3- RESULTS

Electronic absorption spectra of ligands under investigation in buffer solutions of varying pH and spectrophotometric determination of their acid dissociation constant (pK$_a$)

The absorption spectra of both azo dye and Schiff base ligands in buffer solutions of varying pH values are recorded within the wavelength range 200-600 nm. The acid dissociation of the ligand can be represented by the following equilibriums.

$$H_3L \overset{Ka_1}{\rightleftharpoons} H_2L^- + H^+,\ H_2L^- \overset{Ka_2}{\rightleftharpoons} HL^{2-} + H^+ \text{ and } HL^{2-} \overset{Ka_3}{\rightleftharpoons} L^{3-} + H^+ \quad (I_a, I_b, II_a)$$

$$H_2L \overset{Ka_1}{\rightleftharpoons} HL^- + H^+,\ HL^- \overset{Ka_2}{\rightleftharpoons} L^{2-} + H^+ \quad (I_c, II_b, II_c)$$

$$HL \overset{Ka_1}{\rightleftharpoons} L^- + H^+ \quad (II_d)$$

The bands of the compounds were shifted in their position or show variation in extinction whereas other exhibit a new band by increasing pH of the medium as shown in Figs. (   ). The pH-absorbance curve of the ligands at different wavelength corresponding to λ_{max} are of typical Z or S shaped as shown in Figs. (   ). This behaviour is utilized for the determination of the acid dissociation constant (pK$_a$) of these compounds by applying the half-height method (HHM), the modified limiting absorbance method (LAM) The colleter method (CM) and the modified isosbestic point method (IPM).

The values of pK_a were used in calculating the free energy change (ΔG^*) of the dissociation process from the relationship.

$$\Delta G^* = -2.303\ RT \log K \text{ (at 298 K)}$$

1- The half-height method( )

This method is based on the fact that at the half-height of the pH-absorbance curve, the dissociated and undissociated species exist in equivalent quantities, this:

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

where: $A_{1/2} = [(A_{max}-A_{min})/2] + A_{min}$

2- The modified limiting absorbance method( )

This method has the advantage of eliminating any overlaps between absorbance of the two forms, and pK_a is calculated by equation:

$$pH = pK + \log \gamma` + \log [(A-A_{min})/(A_{max}-A)]$$

where:

A = absorbance at a given pH value.

γ = the activity coefficient of the ion present at equilibrium.

A_{min}, A_{max} are the absorbance corresponding to the total concentration of neutral and ionized species liable to exist in solution.

The pK_a value can be evaluated by plotting $\log [(A-A_{min})/(A_{max}-A)]$ vs pH. The pK_a value thus corresponds to the pH value at zero $\log[(A-A_{min})/(A_{max}-A)]$.

3- The colleter method ( )

This method is utilized in the form developed for the determination of the dissociation constants of weak acids. In this method, three absorbance values are taken at three different hydrogen ion concentrations at the same wavelength.

The dissociation constants can be calculated using the following equations

$$K_a = \frac{C_{H_2^+} - MC_{H_3^+}}{M - 1}$$

in which

$$M = \left(\frac{A_3 - A_1}{A_2 - A_1}\right) \cdot \left(\frac{C_{H_1^+} - C_{H_2^+}}{C_{H_1^+} - C_{H_3^+}}\right)$$

Where A_1, A_2, A_3 are the absorbance at three different H^+ ion concentration $C_{H_1^+}$, $C_{H_2^+}$ and $C_{H_3^+}$ respectively

4- The modified isosbestic point method( )

For acid- base equilibriums

$$R\text{-}OH \leftrightarrow R\text{-}O^- + H^+$$

the following relation can be applied:

$$pH = pK + \log \gamma` + \log [(\varepsilon_{R-O^-}) / (\varepsilon_{R-OH})] + \log[(A - A_{min})_{R-O^-} / (A - A_{min})_{R-OH}]$$

where ε_{R-O^-} and ε_{R-OH} are the extinction coefficients of nonionized and ionized form at λ_1 and λ_2 ,respectively.

The correlation of log [(A-A_{min}) $_{R\text{-}O\text{-}}$/(A – A_{min})$_{R\text{-}OH}$] with pH yield a linear relationship. The intercept of this line at log[(A-A_{min}) $_{R\text{-}O\text{-}}$/(A – A_{min})$_{R\text{-}OH}$] equal zero gives a value equivalent to the following term

$$pK + \log \gamma` + \log [(\varepsilon_{R\text{-}O\text{-}}) / (\varepsilon_{R\text{-}OH})]$$

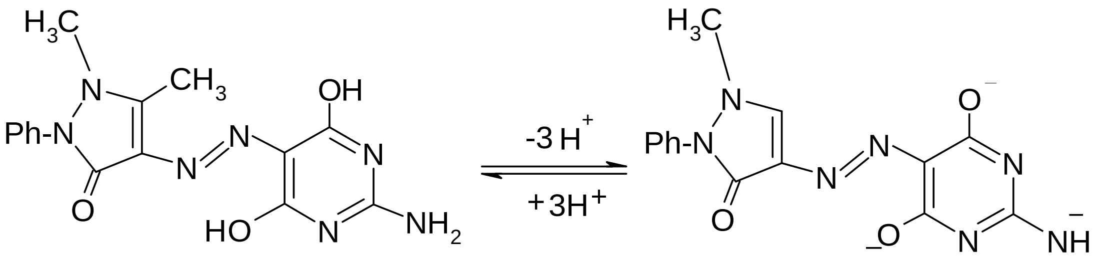
from which pK_a con be calculated

The pK_a values determined by the different methods for ligands $I_{a\text{-}c}$ and $II_{a\text{-}d}$ are given in Table ( ).

The electronic absorption spectra of azo dye ligands in buffer solutions of varying pH

The absorption spectra of 3 x 10^{-5} M of azo ligands $I_{a\text{-}d}$ in universal buffer solutions of varying pH in UV-Vis region (200-600 nm) are shown in Figs. (   ). The spectra obtained indicate that the absorbance values and positions of the absorption bands change with the pH of the medium due to the following:

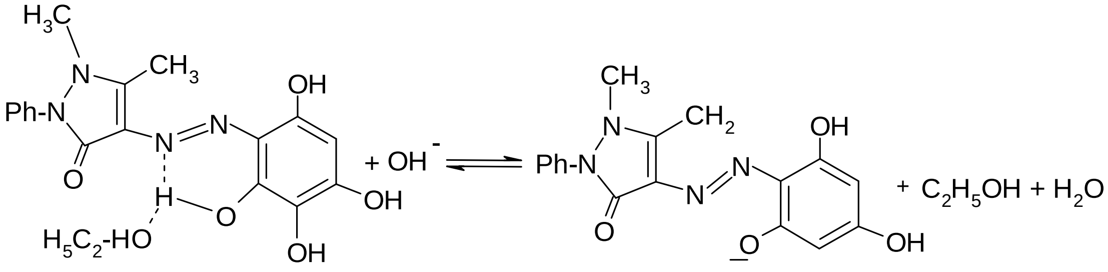
1- In case of I_a, the absorption band with λ_{max} = 232 nm corresponding to H_3L form the extinction of this peak decreases with increasing pH values while another band appeared at λ_{max} = 422 nm corresponding to L^{3-} form. The absorbance of this peak increases with decreases pH values of solution until pH 11.86. At λ_{max} = 395 nm, there a clear isosbestic point which indicates that an acid-base equilibrium occurred between the nonionized and ionized species, this can be represented as follows:



Nonionized form Ionized form

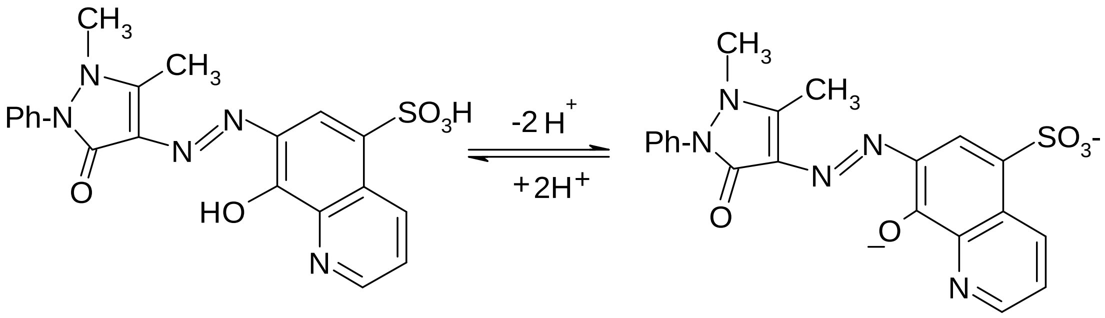
The variation of absorbance with pH at selected wavelength, λ_{max}, gives Z shaped curves as shown in Fig. ( ).

2- The spectra of ligand I_b showed two bands with λ_{max} equals 230 and 425 nm corresponding to H_3L and L^{3-} forms, respectively. The extinction of the first band, due to undissociated and dissociated forms, increases with increasing pH. At neutral pH, the shoulder appears with increasing pH. This shoulder is attributed to the formation of ionized species. This may be explained on the basis of a decrease in strength of the intramolecular hydrogen bond in the presence of ethanol and hydroxyl ions( ). This ionization may be represented as follows:



The variation of absorbance with pH for I_b gives S-shaped curves as shown in Fig. ( ).

3- In case of I_c, the spectra of this ligand shows a band with λ_{max} = 252 nm corresponding to the undissociated form H_2L, the extinction of this band increases with increasing pH values of solution, while another absorption band with λ_{max} = 357 nm which corresponding to L^{2-} form. The absorbance of this band decrease with increasing pH value until pH 10.3. A clear isosbestic point appeared at 244 nm which indicates that an equilibrium state between dissociated and undissociated forms, this can be represented as follows:



From the ΔG* value (Table 2) we show that, the free energy change during the first dissociation step is approximately the same for I_a and I_c whereas higher in case of I_b. This can be attributed to the effect of two hydroxyl group in I_c which strongest the hydrogen bond between O-OH and -N=N- and thus retards, the libration of H^+ proton relative to I_a and I_c ligands$^{()}$.

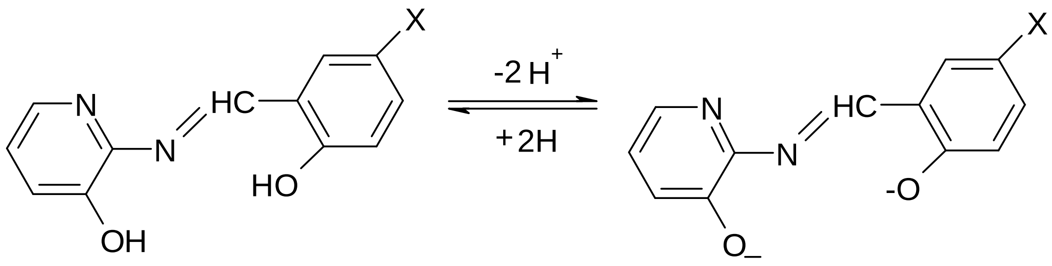
The electronic absorption spectra of Schiff base ligands in buffer solutions of varying pH

The absorption spectra of 3 x 10^{-5} M of ligands II_{a-d} in universal buffer solutions of varying pH in UV-Vis region (200-600 nm) are shown in Figs. ( ).

The spectra obtained indicate that the absorbance values and position of the absorbance bands change with pH of the medium due to the following:

1- In case of ligand II_a, the absorption spectra shows an absorption band with λ_{max} = 230 nm corresponding to H_3L form, the extinction of this band decreases with increasing pH values of solution while another absorption band with λ_{max} = 310 nm corresponding to the H_2L^- form. The absorbance of this band decreases with increasing pH values of solution until pH 10.2. This behaviour indicates that at pH range 4-10.2 the undissociated and dissociated form are present in different ratios.

2- The electronic spectra of ligands II_b and II_c show form different bands with two clear isosbestic points. These bands at λ_{max} = 225, 251, 310 ad 378 nm for ligand II_b and at λ_{max} = 220, 250, 313 and 390 nm for ligand II_c. The first two band in both ligand decrease in absorbance with increase pH values of solution which indicate that these bands for undissociated form H_2L. The bands at higher wavelength increases in absorbance with increase pH values of solution and these bands corresponding to dissociated forms of two ligands. The isosbestic points at λ_{max} = 285 and 347 nm for II_b and at λ= 355 and 278 nm for II_c indicating the existence of an acid base equilibrium between two different form of these compounds as shown in the following:



Where X = H (II_b), Br(II_c)

3- The spectra of ligand II_d show two different bands with λ_{max} equals 244 and 352 nm corresponding to HL and L^- forms, respectively. The extinctions of the two bands increases with increasing pH of the solution due to the change from undissociated form to the dissociated form with increasing pH.

Table ( ): The values of pK_a (dissociation constant) for azo dyes and Schiff base ligands at 298 K.

Ligand		**pK_a**					**λ_{max} (nm)**	**ΔG^* ($kJ\ mol^{-1}$)**
		HHM	**LAM**	**CM**	**IPM**	**Av.V**		
I_a	pK_{a1}	3.81	4.22	4.55	---	4.19	232	23.90
	pK_{a2}	8.55	8.51	---	---	5.53	232	48.67
	pK_{a3}	8.82	8.41	---	7.81	8.35	422	47.64
I_b	pK_{a1}	7.05	6.92	6.81	---	6.93	230	39.54
	pK_{a2}	7.23	7.35	---	---	7.29	425	41.59
	pK_{a3}	10.62	10.41	10.53	---	10.52	230	60.03
I_c	pK_{a1}	3.95	4.12	---	---	4.04	357	23.05
	pK_{a2}	9.12	7.42	8.21	7.91	8.17	252	46.61
II_a	pK_{a1}	3.72	4.05	---	---	3.89	310	22.19
	pK_{a2}	6.20	6.36	7.02	---	6.53	230	37.26
	pK_{a3}	8.64	8.61	---	---	8.63	310	49.24
II_b	pK_{a1}	4.10	5.21	6.11	4.53	4.98	251	28.42
	pK_{a2}	6.20	6.34	---	5.92	6.15	310	35.09
II_c	pK_{a1}	6.82	6.43	---	5.83	6.36	313	36.29
	pK_{a2}	7.28	6.97	6.35	6.71	6.82	250	38.91
II_d	pK_{a1}	7.79	7.21	8.01	---	7.67	352	43.76

HHM: Half height method, **LAM**: Modified limiting absorbance method, **CM**: Colleter method, **IPM**: modified isosbestic point method, **Av.V**: Average value, **ΔG^***: free energy change.

Solvatochromic behaviour of the electronic absorption spectra of the azo dye and Schiff base compounds in different organic solvents

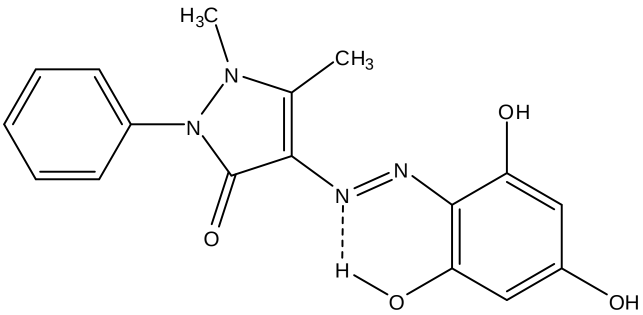
When absorption spectra are measured in solvents of different polarity, it is found that the positions, intensities and shapes of the absorption bands are usually modified by these solvents. These changes are a result of physical intermolecular solute-solvent interaction forces (such as ion-dipole, dipole-dipole, dipole-induced dipole, hydrogen bonding, etc.), which above all tend to alter the energy difference between ground and excited state of the absorbing species containing the chromophore( ). The medium influence on absorption spectra can be considered by comparing the spectra change observed (a) on going from the gas phase to solution, or (b) simply by changing the nature of solvent. Because in most cases it is not possible to measure the absorption spectrum in the gas phase, the treatment of this topic will be restricted to approach (b). All spectral changes which arise from alteration of the chemical nature of the chromophore-containing molecules by the medium, such as proton or electron transfer between solvent and solute, solvent-dependent aggregation, ionization, complexation, or isomerization equilibria. Thus, solvent effects on absorption spectra can be used to provide information about solute-solvent interaction. On the other hand, in order to minimize these effects, it would be preferable to record absorption spectra in less interacting nonpolar solvent, such as hydrocarbons, whereas solubility permits.

The electronic absorption spectra of azo dye and Schiff base compounds under investigation were studied in seven organic solvents. The solvents included polar solvent such as methanol, ethanol and DMF as well as no polar solvents such as diethyl ether, benzene, toluene and cyclohexane.

These studies reveal that the electronic absorption spectra involve bands due to electronic transitions within the various moieties **locally excited (LE)** attached either to the azo group or to the azomethine group leading to absorption in the UV-Vis region and band corresponding to the electronic excitation of the π and n-electrons on the (-N=N-) and (-CH=N-) systems which can be activated by **charge transfer (CT)** interactions.

The electronic absorption spectra of the azo dyes in ethanol

The electronic absorption spectra of azo dye ligands (I_a-I_c) in ethanol (Fig.   ) displays four main bands (Table   ). The first two bands A and B which ranging (223-241 nm) and (182-310 nm) respectively are assigned to the π-π* transitions of the aromatic rings in which ligand I_c gives largest molar absorpativity ε_{max} = 2.11 x 10^4 L mol^{-1} cm^{-1} which due to the presence of three aromatic rings while in ligands I_a and I_b only two aromatic rings are presented with ε_{max} of 0.90 x 10^4 and 1.06 x 10^{-4} L mol^{-1} cm^{-1} respectively. The third band (c) at (332-379 nm) involves π-π* transition of N=N groups. This band appears splitted in the spectra of I_b where the azo group is involved in an intremolecular hydrogen bond which can be shown as follows:



Ligand I_b

This intramolecular hydrogen bond causes a decrease of the π-π* energy of the N=N group and shifted to longer wavelength relative to the other two ligands. The longer wavelength band at (426-437 nm) can be assigned to an intramolecular charge transfer interaction from aromatic group to the N=N group. This can be confirmed by determining the energy of the charge transfer band from λ_{max} values using the relation:

$$E_{CT} = \frac{1241.6}{\lambda_{max}^{CT}}$$

and comparing the values that obtained with those calculated from the **Briegleb relation**( ):

$$E_{CT} = I_p - (E_A + C)$$

in which I_p is the ionization potential of the donor part, E_A is the electron affinity of the N=N acceptor group (-0.96 ev) and (-1.3 eV) for the C=N acceptor group and C is the coulombic force between the electron transferred and the positive hole left behind (C = 5.2 or 5.6 eV)( ). The values obtained for E_{CT} from Eq. ( ) lie between the two values calculated from Eq. ( ) by using the two values of C (Table).

The oscillator strength (f) of the CT band was determined from the relation( ):

$$f = 4.6 \times 10^{-9}\ \varepsilon_{max}\ \Delta\nu_{1/2} \ldots\ldots\ldots \qquad (\quad)$$

in which $\Delta\nu_{1/2}$ is the bandwidth at half absorbance value and ε_{max} is the maximum molar extinction coefficient. In cases when the CT band overlaps with band C, the band envelope was completed by considering it to follow a Gaussian curve. The f-values determined are given in Table (   ). The ionization potentials of 2-amino-pyrimidine-4,6-diol under study were determined from the electronic absorption spectra applying the relation:

$$I_p = a + b\nu \qquad (\quad)$$

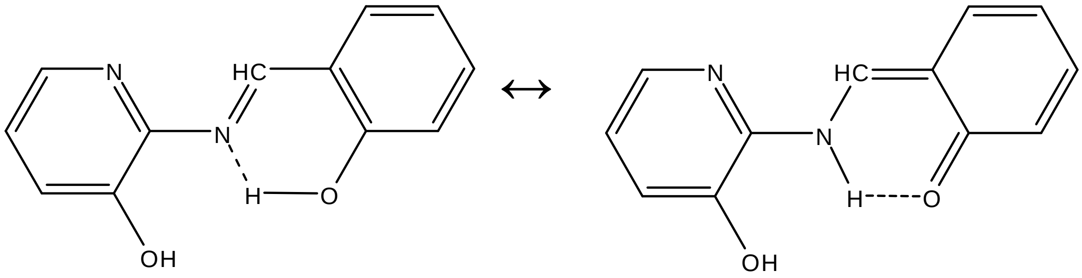
in which a and b are constants having the values (4.930 and 0.857)( ) and ν is the energy of the lowest π-π* transition. The values obtained are given in Table ( ).Despite the fact that the position of the CT band is influenced by the substituent on the aromatic ring being shifted to longer wavelength with increasing donor character of substituent , yet it not possible to have a quantataive treatment because the shift is of a small magnitude. Also the hydrogen bond formation between the N=N and the *o*-OH group of aromatic ring shift the CT band to longer wavelength.( )

The electronic absorption spectra of the Schiff bases in ethanol

The electronic absorption spectra of Schiff bases $II_{a\text{-}d}$ in ethanol display bands as shown in Fig. ( ). The first two bands A and B are observed at range (225-240 nm) and (272-299 nm) are referred to the π-π* transitions of the aromatic rings with ε_{max} 0.67 x

10^4 and 2.33 x 104 L mol^{-1} cm^{-1} for II$_a$ and II$_b$ receptivity. The donor substitute (hydroxyl group) causes a red shift for the pyrimine π-π* band.

The third band (c) ranged (314-343 nm) is due to π-π* transition in the azomethine system (-CH=N-). This band is blue shift in ligands II$_a$ and II$_d$ relative to ligand II$_b$. This can be explained by the inductive effect of the two methyl groups which increases the possibility for the blocking of n N=N electrons with ethanol molecules. For ligand II$_b$ there is a shoulder at 272 nm which may be due to the delocalization of hydrogen atom from (OH) groups to give keto enol form which be represented as follows:



The longer wavelength band (D) at (400-469 nm) can be assigned to an intramolecular charge transfer interaction from aromatic group to the azo-methene group (-CH=N-) at 400, 450, 460 and 469 nm for ligands II$_d$, II$_a$, II$_b$ and II$_c$ respectively which originate, from the substitutents phyenyl ring which increases the dipole moment of the solute during the electronic transition, the Franck-Condon excited state is formed in astrained solvent cage of the oriented dipoles, thus the energy of the ground state is increased and this produces. A bathochromic shift( ). However, the hydrogen bond formation between the C=N group and the *o*-OH groups on the phenyl-ring shifts the CT band to longer wavelength.

Table (   ): Data from UV-Vis spectra of azo dye and Schiff base ligands in ethanol.

	Ethanol							
	A		B		C		D	
	λ_{max} (nm)	ε_{max} x 10^4	λ_{max} (nm)	ε_{max} x 10^4	λ_{max} (nm)	ε_{max} x 10^4	λ_{max} (nm)	ε_{max} x 10^4
I_a	241	0.90	282	0.50	332	0.38	426	0.75
I_b	223	1.06	-	-	379	1.07	428	1.28
I_c	243	2.11	310	0.50	375	0.24	-	-
II_a	225	0.67	299	0.44	-	-	450	0.12
II_b	232	2.33	272	1.34	314	1.35	366	1.42
II_c	228	2.2	-	-	343	0.87	469	0.11
II_d	240	1.03	-	-	340	2.59	400	0.11

The electronic absorption spectra of the azo dye lignads in different organic solvents

The spectra of ligands I_{a-c} are measured in organic solvents of different polarity and the values of molar absorpativities and λ_{max} are listed in Table (   ). The obtained results indicate that the position of the bands due to the localized transitions is slightly influenced by solvent polarity. The CT band displays a general red shift with an increased solvent polarity denoting the higher stability of the excited state with increased solvent polarity. The shift in λ_{max} can be discussed in term of the solvent polarity viz dielectric constant and the possibility of formation of an intermolecular hydrogen bonds between ligand and solvent molecules. The application of the dielectric relations of **Gati** and **Szalay**( ) to the data of the CT band did not lead to linear relationships. This reveals that the dielectric constant of the solvent does not play an important role in the band shift. The plot of E_{CT}^{max} in different solvent as a function of various microscopic solvent parameter: α(acidity), β (basicity), as well as π* (dipolarity)( ) showed nonlinear relations indicating that these solvent parameters are not the main factors affecting the CT band position. Accordingly, it can be assumed that the shift of the CT bond is the resultant of the influence of all these parameters. These effects may be additive, counteracting or even may cancel out each other as said by **Issa**( ).

The electronic absorption spectra of the Schiff base ligands in different organic solvents:

The electronic absorption spectra of the investigated Schiff base ligands are collected in Table ( ). For the spectra of Schiff base compounds, it is apparent that the spectrum of each compound exhibits mainly four bands as shown in Fig. ( ). The lowest transition at (355-469 nm) and is assigned to the intramolecular charge transfer. This band shows positive solvatochromiusm (bathochromic shift) upon increasing the solvent polarity. This means that a pronounced change in position of an electronic absorption bond is accompanying a charge in the polarity of the medium. This observed behaviour is accounted as those molecules in the ground state and in the excited state indicate different polarities. This interpretation involves that highly simplifying assumption that Schiff bases with non-polarized ground state are more strongly polarized in protic solvents, because the high-energy polar structure of the excited state is stabilized. The excited state is lowered. The ground state is hardly affected. The energy difference between ground states and excited states is decreased and the excitation energy is decreased. The approximation of the energy levels expresses itself in a bathochromic shift of the spectrum with increasing polarity of solvents. The other absorption bands corresponding to the highest energy centered at (204-287 nm) are localized in the aromatic rings and are due to a (π-π^*) transition. These bands show a negative solvatochromism in solvent like diethyl ether, benzene and toluene. Those non-protic solvents destabilize the polarized electronic state. This leads to a hyposochromic shifting of the spectrum with decreasing solvent polarity. The UV-Vis spectrum of Schiff bases (II_b-II_c) exhibit mainly two absorption bands. A positive solvatochromism is observed for (n-π^*) absorption in case of the whereas a negative solvatochromism is observed for this band in case of II_c in where there is a Bromide atom. The hyposochromic shift in the band follow the order Br >> H in an agreement with the order of their electronegativities.

The UV-Vis spectra of ligands II_b and II_c in toluene exhibits two absorption bands. A band is formed at about 285 and 288 nm are assigned to a (π-π^*) transition which are blue shifted in all other solvents. Also, the second band at 358 and 345 nm for II_b and II_c respectively are blue shifted in the other solvents. A negative solvatochromism is noticed in all other solvents. The spectral shifts decrease with gradual introduction of the more polar solvent. In these solvents the hydroxyl groups in the pyridine moriety will be the proton acceptor center in the process of hydrogen bonds formation whereas the solvents that have the ability to form hydrogen bonds are the proton donors.

Table ( ) Data from UV-Vis spectra of azo dye and Schiff base compounds in ethanol

Ligand	**E_{CT} (eV) Eq.( )**	**f x10^{-4}**	**I_p (eV)**	**E_{CT} (eV) Eq.( )**	**E_{CT} (eV) Eq.( )**
I_a	2.91	0.33	7.339	3.100	2.699
I_b	2.90	0.55	7.695	3.455	3.055
I_c	2.84	0.05	7.303	3.063	2.663
II_a	2.76	2.00	6.652	2.752	2.252
II_b	3.49	0.16	7.509	3.609	3.209
II_c	2.64	3.20	6.590	2.690	2.290
II_d	3.10	1.00	7.357	3.450	3.057

Conductometric titrations

Conductometry, the measurement of conductance, is a physic-allychemical tool that provides information about the total ionic content of a solution. Changes in the conductance depend on the change in the number and character of the conducting species in solution. Since the metal ions are involved in complex compounds, their conductance should be lower as a result of decreasing value of the diffusion coefficient of the particle as observed from the relation between conductivity and diffusion coefficient

$$D^o = \frac{RT}{ZF^2}.\lambda^2$$

The diffusion coefficient is in turn related by Stocks-Enistien equation to the volume of the diffusing particle, (V_m) thus,

$$D^o = \frac{K}{(V_m)^{1/3}\eta}$$

where D^o is the diffusion coefficient of the conducting species and η the viscosity of the medium used.

The change in the type of conducting species is also an important factor that gives the direction of conductance change. This depends to a large extent on the reaction taking place between the ligands and metal ions in solution. The ions liable to exist in solution are the H^+ ions which are produced by displacement from the ligand molecule by metal ions. Thus, complex formation should take place through a covalent link construction between the metal ion and the oxygen atom of the hydroxyl group( ).

The factors governing the change in conductance are:

1. The increase in the volume of the metal ions on chelate formation.
2. The lowering of the charge on the metal ion through covalent bond formation with the ligand.
3. The liberation of H^+ ions from the ligand through bonding with the metal ion.

The first and second factors lead to the lowering of the conductance, while the third one favors an increase of ionic conductivity. Accordingly, the net effect will be the resultant of all these factors depending on the nature of the metal ion and the medium applied.

Conductometric titration of the azo dye and Schiff base ligands with Ag^+, Cd^{2+}, Cu^{2+}, Hg^{2+} and Zn^{2+} ions at 25 °C.

The liberation of hydrogen ions from the hydroxyl group of ligands during the complex formation is ascertained, leading to the increase in conductance as apparent from the titration of the metal ion solutions with ligands( ). If there was no interaction between ligands and metal ions in solution, the measured conductance values would be expected to the sum of the conductivities of the individual ions in the solution, furthermore the specific conductance would increase linearly with increasing concentration of added ligand concentrations( ). As can be seen from the figures, the specific conductance curves deviates from linearity in all figures for all complexes. The plot of the specific conductance values, after correction for the dilution effect, vs, the mL added of $1x10^{-3}$ M of ligands as shown in Figs. ( ) are characterized by breaks denoting the formation of (1:1) (M:L) types of complexes for all ligands and transition metal ions under investigation. In case of ligands I_b, I_c, II_b and II_c a (2:1) (M:L) complexes are observed with Hg^{2+}, Ag^{+}, Cd^{2+} and Cu^{2+}, respectively. The transition metal ion Cd^{2+} gives (2:3) (M:L) complexes with ligands I_a and II_c whereas Cu^{2+} ion gives (2:3) (M:L) complexes with ligand II_a and II_c only. From these results it is concluded that the complex formation is accompanied by the libration of proton from OH substitutent groups of ligands leading to the formation of a covalent linkage between the transition metal ions and oxygen atom, and a coordinated bond between metal ions and the nitrogen atom of -N=N- or -CH=N- groups. This was supported by the increase in the specific conductance when the reagent is added to the metal ion solution, this can be represented as follow:

$$H_nL + M^{m+} \rightleftharpoons [MH_{(n-1)}L]^{m-1} + [H^+]$$

On the other hand, there are a decrease in conductance when the reagent is added to metal ion in case of (1:1) (M:L) of (Ag-II_b), (Cd^{2+}-II_b), (Hg^{2+}-II_c), (Cd^{2+}-II_c) and (Cu^{2+}-II_d) complexes because the increased weight and volume of metal ion after complex formation. This is due to a decrease in the diffusion coefficient and hence in its conductivity. The results are listed in Tables ( ).

Table ( ): Stoichiometry of complexes of Cu^{2+}, Cd^{2+}, Hg^{2+}, Ag^{+} and Zn^{2+} with reagents under investigation

Reagent	**Types of complexes (M:L) ratios**				
	Cu^{2+}	Cd^{2+}	Hg^{2+}	Ag^{+}	Zn^{2+}
I_a	(1 : 1)	(1 : 1) (2 : 3)	(1 : 1)	(1 : 1)	(1 : 1)
I_b	(1 : 1)	(1 : 1)	(1 : 1) (2 : 1)	(1 : 1)	(1 : 1)
I_c	(1 : 1) (2 : 1)	(1 : 1)	(1 : 1)	(1 : 1) (2 : 1)	(1 : 1)
II_a	(1 : 1) (2 : 3)	(1 : 1)	(1 : 1)	(1 : 1)	(1 : 1)
II_b	(1 : 1)	(1 : 1) (2 : 1)	(1 : 1)	(1 : 1)	(1 : 1)
II_c	(1 : 1) (2 : 1)	(1 : 1) (2 : 3)	(1 : 1)	(1 : 1)	(1 : 1)
II_d	(1 : 1)	(1 : 1)	(1 : 1)	(1 : 1)	(1 : 1)

Study the conductometric titration of Cu^{2+} ion with ligands under investigation at different temperature

A conductometric method for the determination of the stability constants of complexes due to the reaction between ligands and metal ions has been used by several investigators( ). The 1:1 (M:L) binding of a metal cation (M^{n+}) with ligand can be represented by the following equilibrium equation:

$$M^{n+} + L \rightleftharpoons ML^{n+} \qquad (1)$$

$$\alpha\,[M]_t\,[L]_t \rightarrow (1-\alpha)\,[M]_t\,(1-\alpha)\,[L]_t$$

where M^{+}, L, ML^{n+} and α are the metal ion, the ligand, the complex and the fraction of the free metal ion, respectively. The complex formation constant in terms of the molar concentration can be expressed as:

$$K_{ML}{}^{n+} = \frac{[ML^{n+}]}{[M^{n+}][L]} = \frac{1-\alpha}{\alpha[L]} \qquad (2)$$

The observed conductivity, K at each point in the titration can be written as:

$$K = K_M{}^{n+} + K_{ML}{}^{n+} \qquad (3)$$

where $K_M{}^{n+}$ and $K_{ML}{}^{n+}$ are the conductivities of the metal salt and complex, respectively. The molar conductivity is given by:

$$\Omega_{Mn+} = \frac{K_{M^{n+}}}{[M^{n+}]} \approx \frac{K_{M^{n+}}}{\alpha[M^{n+}]_t} \qquad (4)$$

$$\Omega_{MLn+} = \frac{K_{ML^{n+}}}{[ML^{n+}]} = \frac{K_{ML^{n+}}}{(1-\alpha)M_t} \qquad (5)$$

where Ω_{Mn+} and Ω_{MLn+} are the molar conductivities of the metal salt and complex, respectively. As a consequence of Eqs. (4) and (5), Eq.(3) can be transformed into:

$$\Omega = \frac{K}{[M]_t} = \alpha\Omega_{M^{n+}} + (1-\alpha)\Omega_{ML^{n+}} \qquad (6)$$

Substituting from Eq. (6) into Eq. (3) gives the following equation:

$$K_{MLn+} = \frac{\Omega_{M^{n+}} - \Omega}{(\Omega - \Omega_M)[L]} \qquad (7)$$

where:

$$[L] = [L]_t - \frac{[M]_t(\Omega_{M^{n+}} - \Omega)}{\Omega_{M^{n+}} - \Omega_{ML^{n+}}} \qquad (8)$$

All calculated normal stability constants log K_f for (1:1) (Cu^{2+}-L) complexes are tested in Table ( ). Assuming that the activity coefficients of Cu^{2+} and L have the same value, K_f is a thermodynamic equilibrium constant on the molar concentration scale, related to the Gibbs standard energy of complexation reactions, ΔG^o, on the same scale. The Van't Hoff plots of log K_f *versus* 1/T for all of the system investigated were constructed. A typical example of these plots is shown in Figs. ( ).

The changes in the standard enthalpy (ΔH^o_C) for complexation reactions were determined in the usual manner for the slope of van't Hoff plots assuming that ΔC_p is equal to zero over the entire temperature range investigated. The change in standard entropy (ΔS^o_C) were calculated from the relationship ΔG^o_C, 298 = ΔH^o_C-298, ΔS^o_C. The results are summarized in Table ( ).

As is evident from Figs. ( ) addition of the azo dye and Schiff base ($II_{a,b}$) ligands to a solution of copper ion at different temperatures shows an increase in molar conductivity with an increase of the ligand concentration. This indicates that the formed complex is more mobile than the free solvated Cu^{2+} ion.

It is observed from Fig. ( ), the curvature of the plots of (I_c-Cu^{2+}) complex increases at all temperatures than (I_a-Cu^{2+}) and (I_b-Cu^{2+}) complexes which indicates the formation of stronger complex and this observation confirmed from the values of log K_f in Table ( ).

For Schiff base($II_{c,d}$) complexes with Cu^{2+} ion as shown in Fig. ( ), addition of II_c and II_d to solution of copper ion shows a decrease in conductivity at various temperature with an increase of the ligand concentration. This shows that the (II_c-Cu^{2+}) and (II_d-Cu^{2+}) complexes is less mobile than free solvated Cu^{2+} ion.

For ligands II_{b-d} with Cu^{2+} ion at low temperature (25 ^{o}C) only (1:1) (M:L) complexes are formed while with increasing temperature a new complex of stoichiometry (2:1) (M:L) is observed at higher temperatures Figs. ( ). In addition as is evident from Table ( ) the stability of complexes of Cu^{2+} ion with azo dye ligands at 25 ^{o}C decrease in the order $I_c > I_a > I_b$ whereas at higher temperature the order is charged into $I_c > I_b > I_a$. This indicates that as the temperature increases, protons of substituents (-OH, $-NH_2$ and $-SO_3H$) liberate and thus these group don't participate in stability of complexes formed so as there are only one group in I_c ($-SO_3H$) while two group in I_a (-OH, NH_2) and the dihydroxyle groups in ligand I_b, so the electronic cloud of aromatic system stabilize the complex center in order $I_c > I_b > I_a$ at higher temperature.

Also, the order of decrease stability constants for Schiff bases with Cu^{2+} ion is $II_a > II_b > II_c > II_d$ at 25 ^{o}C but this order charged into $II_a > II_c > II_b > II_d$ at higher temperatures

Table ( ): Formation constants of (1:1) (M:L) complexes with azo dye and Schiff base complexes at different temperatures.

Complexes	Log k_f			
	25^{o}C	37 ^{o}C	45 ^{o}C	55 ^{o}C
Cu^{2+}-I_a	1.885	1.935	1.807	1.950
Cu^{2+}-I_b	1.185	2.033	2.015	2.040
Cu^{2+}-I_c	2.580	2.670	2.640	2.560
Cu^{2+}-II_a	2.530	3.690	2.590	2.480
Cu^{2+}-II_b	1.640	1.844	1.620	1.879
Cu^{2+}-II_c	1.567	2.050	1.764	2.025
Cu^{2+}-II_d	1.400	1.340	1.540	1.740

Table ( ): Thermodynamic parameters for Cu^{2+} complexes with azo dye and Schiff bases ligands at 25 °C.

Complexes	$-\Delta G^o_c$ (kJ /ml)	ΔH^o_c (kJ /mol)	ΔS^o_c
$Cu^{2+}-I_a$	10.75	-0.677	33.80
$Cu^{2+}-I_b$	6.763	-0.023	22.62
$Cu^{2+}-I_c$	14.72	0.488	51.03
$Cu^{2+}-II_a$	14.43	1.586	53.74
$Cu^{2+}-II_b$	9.355	-4.503	16.28
$Cu^{2+}-II_c$	8.944	-10.00	-3.543
$Cu^{2+}-II_d$	7.985	-9.625	-5.503

The infrared spectra of the azo dye and Schiff base compounds

This part includes an attempt to obtain the assignment for the important and characteristic bands in the IR spectra of the ligands under investigation. The IR spectra of the azo dye and Schiff base compounds under investigation are recorded in Figs. (   ). The assignment of the important bands is given in Tables ( ).

The infrared spectra of the azo dye ligands

All the azo dye ligands gave an infrared spectral region of 3421-3505 cm^{-1} due to ν_{OH} presence of intramolecular hydrogen bond. This band is broaded in case of ligand I_a while in case of ligands I_b and I_c it appears as a sharp band at 3421 and 3505 cm^{-1}, respectively. The OH deformation bands lie at 1375, 1417 and 1383 cm^{-1} for ligands I_a, I_b and I_c, respectively. All compounds display an intense band at 1599-1653 cm^{-1} corresponding to $\nu_{C=O}$. The aliphatic CH_3-groups lead to two small bands at 1936-1985 cm^{-1} due to the stretching modes, while their deformation vibrations give strong bands at 1144-1190 cm^{-1}. The aromatic rings give a group of intense band due to skeletal and CH deformation at different positions characteristic for the type of substitution. The $\nu_{(C-OH)}$ bands are observed at 1045-1077 cm^{-1}. The N=N bands give $\nu_{N=N}$ (symmetrical) at 1431-1497 cm^{-1}. The asymmetrical N=N band usually overlap with the bands of the aromatic rings and hence difficult to identify$^{( )}$.

The infrared spectra of the Schiff base ligands

The spectra of all compounds exhibit two week intensity bands at 2916-2922 and 2819-2872 cm^{-1} corresponding to asymmetric and symmetric stretching vibrations of the aromatic C-H groups: $\nu_{(C=N)}$ give medium intensity bands at 1547-1572 cm^{-1}. This band being shifted to lower wavenumber due to the contribution of the C=N in an intramolecular hydrogen bond. The spectra of these compounds exhibit the $\nu_{(OH)}$ as week band at 3231-3439 cm^{-1}. While $\nu_{(C-OH)}$ bands are observed as weak intensity at 1065-1096 cm^{-1}. The low values of ν_{OH} reflects the existence of intramolecular hydrogen bands between OH and C=N groups( ).

The IR spectra of the Schiff base ligands under investigation exhibited medium intensity bands within 1292-1312 cm^{-1} are assigned to ν_{C-N}.

6.3. The infrared spectra of metal chelates with ligands under investigations

6.3.1 The IR absorption spectra of the metal chelates with azo ligands at (1:1) (M:L) ratio of complexes

The IR spectra of the azo dye metal complexes are compared with that of the azo dyes itself in order to determine the coordination sites that may be involved in chelation. There are some guide peaks, in the spectrum of the ligands, which enable one to achieve this goal. These peaks change either in their positions and/or their intensities upon chelation. They are listed in Table (44). The spectra are represented in Figs (135-141)

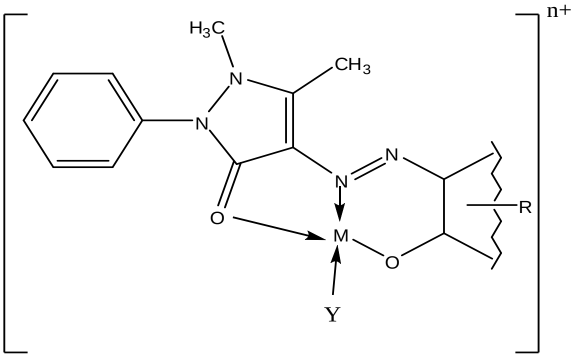
The IR spectrum of azo dye ligands shows strong broaded bands at 3395, 3421 and 3505 cm^{-1} $\nu_{(OH)}$ for I_a, I_b and I_c, respectively. These bands shifted from their position to lower wavenumbers (by 10-112, 1-4 and 1-83 cm^{-1}) for complexes of I_a, I_b and I_c respectively. Also, the disappearance of $\nu_{(OH)}$ bands in the complex Cu^{2+}-I_c reveals the deporotionation of the enolic and phenolic OH group indicating that the proton of the OH group is displayed by the metal ions on complex formation(138).

The IR spectra of the metal chelates of azo dye ligands show shifts to lower wavenumbers of the $\nu_{(C=O)}$ and $\nu_{(N=N)}$ bands compared to the values of the free ligands. These shifts suggest that the carbonyl-O of aromatic ring and an azo-N and phenolic-O atoms are involved in coordination to the metal ions(139).

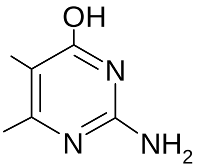
The presence of water in the above mentioned complexes is confirmed by the presence of a weak band in the 870-990 cm^{-1} range which may be attributed to the bending vibration of the water molecules(140).

The two new bands with were intensities are observed in the regions of 413-663 cm^{-1} in the complexes under study. such bands were previously reported to be assignable to $\nu_{(M\text{-}O)}$ and $\nu_{(M\text{-}N)}$ modes.

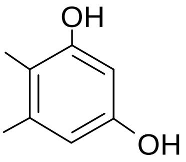
Accordingly, the mode of bonding of the metal ions with ligands under investigation can be represented as follows:



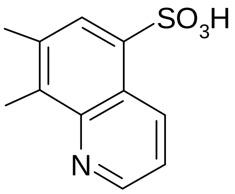
where:
R =



(Ia)



(Ib)



(Ic)

M = Cu^{2+}, Ag^{+}, Zn^{2+}, Cd^{2+} and Hg^{2+}
Y = Number of water molecules coordinated to metal ion
n = Overall charge on the chelates.

It is also worth noting that the weak band ν(N=N) of I_a varies in the range from 1417-1460 cm^{-1} and ν(M-N) varies in the range 433-474 cm^{-1} along with the decrease of transition metal ionic size (attributed to stretching mode) as shown in Figs. (142-143).

Assignments for stretching frequencies can be approximated by the application of **Hook's** law. In the application of the law, two atoms and their connecting bond are treated as simple harmonic oscillator composed of two masses joined by aspiring. The following equation(141), derived from Hook's law states the relationship between frequency of oscillation, atomic masses and the force constant of the bond.

$$\bar{\nu} = \frac{1}{2\pi c}\left[\frac{f}{(M_x M_y)/(M_x + M_y)}\right]^{1/2}$$

where $\bar{\nu}$ = the vibrational frequency (cm^{-1})

c = velocity of light (cm/s)

f = force constant of bond (dyne/cm)

M_x and M_y = mass (g) of atom X and atom Y, respectively.

Force constants obtained in this way for M-O and M-N bonds are mentioned in Tables (44,45).

6.3.2. The IR absorption spectra of metal chelates with Schiff base ligands at (1:1) (M:L) ratio of complexes.

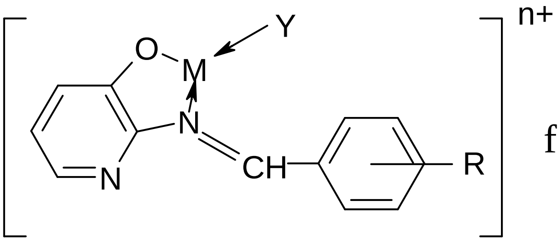
The infrared spectrum of the metal complexes, Table (45), compared with those of the free Schiff base ligands showed that the vibrational frequencies of coordinated functional groups (e.g. $\nu_{(OH)}$, $\nu_{(C=O)}$, $\nu_{(N=N)}$) are affected with different degrees depending on the strength of π-interaction occurring between the metal ion and π electrons of the functional groups(142) .

Upon chelation, the phenolic OH weak band disappears and a new very broad appears near 3430 cm^{-1} which is assignable to ν(OH) of coordinated H_2O molecules in the complexes(143). This may indicate the replacement of hydrogen of OH group by the metal ion.

The imine C=N stretching bands of the free ligands which appear near 1600 cm^{-1} shifted to higher and lower wavenumber for all complexes in range of 3-43 cm^{-1}. This implies the participating of the azomethine N in chelation with metal ions$^{(144)}$. This finding is further confirmed by the appearance of M-N band at 409-475 cm^{-1}.

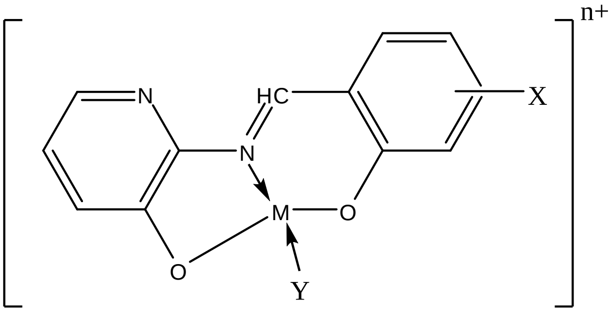
The band, near 1300 cm^{-1} which is assignable to the asym $\nu_{(C\text{-}N)}$ in the free ligands, shifted to different frequencies upon chelation. The new two bands with weak intensities are observed in the region of 409-721 cm^{-1} in the complexes under study. Such bands were previously reported to be assignable to $\nu^{(M\text{-}O)}$ and $\nu_{(M\text{-}N)}$ modes.

So, the structure of (1:1) chelates of ligands II_a, II_b, II_c and II_d with the mutation under study can be represented as follows:



for II_a, II_d

where R = 3, 4 (OH) II_a and 4($N(CH_3)_2$)II_d



for II_b, II_c

where: X = 1(OH) [II_b] and 1(OH), 4 (Br) [II_c]
$M = Cu^{2+}$, Ag^{+}, Zn^{2+}, Cd^{2+} and Hg^{2+}
Y = Number of water molecules coordinated to metal ion
n = Overall charge on the chelates