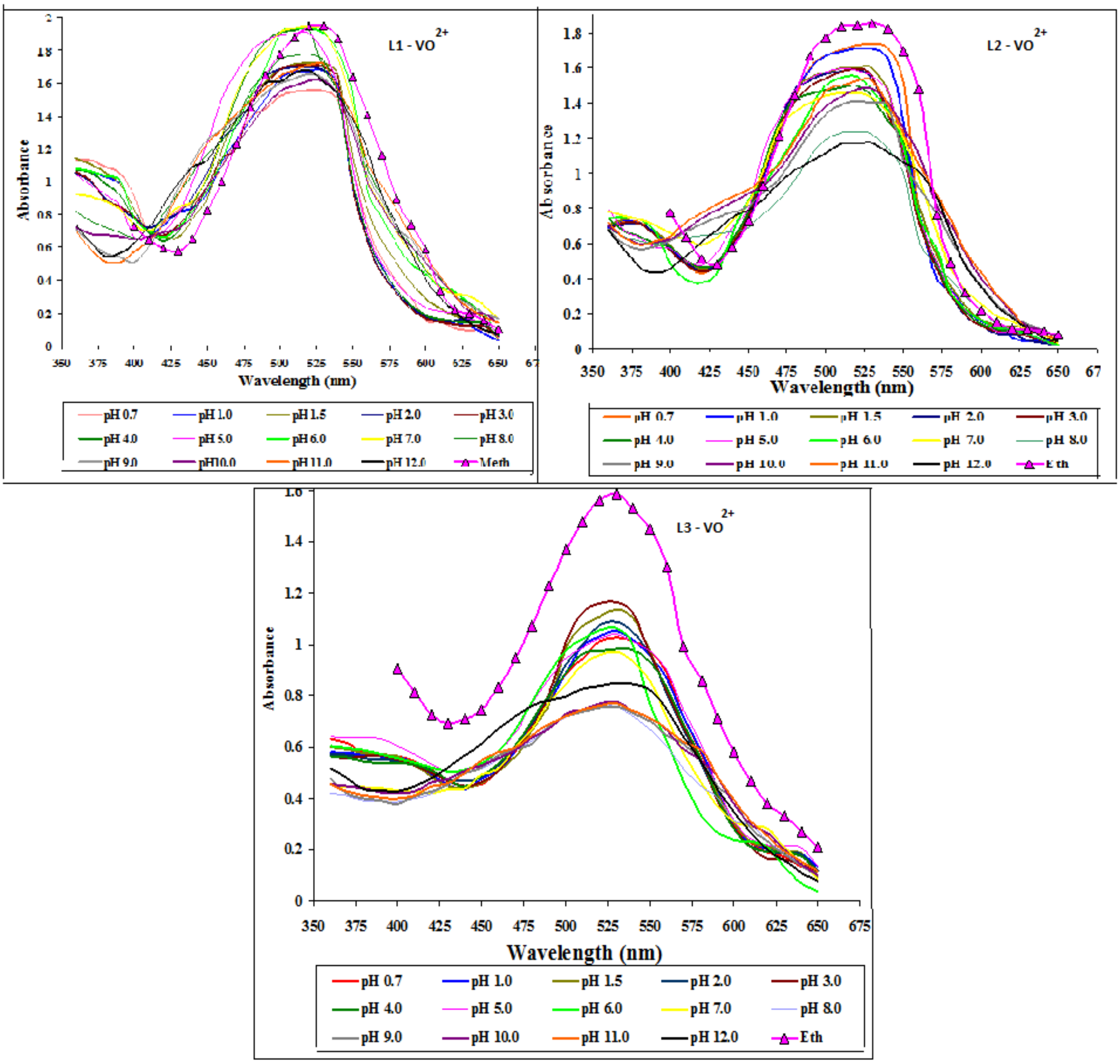


Fig.-8: Effect of pH on complexes (C_1 and C_2) spectra. ($[VO^{2+}] = [L] = 8.0 \times 10^{-5}$ M)

Squence of additions

It was found from Table – 4 that is no effect of Squence of additions of reagent on the absorbance of the azo dyes complexes.

Table - 4: Sequence of addition of reagents ([L] = [VO^{2+}] = 8 x 10^{-3} M

	Sequence of addition	Absorbance at wavelength of 530 nm.		
		$L_1 - VO^{2+}$	$L_2 - VO^{2+}$	$L_3 - VO^{2+}$
1	Dye + VO^{2+} + alcohol	1.430	1.656	1.532
2	Dye + alcohol + VO^{2+}	1.395	1.664	1.587
3	VO^{2+} + alcohol + Dye	1.389	1.659	1.541

The composition of the complexes (stoichiometry)

The composition of the complexes formed has been established by continues variation method (job method). From Fig.-9 it was found that the (VO^{2+} : azo dye) equal to (1 : 2).

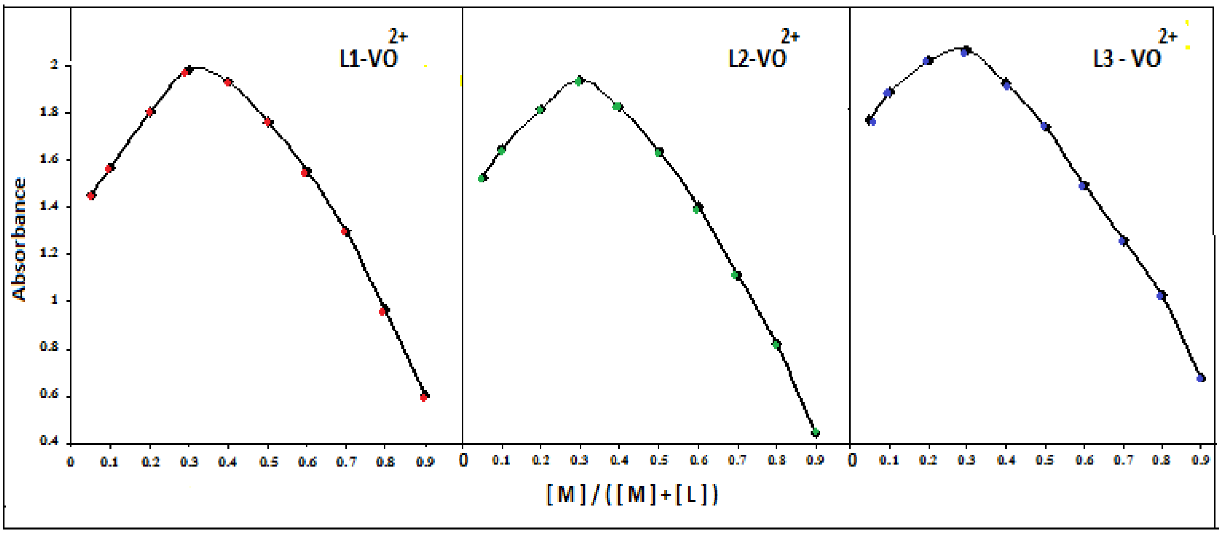


Fig.-9: Continues variation method for complexes (C_1 and C_2) , ([VO^{2+}] = [L] = 8.0 x 10^{-5} M)

Beer's law and sensitivity

To get better results for beer's law, the optimum blank composition technique[28] was applied (i.e. using unreacted dye as blank solution from knowledgement of stoichiometry of comolexes) . The calibration curve shows that Beers law is obeyed up to concentration range 8.03, 6.69 and 6.69 µg ml^{-1} for vanadium in complexes $C_1 - C_3$ respectively . Table (5) shows the data obtained , that represented by λ_{max} , the molar absorbitivity coefficient (ε , $L.mol^{-1}.cm^{-1}$) and sensitive index (S , $µg.cm^{-2}$), with higher precision that represented by the results of standard deviation (S.D), and high linearity of Beer's law which represent by the correlation coeff. (r) which is nearly to unity. And the detection limit (DL µg.ml) of the complexes.

Table –5: Some results obtained from Beers law

complexes	**λ_{max} nm.**	**l/mol.cmε**	**S.D**	**S µg/ml**	**DL µg/ml**	**r**	**Beer's law limt ppm**
C_1	530	7699.4	0.0079	0.0087	0.115	0.984	8.03
C_2	530	7398.6	0.0070	0.0095	0.178	0.913	6.69
C_3	530	7547.8	0.0073	0.0089	0.253	0.975	6.69

Interferences of foreign ions

The effect of interferences of foreign ions , on the absorbance of VO^{2+} - complexes, was studied at 1-fold , 5-fold and 10-fold concentrations of foreign ions (Table -6).

Table -6: Effect of Interferences of foreign ions on the absorbance of VO^{2+} - complexes. ([M] = [L_1]= [L_2] = [L_3] = 8 x 10^{-5} M) and the absorbance of L_1, L_2 and L_3 (in absence of foreign ions) are 1.347 , 1.445 and 1.054 respectively .

ion	**Absorbance of $L_1 – VO^{2+}$**			**Absorbance of $L_2 – VO^{2+}$**			**Absorbance of $L_3 – VO^{2+}$**		
	1-fold	**5-fold**	**10-fold**	**1-fold**	**5-fold**	**10-fold**	**1-fold**	**5-fold**	**10-fold**
K^{+}	1.341	1.309	1.301	1.420	1.437	1.395	1.100	1.125	1.111
Na^{+}	1.309	1.301	1.292	1.400	1.412	1.399	1.099	1.101	1.112
Ag^{+}	1.225	1.221	1.219	1.251	1.250	1.195	1.024	1.063	0.984
Ti^{+}	1.355	1.313	1.297	1.297	1.291	1.280	0.996	0.994	0.984
Co^{+2}	1.333	1.352	1.349	1.413	1.452	1.397	1.099	1.062	1.099
Cu^{+2}	1.124	1.151	0.954	1.404	1.397	1.392	1.176	1.219	1.207
Ni^{+2}	1.589	1.558	1.599	1.588	1.510	1.504	1.355	1.317	1.365
Zn^{+2}	1.667	1.640	1.733	1.367	1.380	1.370	1.563	1.503	1.474
Ba^{+2}	1.439	1.445	1.401	1.496	1.493	1.410	1.092	1.099	1.098
Pb^{+2}	1.344	1.337	1.401	1.318	1.357	1.343	1.100	1.117	1.108
Cd^{+2}	1.289	1.126	1.107	1.332	1.245	1.309	1.167	1.120	1.096
Pt^{+2}	1.046	1.086	1.032	1.318	1.357	1.343	1.063	0.997	1.088
Mn^{+2}	1.259	1.249	1.226	1.401	1.428	1.410	1.064	1.117	1.091
Hg^{+2}	1.227	1.224	1.219	1.349	1.359	1.289	1.027	1.021	0.994
Fe^{+3}	1.498	1.488	1.490	1.406	1.397	1.389	1.070	1.074	1.069
Cr^{+3}	1.143	1.139	1.158	1.358	1.396	1.356	1.080	1.099	1.076
Al^{+3}	1.218	1.217	1.211	1.267	1.280	1.205	1.047	1.089	0.976
La^{+3}	1.261	1.243	1.214	1.342	1.328	1.324	1.026	1.029	0.978
Zr^{+4}	1.294	1.286	1.289	1.390	1.446	1.501	0.973	0.980	0.971
Re^{+7}	1.320	1.311	1.329	1.399	1.390	1.381	1.071	1.110	1.082
EDTA	1.115	1.110	1.183	1.190	1.174	1.181	1.093	1.114	1.084
Cl^{-}	1.311	1.319	1.317	1.401	1.449	1.435	1.057	1.065	1.059
NO_3^{-}	1.325	1.334	1.329	1.387	1.400	1.379	1.111	1.119	1.101
SO_4^{-2}	1.341	1.354	1.351	1.411	1.470	1.461	0.997	1.109	1.000
PO_4^{-3}	1.357	1.371	1.369	1.466	1.479	1.464	0.956	0.999	0.952

It was found from Table -6 , the presence of (K^{+} ، Na^{+}، Ti^{+} ، Ba^{+2} ،Mn^{+2} ، Fe^{+3} ، Hg^{+2}، Cd^{+2} ،Co^{+2} ، Pb^{+2} ، Zr^{+4} ، Re^{+7} ، Cl^{-} ، NO_3^{-} ، SO_4^{-2} ، PO_4^{-3}) do not effected on the absorbance that means not interfered) on L_1- complex. Otherwise the ions (Pt^{+2} ، Zn^{+2} ، Ni^{+2} ، Cu^{+2} ، Ag^{+} ، La^{+3} ، Al^{+3}، Cr^{+3} ،EDTA) will interfere.

The ions (K^{+} ، Na^{+} ، ، Ti^{+} ، Ni^{+2} ، Zn^{+2} ، Pb^{+2} ، Cd^{+2} ، Pt^{+2} ، Hg^{+2} ، Cr^{+3}، Co^{+2} ، Cu^{+2} ، Ba^{+2} ، Mn^{+2} ،La^{+3} ، Fe^{+3} ، Zr^{+4} ، Re^{+7} ، Cl^{-} ، NO_3^{-} ، SO_4^{-2} ، PO_4^{-3}) were not interfered with L_2-complex but the ions (Ag^{+}، Al^{+3} ، EDTA) will interfere. In case of L_3-complex ,the ions (K^{+} ، Na^{+} ، Ag^{+} ، Ti^{+} ،Co^{+2} ، Ba^{+2} ، Pb^{+2} ، Cd^{+2} ، Pt^{+2} ، Mn^{+2}، Cu^{+2} ، Hg^{+2} ، Fe^{+3} ، Cr^{+3} ، Al^{+3} ، La^{+3} ،Zr^{+4} ، Re^{+7} ، EDTA ، Cl^{-} ، NO_3^{-} ، SO_4^{-2} ، PO_4^{-3}) not interfered. But the (Ni^{+2} ، Zn^{+2}) ions interfering.

The stability of the complexes

The stability constants of complexes C_1 – C_3 were determined by using Corresponding Solutions method , which depends on aid of half- value method [28]. This method required two series of solutions of total metal ion concentration $C_{1M} = 1 \times 10^{-4}$ M (concentrated series) and $C_{2M} = 0.5 \times 10^{-4}$ M (diluted series) and varying ligand concentrations C_{1L} (0.2 – 2.2 x 10^{-4}) and C_{2L} (0.1 – 1.1 x 10^{-4} M) . Then the absorbance of diluted series was multiplied by the factor (C_{1M} / C_{2M} which equal 2) .The corresponding solutions are those which have the same absorbance at different ligand (dye) concentration. From the absorbance - C_L plots (Fig.-10) , many pairs of C_{1L} and C_{2L} consequently, ñ (complex formation function) and [L] (free ligand concentration) can be determined where:

$\tilde{n} = (C_{1L} - C_{2L}) / (C_{1M} - C_{2M})$ and $[L] = (C_{1M} C_{2L} - C_{2M} C_{1L}) / (C_{1M} - C_{2M})$

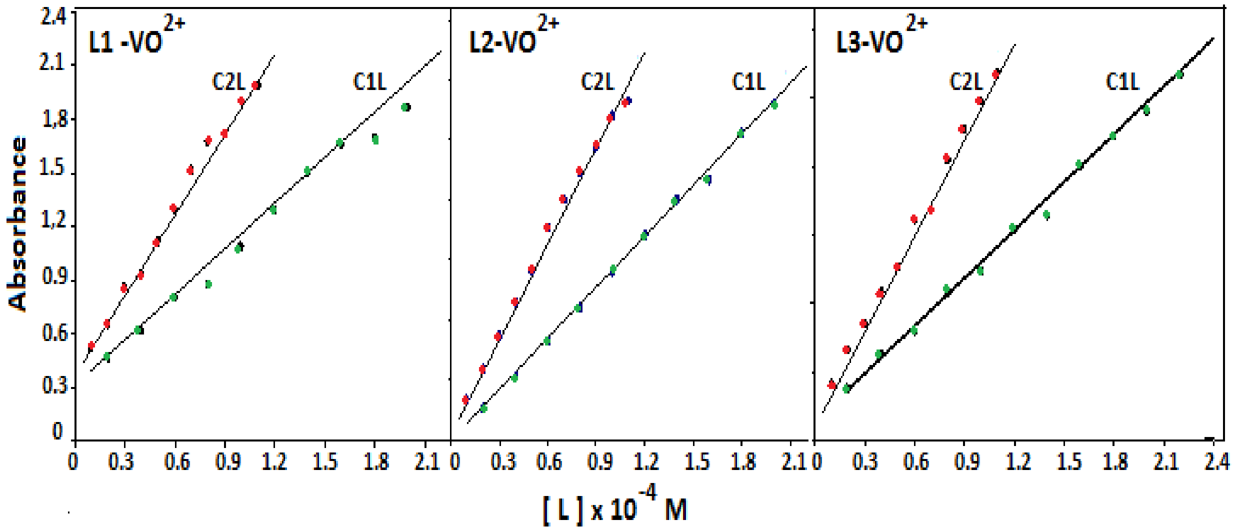


Fig.-10: Absorbance – Cl plot of complexes VO^{2+} - complexes (C_1-C_3) at λ_{max} of each of them

Then ñ – pL was ploted (Fig.-11) and by using the half value method, the log β_1 and log β_2 are obtained (Table –7).When ñ = 0.5 gives log β_1 (log K_1) and ñ =1.5 gives log β_2 (log K_1+ log K_2) (where K and β are step stability and overall stability constants).

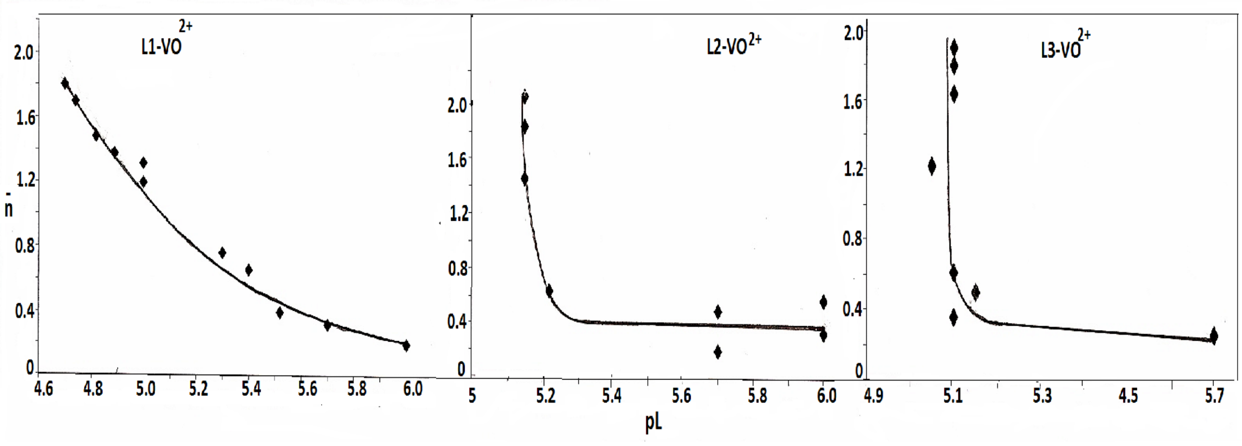


Fig.-11: ñ – pL curves for complexes ($C_1 – C_3$)

Table -7: Log β_1 and Log β_2 of ($C_1 – C_3$)complexes

Log β	**$L_1 – VO^{2+}$**	**$L_2 – VO^{2+}$**	**$L_3 – VO^{2+}$**
Log β_1	5.45	5.27	5.13
Log β_2	10.35	10.44	10.22

It was found from Table -7, the sequence of azodyes complexes stability are $L_2 + VO^{+2} > L_1 + VO^{+2} > L_3 + VO^{+2}$ and also found log K_1 is nearly equal to the log K_2. That means the azo dyes complex reaction is spontaneous and happened in one step.

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