3-Results and Discussion

3.1. Studies on the organic ligands

3.1.1.The spectral chartacteristics of the organic ligands

3.1.1.1 The electronic absorption spectra of Schiff bases compounds:

The electronic absorption spectra of Schiff base compounds under consideration were studied in different organic solvents. When absorption spectra are measured in solvents of different polarities, it is found that the positions, intensities and shapes of the absorption bands are usually modified by these solvents. The changes in displacements of bands are due to the following reasons:

1-The physical properties of the organic solvent such as dipole moment, dielectric constant and its ability to interact through hydrogen bonding with the solute molecules.

2-The difference in solvation energy from one solvent to another and in the ground state to the excited state during the excitation of the same solvent.

3-The changes in polarities and dipole moments of the solute on excitation.

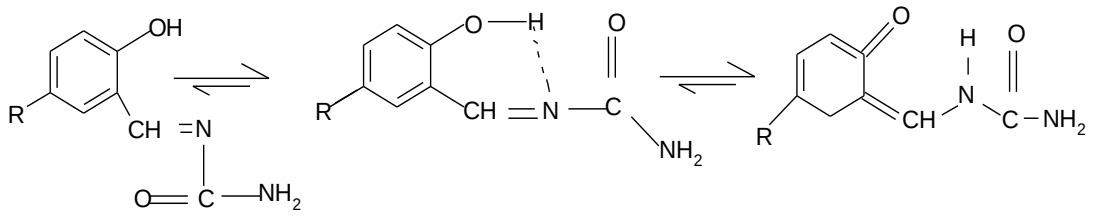
The spectra of the ligands under investigation were studied in different organic solvents. The solvents include polar solvents such as ethanol and non polar solvents such as benzene .

These studies imply that the electronic absorption spectra exhibit bands due to electronic transition within the various moieties locally excited 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-) groups which can be activated by charge transfere (CT) interactions.

3.1.1.2. The electronic absorption spectra of the Schiff bases in ethanol

The electronic absorption spectra of considered Schiff bases (I_a,I_b,I_c and I_d) in ethanol as shown in Figs (1-4) and Table (2) exhibits mainly four bands, the two bands on the higher energy side within the 227-250 nm and 268-289 nm ranges, are referred to the excitation of the π electrons ($\pi-\pi*$ transitions) of the aromatic rings with ε_{max} 0.7 ,0.48 and 0.84 x 10^5 L mol^{-1} cm^{-1} at 270 , 270 and 260 nm for ligands I_a,I_b and I_c respectively .For ligand I_d there is a shoulder at 240 nm .The donner substitute of hydroxyl group causes a red shift for the $\pi-\pi*$ band .

The third band within the 317-351 nm range is due to the $\pi-\pi*$ transition in the azomethine group (-CH=N) with ε_{max} 1.6, 0.6, 0.79 and 1.37 x 10^5 L mol^{-1} cm^{-1} at 340, 320, 320 and 320 nm for ligands I_a,I_b,I_c and I_d, respectively. This band is attributed to a blue shift in ligands.The delocalization of hydrogen atom from (OH) groups is carried out to give keto-enol form which may be represented as follows:



Enol form **Keto form**

The longer wavelength band around 400 nm shoulder of CT band which can be assigned to an intramolecular charge-transfer interaction from aromatic ring to the azomethine group at 420, 425, 425 and 500 nm for ligands I_a,I_b,I_c and I_d, respectively which originate from the substitutents phenyl ring which increases the dipole moment of the solute during the electronic transition, the Frank-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[176]. However, the hydrogen bond formation between the CH=N group and the o-OH groups on the phenyl-ring shifts the CT band to longer wavelength.

3.1.1.3. The electronic absorption spectra of the Schiff bases in different organic solvents

The electronic absorption spectra of the investigated Schiff base ligands were studied in different organic solvents. For the spectra of Schiff base compounds, it is apparent that the spectrum of each compound exhibits mainly four bands as shown in Figs. (1 - 4) and Table (2). The lowest transition at (355-469 nm) is assigned to the intramolecular charge transfer (CT band) such bands are observed at 370, 365, 380, 360, 379 and 360 nm for methanol, chloroform, benzene, 2-propanol, carbon tetrachloride and cyclohexane, respectively when studied with ligand Ia but when studying the related bands appeared using the same mentioned solvents with the rest ligands, it was found that they are 350,350,380,360,380 and 370 nm with Ib, 360, 370, 350, 450,400,390 nm with Ic and 370, 370, 370, 360, 370, 360 nm with Id. 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 change 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. Some shoulders appeared at 405-455 nm for Ia, 400-450 nm for Ib, 400-500 for Ic and at 425-500 nm for Id with the worked solvents. The other absorption bands corresponding to the highest energy centered at (210-290 nm) are localized in the aromatic rings and are due to a ($\pi - \pi*$) transition. These bands show a negative solvatochromism in solvent like benzene, cyclohexane and carbon tetrachloride. Those nonprotic solvents destabilize the polarized electronic state. This leads to a hyposochromic shifting of the spectrum with decreasing solvent polarity.

Table 2: Band assignment of (I_{a-d}) ligands in different solvents

Band assignment								
Ligand I_a								
Solvent	**A**		**B**		**C**		**D**	
	λ_{max} (nm)	* ε_{max} (x10^5)	λ_{max} (nm)	ε_{max} (x10^5)	λ_{max} (nm)	ε_{max} (x10^5)	λ_{max} (nm) sh.	ε_{max} (x10^5)
Ethanol	270	0.7	340	1.6	380	0.62	420	0.20
Methanol	281	0.45	322	0.82	370	0.65	410	0.22
Chloroform	295	0.14	345	0.43	365	0.59	425	0.1
Benzene	294	0.17	332	0.41	380	0.70	428	0.12
2-propanol	291	0.07	350	0.39	360	0.24	450	0.08
CCl 4	296	0.16	344	0.2	379	0.17	405	0.04
Cyclohexane	290	0.05	325	0.5	360	0.75	455	0.06
Ligand I_b								
Ethanol	270	0.48	320	0.60	360	0.59	425	0.18
Methanol	220	1.17	321	1.39	350	1.37	450	0.096
Chloroform	260	0.61	320	0.62	350	0.48	445	0.054
Benzene	280	0.43	360	0.66	380	0.46	425	0.08
2-propanol	240	0.07	290	0.31	360	0.14	400	0.02
CCl 4	299	0.02	340	0.11	380	0.189	440	0.06
Cyclohexane	298	0.09	350	0.75	370	0.75	430	0.07
Ligand I_c								
Ethanol	260	0.84	320	0.79	340	0.73	425	0.088
Methanol	220	1.17	320	1.39	360	1.5	450	0.26
Chloroform	270	0.5	325	0.64	370	0.56	425	0.18
Benzene	280	0.43	340	0.59	350	0.6	450	0.04
2-propanol	240	0.07	350	2.1	450	0.36	500	0.12
CCl 4	310	0.22	370	0.15	400	0.04	450	0.02
Cyclohexane	270	0.44	320	0.66	390	0.12	425	0.03
Ligand I_d								
Ethanol	240	0.08	320	1.37	350	1.3	500	0.09
Methanol	280	0.49	310	0.69	370	0.30	425	0.09
Chloroform	270	0.07	320	0.61	370	0.286	425	0.08
Benzene	285	0.05	340	0.28	370	0.213	430	0.06
2-propanol	280	0.04	340	0.34	360	0.33	428	0.07
CCl 4	310	0.06	350	0.22	370	0.2	425	0.08
Cyclohexane	280	0.07	320	0.19	360	0.3	450	0.05

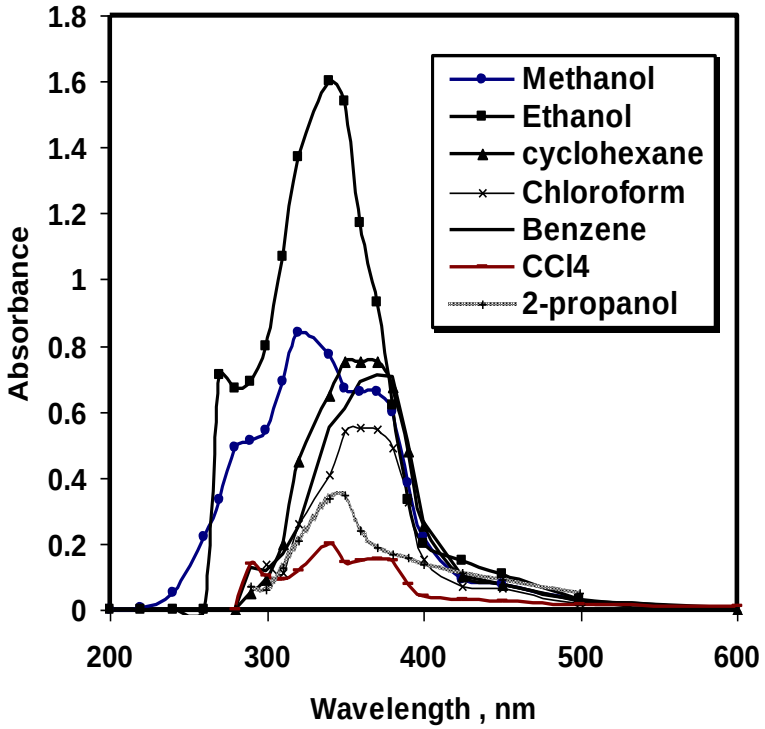


Fig.(1) Effect of solvents on Schiff base derived from p-amino benzoic acid (reagent $\mathbf{I_a}$) at wavelength rage from 200 to 600 nm

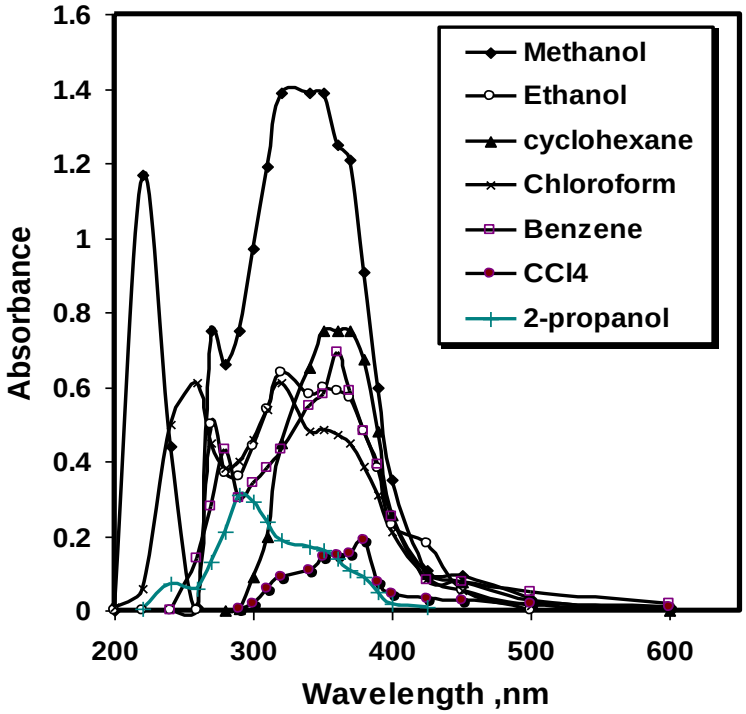


Fig.(2) Effect of solvents on (reagent$\mathbf{I_b}$)at wavelength range from 200 to 600 nm

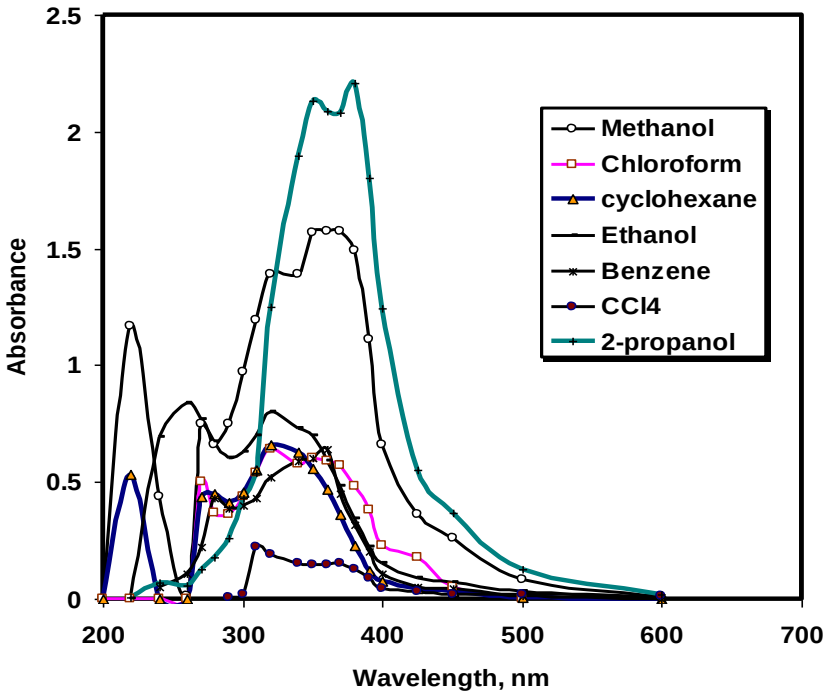


Fig .(3) Effect of solvents on (reagent$\mathbf{I_c}$)at wavelength range from 200 to 600 nm

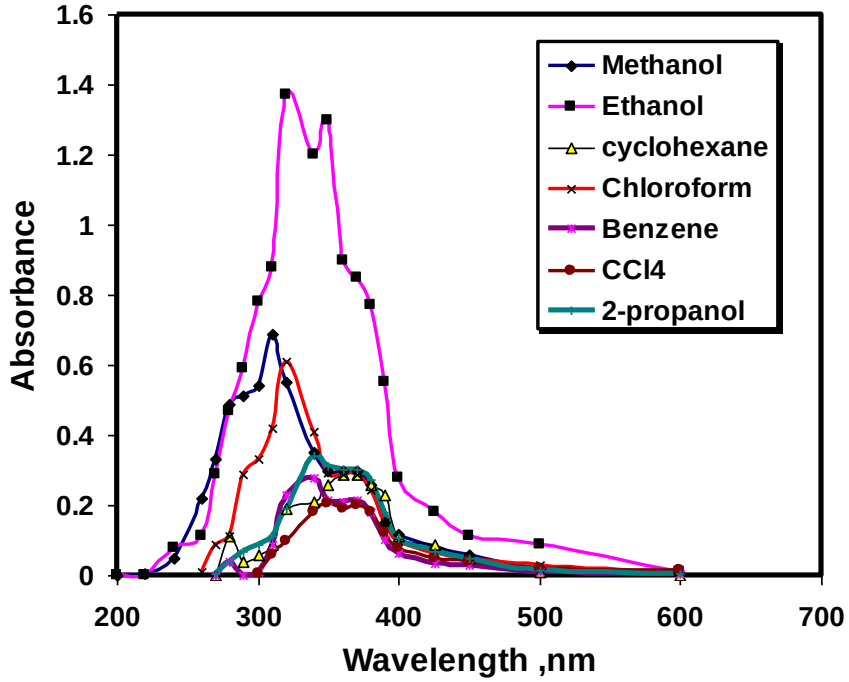


Fig .(4) Effect of solvents on (reagent$\mathbf{I_d}$)at wavelength range from 200 to 600 nm

3.1.1.4.The spectral behavior of ligands under consideration in buffer solutions and the determination of their acid ionization constants

The acid ionization constants (pK_a) of the ligands under investigation were determined spectrophotometrically in universal buffer solutions covering the range 350-600 nm.

The bands of the compounds were shifted in their position or show variation in extinction whereas a new band is observed by increasing the pH of the medium .

The change of absorbance with pH can be utilized for determination of the dissociation constants by the following method:

1-Half-height method (HHM)

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

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

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

2-The modified limiting absorbance method(LAM)

This method has the advantage of eliminating any overlaps brtween absorbance of the two forms , and pka is calculated by the 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}=the absorbance corresponding to the concentration of neutral species

A_{max}=the absorbance corresponding to the concentration of ionized species.The pK_a value can be evaluated by plotting log [(A-Amin) / (Amax-A)] vs pH. The pK_a value corresponds to the pH value at zero log [(A-Amin) / (Amax-A)] as shown in Figs.(6,8,10,12). Table (3) shows the values of pK_a of studied ligands.

3.1.1.5. The electronic absorption spectra of the Schiff base ligands in buffer solutions

The acid base equilibrium of the studied Schiff bases can be schemed as:

$H_3L \overset{K_1}{\rightleftharpoons} H_2L^- + H^+$, $H_2L^- \overset{K_2}{\rightleftharpoons} HL^{2-} + H^+$ and $HL^{2-} \overset{K_3}{\rightleftharpoons} L^{3-} + H^+$ (Ia)

$H_2L \overset{K_1}{\rightleftharpoons} HL^- + H^+$ and $HL^- \overset{K_2}{\rightleftharpoons} L^{2-} + H^+$ (Ib, Ic, Id)

The absorption spectra of ligands I_a,I_b,I_c and I_d in universal buffer solutions varying pH are shown in Figs. (5, 7, 9, 11) and Table (3). 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 I_a, the absorbance spectra show an absorption band with λ_{max} = 395 nm in the strong acid medium corresponding to the non ionic form of the ligand H_3L, the extinction of this band decreases with increasing pH showing the absorbance of the ionic form of the ligand .

2-The electronic spectra of ligand I_b show an absorption band at λ_{max} = 390 nm corresponding to the H_2L form, by increasing the pH, the absorption decreased indicating that the ionic form HL^- is present .

3-The electronic spectra of ligand $I_c$and I_d show absorption bands at λ_{max} = 450 and 380 nm respectively, by increasing the pH, the absorption decreased that indicate the ionic and non ionic forms of the ligands are present when dissolved in universal buffer.

Table 3:The values of pK_a(dissociation constant) for studied ligands

Ligand		**pK_a**		**λ_{max} (nm)**
		HHM	**LAM**	
I_a	**pK_a1**	**3.8**	**-**	**390**
	pK_a2	**6.3**	**7.7**	**390**
I_b	**pK_a1**	**4.5**	**-**	**410**
	pK_a2	**8.36**	**7.8**	**410**
I_c	**pK_a**	**7.0**	**8.0**	**450**
I_d	**pKa1**	**3.29**	**-**	**380**
	pK_a2	**7.5**	**7.5**	**380**

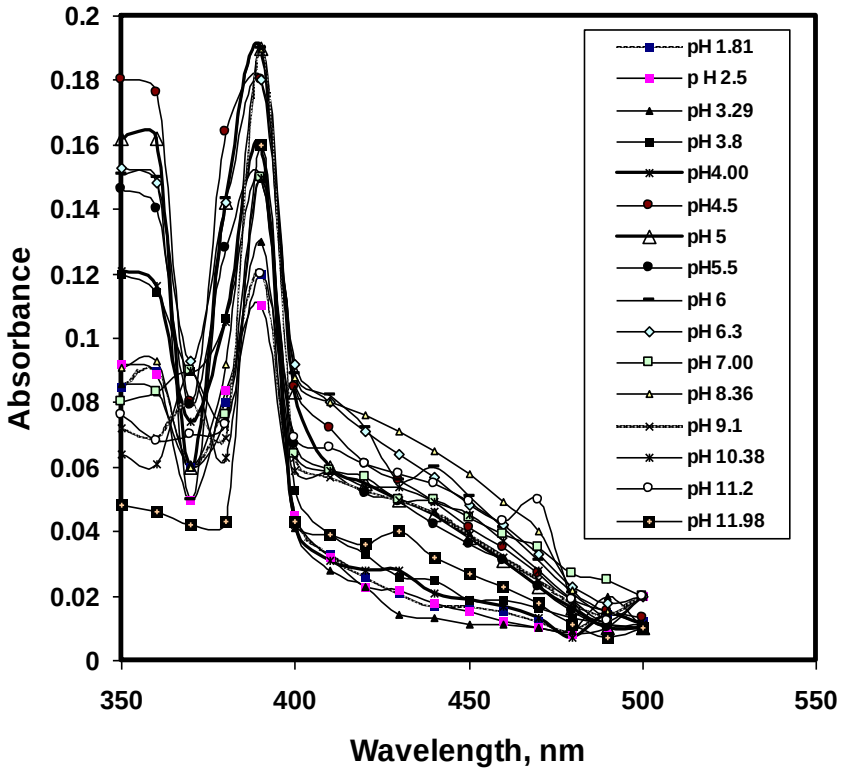


Fig. (5) Effeect of pH on (reagent I_a) using universal buff

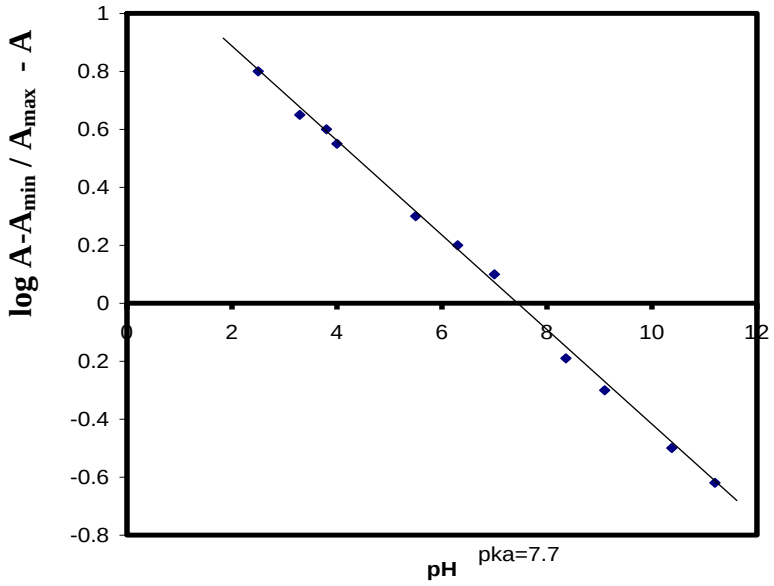


Fig.(6) pK_a of (reagent I_a) at 390 nm using universal buffer

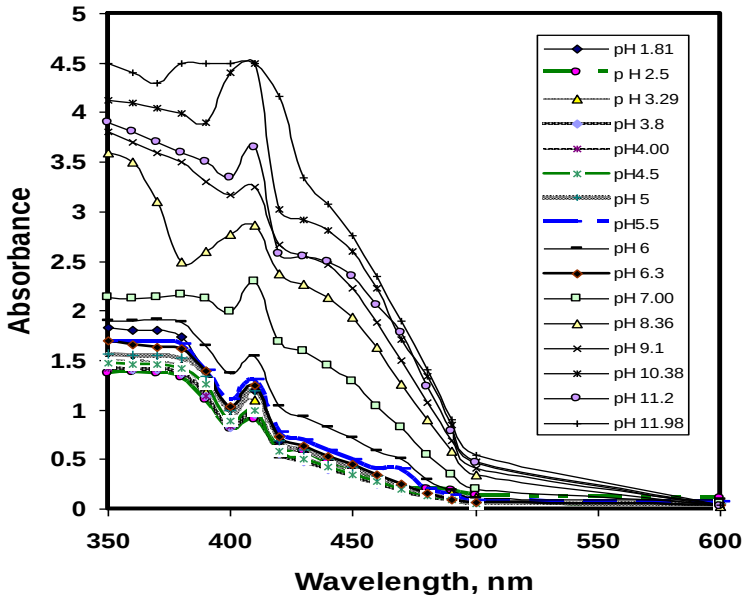


Fig. (7) : Effect of pH on reagent (I_b) using universal buffer

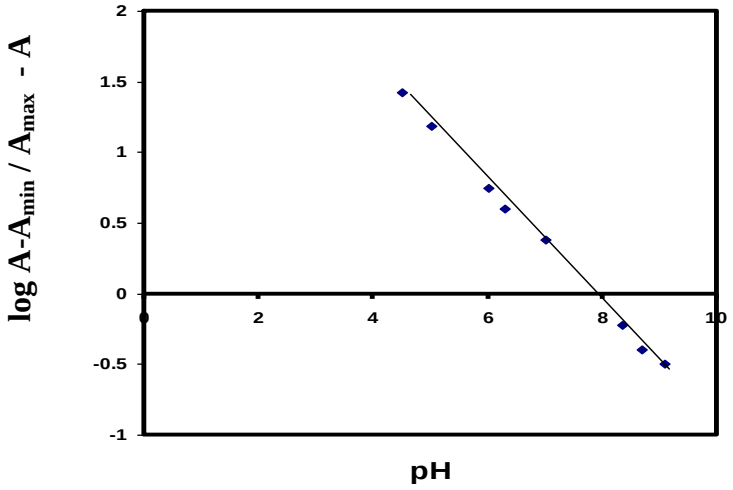


Fig. (8) pK_a of (ligand I_b) at 410 nm using universal buffer

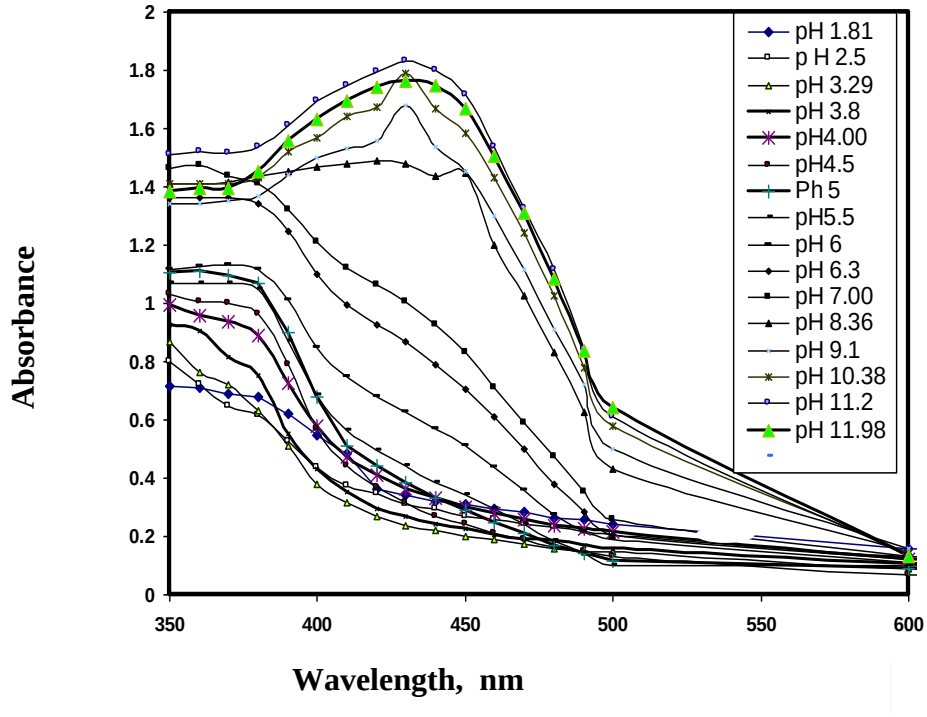


Fig. (9): Effect of pH on reagent (I_c) using universal buffer

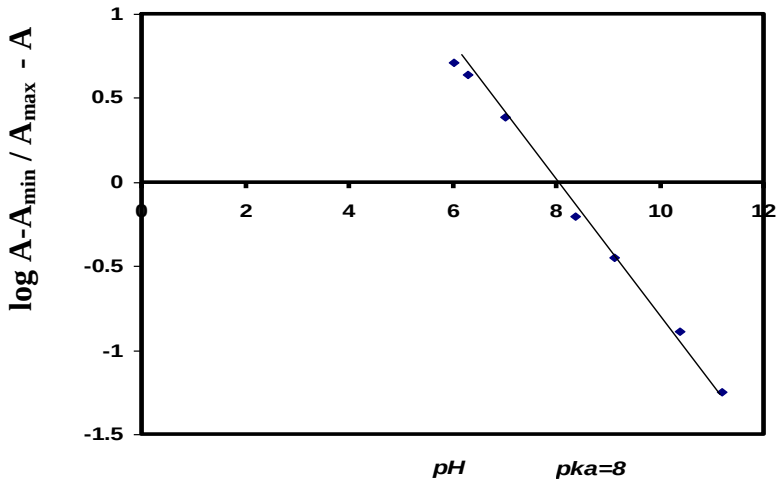


Fig. (١٠): pK_a of ligand I_c using universal buffer at 450 nm

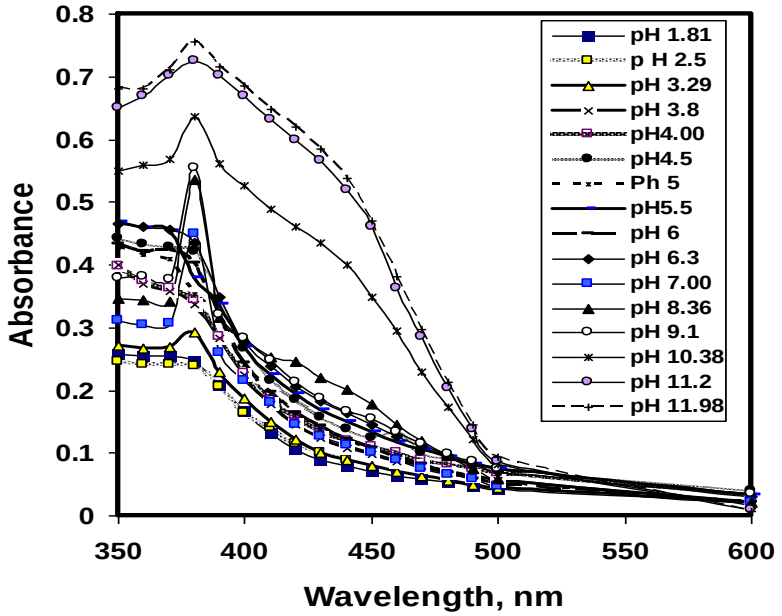


Fig. (11) : Effect of pH on reagent I_d using universal buffer

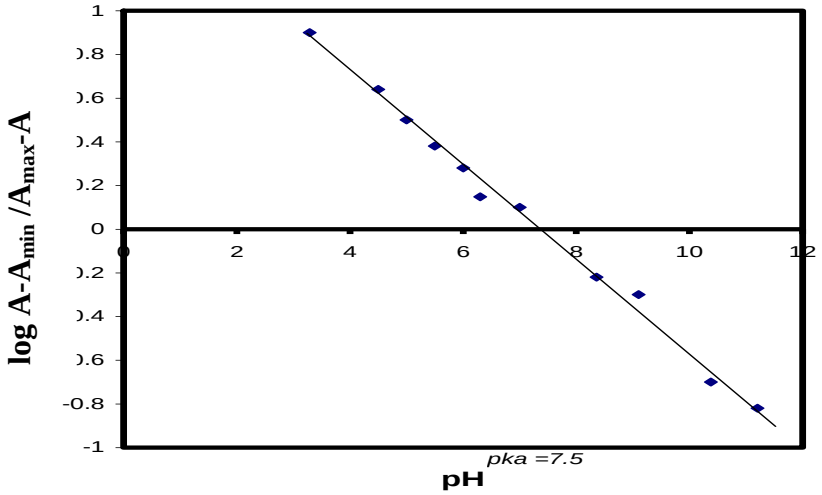


Fig. (12): pK_a of (reagent I_d) at 380 nm using universal buffer

3.1.1.6. Infrared spectra of the studied schiff base compounds

For ligands I_{a-d} in region 3500-3300 cm^{-1}, the bands due to the (OH) stretching vibration appeared at 3420, 3433, 3490 and 3358 cm^{-1} for I_a, I_b, I_c, and I_d, respectively. The in-plan bending modes of OH group appeared at 1345, 1343, 1385 and 1341 cm^{-1} for ligands I_a, I_b , I_c and I_d respectively.

The aromatic C-H stretching vibrations bands occur in region 3080-3010 cm^{-1} for ligands I_a, I_b, I_c and I_d, respectively.

The spectra of Schiff base compounds in range 1700-1200 cm^{-1} show bands due to ν c-o and ν sy C=N where the symmetric vibrations of C=N group for Schiff base ligands at 168, 1683, 1690 and 1687 cm^{-1} for I_a, I_b, I_c and I_d respectively and ν c-o appeared at 1221, 1227, 1161 and 1225 cm^{-1} for I_a, I_b , I_c and I_d, respectively.

The spectra in the range(2500-3000) is attributed to OH in carboxylic group as shown in reagnt I_a while the spectra in the range 1554 - 1349 cm^{-1} are due to the NO_2 group as found in reagent I_c.The spectra of Br atom is appeared at 1625 cm^{-1} which present in reagent I_d. The aromatic C=C bending which exhibits band in the range 1700-1500 cm^{-1} can also confirm the structure of the studied ligands. The IR spectra of investigated ligands are shown in Fig. (13) and the assignment of most important bands are collected in Table(4).

Table (4) : Assignment of the important bands in the IR spectra of I_a, I_b, I_c and I_d, ligands

Compound	ν **-OH**	δ **OH**	ν **-C=N**	ν **-N=N-**	ν **C-O**	ν **NO2**	ν **Br**
I_a Free	3412	1378	1573	1455	1156	-	-
I_b Free	3440	1366	1586	1482	1151	-	-
I_c Free	3742	1344	1576	1480	1145	1518	-
I_d Free	3691	1380	1619	1475	1143	-	1625

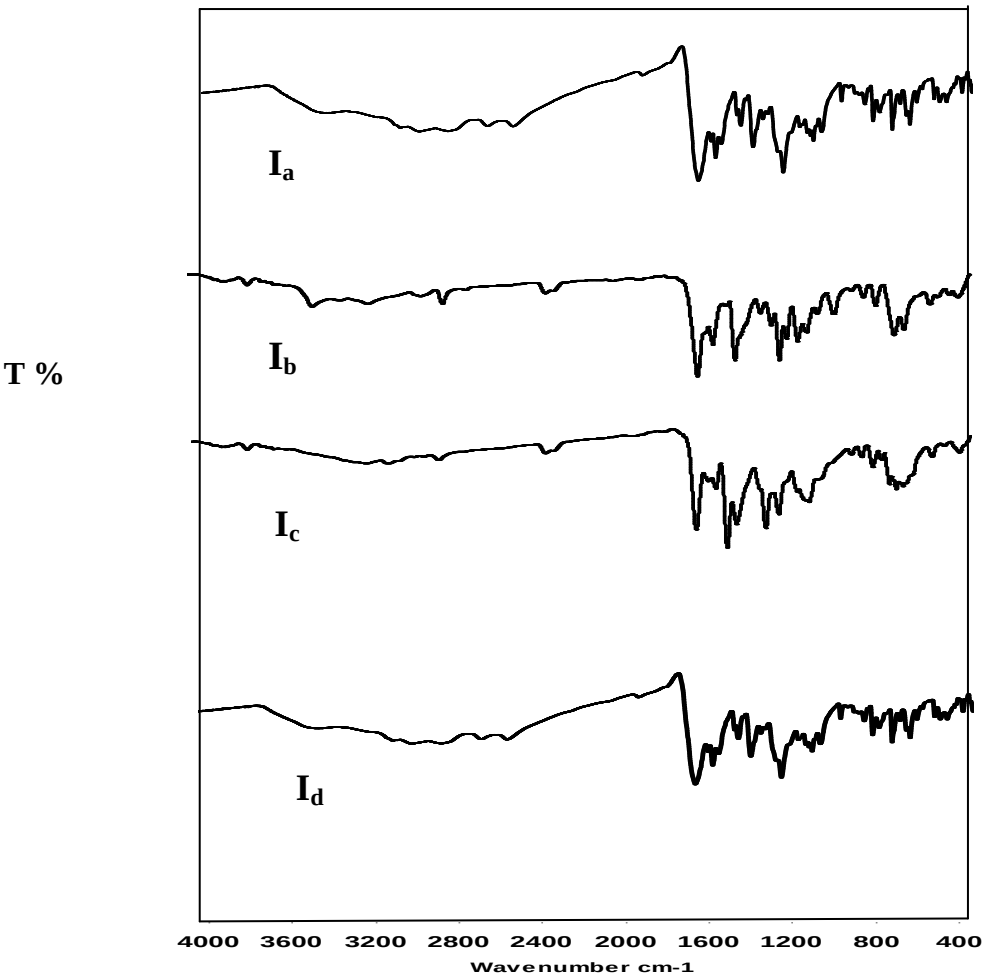


Fig. (13): IR spectra of investigated free ligands

3.1.1.7. H-NMR spectra of studied Schiff base compounds

The H-NMR spectra of I_a, I_b, I_c and I_d are shown in Fig.(14) and chemical shifts of the different signals are recorded in Table (5).

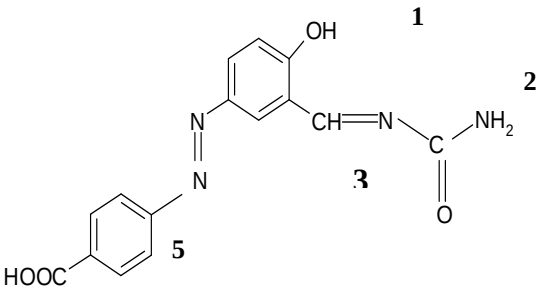
It is clear from H-NMR spectra of these ligands that signals lying at 10.392 , 10.37 , 10.42 and 10.396 ppm give evidence that they are due to the OH group attached to the phenyl ring of I_a, I_b, I_c and I_d reagents respectively.A new multiple signals at range 6.37-7.713 ppm are due to the protons of the phenyl group.

The signals lying in the range of ٨.١٨ – ٩.٢ ppm refer to the proton of azomethine group of these Schiff base compounds. A signal appeared at ٣.٩٦ ppm which attributed to protons of -OCH_3 group which confirmed the structure of I_b reagent.

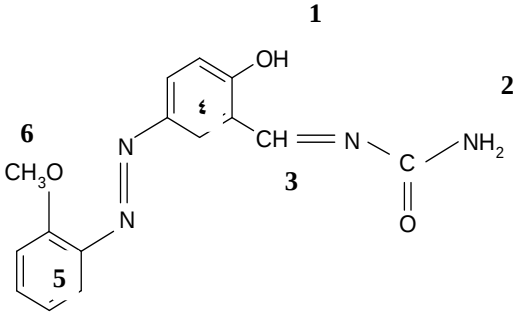
Table (5): Assignment and chemical shift (ppm) of different types of protons of ligands under consideration

Compound	**Chemical shift (δ), ppm of protons**					
	H (1) OH	**H(2)$_{NH2}$**	**H(3) CH=N**	**H(٤)**	**H(٥)**	**H(٦)**
I_a	١٠.٣٩٢	٦.٠٥	٨.١	٧.٩٠١	٧.٣٢	-
I_b	**10.37**	٦.٠٤	٨.١٣	**8.03**	**7.24**	**3.96**
I_c	**10.42**	٦.٠٥	٨.١٨	**7.84**	**7.30**	-
I_d	١٠.٣٩٦	٦.١٠	٩.١	٧.٧٩	٧.٣٢	-

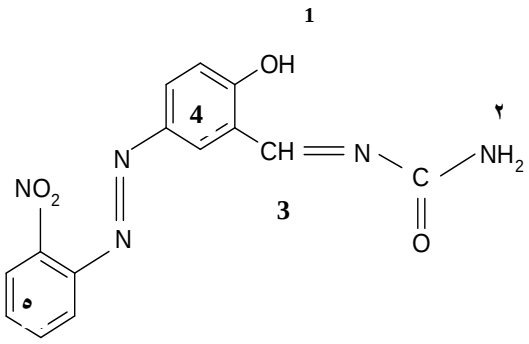
The support for conclusion obtained from elemental analysis, IR spectra and H-NMR for the structure of the ligands under consideration is gained. The different types of hydrogens which are expected for some compounds under investigation can be formulated as follows:



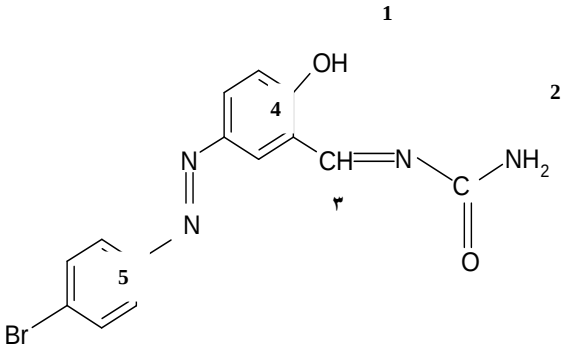
I_a reagent



I_b reagent



I_c reagent



I_d reagent

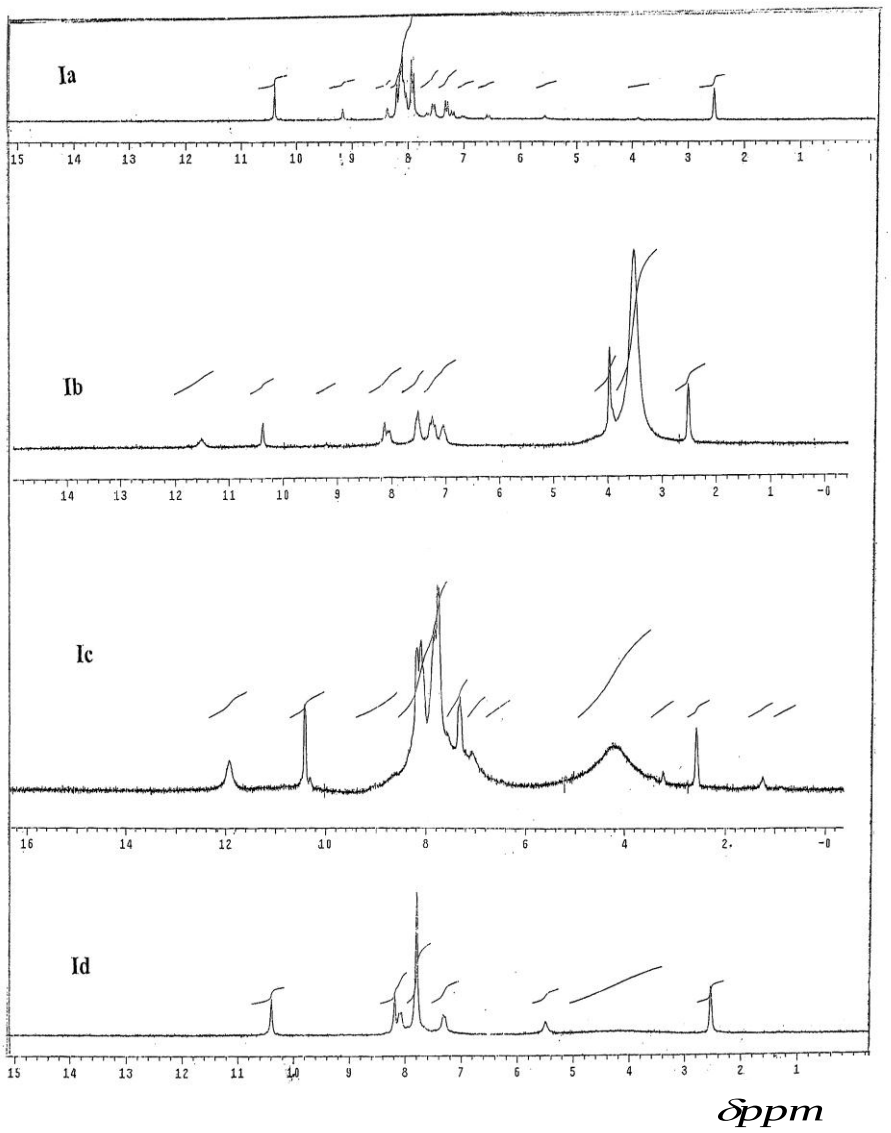


Fig. (14): H-NMR spectra of investigated free ligands

3.2. Studies of the complexes in solution

3.2.1.Conductometric titration studies

In the present work, conductometric titrations were carried out for transition metal ions Cu(II), Zn(II), Ag(I), V(V) and Hg(II) with the studied ligands.

Changes in the conductance depend on the change in the number and character of the conducting species in solution. The relation between the diffusion coefficient of these species and their conductivity is given by Stocks-Enistien equation:

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

Where D°is the diffusion coefficient of the conducting species, V_m the volume of the diffusing particles and η the viscosity of the used medium

Factors affecting 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 plot of the specific conductance values, after correction for the dilution, vs the ml added as shown in Fig (١٥) are characterized by breaks denoting the formation of (1:1), (1:2), (2:1) and (2:3) (M:L) types of the complexes with the metal ions under investigation as shown in Table (6).

٣.2.1.1. Conductometric titration of studied transition metal ions with Schiff base derived from p-aminobenzoic acid [I_a]

50 ml of metal ions ($1x10^{-4}$ M) was titrated with ($1x10^{-3}$ M) of the above reagent. From the resulted curve it was found that M:L ratio of the complex is 1:1 and 1:2 with all metal ions, except Ag(I) form 2 : 1

3.2.1.2. Conductometric titration of studied transition metal ions with Schiff base derived from o-Methoxyaniline [I_b]

50 ml of metal ions ($1x10^{-4}$ M) was titrated with ($1x10^{-3}$ M) of the above reagent. From the resulted curve it was found that copper ions form 1:1, 1:2, 2:1 and 2:3 (M:L) complexes with the studied ligand, mercury form 1:1, 1:2, 2:1, zinc form 1:1, 1:2 and 2:1 and silver ion form 1:1, 1:2, 2:1 complexes and vanadium form 1:1, 1:2, 2:1 and 2:3.

3.2.1.3. Conductometric titration of studied transition metal ions with Schiff base derived from o-Nitroaniline [I_c]

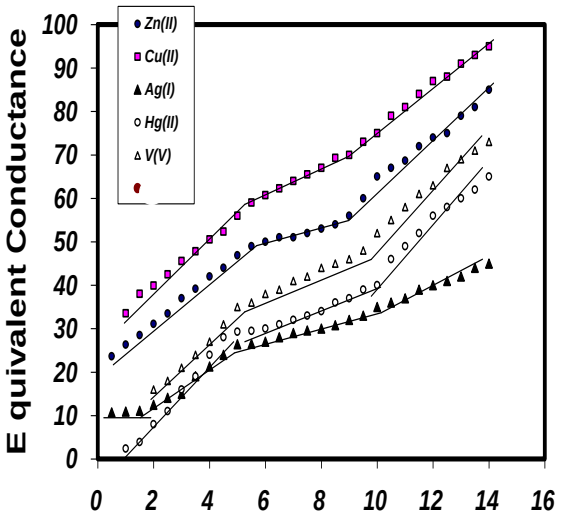
50 ml of metal ions ($1x10^{-4}$ M) was titrated with ($1x10^{-3}$ M) of the above reagent. From the resulted curve it was found that zinc, mercury and copper ions form 1:1, 1:2 and 2:1 (M:L) complexes with the studied ligand while, silver ion form 1:1, 1:2 (M:L) complexes and vanadium ions form 1:1, 1:2 (M:L) complexes .

3.2.1.4 Conductometric titration of studied metal ions with Schiff base derived from p-Bromoaniline derived Schiff base [I_d]

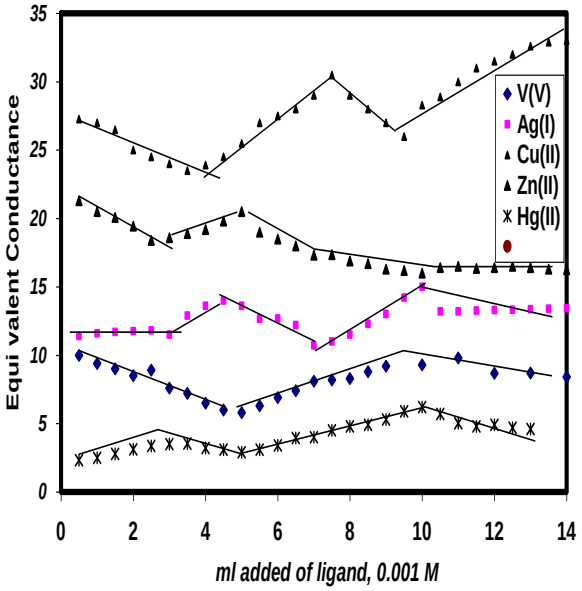
50 ml of metal ions ($1x10^{-4}$ M) was titrated with ($1x10^{-3}$ M) of the above reagent. From the resulted curve it was found that all metal ions form 1:1 (M:L) and 1:2 complexes with the studied ligand.

Table (٦) The stoichiometry of complexes of Ag(I), Cu(II), Zn(II), V(V), and Hg(II) with the studied ligands Hg^{2+} with the studied ligands

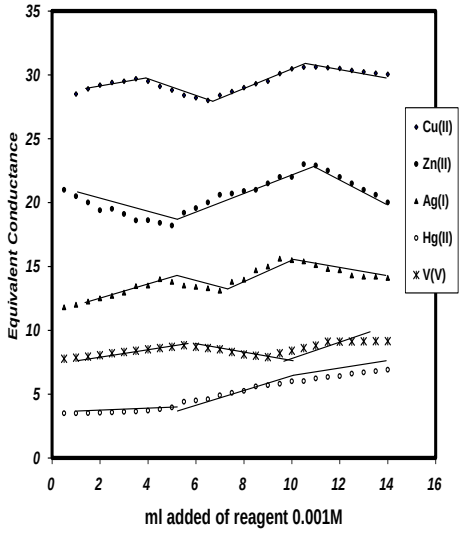
Ligand	Types of complexes (M:L)				
	Ag(I)	Cu(II)	Zn(II)	Hg(II)	V(V)
I_a	**1:1**	**1:1**	**1:1**	**1:1**	**1:1**
	2:1	**1:2**	**1:2**	**1:2**	**1:2**
I_b	**1:1**	**1:1**	**1:1**	**1:1**	**1:1**
	١: ٢	**1:2**	**1:2**	١: ٢	**1:2**
	٢:١	٢:١	٢:١	٢:١	٢:١
	--	**2:3**	**- -**	**--**	**2:3**
I_c	**1 :1**	**1:1**	**1:1**	**1 :1**	**1 :1**
	1:2	**1:2**	**1 :2**	**1:2**	**1:2**
	2:3	٢:١	٢:١	٢:١	**-**
I_d	**1:1**	1:1	1:1	1:1	1:1
	1:2	1:2	1:2	**١:٢**	**١:٢**



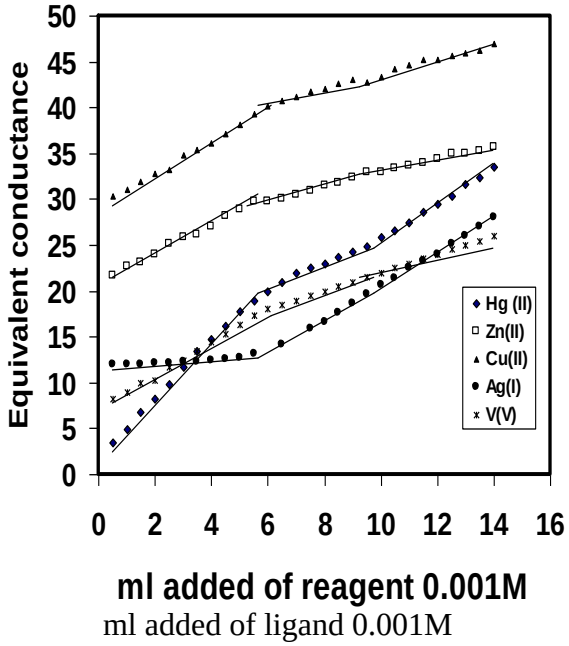
I_a reagent with metal ion



I_b reagent with metal ion



I_c reagent with metal ion



I_d reagent with metal ion

Fig. (15) Conductometric titration curves of studied metal ions with I_a, I_b, I_c and I_d ligands to form complexes

3.2.2. Potentiometric titration studies

The potentiometric technique has been used in many fields of chemistry .There are three types of potentiometric procedures:

1-**Bjerrum**[177] adding the ligand to an acidic solution of metal ions

2-**Calvin and Willson**[178] titrating a solution of metal ion and ligand with a solution of alkali.

3-**Fronaeus**[179] titrating the acidified metal-ion solution with a buffer mixture containing the acid and its sodium salt.

The titration procedure used in this work is developed by Calvin and Bjerrum and the proton-reagent stability constants (k_n^H) were determined.

The average number of protons associated with the reagent molecules $\bar{n}_A$ was determined using the equation:

$$\bar{n}_A = Y + \frac{(V_1 - V_2)(N^\circ + E^\circ)}{(V^\circ + V_1)\ TC_{L^\circ}}$$

Where V_1 and V_2 are the volumes of alkali required to reach the same pH in the titration of acid solutuion and ligand. respectively. V° is the initial volume of the mixture (50 ml), N°is the normality of sodium hydroxide, E° is the concentration of free acid and TC_{L° is the total concentration of the reagent Y is the total number of dissociable protons attached with the reagent molecule. The values of $\bar{n}_A$ were plotted against pH and the values of proton-ligand stability constants were determined by interpolation of half $\overline{n_A}$ values. The average number of molecules attached per metal ion $\bar{n}$ and free ligand exponent pL are calculated using The quations:

$$\bar{n} = \frac{(V_3 - V_2)(N^\circ + E^\circ)}{(V^\circ + V_1)n^-{}_A TC_{M^\circ}}$$

$$pL = \log_{10} \frac{\sum_{n=o}^{n=j} \beta^H_n \left(\frac{1}{\text{antilog} pH} \right)^n}{TC_{L^o} - n^- TC_{M^o}} \times \frac{V^o + V_3}{V^o}$$

Where TC_{M°, the total concentration of the metal present in the solution $\beta^H{}_n$ overall proton-reagent stability constant, V_1, V_2 and V_3 are the volumes of alkali required to reach the same pH in the titration curves of nitric acid, ligand and the complex respectively.

Plotting the values of $\bar{n}$, against the pL values and interpolation at the half $\bar{n}$ values the stability constants of complexes were determined.

Potentiometric titration of studied transition metal ions with ligands under investigation

The potentiometric titration of an acid mixture, ligand soltions under consideration and ligand-metal solutions was carried out against NaOH for determination of stability constants of studied complexes.

Mixture A 5.0 ml of 0.1 M HNO_3 and 5.0 ml of 1 M KNO_3 then completed to 50 ml by (40% v/v) alcoholic water mixture.

Mixture B consists of mixture A and 25 ml of ligand solution ($1x10^{-3}$ M) then complete the mixture to 50 ml by (40% v/v) alcoholic water mixture.

Finally mixture C consists of mixture B and 5 ml of metal solution ($1x10^{-4}$ M) then completed to 50 ml by the same alcoholic water solution(40 % v/v). The metal mixture (C) of Zn(II), V(V), Cu(II), Ag(I) and Hg(II) was titrated with larger volumes of sodium hydroxide than that in case of acid and ligand mixtures as shown in Figs. (16,19,22,25).

The formation curves of the plot $\bar{n}$ against pL for the solution containing the metal ions Zn(II), V(V), Cu(II), Ag(I) and Hg(II) are represented in Figs. (18), (21), (24) and (27). From these curves the values of stability constants pK_1 and pK_2 were determined at $\bar{n}$ =0.5 and 1.5 in case of I_a reagent while in case of I_b, I_c and I_d reagents pK_1 only was determined at $\bar{n} = 0.5$ depending on the number of replaceable protons in the ligand as shown in Figs. (17,20,23,26) .

The proton ionization constants and stability constants of metal ligand complexes are recorded in Table (٧) which indicate that pK_1 values decrease in the order $I_c > I_d > I_a > I_b$. It is clear also that the chelates with Zn(II), V(V), Cu(II), Ag(I) and Hg(II) ions of stability in order V(V) > Cu(II) > Zn(II)> Hg(II)> Ag(I) for I_c and I_d which indicate that as the oxidation state of the metal increase the overall stability constant of the formed complex increase whereas the other orders of I_a , I_b with metal ions under consideration differ in their sequences indicating that such complexes are formed through covalent bonding between the central metal ion and ligand molecules.

Table (٧) Proton ionization constant and metal-ligand constant deducted from potentiometric titrations

Ligand	Proton ionization constsnt		Metal–ligand stability constant									
			Ag(I)		Hg(II)		Cu(II)		Zn(II)		V(V)	
	pK_1^H	pK_2^H	log β_1	log β_2	log β_1	log β_2	log β_1	log β_2	log β_1	log β_2	log β_1	log β_2
I_a	**7.2**	**8.4**	**3.6**	**5.6**	**3.5**	**6.6**	**4.6**	**7.1**	**4.4**	**6.8**	**4.7**	**7.3**
I_b	**5.5**	**--**	**3.9**	**--**	**4.3**	**--**	**4.4**	**--**	**4.1**	**--**	**4.9**	**--**
I_c	**8.2**	**--**	**4.2**	**--**	**5.2**	**--**	**5.8**	**--**	**5.6**	**--**	**6.3**	**--**
I_d	**7.3**	**--**	**3.2**	**--**	**3.6**	**--**	**3.9**	**--**	**3.8**	**--**	**4.5**	**--**

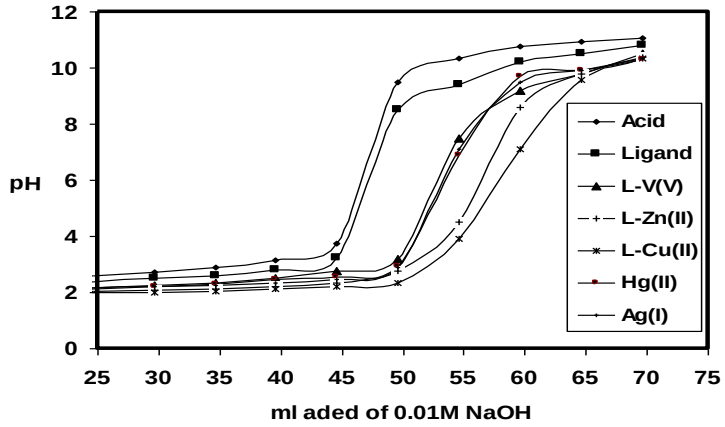


Fig. (16) Potentiometric titration of Schiff base (reagent I_a) in presence of metal ions

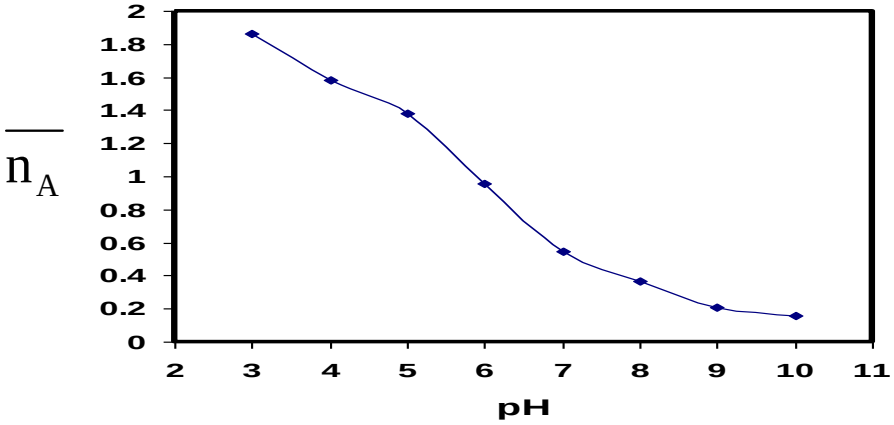


Fig. (17) Formation curve of proton- ligand I_a

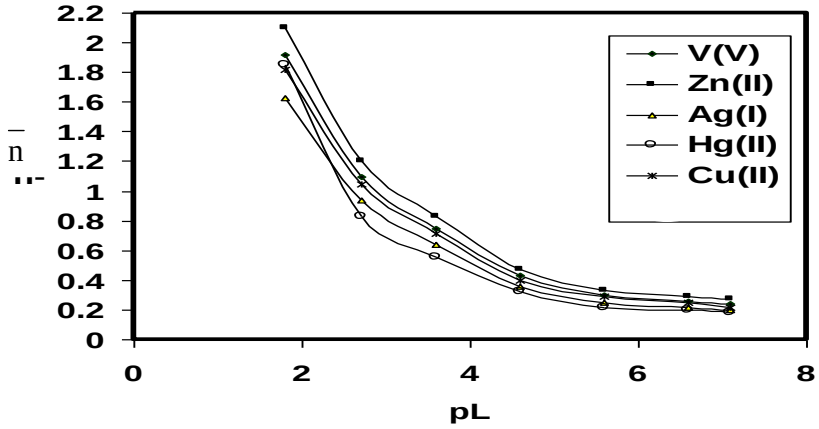


Fig. (18) Formation curve of studied metal ions with ligand I_a

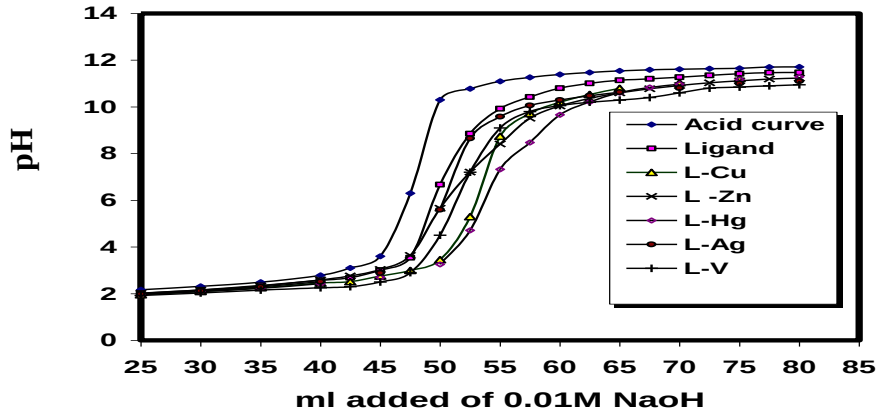


Fig. (19) Potentiometric titration of o-methoxyaniline derived Schiff base (ligand I_b) in presence of metal ions

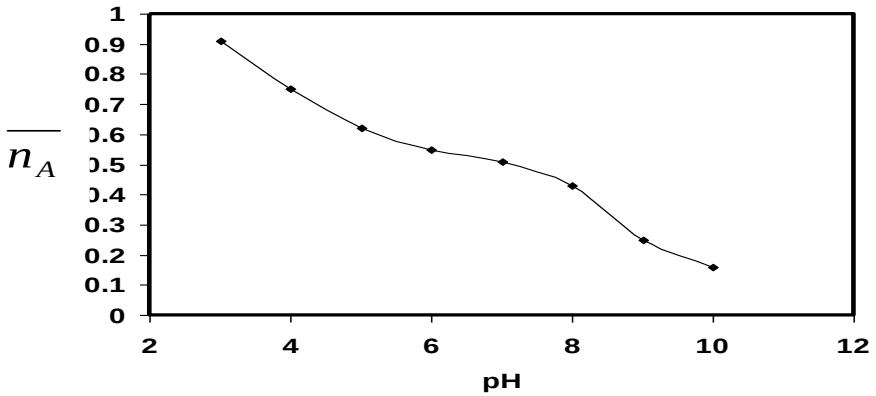


Fig. (20) Formation curve of proton- ligand I_b

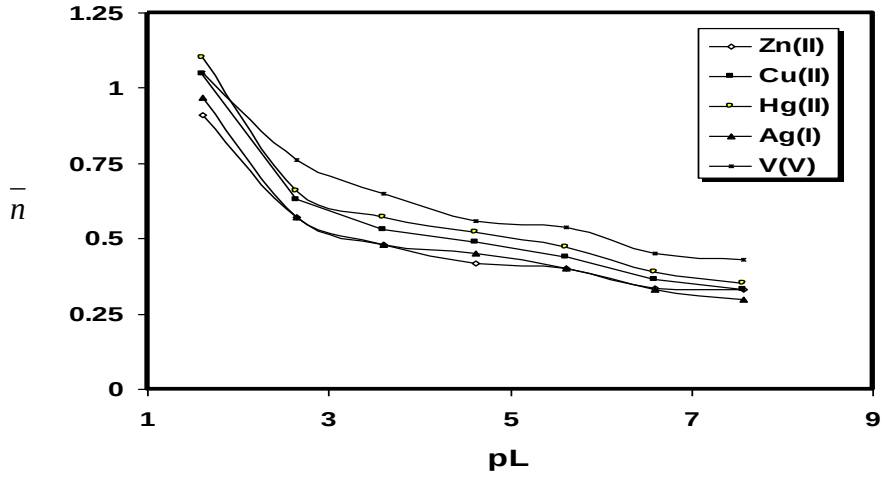


Fig. (21) Formation curve of metal ions with ligand I_b

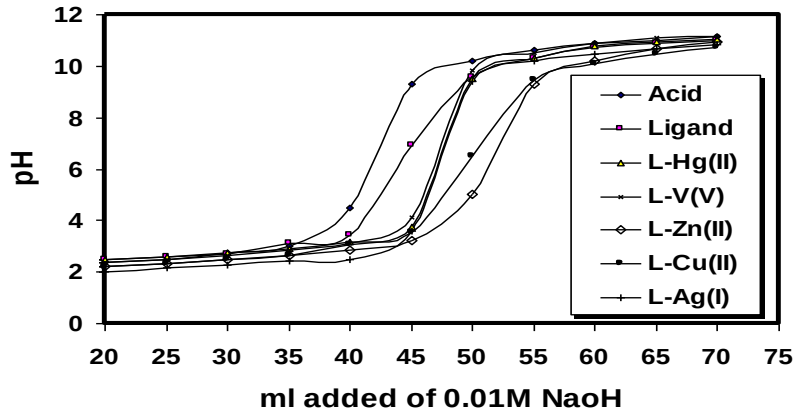


Fig. (22) Potentiometric titration of o-nitroaniline derived Schiff base(ligand I_c) in presence of metal ions

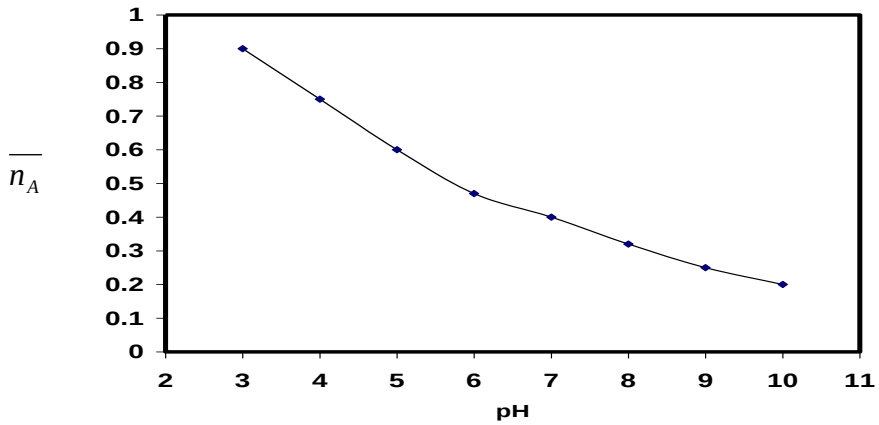


Fig. (23) Formation curve of proron-ligand I_c

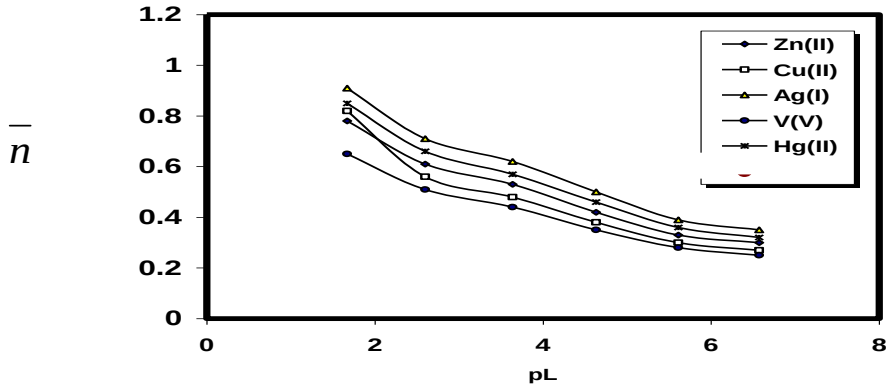


Fig. (24) Formation curve of metal ions with ligand I_c

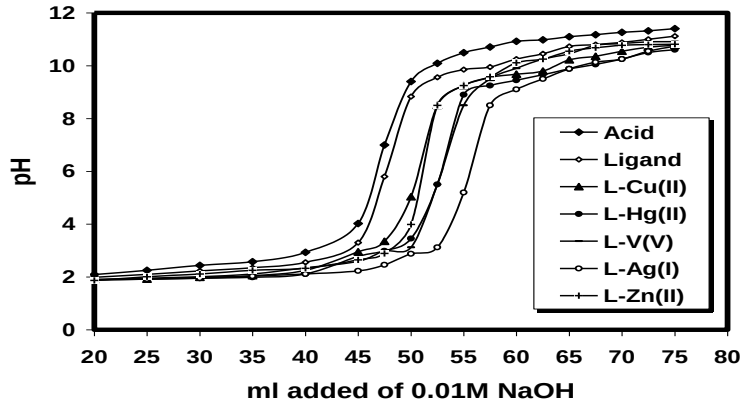


Fig. (25) Potentiometric titration of p-bromo aniline derived Schiff base (ligand I_d) in presence of metal ions

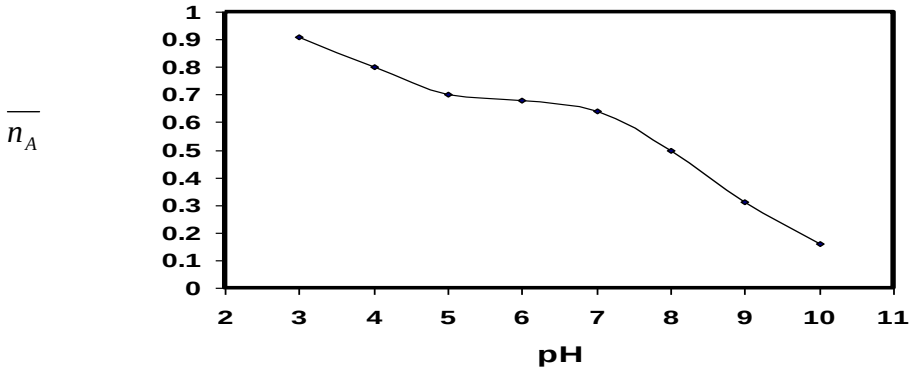


Fig. (26) Formation curve of proton- ligand I_d

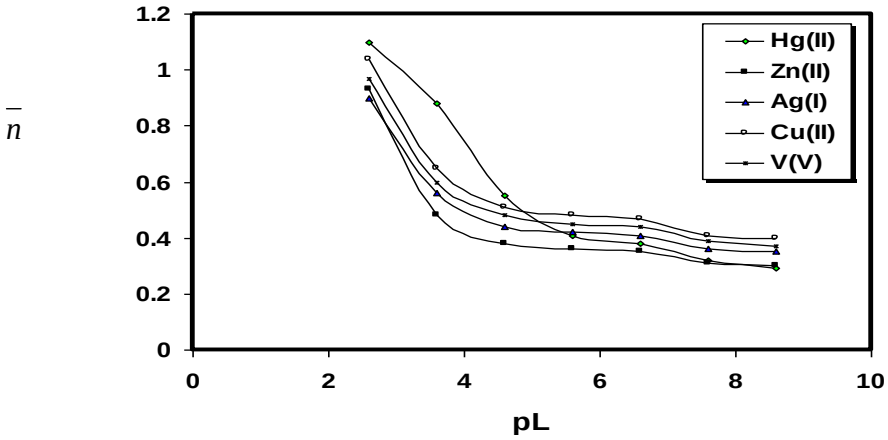


Fig. (27) Formation curve of studied metal ions with ligand I_d

3.2.3. Spectrophotometric studies

3.2.3.1. Spectrophtometric studies of Cu(II), Zn(II), Ag(I), V(V) and Hg(II) with 4-(3-carbamoyliminomethyl-4hydroxy-phenylazo) benzoic acid(I_a)

3.2.3.1 .1. The optimum conditions for complex formation

3.2.3.1.1.1. Effect of pH

The effect of pH on the formation of reagent I_a complexes with the metal ions under investigation was studied in universal buffer solution of the pH range 1.81-11.98 for Cu(II), Zn(II), Ag(I), V(V) and Hg(II) to obtain best colour development for complex formation. The most suitable pH values for the formation of Zn(II), Cu(II) and Ag(I) complexes with reagent I_a are determined by mixing a constant volume 1.5 ml of 3 $x10^{-3}$ M of reagent and different volumes of buffer solution of different pH values and 1 ml of 3×10^{-3} M metal ion. The absorption spectra were recorded using a blank solution prepared in the same manner without metal ion. In case of V(V) and Hg(II) 2.0 ml reagent was needed with 1 ml of metal ion at different pH values.From this analysis it was found that the best pH values were 6.5 , 7.8, 3.6, 5.5 , 4.6 with complete colour development at λ_{max} 450, 400, 390, 500 and 425 nm during the determination of Zn(II), Cu(II), V(V), Ag(I) and Hg(II) respectively, these wavelengths represent λ_{max} of C curve as shown in Fig. (28) and Table (8). The absorbance-pH curves of ligand I_a with metal ions under investigation in universal buffer solutions of varying pH values are represented in Fig.(29) where the suitable pH was detected for each metal ion complex .

3.2.3.1.1.2. Effect of time

Experiments on the effect of time on the absorbance of formed complexes, as in Fig.(30) showed that complexes of Zn(II) and Cu(II) are completely developed but after 5 minutes their absorbances decrease

while those of Ag(I) and Hg(II) are stable up 10 minutes. In case of V(V), the absorbance of the formed complex increased by time up to 50 minutes.

3.2.3.1.1.3. Effect of temperature

The stability of complex colour is studied against temperature. The absorbance of V(V)-I_a complex was still stable up to 50 °C after that it becomes pale light yellow while the absorbsnces of I_a complexes with Zn(II) and Cu(II) were stable by increasing temperature up to 35 °C then decreased sharply. In case of Hg(II) and Ag(I), as these complexes were subjected to temperature their absorbencies decreased as shown in Fig(31).

3.2.3.1.1.4. Stoichiometry of metal ion complexes

Contiuous variation method[(180)]

A serious of solutions which were obtained by mixing equimolecular solution of metal ion solution and ligand in varied proportions keeping the total molar concentration constant and measure the absorbance. From this study, it was concluded that all investigated metal ions**,** Cu(II), Zn(II), Ag(I), V(V) and Hg(II) form (1:1) complexes with reagent I_a which was showed in Fig. (32).

3.2.3.1.15. Molar ratio method[(181)]

The metal ion concentration was kept constant while ligand was increased and measure the corresponding concentration. This method confirmed the continuous variation method in that all the formed complexes are of (1:1) in their metal–reagent ratio which indicated in Fig. (33).

3.2.3.1.1.6. Determination of stability constant

Spectrophotometric techniques can be useful for the determination of the stability constant of metal ion complexes. Generally, the

spectrophotometric methods that are used for stoichiometric determination of the complex can be used for the determination of its stability constant as shown in Table (8). The data of the mole ratio and continuous variation methods aid in gaining the stability constant by substituting in the following equation[182]:

$$K_n = \frac{A/A_m}{(1-A/A_m)^{n+1} C_R{}^n n^2}$$

Where ;

A, is the absorbance at reagent concentration C_R

A_m, is the absorbance at complete colour development

n, is the stoichiometric ratio of the complex

K_n, is the stability constant

3.2.3.1.1.7. Obeyence to Beer`s law:

The obeyence of Cu(II), Zn(II), Ag(I), V(V) and Hg(II) complexes with the reagent I_a to Beer`s law was studied to verify such complexes for spectrophotometric determination of these metal ions. The relation drawn between the concentration of metal ions studied and the absorbances of their complexes can be used as calibration curve for the spectrophotometric determination purpose. The reagent concentration was constant, for each metal ion, for both blank and sample while the concentration of metal ion was varied, the pH is adjustd to the suitable value for each metal ion using universal buffer and absorbencies were measured at definite wavelength for each studied metal ion,Fig. (34). The molar absorptivity (ε) values expressed in (L mol^{-1} cm^{-1}) are obtained as slopes of the constructed lines. Intercept, slope and correlation coefficient are also obtained from the same lines , all these values are calculated and recorded in Table (8).

3.2.3.1.1.8. Ringbom optimum range[183]

For accurate spectrophotometric analysis, Ringbom plot has been drawn Fig. (35). The results indicate that the optimum ranges are 1.5-4.9 1.0-5.4, 2.9-16.2, 1.1-8.3, and 1.7-8.9 for Zn(II), Cu(II), V(V), Ag(I) and Hg(II) complexes respectively with reagent I_a with relative standard deviation (RSD) from 0.61-1.29 % as shown in Table (8).

3.2.3.1.1.9. Effect of interference

The influence of interference ions on the determination of Zn(II), Cu(II), V(V), Ag(I) and Hg(II) with reagent I_a was tested for some cations and anions. An error of less than ± 3 % in the absorbance reading was considered to be tolerable. The tolerance limit was defined as the concentration of the foreign caused an error less than 3 % in the absorbance value of the metal ion complex. So, As shown in Table (9), for V(V)-I_a complex, the tolerance values for ions Na^{+}, Mg^{2+}, Sr^{2+}, K^{+} ,Ca^{2+},Mn^{2+} I^{-} ,NO_2^{-}, ,SO_3^{2-} are mor than 2000 µg ml^{-1}. From these tolerance values it was suggested that the application of reagent I_a for the determination of V(V) in presence of high amount of these ions. Whereas in case of Fe^{3+}, Pb^{2+}, $NH_4^{+}$the tolerance values are less than 200 µg ml^{-1} so these ions should be masked befor determination of V(V). The tolerance values of other complexes are listed in Table (9).

Table(8): Cumulative data of the analytical conditions for spectrophotometric determination of Zn(II), Cu(II), V(V), Ag(I) and Hg(II) ions with reagent I_a

Parameter	Reagent I_a				
	Zn(II)	Cu(II)	V(V)	Ag(I)	Hg(II)
pH	6.5	7.8	3.6	5.5	4.6
λ_{max} (nm),A curve	360	360	380	360	360
λ_{max} (nm),B curve	355	370	360	370	380
λ_{max} (nm),C curve	450	400	390	500	425
Beer'Law range,(µg ml^{-1})	1.5-5.0	1.0-5.5	2.5-16.5	1.0-8.5	1.5-9.0
Ringbom range, (µg ml^{-1})	1.5-4.9	1.0-5.4	2.9-16.2	1.1-8.3	1.7-8.9
Standard deviation(SD)	0.077	0.059	0.097	0.084	0.068
Relative standard deviation(RSD)	0.61	0.85	1.29	0.52	0.59
Variance $(SD)^2$ x 10^{-3}	5.92	3.48	9.4	7.05	4.62
Slop (b)	0.04	0.071	0.057	0.1114	0.023
Intercept (a)	-0.01	-0.0013	-.0024	-.0017	-.0018
Correlation coefficient	1.0	0.997	0.997	0.997	0.992
Molar absorptivity , L $mol^{-1}cm^{-1}$	3.7 X 10^4	**7.5 X10^4**	3.57 x 10^3	2.3X10^5	1X10^4
Stability constant [a]	4.43	3.94.	4.29	3.85	3.8
Stabilit`y constant [b]	6.2	4.78	5.21	4.77	5.6
Average of stability constant	5.3	4.36	4.75	4.31	4.7
Stoichiometry(M :L)	(1:1)	(1:1)	(1:1)	(1:1)	(1:1)

[a] : Stability constant using continuous variation method
[b] : Stability constant using Mole ratio method

Table (9): Tolerance limits for the influence of interference ions on the determination of Zn(II), Cu(II), V(V), Ag(I) and Hg(II) with reagent I_a

Foreign ion	Zn(II)-I_a	Cu(II)-I_a	V(V)-I_a	Ag(I)-I_a	Hg(II)-I_a
K^+	500	2500	3000	1600	2200
Ca^{2+}	1000	2100	2200	2900	2600
Mn^{2+}	400	1000	900	850	1300
NO_2^-	2000	1300	500	200	1000
SO_3^{2-}	1600	700	600	2500	3000
Fe^{2+}	20	50	150	400	100
Pb^{2+}	50	100	50	150	200
$NH4^+$	200	1000	20	600	100
Al^{3+}	20	500	300	1000	2500
$C_2O_4^{2-}$	2000	1300	200	500	400
Cr^{3+}	100	50	1500	150	200
SO_4^{2-}	150	200	750	2000	500
Ni^{2+}	1100	200	500	100	50
Co^{2+}	300	2500	1500	1000	1200
Na^+	5000	2000	4000	1000	3000
Mg^{2+}	3500	300	2500	100	300

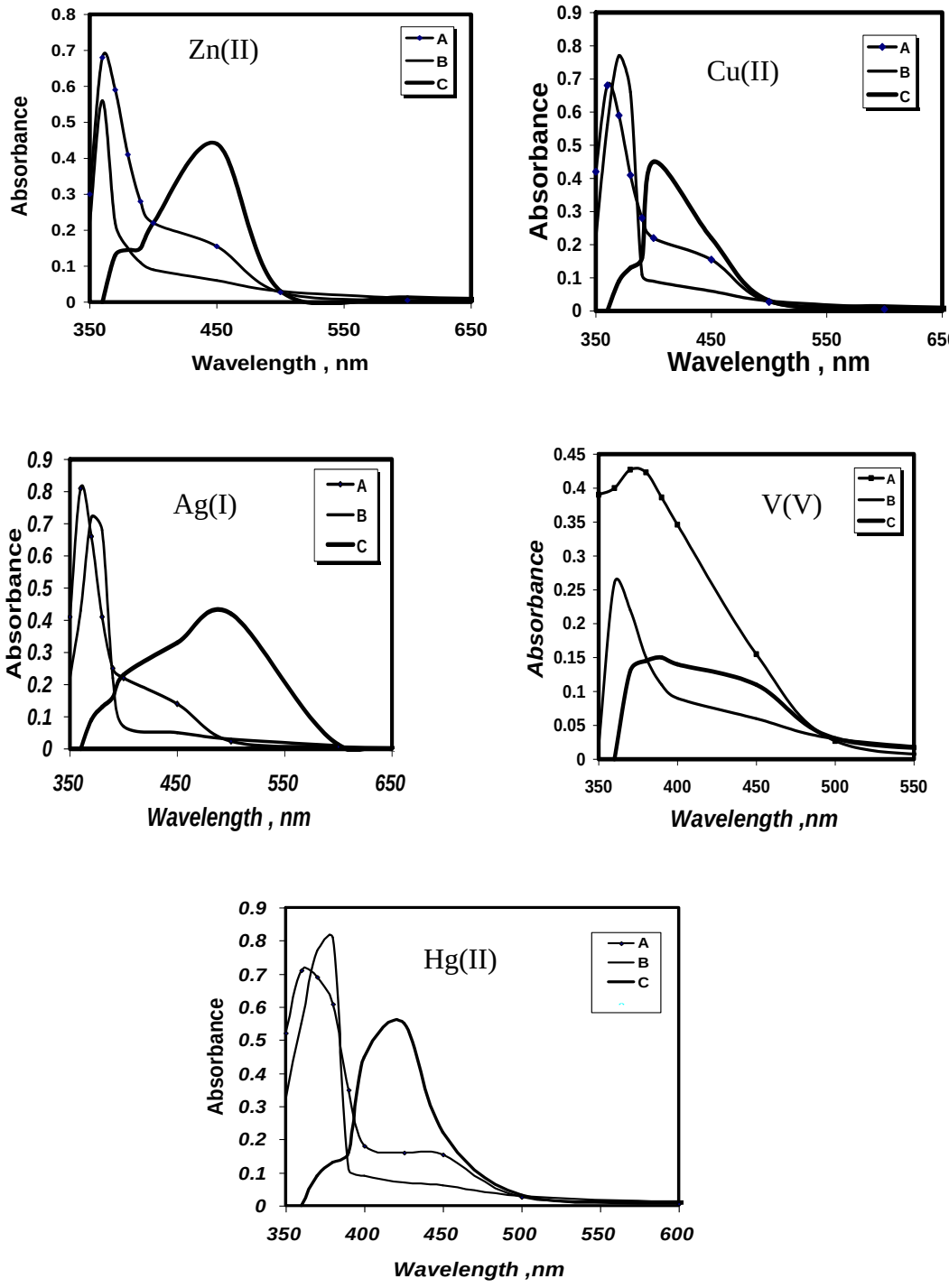


Fig. (28) Absorption spectra of reagent I_a with Zn(II), Cu(II), V(V), Ag(I) and Hg(II) where A:reagent + buffer against buffer B:Reagent + M^{n+} + buffer against buffer ,C: reagent + M^{n+} + buffer against reagent + buffer

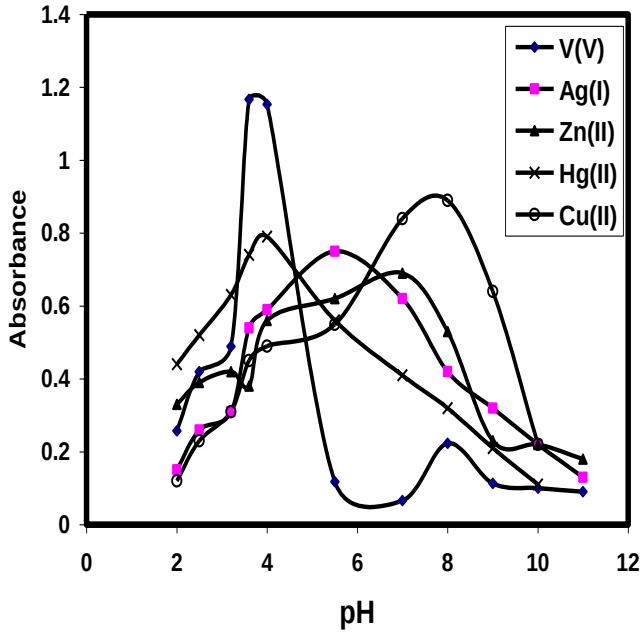


Fig. (29): Effect of pH on the absorbance of metal ion complexes with reagent I_a

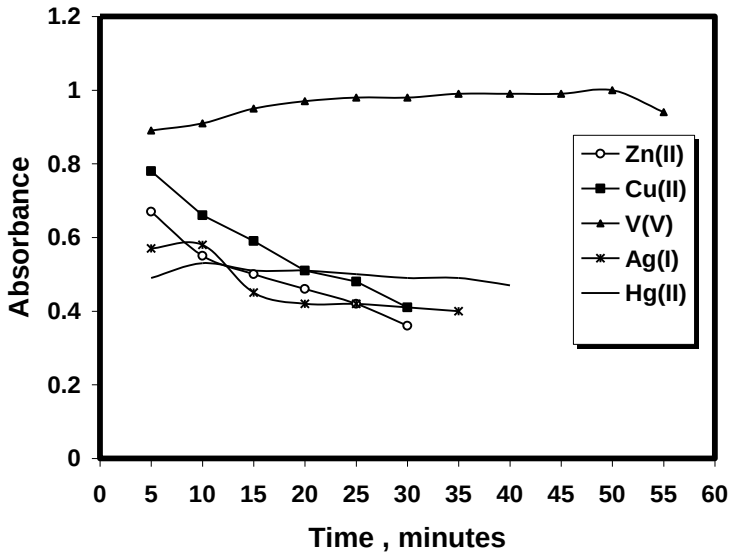


Fig. (30): Effect of Time on the absorbance of metal ion complexes of reagent I_a

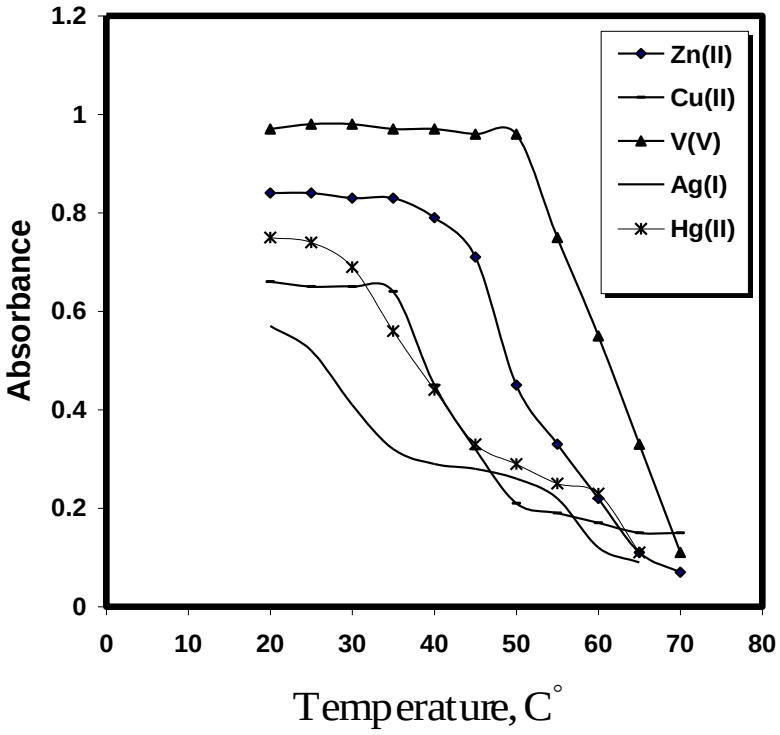


Fig. (31): Effect of Temperature on the absorbance of metal ion complexes of reagent I_a

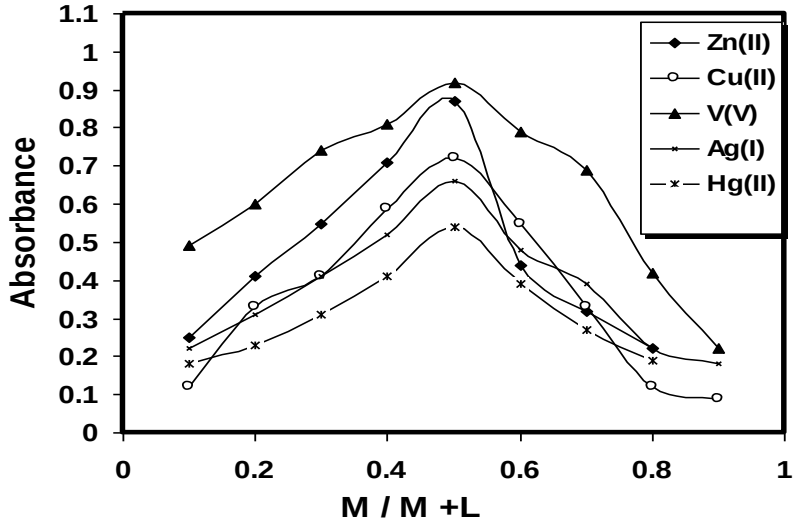


Fig. (32): Continuous variation method for metal chelates with reagent I_a

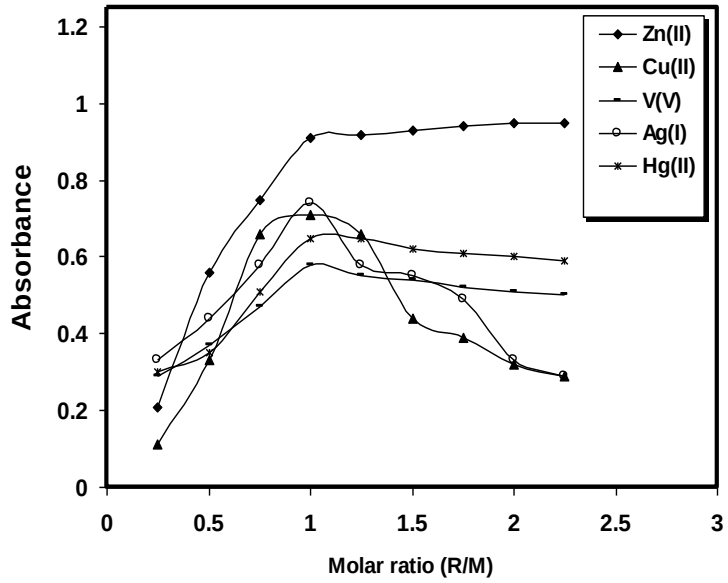


Fig. (33): Molar ratio method for metal chelates with reagent I_a

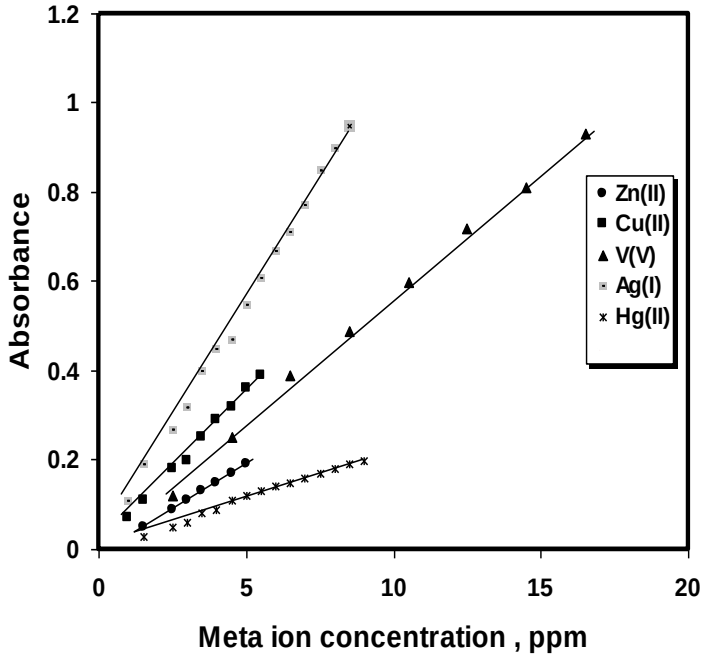


Fig. (34): Application of Beer´s law for studied complexes at the suitable conditions of reagent I_a

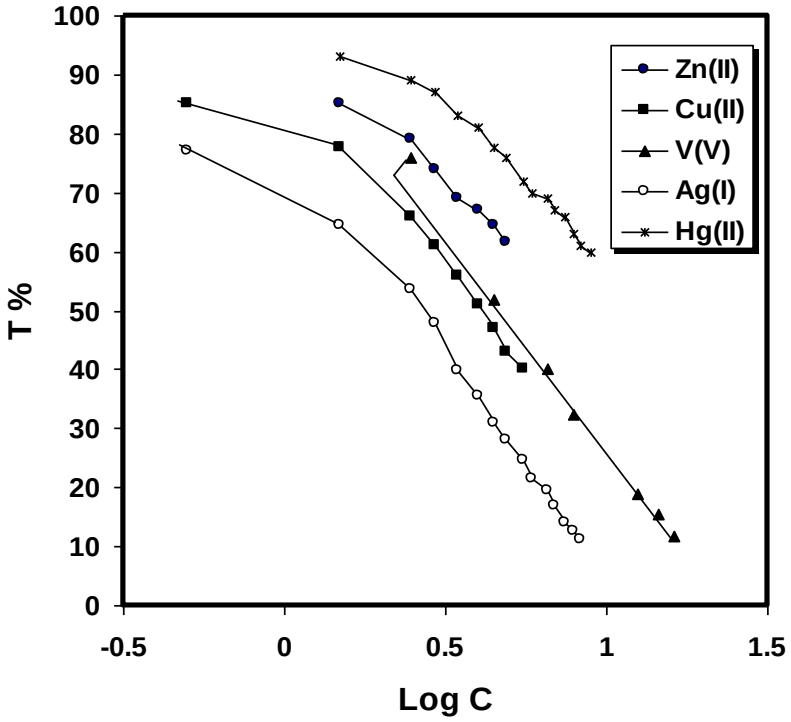


Fig. (35): Ringbom plot for Zn(II), Cu(II), V(V), Ag(I) and Hg(II) complexes with I_a

3.2.3.2. Spectrophtometric studies of Zn(II), Cu(II), V(V), Ag(I) and Hg(II) with 1-[2-hydroxy-5-(methoxyphenyldiazenyl) benzylidene] urea (I_b)

3.2.3.2.1. The optimum conditions for complex formation

3.2.3.2.1.1. Effect of pH

The effect of pH on the formed complexes of reagent I_b with the metal ions under investigation was studied in universal buffer solution of the pH range 1.81-11.98 for Cu(II), Zn(II), Ag(I), V(V) and Hg(II) to obtain best absorbance for complex formation. The most suitable pH values for the formation of Zn(II) and Cu(II) complexes with reagent I_b are determined by mixing a constant volume 1.0 ml of 3 $x10^{-3}$ M of reagent and different volumes of buffer solution of different pH values and 0.5 ml of 3×10^{-3} M metal ion while Hg(II) -complex with reagent I_b needs 2.5 ml of the reagent and 1 ml of the metal ion. The absorption spectra were recorded using a blank solution prepared in the same manner without metal ion. In case of V(V) and Ag(I) 2.0 ml reagent was needed with 1 ml of metal ion at different pH values .From this analysis it was concluded that the best pH values were 6.0, 4.7, 4.4, 5.3 and 7.0 during the determination of Zn(II) and Cu(II), V(V), Ag(I), and Hg(II) with λ_{max} 425, 450, 410, 390 and 400 nm respectively, these wavelengths represent λ_{max} of C curve as shown in Fig.(36) and in Table (10). The absorbance-pH curves of ligand I_b with metal ions under investigation in universal buffer solutions of varying pH values are represented in Figs. (37) where the suitable pH value was detected for each metal ion complex.

3.2.3.2.1.2. Effect of time

The effect of time on I_b complexes of metal ions was studied by measuring the absorbance of solution containing the metal ion and the reagent against blank solution prepared by the same way without metal ions after adjusting the pH to the suitable values using universal buffer

.This study confirmed that the complexes between I_b and Cu(II), Zn(II) and Ag(I) were completely formed and remained stable up to 60 min, 30 and 20 min respectively while those of V(V) and Hg(II) were affected by time after 5 min where their absorbencies were sharply decreased as shown in Fig. (38).

3.2.3.2.1.3. Effect of temperature

The effect of temperature was also studied for the metal ion complexes with reagent I_b by heating the sample solution and the blank at different temperatures. This test showed that raising the temperature also affects the stability of Cu(II), Zn(II) and Ag(I) complexes while those of V(V) and Hg(II) were stable up to 40 °C which is shown in Fig.(39).

3.2.3.2.1.4. Stoichiometry of metal ion complexes

Contiuous variation method

A serious of solutions which were obtained by mixing equimolecular solution of metal ion solution and ligand in varied proportions keeping the total molar concentration constant and measure the absorbance. From this study, it was concluded that Zn(II), Cu(II), V(V) ions form (1:2) M:L complexes with reagent I_b while Ag(I) and Hg(II) form (1:1) complexes which was showed in Fig. (40) and Table (10).

3.2.3.2.1.5. Molar ratio method

The metal ion concentration was kept constant while ligand was increased and measure the corresponding concentration .This method confirmed the continuous variation method in that Zn(II), Cu(II), V(V) ions form (1 : 2) M : L complexes with reagent I_b while Ag(I) and Hg(II) form (1:1) complexes which was showed in Fig. (41).

3.2.3.2.1.6. Determination of stability constant :

Spectrophotometric techniques can be useful for the determination of the stability constant of metal ion complexes. Generally, the spectrophotometric methods that are used for stoichiometric determination of the complex can be used for the determination of its stability constant. The data of the mole ratio and continuous variation methods aid in gaining the stability constant of the metal ion complexes as shown in Table (10).

3.2.3.2.1.7. Obeyence to Beer`s law:

The obeyence of Zn(II), Cu(II), Ag(I), V(V) and Hg(II) complexes with the reagent I_b to Beer`s law was studied to verify such complexes for spectrophotometric determination of these metal ions. The relation drawn between the concentration of metal ions studied and the absorbances of their complexes can be used as calibration curve for the spectrophotometric determination purpose, Fig. (42). The reagent concentration was constant at 1 ml of 3 x 10^{-3} M for both blank and sample while the concentration of metal ion was varied in case of Zn(II), Cu(II) ions, 2.0 ml reagent must be used with V(V), Ag(I) ions and 2.5 ml reagent was needed with Hg(II) ions. The pH was adjusted to the suitable value for each metal ion using universal buffer and absorbencies were measured at definite wavelength for each studied metal ion. The molar absorptivity (ε) values expressed in (L mol^{-1} cm^{-1}) are obtained as the slopes of the constructed curves. Intercept, slope and correlation coefficient are also obtained from the same curves. The values of molar absorptivity and Beer ´law obeyence range, all these values are calculated and recorded in Table (10).

3.2.3.2.1.8. Ringbom optimum range

For accurate spectrophotometric analysis, Ringbom plot has been drawn Fig.(43).The results indicate that, the optimum ranges are 0.6-4.8, 0.9-8.7, 0.6-4.4, 1.6-6.4 and 0.5-4.9 for Zn(II), Cu(II), Ag(I), V(V) and Hg(II) complexes respectively with reagent I_b with RSD from 0.58-1.1 % as shown in Table (10).

3.2.3.2.1.9. Effect of interference

The influence of interference ions on the determination of Zn(II), Cu(II), Ag(I), V(V) and Hg(II) with reagent I_b was tested for some cations and anions An error of less than ± 3 % in the absorbance reading was considered to be tolerable. So, As shown in Table (11), for Cu(II)-I_b complex, the tolerance values for ions Na^+, Mg^{2+}, ,K^+ ,Ca^{2+}, Mn^{2+},NO_2^-, ,SO_3^{2-} are more than 1000 µg ml^{-1}.From these tolerance values it was suggested that the application of reagent I_b for the determination of Cu(II) in presence of high amount of these ions .Whereas in case of Sr^{2+},Co^{2+},Cr^{3+},Al^{3+},$C_2O_4^{2-}$ and NH_4^+ the tolerance values are less than 100 µg ml^{-1} so these ions should be masked befor determination of Cu(II).The tolerance values of other complexes are listed in Table (11).

Table(10): Cumulative data of the analytical conditions for spectrophotometric determination of Zn(II), Cu(II), Ag(I), V(V) and Hg(II) ions with reagent I_b

Parameter	Reagent I_b				
	Zn(II)	Cu(II)	V(V)	Ag(I)	Hg(II)
pH	6.0	4.7	4.4	5.3	7.0
λ_{max} (nm),A curve	370	360	360	370	370
λ_{max} (nm),B curve	390	400	380	360	380
λ_{max} (nm),C curve	425	450	410	390	400
Beer'Law range,(µg ml^{-1})	0.5-4.8	0.8-8.8	0.5-4.5	1.5-6.5	0.5-5.0
Ringbom range, (µg ml^{-1})	0.6-4.8	0.9-8.7	0.6-4.4	1.6-6.4	0.5-4.9
Standard deviation(SD)	0.055	0.061	0.097	0.082	0.049
Relative standard deviation(RSD)	1.10	0.58	0.86	0.79	0.63
Variance x 10^{-3}	3.02	3.72	9	6.72	2.4
Slop (b)	0.1133	0.0926	0.4	0.125	0.205
Intercept (a)	0.037	0.0092	0.0019	-0.017	0.0033
Correlation coefficient	0.994	0.998	0.998	0.999	0.999
Molar absorptivity,L $mol^{-1}cm^{-1}$	8.4×10^3	9.8×10^3	3.57×10^3	2.5×10^4	1.3×10^4
Stability constant [a]	6.92	6.93	6.75	3.49	3.52
Stabilit`y constant [b]	8.29	8.86	8.7	5.69	5.56
Average of stability constant	7.6	7.8	7.72	4.59	4.54
Stoichiometry(M:L)	(1:2)	(1:2)	(1:2)	(1:1)	(1:1)

[a] : Stability constant using continuous variation method
[b] : Stability constant using Mole ratio method

Table (11): Tolerance limits for the influence of interference ions on the determination of Zn(II), Cu(II), Ag(I), V(V) and Hg(II) with reagent I_b

Foreign ion	Zn(II)-I_b	Cu(II)-I_b	V(V) -I_b	Ag(I)-I_b	Hg(II)-I_b
K^+	500	3000	3000	1600	2200
Ca^{2+}	1000	2500	2200	2900	2600
Mn^{2+}	400	2500	900	850	1300
NO_2^-	2000	1300	500	200	1000
SO_3^{2-}	1600	1200	600	2500	3000
Fe^{2+}	20	1500	150	400	100
Pb^{2+}	50	800	50	150	200
$NH4^+$	200	40	20	600	100
Al^{3+}	20	25	300	1000	2500
$C_2O_4^{2-}$	2000	50	200	500	400
Cr^{3+}	100	50	1500	150	200
SO_4^{2-}	150	800	750	2000	500
Ni^{2+}	1100	1000	500	100	50
Co^{2+}	300	50	1500	1000	1200
Na^+	5000	2000	4000	1000	3000
Mg^{2+}	3500	2500	2500	100	300
Sr^{2+}	200	20	100	300	1000

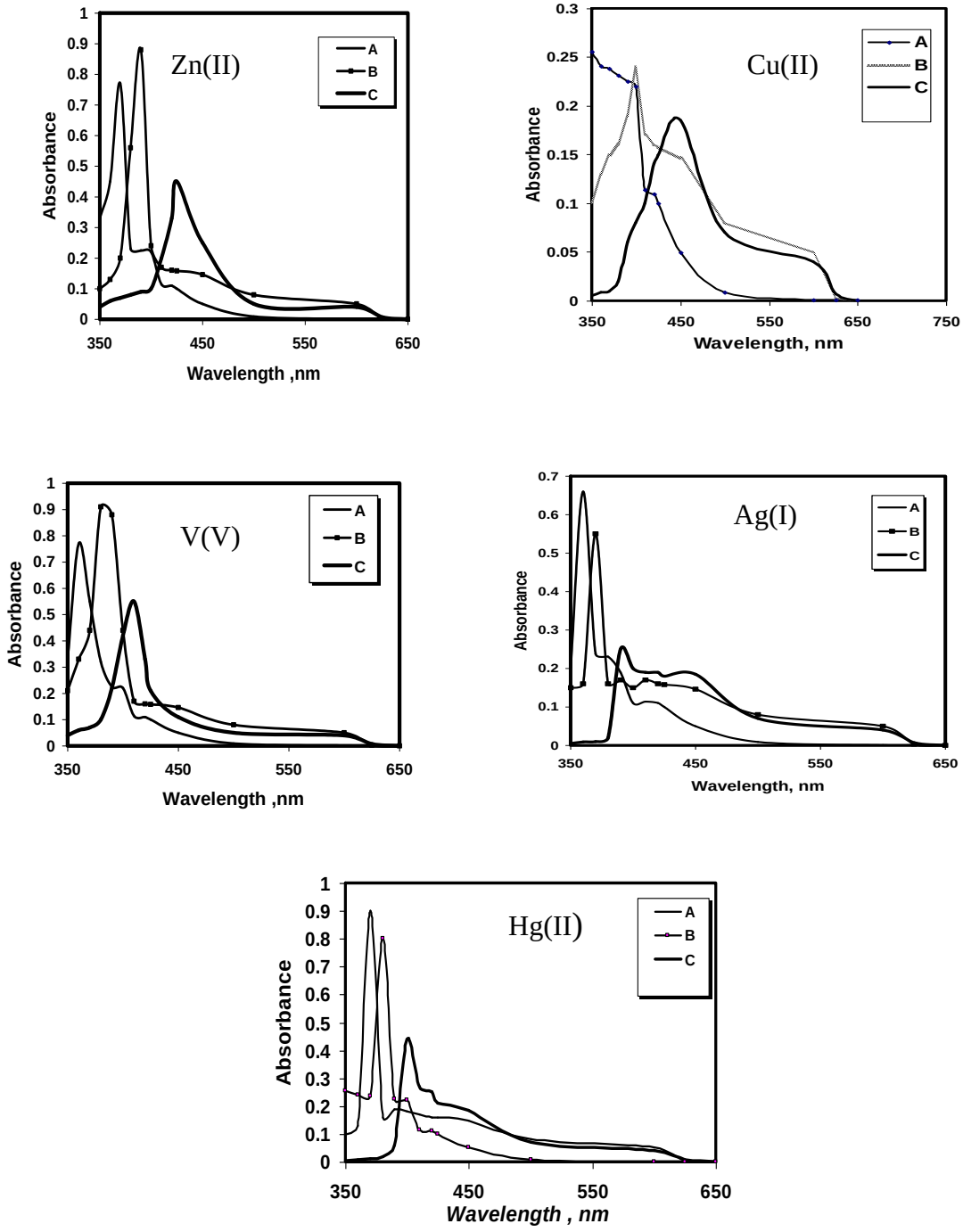


Fig. (36) Absorption spectra of reagent I_b with Zn(II), Cu(II), Ag(I), V(V) and Hg(II) where A:reagent + buffer against buffer B:Reagent + M^{n+} + buffer against buffer ،C: reagent + M^{n+} + buffer against reagent + buffer

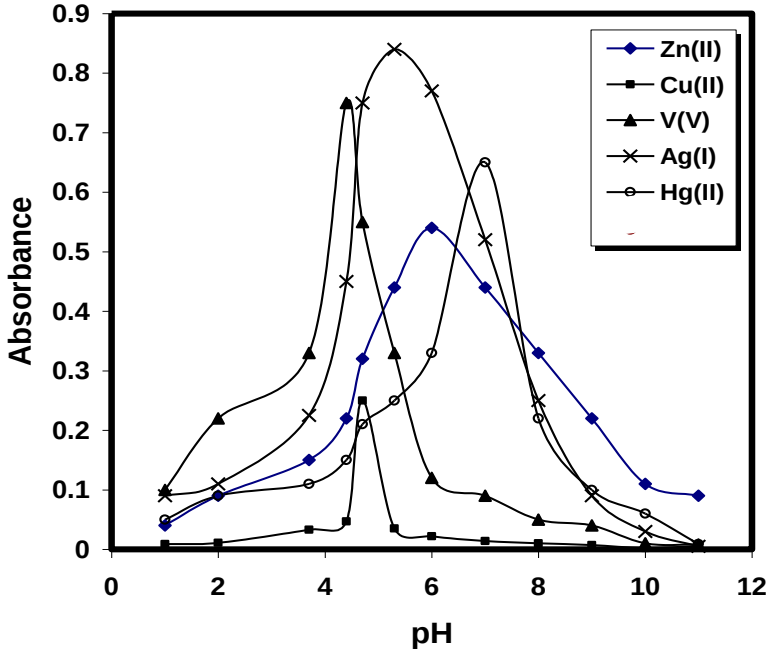


Fig. (37): Effect of pH on the absorbance of I_b complexes

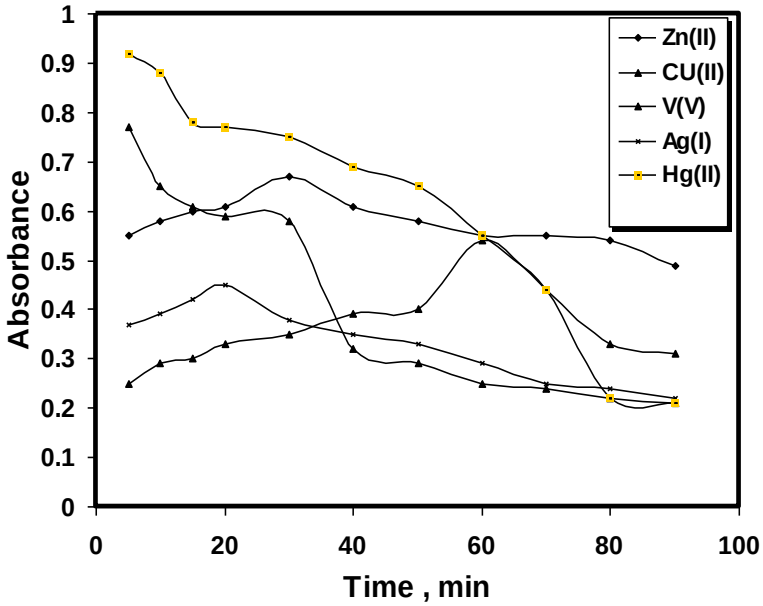


Fig. (38) : Effect of time on complexes formed between reagent I_b and studied metal ions

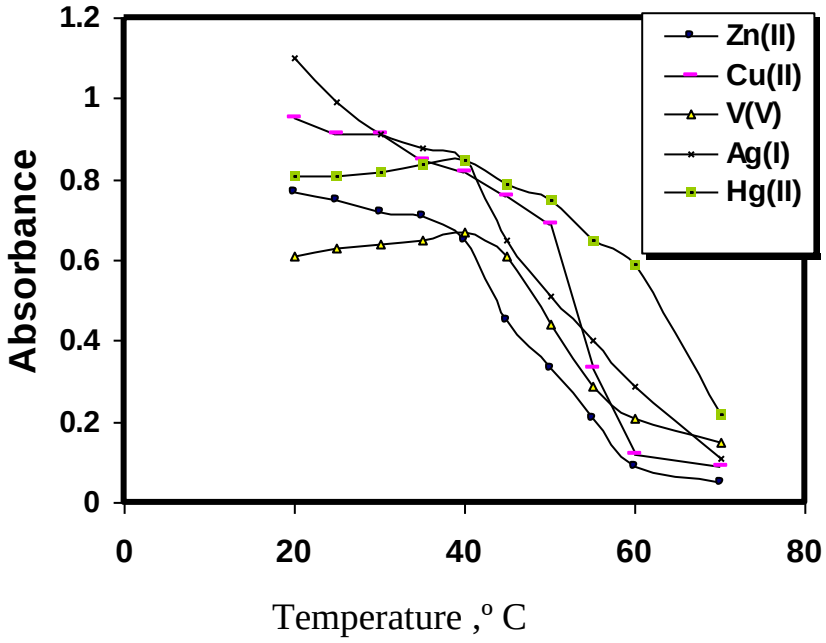


Fig. (39): Effect of temperature on formed complexes between reagent I_b and studied metal ions

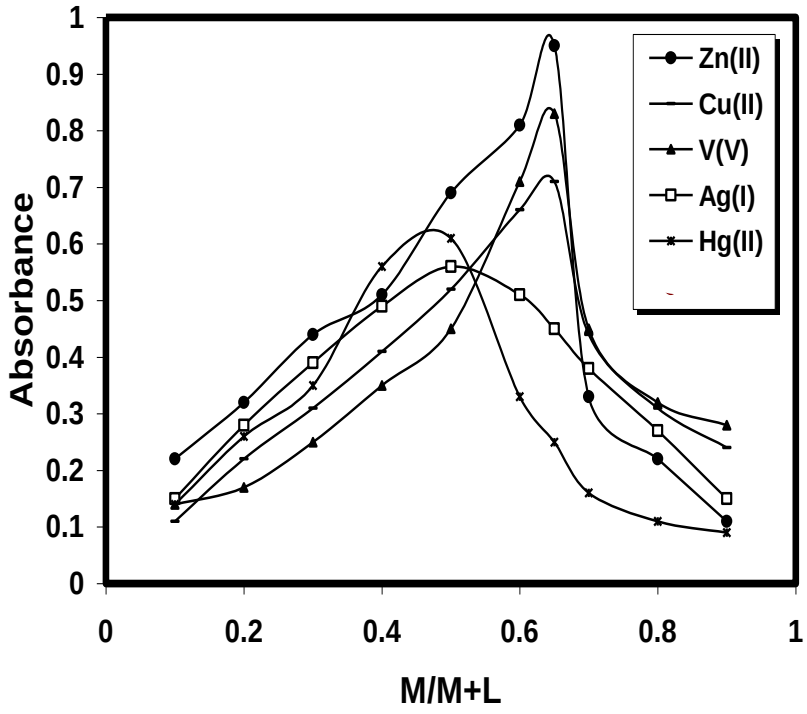


Fig. (40): Continuous variation method for reagent I_b with different metal ions

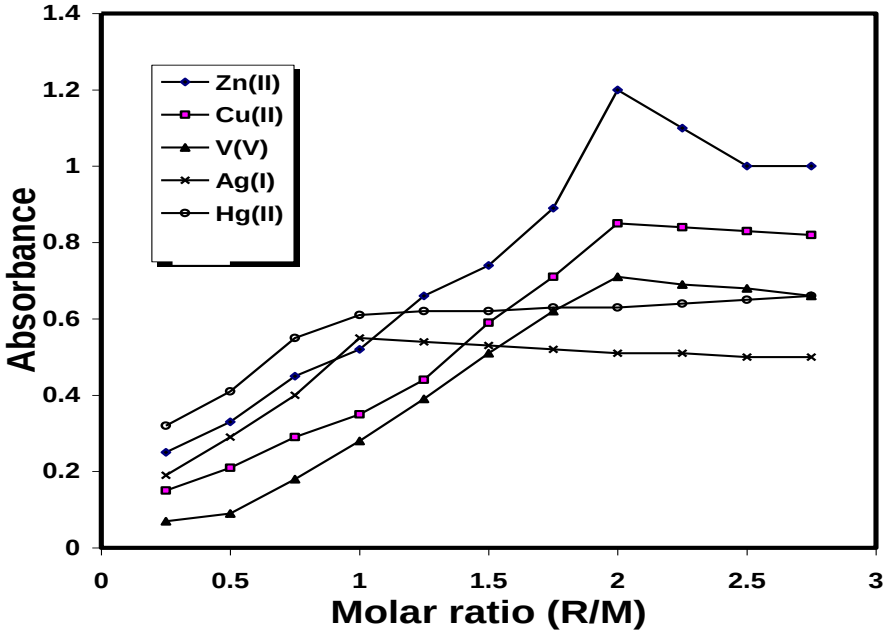


Fig. (41) : Molar ratio method for reagent I_b with different metal ions

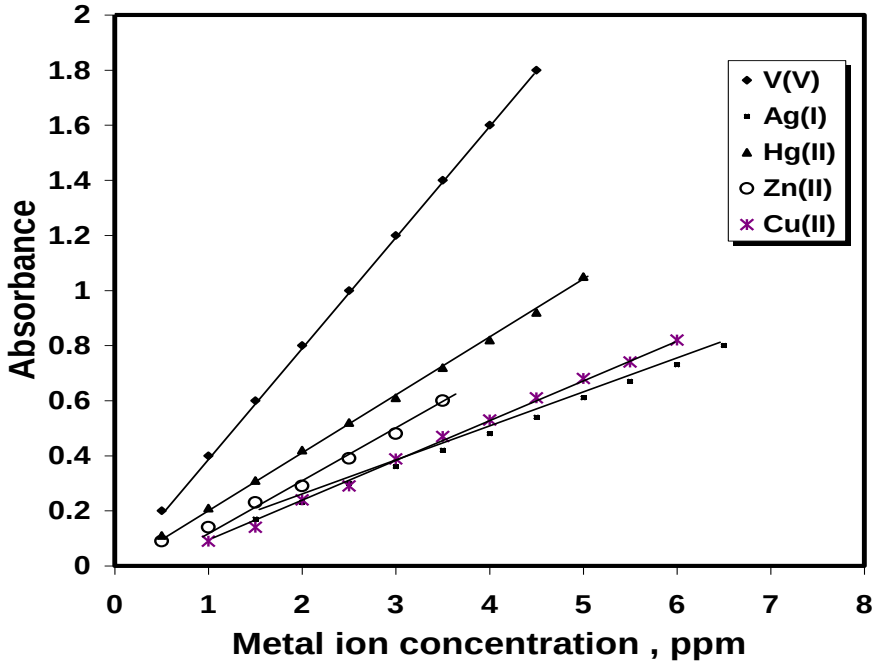


Fig. (42) : Application of Beer 's law for the determination of Zn(II), Cu(II), Ag(I), V(V) and Hg(II) metal ions using the optimum conditions of reagent I_b

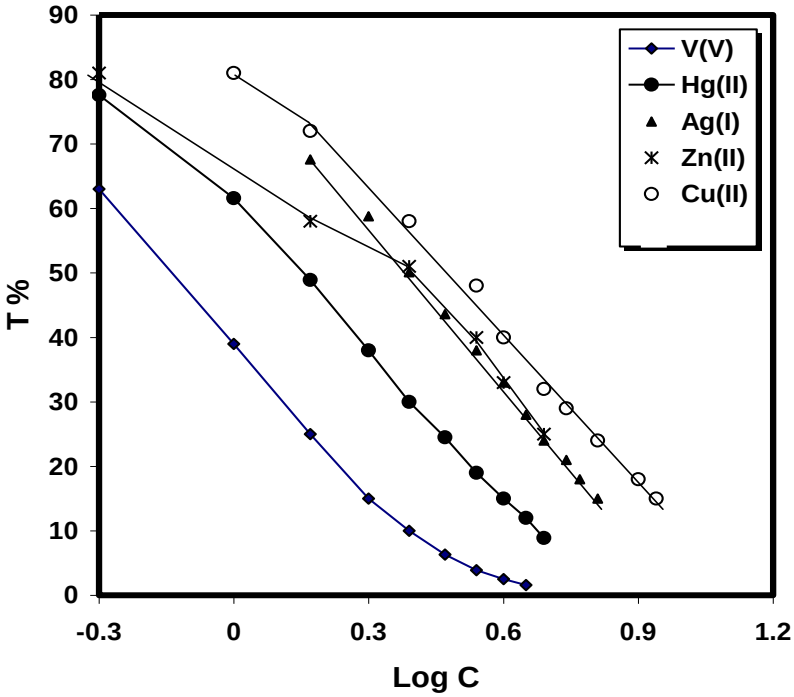


Fig. (43): Ringbom plot for Zn(II), Cu(II), Ag(I), V(V) and Hg(II) complexes with I_b

3.23.3. Spectrophtometric studies of Zn(II), Cu(II), Ag(I), V(V) and Hg(II) with 1-[2-hydroxy-5-(2-nitrophenyldiazenyl)benzylidene] urea (I_c)

3.2.3.3 .1. The optimum conditions for complex formation

3.2.3.3.1.1-Effect of pH

The effect of pH on the formed complexes of reagent I_c with the metal ions under investigation was studied in universal buffer solution of the Ph range 1.81-11.98 for Zn(II), Cu(II), Ag(I), V(V) and Hg(II) to obtain best absorbance for complex formation. The most suitable pH values for the formation of Zn(II) and Cu(II) complexes with reagent I_c are determined by mixing a constant volume 1.5 ml of 3 $x10^{-3}$ M of reagent and different volumes of buffer solution of different pH values and 1.0 ml of 3×10^{-3} M metal ion. While Hg(II)-complex with reagent I_c needs 2.0 ml of the reagent and 1 ml of the metal ion. The absorption spectra were recorded using a blank solution prepared in the same manner without metal ion. In case of V(V) and Ag(I) 1.0 ml reagent was needed with 1 ml of metal ion at different pH values.From this analysis it was concluded that the best pH values were 6.8, 4.5, 5.7, 3.5 , 7.2 with λ_{max} 450, 425, 400, 390 and 410 nm during the determination of Zn(II) Cu(II), V(V), Ag(I), and Hg(II) respectively at complete colour development as shown in Fig.(44) and in Table (12).The mentioned wavelengths above represent C curve shown in the same Fig. and Table The absprbamce-pH curves of ligand I_c with metal ions under investigation in universal buffer solutions of varying pH values are represented in Fig.(45) gaining the best pH value for each metal ion complex .

3.2.3.3.1.2. Effect of time

The effect of time on I_c complexes of metal ions was studied by measuring the absorbance of solution containing the metal ion and the reagent against blank solution prepared by the same way without metal

ions after adjusting the pH to the suitable values using universal buffer. This study confirmed that the complexes between I_c and Cu(II) and Zn(II) were unstable after waiting few time while those of V(V), Ag(I) and Hg(II) were affected by time after 5 min where their absorbencies were sharply decreased as shown in Fig. (46).

3.2.3.3.1.3. Effect of temperature

The effect of temperature was also studied for the metal ion complexes with reagent I_c by heating the sample solution and the blank at different temperatures. This test showed that raising the temperature also affects the stability of Cu(II), Zn(II), complexes after heating up to 40 °C while those of V(V), Ag(I) and Hg(II) were unstable by increasing temperature above room temperature which is shown in Fig. (47).

3.2.3.3.1.4. Stoichiometry of metal ion complexes

Contiuous variation method

A serious of solutions which were obtained by mixing equimolecular solution of metal ion solution and ligand in varied proportions keeping the total molar concentration constant and measure the absorbance. From this study, it was concluded that Cu(II) ions form (1:2) M:L complexes with reagent $I_c$while Ag(I), Zn(II), V(V) and Hg(II) form (1:1) complexes which was showed in Fig(48).

3.2.3.3.1.5. Molar ratio method

The metal ion concentration was kept constant while ligand was increased and measure the corresponding concentration .This method confirmed the continuous variation method in that Zn(II), V(V) Ag(I), Hg(II), ions form (1:1) M:L complexes with reagent I_c while Cu(II) form (1:2) complex which was showed in Fig. (49). The stoichiometric ratios of different studied complexes deduced from both continuous and molar methods are collected in Table (12).

3.2.3.3.1.6. Determination of stability constant :

Spectrophotometric techniques can be useful for the determination of the stability constant of metal ion complexes. Generally, the spectrophotometric methods that are used for stoichiometric determination of the complex can be used for the determination of its stability constant. The data of the mole ratio and continuous variation methods aid in gaining the stability constant of the metal ion complexes as shown in Table (12).

3.2.3.3.1.7. Obeyence to Beer`s law:

The obeyence of Zn(II), Cu(II), Ag(I), V(V) and Hg(II) complexes with the reagent I_c to Beer`s law was studied to verify such complexes for spectrophotometric determination of these metal ions. The relation drawn between the concentration of metal ions studied and the absorbances of their complexes can be used as calibration curve for the spectrophotometric determination purpose as shown in Fig. (50). The reagent concentration was constant at 1.5 ml of 3×10^{-3} M for both blank and sample while the concentration of metal ion was varied in case of Zn(II), Cu(II) ions. 2.0 ml reagent must be used with V(V), Ag(I) ions and 1.0 ml reagent was needed with Hg(II) ions. The pH was adjusted to the suitable value for each metal ion using universal buffer and absorbencies were measured at definite wavelength for each studied metal ion. The molar absorptivity (ε) values expressed in (L mol^{-1} cm^{-1}) are obtained as the slopes of the constructed curves. Intercept, slope and correlation coefficient are also obtained from the same curves. The values of molar absorptivity and Beer ´law obeyence range, all these values are calculated and recorded in Table (12).

3.2.3.3.1.8. Ringbom optimum range

For accurate spectrophotometric analysis, Ringbom plot has been drawn Figs.(51) .The results indicate that, the optimum ranges are 1.3-11.7, 1-4.8 , 1.1-5.8 , 1.2-9.3 and 1.0-7.9 for Zn(II), Cu(II), V(V), Ag(I) and Hg(II) complexes respectively with reagent I_c with RSD from 0.55-1.29 % as shown in Table (12).

3.2.3.3.1.9. Effect of interference

The influence of interference ions on the determination of Zn(II), Cu(II), V(V), Ag(I) and Hg(II) with reagent I_c was tested for some cations and anions An error of less than ± 3 % in the absorbance reading was considered to be tolerable. For Zn^{2+}- I_c complex, the tolerance values for ions Na^{+}, Mg^{2+},K^{+}, Ni^{2+}, Mn^{2+},NO_2^{-}, ,SO_3^{2-} $SO_4^{2-}$are more than 1000 µg ml^{-1}. From these tolerance values it was suggested that the application of reagent I_c for the determination of Zn^{2+} in presence of high amount of these ions .Whereas in case of Sr^{2+}, Fe^{2+}, Co^{2+},$Ca^{2+,}$,Al^{3+},$C_2O_4^{2-}$ and NH_4^{+} the tolerance values are less than 100 µg ml^{-1} so these ions should be masked befor determination of Zn(II). The tolerance values of other complexes are listed in Table (13).

Table(12): Cumulative data of the analytical conditions for spectrophotometric determination of Zn(II), Cu(II), V(V), Ag(I) and Hg(II) ions with reagent I_c

Parameter	Reagent I_c				
	Zn(II)	Cu(II)	V(V)	Ag(I)	Hg(II)
pH	6.8	4.5	5.7	3.5	7.2
λ_{max} (nm),A curve	360	380	360	360	370
λ_{max} (nm),B curve	370	370	380	370	380
λ_{max} (nm),C curve	450	425	400	390	410
Beer'Law range,(µg ml^{-1})	1.0-12	1.0-5.0	1.0-6.0	1.0-9.5	1.0-8.0
Ringbom range, (µg ml^{-1})	1.3-11.7	1.0-4.8	1.1-5.8	1.2-9.3	1.0-7.9
Standard deviation(SD)	0.048	0.073	0.097	0.065	0.081
Relative standard deviation(RSD)	0.55	0.68	1.29	0.79	0.99
Variance x 10^{-3}	2.3	5.32	9.4 x10^{-3}	4.22	6.56
Slop (b)	0.0904	0.18	0.153	.043	0.06
Intercept (a)	0.0009	0.0001	0.0019	-.0008	0.0005
Correlation coefficient	0.998	0.9908	0.998	0.999	0.999
Molar absorptivity, L mol^{-1}cm^{-1}	**7.8×10^3**	**1.4x10^4**	**3.57 x 10^3**	**4.0x10^4**	**3.5x10^4**
Stability constant [a]	4.11	5.83	4.18	4.37	3.95
Stabilit`y constant [b]	5.91	8.64	5.74	5.58	5.56
Average of stability constant	5.01	7.23	4.96	9.95	4.75
Stoichiometry(M:L)	(1 :1)	(1 :2)	(1 :1)	(1 :1)	(1 :1)

[a] : Stability constant using continuous variation method
[b] : Stability constant using Mole ratio method

Table (13): Tolerance limits for the influence of interference ions on the determination of Zn(II), Cu(II), V(V), Ag(I) and Hg(II) with reagent I_c

Foreign ion	Zn(II)-I_c	Cu(II)-I_c	V(V)-I_c	Ag(I) -I_c	Hg(II)-I_c
K^+	1500	2500	3000	1000	2000
Ca^{2+}	80	3000	2000	2500	1500
Mn^{2+}	1000	200	500	1000	250
NO_2^-	1500	100	1000	100	2200
SO_3^{2-}	2000	1500	800	50	2000
Fe^{2+}	20	200	50	1000	2500
Pb^{2+}	50	500	100	100	20
NH_4^+	100	200	1000	50	1000
Al^{3+}	20	50	300	1000	2500
$C_2O_4^{2-}$	50	200	200	500	400
Cr^{3+}	100	100	100	50	200
SO_4^{2-}	1100	200	750	2000	500
Ni^{2+}	1000	50	500	100	50
Co^{2+}	20	20	1500	1000	50
Na^+	4000	2000	4000	1000	3000
Mg^{2+}	2500	2500	2500	100	300
Sr^{2+}	50	100	100	20	1000

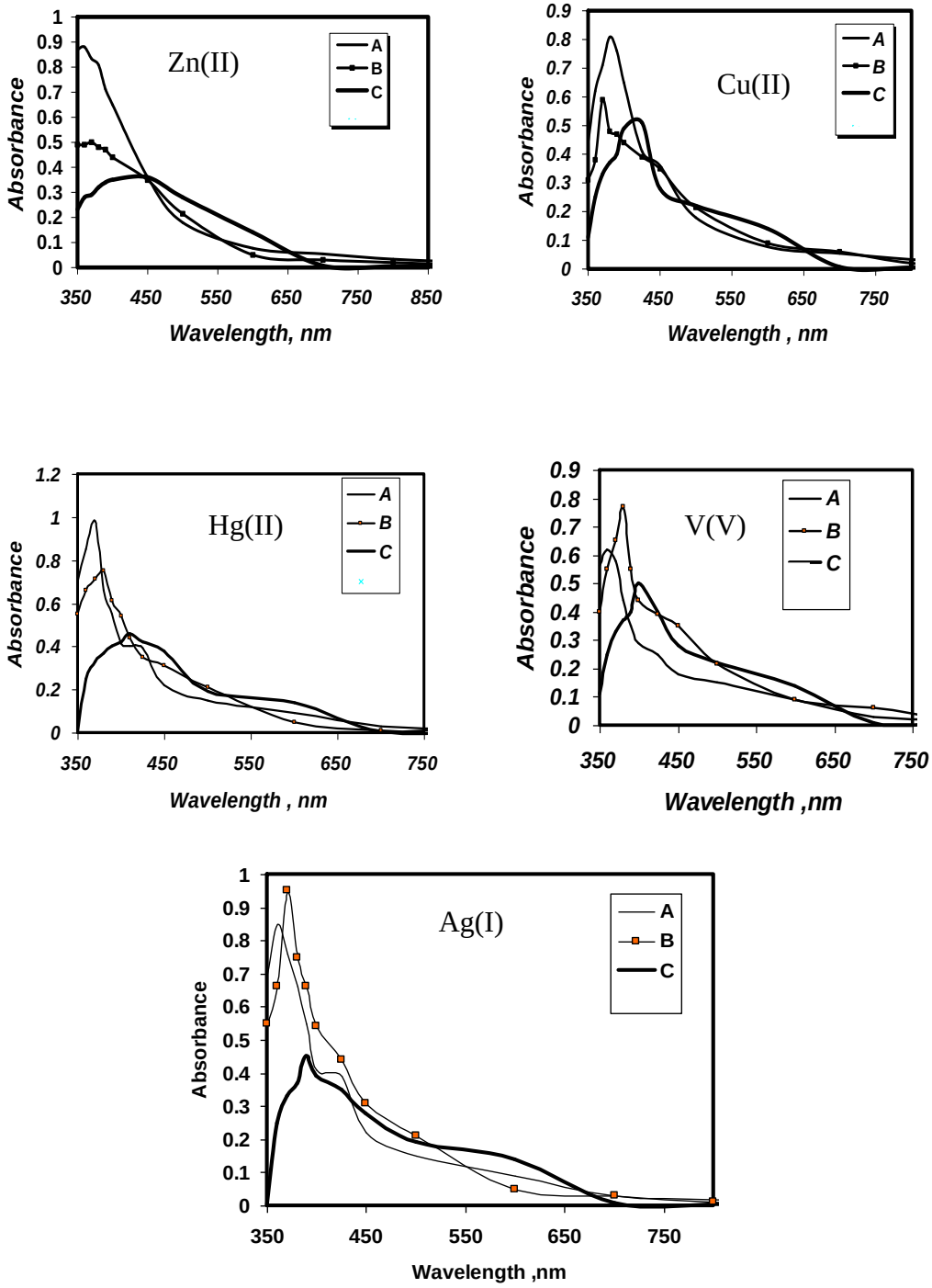


Fig. (44) Absorption spectra of reagent $\mathbf{I_c}$ with Zn(II), Cu(II), V(V), Ag(I) and Hg(II) where A:reagent + buffer against buffer B:Reagent + M^{n+} + buffer against buffer ،C: reagent + M^{n+} + buffer against reagent + buffer

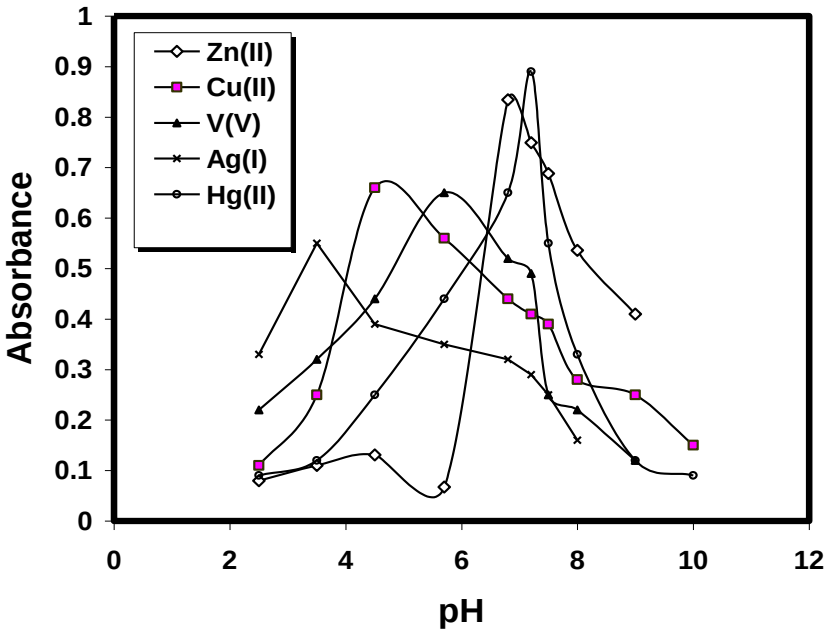


Fig. (45) Effect of pH on the absorbance of I_c complexes

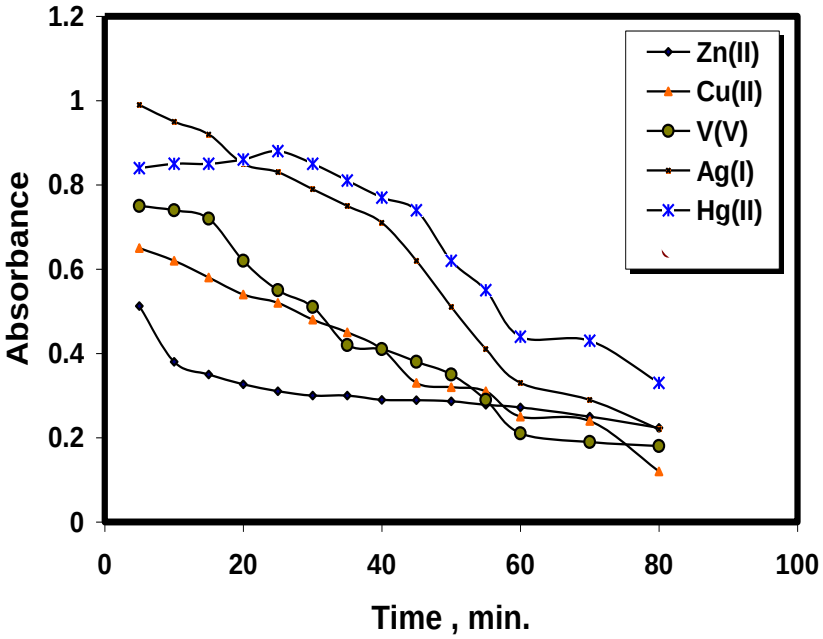


Fig. (46): Effect of Time on the studied complexes of reagent I_c

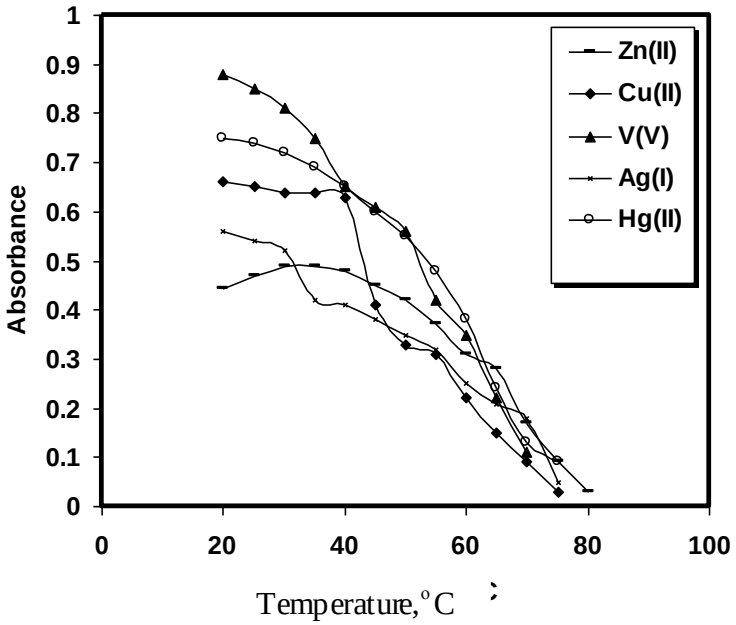


Fig. (47) : Effect of temperature on formed complexes between reagent I_c and studied metal ions

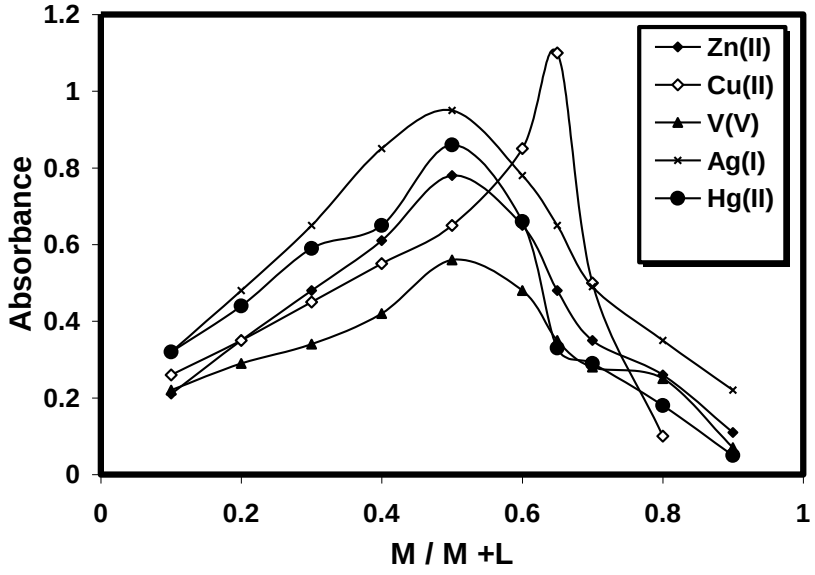


Fig. (48): Continuous variation method for reagent I_c with the studied metal ions

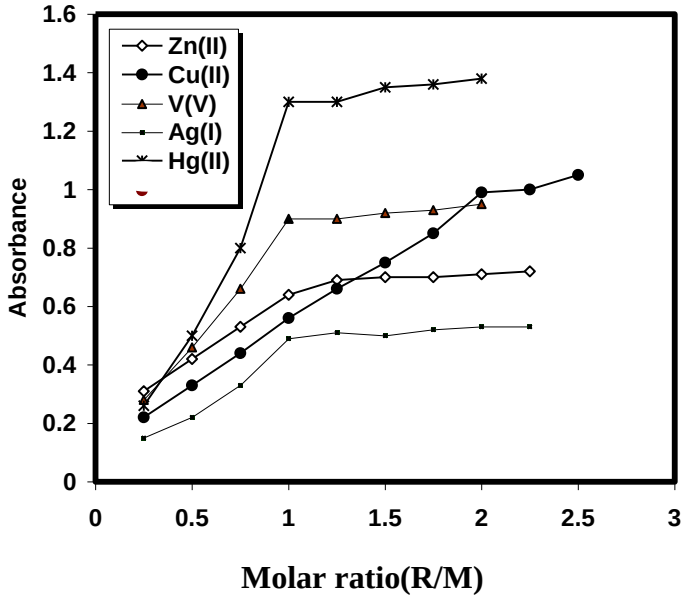


Fig. (49) : Molar ratio method for reagent I_b with the studied metal ions

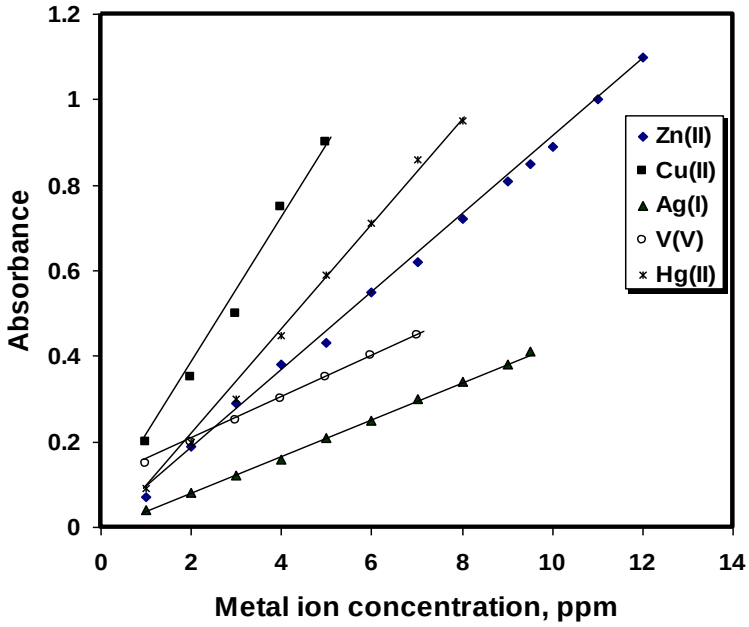


Fig. (50) : Application of Beer 's law for the determination of Zn(II), Cu(II), V(V), Ag(I) and Hg(II) with I_c

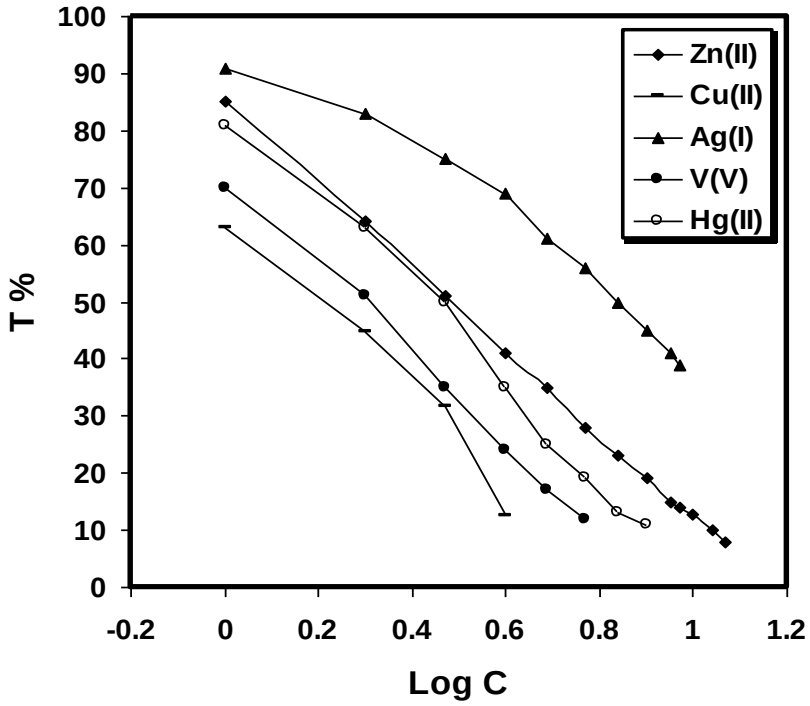


Fig. (51): Ringbom plots for Zn(II), Cu(II), V(V), Ag(I) and Hg(II) complexes, with I_c

3.2.3.4. Spectrophtometric studies of Zn(II), Cu(II), V(V), Ag(I) and Hg(II) with [2-hydroxy-5(4 bromo phenylazo) benzylidene] urea (I_d)

3.2.3.4.1. The optimum conditions for complex formation

3.2.3.4.1.1. Effect of pH

The effect of pH on the formed complexes of reagent I_d with the metal ions under investigation was studied in universal buffer solution of the pH range 1.81-11.98 for Zn(II), Cu(II), V(V), Ag(I) and Hg(II) **[**to obtain best colour develpment for their complexes. The most suitable pH value for the formation of Hg(II) complex with reagent I_d is determined by mixing a constant volume 3.0 ml of 3 $x10^{-3}$ M of reagent and 1.0 ml of 3×10^{-3} M metal ion. While Zn(II)-complex with reagent I_d needs 2.0 ml of the reagent and 1 ml of the metal ion. The absorption spectra were recorded using a blank solution prepared in the same manner without metal ion. In case of V(V), Cu(II) and Ag(I) 1.0 ml reagent was needed with 1 ml of metal ion at different pH values.From this analysis it was concluded that the best pH values were 6.0, 5.5, 5.8, 4.0 and 7.5 with λ_{max} 425, 450, 400, 385 and 400 nm during the determination of Zn(II), Cu(II), V(V), Ag(I) and Hg(II) respectively reaching the the high colour stability ,C curve, as shown in Fig. (52) and in Table(14). Fig(52) shows also A and B curves which indicat the differenc and shift of λ_{max} according to the presence or absence of the metal ion in the studied solution.The absorbamce-pH curves of ligand I_d with metal ions under investigation in universal buffer solutions of varying pH values are represented in Figs. (53) gaining the suitable pH value of each metal ion complex.

3.2.3.4.1.2. Effect of time

The effect of time on I_d complexes of metal ions was studied by measuring the absorbance of solution containing the metal ion and the reagent against blank solution prepared by the same way without metal

ions after adjusting the pH to the suitable values using universal buffer .This study confirmed that the complexe between I_d and Hg(II) was stable up to 40 min while those of Zn(II), Cu(II), V(V), Ag(I) were stable for 20, 10, 5, 30 min respectively where their absorbencies were decreased after waiting the mentioned times as shown in Fig (54)

3.2.3.4.1.3. Effect of temperature

The effect of temperature was also studied for the metal ion complexes with reagent I_d by heating the sample solution and the blank at different temperatures. This test showed that raising the temperature also affects the stability of Hg(II) complexe after heating up to 30 °C while those of Cu(II), Zn(II) were stable by heating their blank and sample solutions up to 50°C. In case of V(V) and Ag(I) were unstable by increasing temperature above room temperature which was shown in Fig.(55).

3.2.34.1.4. Stoichiometry of metal ion complexes

Contiuous variation method

A serious of solutions which were obtained by mixing equimolecular solution of metal ion solution and ligand in varied proportions keeping the total molar concentration constant and measure the absorbance. From this study , it was concluded that Hg^{2+} ions form (1:2) M:L complexes with reagent I_d while Ag(I), Zn(II), V(V) and Cu(II) form (1:1) complexes which was showed in Fig (56).

3.2.34.1.5. Molar ratio method

The metal ion concentration was kept constant while ligand was increased and measure the corresponding concentration. This method confirmed the continuous variation method in that Zn(II), V(V) Ag(I), Cu(II), ions form (1:1) M:L complexes with reagent I_d while Hg(II) form (1:2) complex which was showed in Fig. (57). The stoichiometric ratios of studied metal ion complexes are recorded in table (14).

3.2.34.1.6. Determination of stability constant

Spectrophotometric techniques can be useful for the determination of the stability constant of metal ion complexes. Generally, the spectrophotometric methods that are used for stoichiometric determination of the complex can be used for the determination of its stability constant. The data of the mole ratio and continuous variation methods aid in gaining the stability constant of the metal ion complexes as shown in Table (14).

3.2.3.4.1.7. Obeyence to Beer`s law

The obeyence of Zn(II), Cu(II), V(V), Ag(I) and Hg(II) complexes with the reagent I_d to Beer`s law was studied to verify such complexes for spectrophotometric determination of these metal ions. The relation drawn between the concentration of metal ions studied and the absorbances of their complexes can be used as calibration curve for the spectrophotometric determination purpose, Fig (58) .The reagent concentration was constant at 2.0 ml of 3 x 10^{-3} M for both blank and sample while the concentration of metal ion was varied in case of Zn(II) ions but 1.0 ml reagent must be used with V(V), Cu(II) , Ag(I) ions and 3.0 ml reagent was needed with Hg(II) ions. The pH was adjusted to the suitable value for each metal ion using universal buffer and absorbencies were measured at definite wavelength for each studied metal ion. The molar absorptivity (ε) values expressed in(L mol^{-1} cm^{-1}) are obtained as the slopes of the constructed curves. Intercept, slope and correlation coefficient are also obtained from the same curves and recorded in Table (14).

3.2.3.4.1.8. Ringbom optimum range

For accurate spectrophotometric analysis, Ringbom plot has been drawn Fig.(59) .The results indicate that, the optimum ranges are 0.7-6.4,

, 0.6-3.9, 1.1-4.8 ,and 1.0-3.4 for Zn(II), Cu(II), V(V), Ag(I) and Hg(II) complexes respectively with reagent I_d with RSD from 0.77-1.2 % as shown in Table(14).

3.2.3.4.1.9. Effect of interference

The influence of interference ions on the determination of Zn(II), Cu(II), V(V), Ag(I) and Hg(II) with reagent I_d was tested for some cations and anions An error of less than ± 3 % in the absorbance reading was considered to be tolerable. For Hg^{2+}- I_d complex, the tolerance values for ions Na^{+}, Ca^{2+},Mg^{2+},K^{+}, Ni^{2+}, Mn^{2+},NO_2^{-}, $SO_4^{2-}$are more than 1000 µg ml^{-1}. From these tolerance values it was suggested that the application of reagent I_d for the determination of Zn(II) in presence of high amount of these ions .Whereas in case of Sr^{2+}, Fe^{2+}, Co^{2+}, $C_2O_4^{2-}$ and the tolerance values are less than 100 µg ml^{-1} so these ions should be masked befor determination of Zn(II). The tolerance values of other complexes are listed in Table (15).

Table(14): Cumulative data of the analytical conditions for spectrophotometric determination of Zn(II), Cu(II), V(V), Ag(I) and Hg(II) ons with reagent I_d

Parameter	Reagent I_d				
	Zn(II)	Cu(II)	V(V)	Ag(I)	Hg(II)
pH	6	5.5	5.8	4.0	7.5
λ_{max} (nm),A curve	360	350	350	355	370
λ_{max} (nm),B curve	380	380	380	360	380
λ_{max} (nm),C curve	425	450	400	385	400
Beer'Law range,(µg ml^{-1})	0.5-6.5	0.5-4.0	1.0-5.0	1.0-3.5	1.0-4.5
Ringbom range, (µg ml^{-1})	0.7-6.4	0.6-3.9	1.1-4.8	1.0-3.4	1.0-4.3
Standard deviation(SD)	0.066	0.074	0.056	0.068	0.035
Relative standard deviation(RSD)	**0.77**	1.2	0.88	0.91	1.104
Variance $(SD)^2$	**$4.35x10^{-3}$**	**$5.47x10^{-3}$**	**$3.13x10^{-3}$**	**$4.62x10^{-3}$**	**$1.22 x10^{-3}$**
Slop (b)	0.107	0.056	0.066	0.11	0.089
Intercept (a)	0.03	0.0012	0.0041	0.0001	**0.0002**
Correlation coefficient	0.990	0.997	0.995	0.997	**0.9965**
Molar absorptivity,L $mol^{-1}cm^{-1}$	**2.33×10^4**	**7.5×10^4**	**5.6×10^4**	**3.5×10^4**	**6.06 x 104**
Stability constant [a]	4.15	4.02	3.99	4.16	7.37
Stabilit`y constant [b]	6.49	6.07	5.18	4.82	8.84
Average of stability constant	5.32	5.04	4.58	4.49	8.1
Stoiciometry(M:L)	(1 :1)	(1 :1)	(1 :1)	(1 :1)	(1 :2)

[a] : Stability constant using continuous variation method
[b] : Stability constant using Mole ratio method

Table (15): Tolerance limits for the influence of interference ions on the determination of Zn(II), Cu(II), V(V), Ag(I) and Hg(II) with reagent I_d

Foreign ion	Zn(II)-I_d	Cu(II)-I_d	V(V)-I_d	Ag(I) –I_d	Hg(II)-I_d
K^+	1500	2500	3000	1000	2500
Ca^{2+}	80	3000	2000	2500	2000
Mn^{2+}	1000	200	500	1000	1500
NO_2^-	1500	100	1000	100	1800
SO_3^{2-}	2000	1500	800	50	1250
Fe^{2+}	20	200	50	1000	25
Pb^{2+}	50	500	100	100	200
$NH4^+$	100	200	1000	50	1000
Al^{3+}	20	50	300	1000	2500
$C_2O_4^{2-}$	50	200	200	500	50
Cr^{3+}	100	100	100	50	200
SO_4^{2-}	1100	200	750	2000	1500
Ni^{2+}	1000	50	500	100	1000
Co^{2+}	20	20	1500	1000	20
Na^+	4000	2000	4000	1000	4000
Mg^{2+}	2500	2500	2500	100	2000
Sr^{2+}	50	100	100	20	50

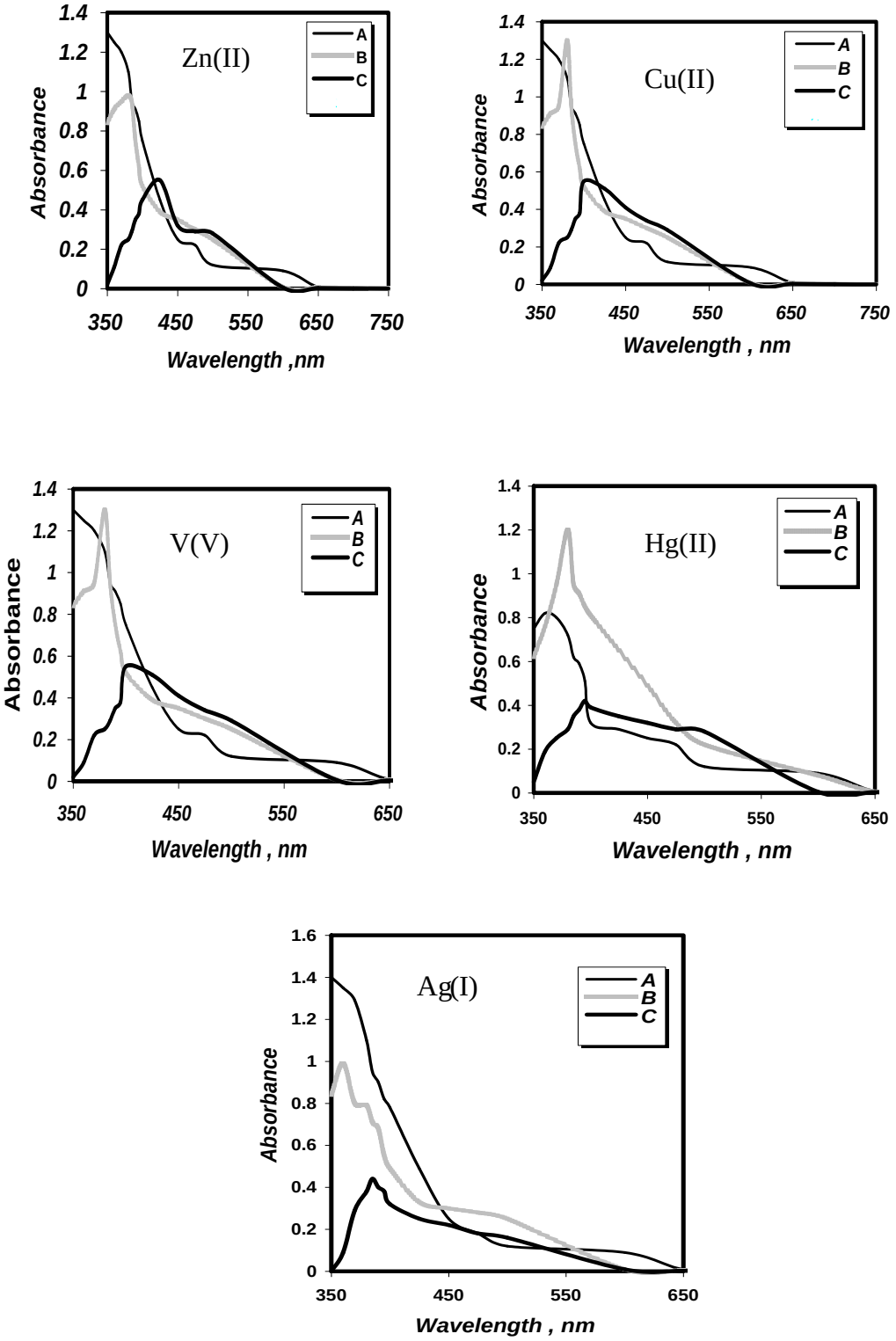


Fig. (52) Absorption spectra of reagent $\mathbf{I_d}$ with Zn(II), Cu(II), V(V), Ag(I) and Hg(II) where A:reagent + buffer against buffer B:Reagent + M^{n+} + buffer against buffer ,C: reagent + M^{n+} + buffer against reagent + buffer.

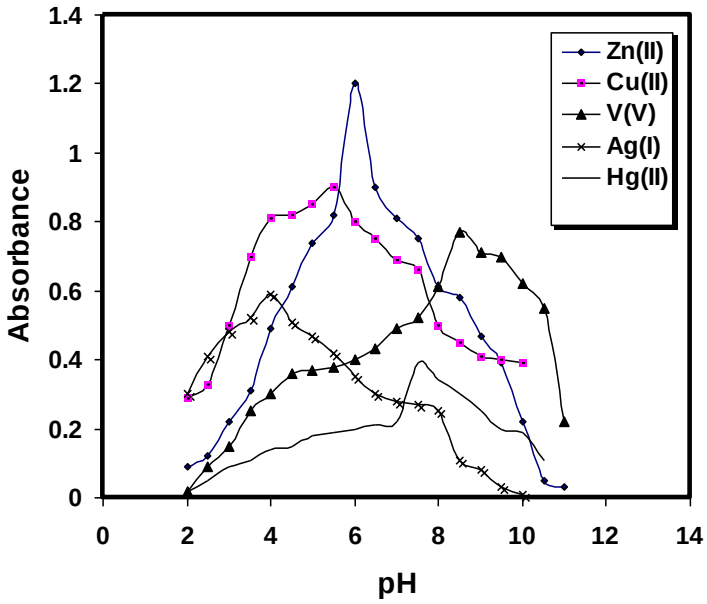


Fig. (53): Effect of pH on the absorbance of metal ion complexes of reagent I_d

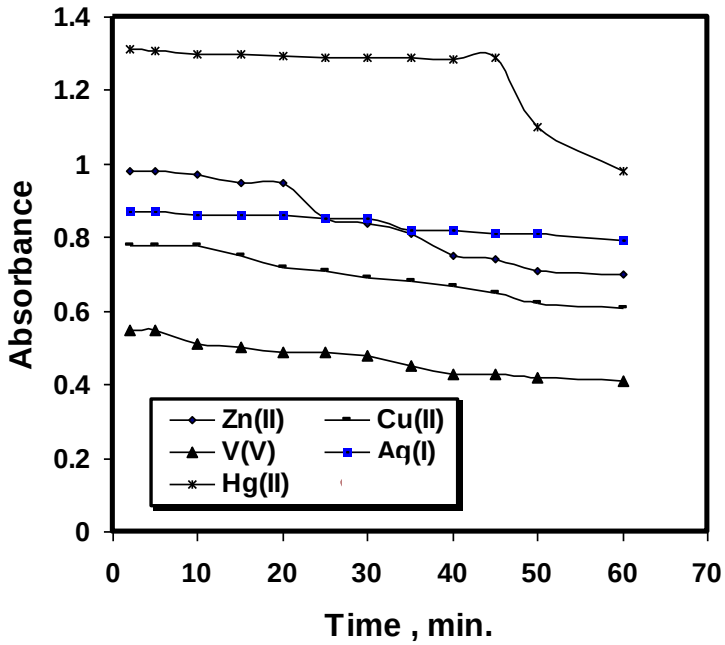


Fig. (54) : Effect of time on the absorbance of metal ion complexes with reagent I_d

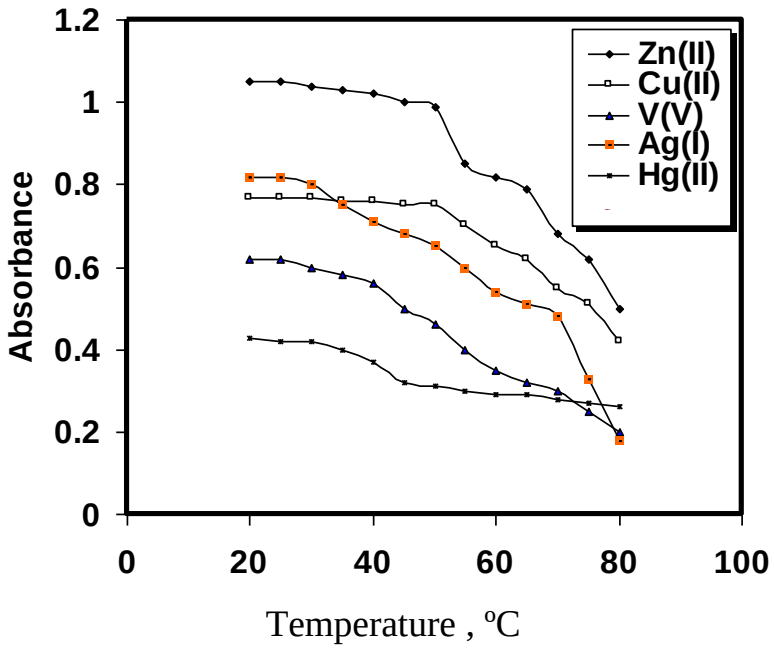


Fig. (55): Effect of temperature on complexes formed between reagent I_d and metal ion

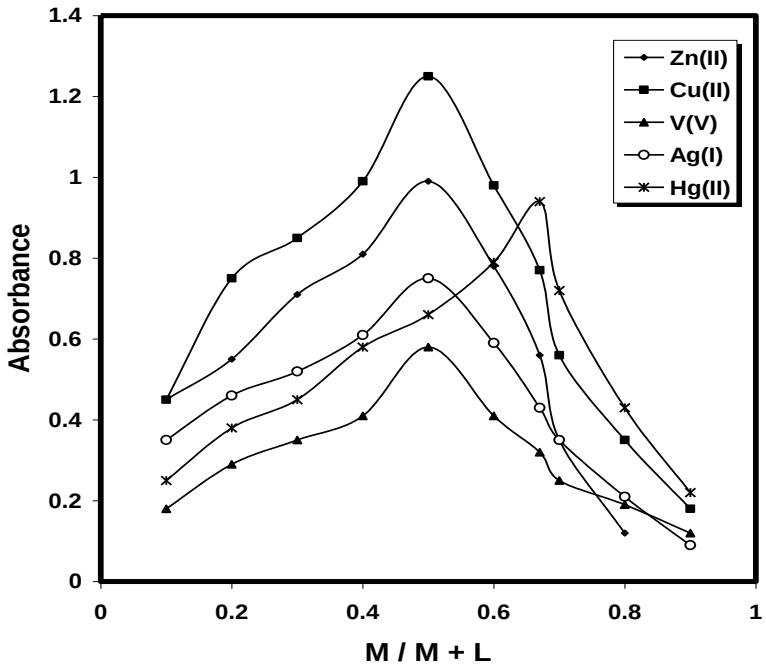


Fig. (56): Continuous variation method for metal ion complexes of reagent I_d

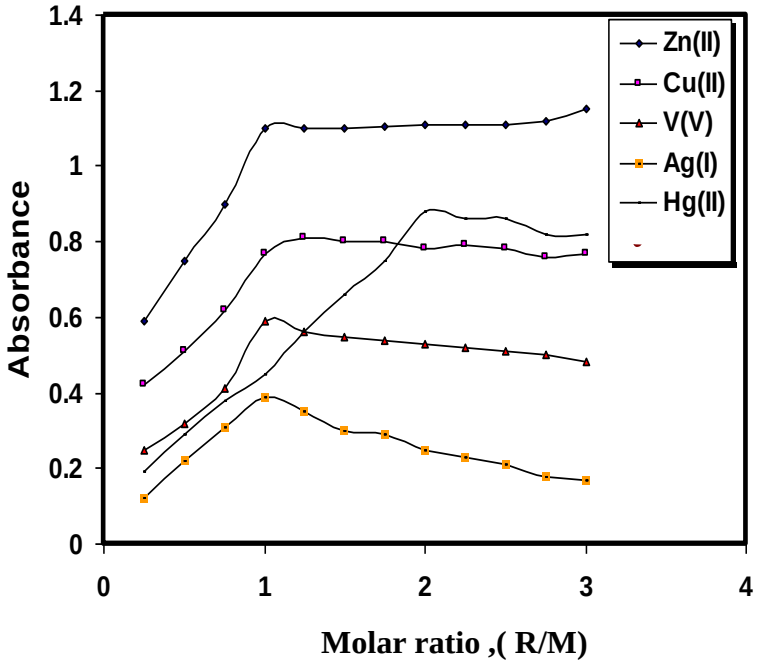


Fig. (57) : Molar ratio method for metal ion complexes of reagent I_d

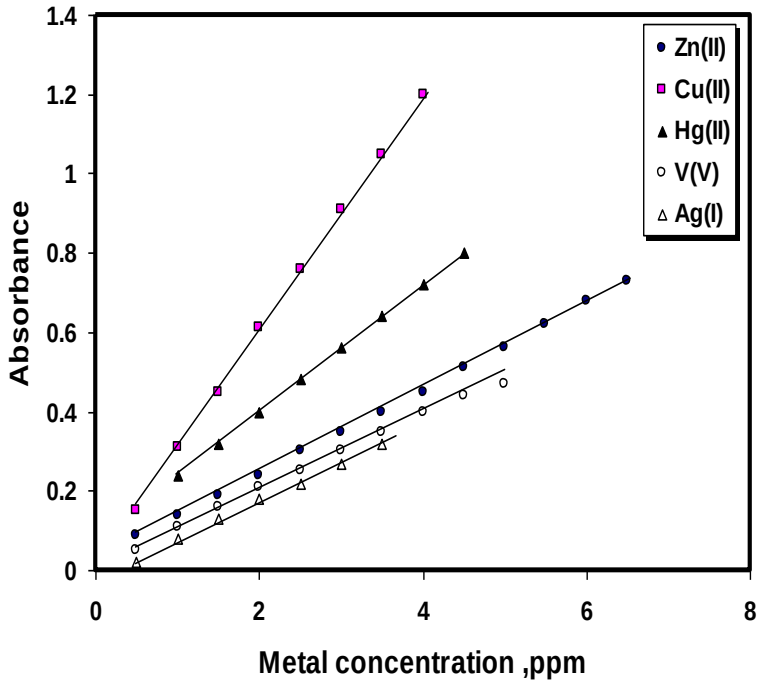


Fig. (58): Application of Beer´s law for Zn(II), Cu(II), V(V), Ag(I) and Hg(II) complexes using the optimum conditions of reagent I_d

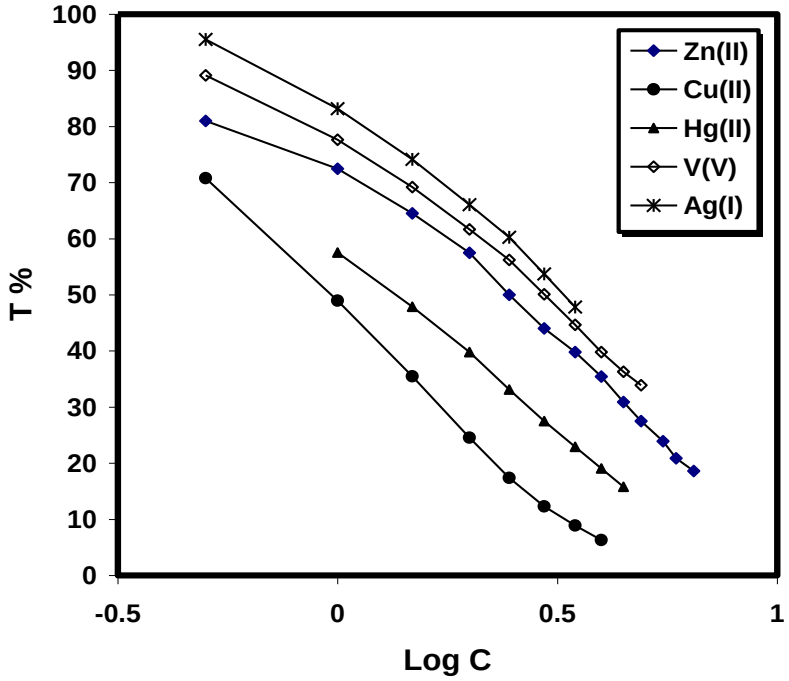


Fig. (59): Ringbom plots for Zn(II), Cu(II), V(V), Ag(I) and Hg(II) complexes with reagent I_d

3.2.3.5. Application

3.2.3.5.1 Determination of vanadium in the deposites of outer surfaces of superheaters and inner part of chimney

The results obtained for the spectrophotometric determination of V(V) considered in the present work show that 2.5-16.5 ppm of V(V) can be accurately determined under optimum experimental conditions. This encouraged us to apply the method for the determination of V(V) in industrial materials and polluted samples .

The determination of the sample and preparation of the solution for spectrophotometric measurements was as given on page (56). The solution was also analysed by a recommended method.

The results of analysis are given, the data for both methods are in satisfactory agreement which proves the possible application of the method developed for the determination of vanadium in industrial materials.

Determination of vanadium in deposits covering the outer surface of superheaters and the inner parts of chimney of steam power plant.

A- Determination of vanadium in deposites of superheaters

when vanadium ion was determined in the deposites of superheaters by the proposed method, it was found that V(V) ion concentration value was 160 μg ml^{-1} .Using the reference method, V(V) ion concentration value was 155 μg ml^{-1}.

B-Determination of vanadium in deposites of chimney

when vanadium ion was determined in the deposites of chimney by the proposed method ,it was found that V(V) ion concentration value was 250 μg ml^{-1} .Using the reference method, V(V)ion concentration value was 244 μg ml^{-1}.

3.2.3.5.2. Determination of copper in waste water and in authentic solution

The results obtained for the spectrophotometric determination of Cu(II) considered in the present work show that 0.8-8.8 ppm of Cu(II) can be accurately determined under optimum experimental conditions.This encouraged us to apply the method for the determination of Cu(II) in industrial samples.

The determination of the sample and preparation of the solution for spectrophotometric measurements was as given in page (57). The solution was analysed by a recommended method.

The results of analysis are given. The data for both methods are in satisfactory agreement which proves the possible application of the method developed for the determination of Cu(II) in an industrial sample and an authentic solution.

A- Cu(II) metal ion is determined in waste water of Steam power plant

The copper ion concentration which was determined by the present method is 1.25 μg ml^{-1}.The reference method confirm this value where Cu^{2+} ion is 1.2٢.

B-Determination of Cu(II) in an authentic solution

The copper ion concentration which was determined by the present method is 7.6 μg ml^{-1}.The reference method confirm this value where Cu(II) ion is 7.4.

3.2.3.5.3. Determination of zinc ions

The results obtained for the spectrophotometric determination of Zn(II) considered in the present work show that 1-12 ppm of Zn(II) can be accurately determined under optimum experimental conditions.This encouraged us to apply the method for the determination of Zn(II) in industrial sample.

The determination of the sample and preparation of the solution for spectrophotometric measurements was as given in page (57).The solution was analysed by a recommended method.

The results of analysis are given, the data for both methods are in satisfactory agreement which proves the possible application of the method developed for the determination of Zn(II) in industrial sample

Zn(II) metal ion was determined in the material of some anodes used in industrial field which known as cathodic protection.The analyzed sample refers that the measured Zn(II) ions were 4.92 % while 5 % was obtained using the reference method.

3.2.3.5.4. Determination of silver ions

The results obtained for the spectrophotometric determination of Ag(I) considered in the present work show that 1.0-9.5 ppm of Ag(I) can be accurately determined under optimum experimental conditions.This encouraged us to apply the method for the determination of Ag(I) in authentic solution of silver nitrate

The determination of the sample and preparation of the solution for spectrophotometric measurements was as given in page (57). The solution was analysed by a recommended method.

The results of analysis are given, the data for both methods are in satisfactory agreement which proves the possible application of the method developed for the determination of Ag(I) in authentic solution. The taken concentration of silver ions was 8.0 ppm and the found concentration of the same ions was 7.8 ppm.

3.2.3.5.5. Determination of mercury ion

The results obtained for the spectrophotometric determination of Hg(II) considered in the present work show that 0.5-4.5 ppm of Hg(II) can be accurately determined under optimum experimental

conditions.This encouraged us to apply the method for the determination of Hg(II) in an authentic solution.

The determination of the sample and preparation of the solution for spectrophotometric measurements was as given in page (57). The solution was analysed by a recommended method.

The results of analysis are given, the data for both methods are in satisfactory agreement which proves the possible application of the method developed for the determination of Hg(II) in an authentic solution.

Hg(II) ions was determined in an authentic solution to be found 2.47 while the taken Hg(II) ion concentration was 2.5 ppm.

3.3. Studies on the solid complexes

3.3.1. Elemental analysis

The chemical composition and the percent of the metal ion and water molecules in the solid complexes can be detected by elemental analysis. The content of sulphate ion was determined by precipitation, the Ag(I) ion was gravimetrically determined as oxide [184], whereas the percent of Cu(II), Zn(II) Hg(II) ions were determined by EDTA titration [185] under the appropriate condition. The number of water molecules contributed to coordination sphere was determined by dehydration method. The results listed in Table (16) are in a good agreement with that calculated for the suggested formula, thus supporting this suggestion.

3.3.2. Molar conductivity

Conductivity in nonaquous solutions had frequently been used in the structure studies of metal complexes within the limits of their solubilities.It provides a method of testing the degree of ionization of the complexes. The more ions that a complex liberates in solution, the higher will be its molar conductivity and vice verse. In the present work, the molar conductivities of the prepared metal complexes were measured in dimethyl formamide(DMF) as a solvent. The molar conductance Λ_M ($ohm^{-1}\ cm^2\ mol^{-1}$) is given by the relation.

$$\Lambda_M = K\ 1000 / C$$

Where K is the specific conductivity ($ohm^{-1}\ cm^2$) and C is molar concentration of complex (mol L^{-1}).

All complexes were intensely coloured , soluble in DMF. The molar conductance values of Zn(II), Hg(II), Ag(I), V(V), Cu(II) complexes lie within different ranges depending on the stoichiometric ratio of the formed complexes and the number of ions formed during dissolution.

Some complexes were selected for carrying out this study. It is clear from the conductivity data, shown in table (16), that most the complexes

present behave as stong electrolytes. It is concluded from the results that Cu(II), Hg(II), Ag(I) and Zn(II) chelates with ligand I_a (M:L) (1:1)are found to have molar conductance values in the range of 62.9 to 92.7 ohm^{-1} cm^2 mol^{-1} indicating the ionic nature of these chelates. Furthermore, it indicates the nonbonding of the nitrate and sulphate anions to Cu(II), Hg(II), Ag(I).. It is clear that Cu(II), Hg(II), Ag(I) and Zn(II) chelates with ligand I_b (M:L) (1:1) have Λ_M in the range of 67 to 82.8 ohm^{-1} cm^2 mol^{-1} indicating the ionic nature of these chelates. The studied Zn(II) chelate with ligand I_c (M:L) (1:1) have molar conductivity 88.5 ohm^{-1} cm^2 mol^{-1} indicating the ionic nature of this chelate. Also Hg(II) chelate with ligand I_d have molar conductivity 84.7 ohm^{-1} cm^2 mol^{-1} indicating the ionic nature of this chelate.

The molar conductance values of the metal chelates of Cu(II), Hg(II), Ag(I) and Zn(II) with ligand I_a,I_b,I_c and I_d (M:L) (1:2), are ranged from 13.4 to 33 ohm^{-1} cm^2 mol^{-1} indicating the non-electrolytic nature of these chelates.

It is clear from conductivity data that most of the complexes present behave as strong electrolytes. Also, the molar conductance values indicate that some anions are present outside the coordination sphere specially the sulphate ion. This is confirmed from the chemical analysis where SO_4^{2-} ion is precipitated as $BaSO_4$ by addition of $BaCl_2$ solution to the soluble complex in DMF. Based on these results the corresponding probable constitutional formulae for the different complexex are suggested as given in Table (16).

Table (16) Elemental analysis and Molar conductivities of some selected complexes

No	Complex	Chemical formula	% SO_4^{2-}		%M^{n+}		% H_2O		Mole
			Found	Taken	Found	Taken	Found	Taken	
1	Zn –I_a	[Zn.L.H_2O]$CH_3COO.H_2O$	-	--	13.66	13.89	7.42	7.63	
2	Ag- I_a	[Ag.L.H_2O]NO_3	-	-	20.5	21.64	3.5	3.6	
3	Cu -I_b	[Cu.L_2.2H_2O]SO_4.3H_2O		11.38	7.25	7.53	10.12	10.66	
4	Zn -I_a	[Zn.L_2.]$CH_3COO.H_2O$	-	-	8.2	8.5	2.13	2.35	
5	Ag - I_b	[Ag.L_2.H_2O].NO3	-	-	13.54	13.79	2.10	2.29	
6	Ag- I_b	[Ag.L.H_2O] NO3.H_2O	-	-	20.99	21.47	6.90	7.15	
7	Zn - I_c	[Zn.L.H_2O]$CH_3COO.H_2O$	-	-	13.25	13.77	7.33	7.61	
8	Hg - I_a	[Hg.L.H_2O].NO3.H_2O	-	-	31.96	32.9	5.6	5.9	
9	Cu - I_b	[Cu.L.H_2O]SO4.H_2O		19.51	12.6	12.9	7.11	7.31	
10	Zn - I_b	[Zn.L_2.2H_2O]SO_4.3H_2O		15.24	10.11	10.33	13.90	14.29	
11	Zn -I_b	[Zn.L.H_2O]SO4.H_2O		19.41	12.96	13.14	6.99	7.28	
12	Hg - I_b	[Hg.L.H_2O]SO4.H_2O		15.24	31.23	31.86	5.5	5.71	
13	Cu- I_a	[Cu.L.H_2O]SO4.H_2O		18.95	12.36	12.53	6.85	7.1	
14	Cu-I_a	[Cu.L_2.2H_2O]SO_4.3H_2O		11.01	7.14	7.29	10.12	10.32	
15	Hg- I_d	[Hg.L.H_2O]NO3.H_2O	-	-				5.58	
16	Hg-I_d	[Hg.L_2.2H_2O]NO3.3H_2O	-	-				8.61	
17	Zn-I_c	[Zn.L_2.2H_2O]CH_3COO.3H_2O	-	-				10.73	

3.3.3. Thermal Analysis

3.3.3.1. Thermogravimetric and differential thermal analyses of some metal chelates

Thermal methods of analysis introduce a new possiblility for investigation of metal chelates[186]. They include such technique as thermogravimetric (TG) and differential thermal analysis (DTA). The TG and DTA curves give interesting information about the various unexpected phenomena observed during thermal degradation. It is important to take into account that the TG curves reveal the variation in weight, whereas the DTA is concerned calorimetrically with weight changes which often occur without observed detection.

From TG curves, one can calculate the percentage of water molecules and metal ion in the chelates, whereas those of DTA make it possible to characterize, thermographically, the process of phase transformation in the examined system. To understand the thermal decomposition of the chelates under investigation, which were studied by TG-DTA techniques , the mechanism of the decomposition has been estabilished from TG-DTA data.The kinetic parameters : activation energy (E_a) and pre-expontial factor (A) are calculated from TG-curves in the temperature range 35-1000 ºC using different methods.

3.3.3.2. Kinetic methods

All kinetic informations can be extracted from dynamic experiments by means of various methods .All kinetic studies assume that the isothermal rate of conversion, dα /dt is a linear function of a temperature dependant rate constant, K, and a temperature –independent function of the conversion, α that is:

$$\frac{d\alpha}{dt} = kf(\alpha) \qquad (1)$$

that express the rate of conversion, dα /dt, at a constant temperature (T) is a function of the reactant concentration loss and rate constant

According to Arrhenius equation

$k = A\, e^{-E_a/RT}$ (2)

Where A is the pre-expontial factor, assumed to be independent of temperature, E_a is the activation energy, T is the absolute temperature, and the gas constant R.

Combination of Eqs. (1) and (2) gives

$$\frac{d\alpha}{dt} = Af(\alpha)\exp - E_a/RT) \qquad (3)$$

in the case of complex degradation, it is assumed that the rates of conversion is proportional to the concentration of material that has to react ,

$$f(\alpha) = (1-\alpha)^n \qquad (4)$$

$$d\alpha/dt = A(1-\alpha)^n \exp(-E_a/RT) \qquad (5)$$

If the sample temperature is changed by a controlled and constant heating rate, $\beta = dT/dt$ it will be dpendent on the time of heating

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta}\exp\left(\frac{E_a}{RT}\right)dT \qquad (6)$$

This is the fundamental expression of analytical methods to calculate kinetic parameters on the basis of TG data. These methods can be distinguished as based on the degree of conversion measurement, α and based on heating rate β.

The variation in the degree of conversion can be analysed as a function of temperature , this temperature being dpendent on the time of heating.Therfore, the rate of conversion may be written as follows :

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT}\frac{dT}{dt} = \beta\frac{d\alpha}{dT} \qquad (7)$$

A combination of Eqs. (3) and (7) leads to :

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E_a}{RT}} f(\alpha) \qquad (8)$$

integration of this equation from an initial temperature ,$T_{o,}$ corresponding to a degree of conversion α_o to the inflection temperature,Tp, where $\alpha = \alpha_o$ gives

$$\int_{\alpha_o}^{\alpha\rho} \frac{d\alpha}{f(\alpha($$ $$= \frac{A}{\beta} \int_{\alpha_o}^{\alpha\rho} e^{-\frac{E_a}{RT}} dT \qquad (9)$$

if T_o is low , it may be reasonably assumed that $\alpha_o = 0$ and considering that there is no reaction between 0 and T_o .

$$g(\alpha) = \int_{a_o}^{ap} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{\alpha_o}^{ap} e^{-\frac{E_a}{RT}} dT \qquad (10)$$

where $g(\alpha)$ is the integral function of conversion as shown in the following table.(Table 17). Where α values are calculated for different thermal degradation processes, for the present selected complexes , then their activation energies can be gained.

Table (17). Algebric expressions for g(α) for the most frequently used mechanisms of solid state processes.

	symbol	g(α)	Solid state process
Sigmoidal curves	A2	$[-\ln(1-\alpha)]^{1/2}$	Nucleation and growth(Avrami equation 1)
	A3	$[-\ln(1-\alpha)]^{1/3}$	Nucleation and growth(Avrami equation 1)
	A4	$[-\ln(1-\alpha)]^{1/4}$	Nucleation and growth(Avrami equation 1)
Deceleration curves	R1	α	Phase boundary controlled reaction(one dimentional movement)
	R٢	$[1-(1-\alpha)]^{1/2}$	Phase boundary controlled reaction(contraction area)
	R3	$[1-(1-\alpha)]^{1/3}$	Phase boundary controlled reaction(contraction volume
	D1	α^2	One-dimentional diffusion
	D2	$(1-\alpha)\ln(1-\alpha)+\alpha$	Two-dimentional diffusion
	D3	$\left[1-(1-\alpha)^{1/2}\right]^2$	Three-dimentional diffusion (Jander equation)
	D4	$(1-2/3\alpha)(1-\alpha)^{2/3}$	Three-dimentional diffusion (Ginstling-Brounshtein equation)
	F1	$-\ln(1-\alpha)$	Random nucleation with one nucleus on the individual particle
	F2	$1/(1-\alpha)$	Random nucleation with two nucleus on the individual particle
	F3	$1/(1-\alpha)^2$	Random nucleation with three nucleus on the individual particle

3.3.3.3. Kissinger method [187]

Kissinger method has been used in the literature to determine the activation energy of solid state reactions from plots of the logarithm of the heating rate versus the inverse of the temperature at the maximum reaction rate in constant heating rate experiments.

The activation energy can be determined by the Kissinger method using the following equation

$$\ln \frac{\beta}{T_p^2} = \ln \frac{AR}{E_a} + \ln\left[n(1-\alpha_P)^{n-1}\right] - \frac{E_a}{RT_P} \qquad (11)$$

where β is the heating rate, T_p and α_p are the absolute temperature and weight loss at the maximum weight-loss rate (dα /dt)p,respectively.A is the pre-expontial factor, and n is the reaction order.

From a plot of ln (β / T^2_P) versus 1/ T_p and fitting to a straight line, the actination energy E_a can be calculated from the slope .

3.3.3.4.Flynn-wall- method[188]

Equation (10) is integrated using the Doyle approximation[189]**.** The result of the integration after taking the logarithm is :

$$\log\beta = \log \frac{AE_a}{g(\alpha)\,R} - 2.315 - \frac{0.457E_a}{RT} \qquad (12)$$

Where β, A, E_a and T have the known meanings.

This is one of the integral methods that can determine the activation energy without a knowledge of the reaction order. It is used to determine the activation energy for given values of conversion. The activation energy for different conversion values can be calculated from a log β versus 1000 /T plot.

3.3.3.5. Friedman method [190]

This method is probably the most general of the derivative techniques and is based on the intercomparison of the rates of conversion dα / dt for a given degree of conversion α determined using different heating rates β this method utilizes the following logarithmic differential equation derived from Eq.(5).

$$\ln A = \ln (d\alpha / dt) - n \ln (1-\alpha) + E_a / (RT) \qquad (13)$$

Using this equation , it is possible to obtain values for E_a over a wide range of conversions by plotting ln (dα / dt) versus 1 / T for a constant α value .

3.3.3.6. Coats-Redfern method [191]

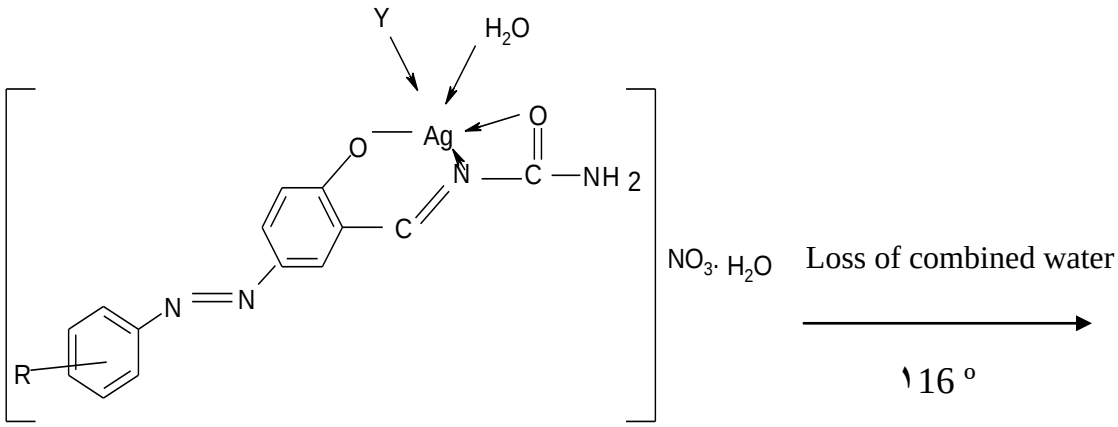
Coata-Redfern used an approximation for thre resolution of Eq.(10) to obtain the equation

$$\ln \frac{g(\alpha)}{T^2} \ln \frac{AR}{\beta E_a} - \frac{E_a}{RT} \qquad (14)$$

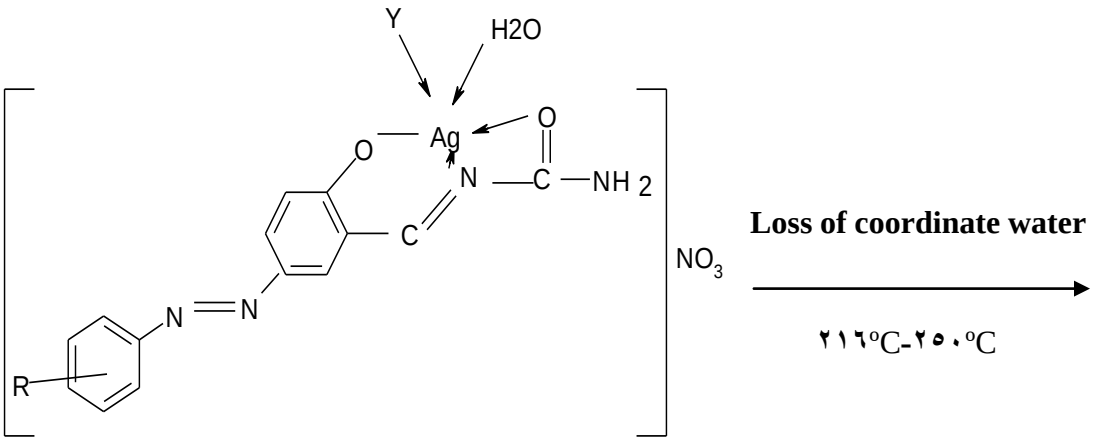
Activation energy for every degradation process can be determined from a plot of $\ln g(\alpha) / T^2$ versus $1000 / T$.

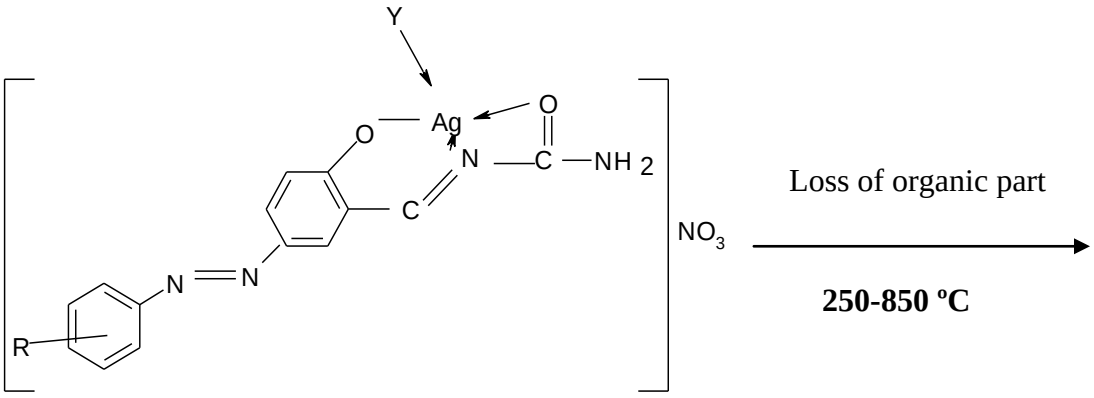
3.3.3.7. The thermal analysis of (1:1) Ag(I) chelate with I_a ligand

TG/DTA analysis for [Ag–Ia·H_2O]NO_3. H_2Ocomplex (1:1) Fig (60) ,shows that the water rmolecules were expelled after raising temperature up to 216 ◦C with weight loss 14.11% (theoretically13.36%) corresponding to the loss of four molecules of water. This step is accompanied by an endothermic peak in the DTA curve ,the second weight loss(found11.90%) takes place between 216 and 336 ◦C having endothermic peak in the DTA curve at 336 ◦C which is attributed to elimination of nitrate ion (theoretically 11.45%) the final step which is shown in the TG curve in the range 350–850 ◦C with weight loss 54.50% (theoretically54.93%) and this corresponding to the decomposition of the organic part of the complex having exothermic peak in DTA curve at 750 ◦C. The metal oxide is formed at 850 ◦C and the activation energy of degradation process is 32.39 $kJmol^{-1}$ which deducted from Fig.(64) after gaining the slope and intercept of the curve. Table (18) contains the degradation steps of that chelate. The different thermal parameters such as ΔH*, ΔS* and ΔG* are calculated and recorded in Table (19).



where R=p-COOH, Y =$OCOCH_3$, $SO4^{2-}$ or Cl^- coordinated to metal ion

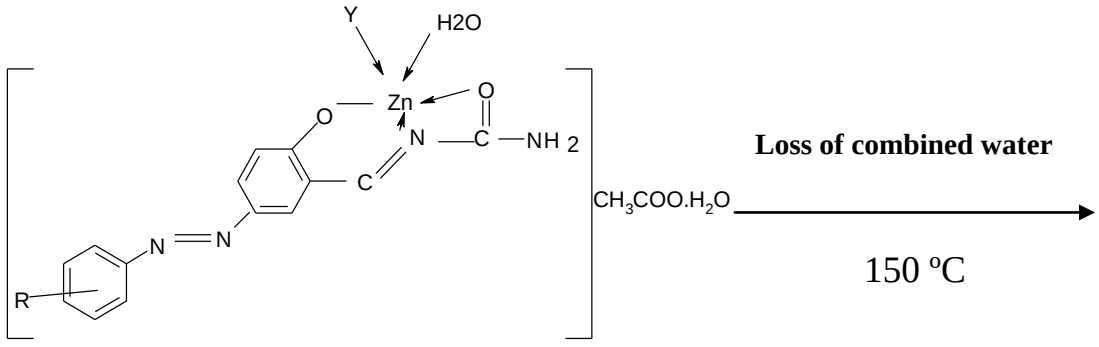

Y
H2O
O
Ag
O
N
C
NH 2
C
N
N
R
NO3
Loss of coordinate water
٢١٦°C-٢٥٠°C


Y
O
Ag
O
N
C
NH 2
C
N
N
R
NO3
Loss of organic part
250-850 °C

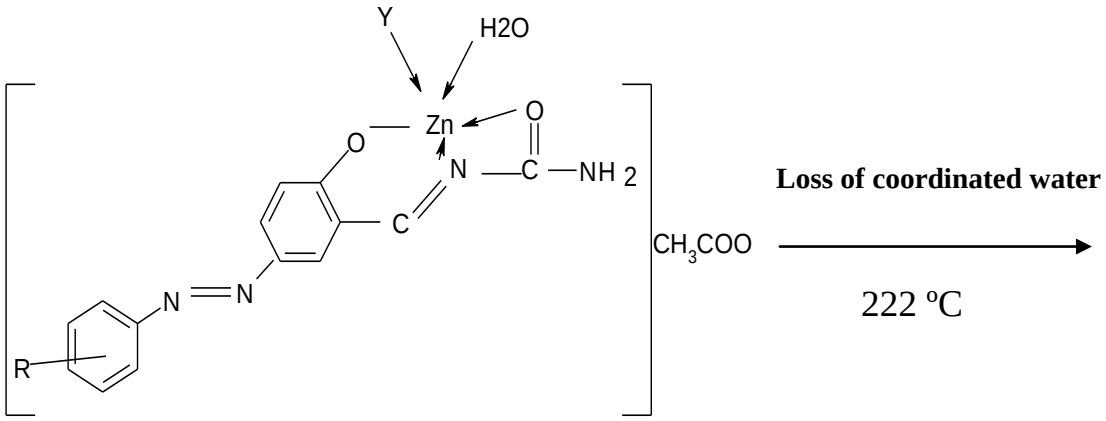
Ag_2O

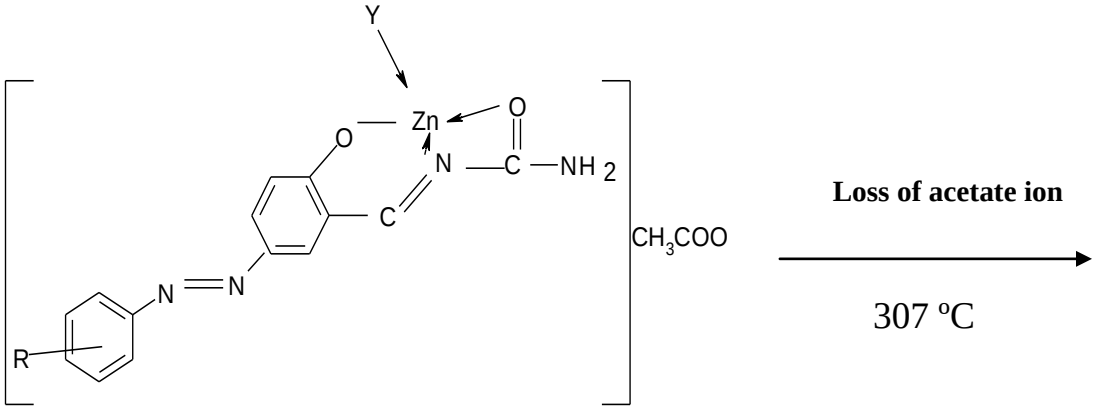
3.3.3.8. The thermal analysis of (1:1) Zn(II) chelate with I_c ligand :

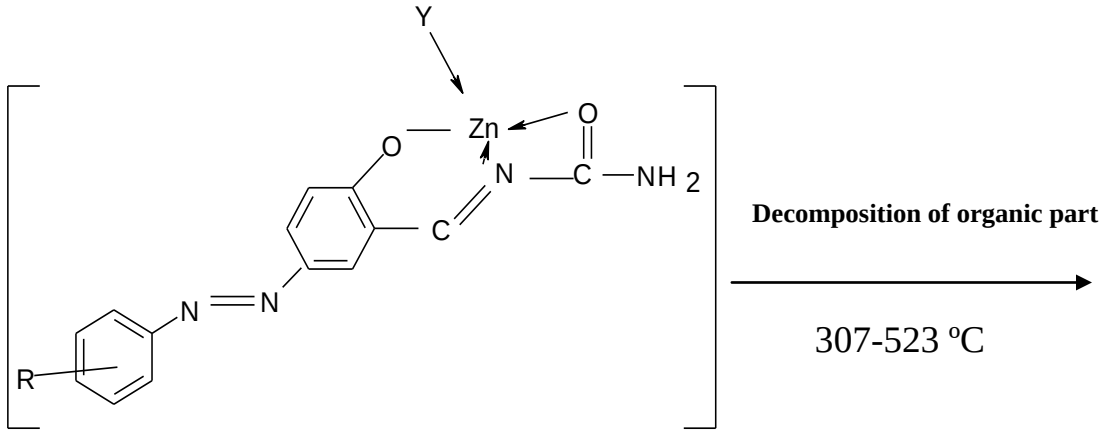
Thermal analysis has been carried out on[Zn·Ic·4H_2O] $CH_3COO·H_2O$ complex. From TG-curves as shown in Fig. (61), the weight losses were calculated for the different overlapping steps and compared with those theoretically calculated for the suggested formula. The first weight loss at temperature up to 120 ◦C is attributed to dehydration of one hygroscopic water molecule ,the found weight losses is 3.25% (calc.3.56%), having broad endothermic peak in DTA at 100 ◦C where as the second step of weight loss within the range 120–220 ◦C is attributed to release of four water molecules coordinated with metal ion with endothermic peak, the third weight loss within the range 220–320 ◦C is attributed to one acetate ion with exothermic peak in DTA curve at 280 ◦C. The found weight losses of the complex amount to 14.75 and 13.25% compared with the calculated values (14.65 and 11.95%) for four water molecule and acetate ion, respectively. The organic part of the complex is decomposed in range 307–523 ◦C, the found weight loss of organic part is 56.16% (theoretically53.41%), and having sharp exothermic peak at 500 ◦C. The activation energy of degradation process is 46.7 $kJmol^{-1}$ which deducted from Fig.(65) after gaining the slope and intercept of the curve. Table(18) contains the degradation steps of that chelate.The different thermal parameters such as ΔH*, ΔS* and ΔG* are calculated and recorded in Table (19).



where R=O-NO_2 , Y =$OCOCH_3$, $SO4^{2-}$ or Cl^- coordinated to metal ion

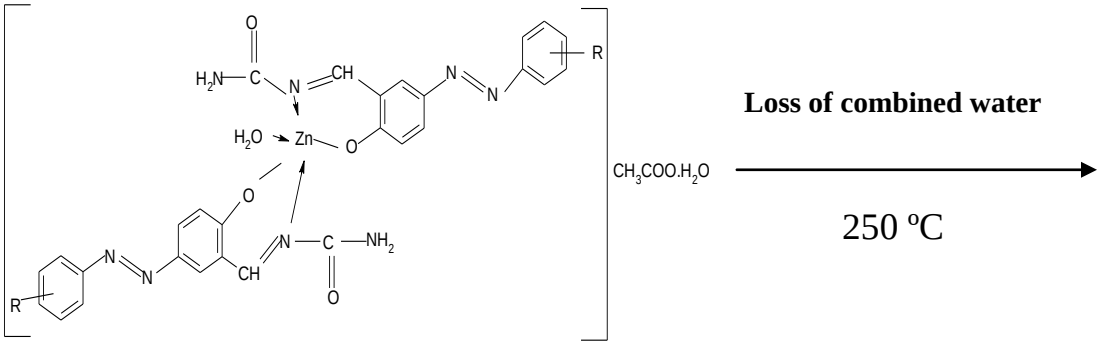

Y
H2O
Zn
O
O
N
C
NH 2
C
N
N
R
CH3COO
Loss of coordinated water
222 ºC


Y
Zn
O
O
N
C
NH 2
C
N
N
R
CH3COO
Loss of acetate ion
307 ºC

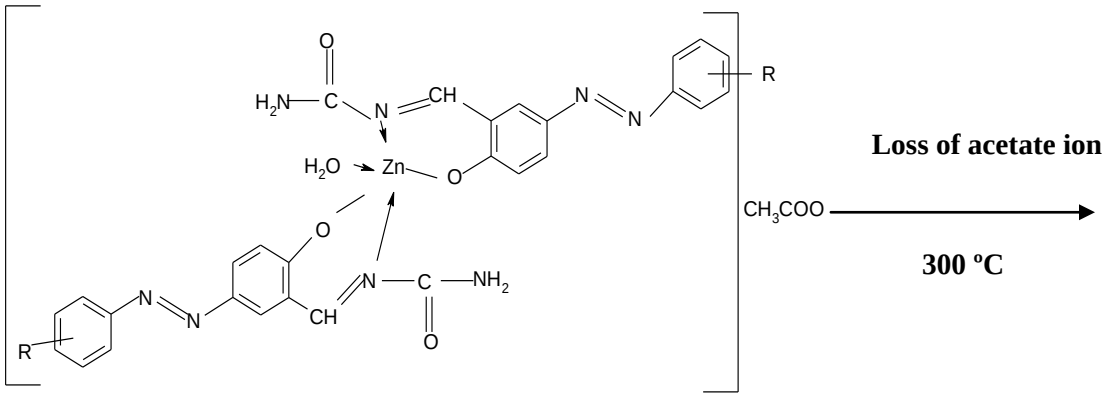

Y
Zn
O
O
N
C
NH 2
C
N
N
R
Decomposition of organic part
307-523 ºC
ZnO

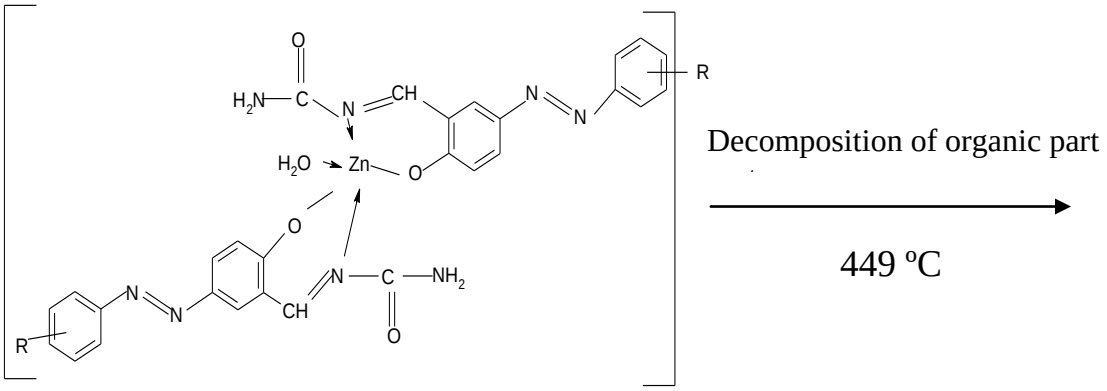
3.3.3.9. The thermal analysis of (1:2) Zn(II) chelate with $I_a$ligand

The thermal decomposition of [Zn·2Ia] $4H_2O$ complex in ratio (1:2) (M:L) has been carried out in temperature range 30–1000 ◦C in nitrogen atmosphere with heating rate of 10 ◦C/ min. From TGA curve in Fig.(62), the weight losses were calculated and compared with those theoretically calculated for the suggested formula. The first weight loss at temperature up to 120 ◦C is attributed to elimination of four water molecules, having broad endothermic peak in DTA at 100 ◦C where as the second step of weight loss within the range 120–550 ◦C is attributed to organic part with exothermic peak in DTA curve at 499 ◦C. The found weight losses of the complex amount to 10.55% compared with the calculated values (10.26%) for four water molecules. The organic part of the complex is decomposed in range 120–523 ◦C, the found weight loss of organic part is 77.16% (cal.77.86%), and having sharp exothermic peak at500 ◦C with forming zinc oxide 11.21 (cal.11.59%). The activation energy of thermal degradation process is 41.33 $kJmol^{-1}$ which deducted from Fig.(66) after gaining the slope and intercept of the curve.



Where R=p-COOH

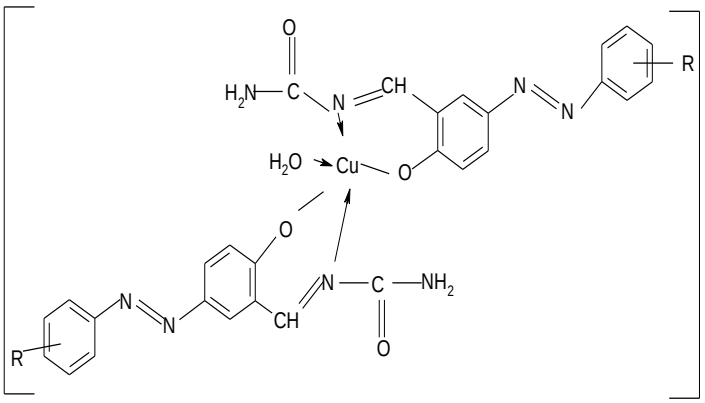

Loss of acetate ion
CH3COO
300 ºC


Decomposition of organic part
449 ºC

ZnO

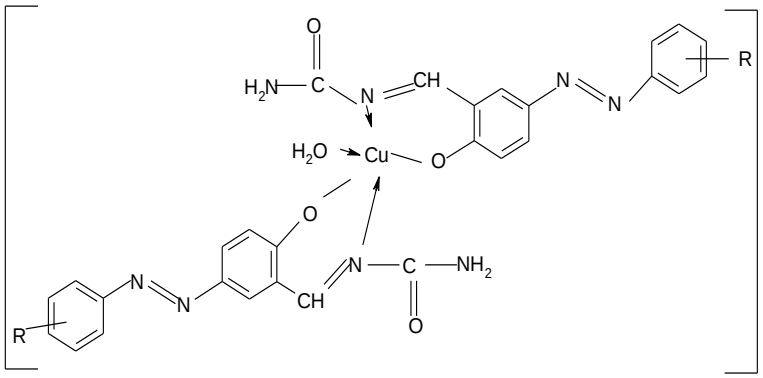
3.3.3.10. The thermal analysis of (1:2) Cu(II)chelate with I_b ligand

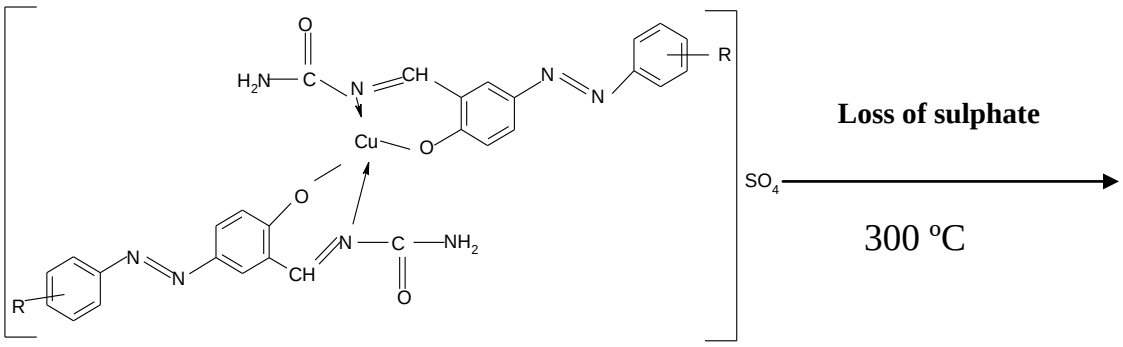
TGA/DTA analysis of the [Cu·2Ib] H_2O complex in ratio(1:2) (M:L) has been carried out, as shown in Fig.(63), with heating rate 10 ◦C/min. in nitrogen atmosphere. The found weight losses of the complex amount to 2.12% compared to calculated 2.62 % for one water molecule having endothermic peak in DTA at 120 ◦C. The organic part of the complex is decomposed in range 120–423 ◦C, the found weight loss of organic part is 87.16% (cal.88.14%), and exothermic peak observed at 400 ◦C with forming copper oxide 11.21 (cal.11.58%). The activation energy of degradation process is 33.2kJmol^{-1} which deducted from Fig. (67) after gaining the slope and intercept of the curve. Table (18) contains the degradation steps of that chelate.The different thermal parameters such as ΔH*, ΔS* and ΔG* are also calculated and recorded in Table (19).

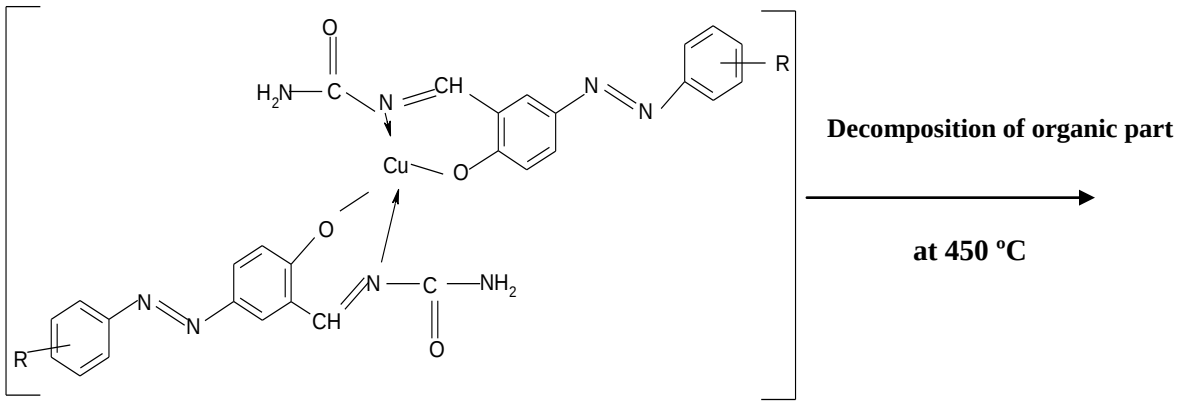


SO_4. H_2O → **Loss of combined water** **221 °C**

where R= o-OCH_3


Loss of coordinate water
SO4
256 ºC


Loss of sulphate
SO4
300 ºC


Decomposition of organic part
at 450 ºC

CuO

-Table.(18) Thermogravimetric analysis of chelates with transition metal ions

chelate	Temperature range, °C	Weight loss %		Type of peak	Assignment
		Cal.	found		
Ag^{+}-I_a (1:1)	30-216	١٣.٤١	١٣.٦٦	endo	Four water molecules
	216-336	١١.٥٤	١١.٩٠	endo	Nitrate ion
	336-850	٥٤.٩٣	٥٤.٥٠	exo	Organic part
Zn^{2+}-I_c (1:1)	35-180	8.22	8.75	endo	$2H_2O$
	180 -222	13.35	13.25	endo	$3H_2O$
	222-307	12.41	12.36	exo	Acetate ion
	307-523	70.41	70.36	exo	Organic part
Zn^{2+}-I_a (1:2)	40-150	2.57	2.3	endo	One coordinated water
	150-350	5.14	4.95	exo	$2H_2O$
	350-600	80.16	80.25	exo	Part of ligand
Cu^{2+}-I_b (1 :2)	40-125 C	4.98	5.12	endo	$2H_2O$.
	120-250 C	2.49	2.6	endo	H_2O
	250-600 C	81.6	82.4	exo	Organic part

Table (19): The kinetic parameters of thermal decomposition of some selected chelates:

Complex	Step	T,k	Correlation factor	E_a kJ mol^{-1}	ΔH* kJ mol^{-1}	Preexponential-factor, $ASec^{-1}$	-ΔS* kJ mol-$1k^{-1}$	ΔG* kJ mol^{-1}
Ag^{+} -I_a (1 : 1)	١	580	٠.٩٩٨	61.27	56.16	$2.13x10^{6}$	129.28	$7.5x10^{4}$
	٢	775	٠.٩٦٦	17.07	10.63	$4.02x10^{3}$	183.91	$14.3x10^{4}$
	٣	١٥١	٠.٩٠٩	42.66	33.09	$2.1x10^{4}$	173.42	$20.0x10^{4}$
Zn^{2+}-I_a (1:2)	1	٤٤١	٠.٩٩٦	٣١.٧٧	٢٨.١	٣.٥×$10^{٤}$	١٦١.٢١	$7.1x10^{4}$
	2	٥٧٤	٠.٩٩٢	٢٢.٤٨	١٧.٧١	١.٢×$10^{٤}$	١٧٢.٢٩	$9.9x10^{4}$
	٣	٧٦٦	٠.٩٩	٣٣.٠٧	٢٧.٢٤	$4.06x10^{4}$	١٦٤.٥٦	$12.6x10^{4}$
Cu^{2+}-I_b (1 :2)	١	٦٩٦	٠.٩٦٢	28.2	24.08	$2.63x10^{4}$	164.57	$8.14x10^{4}$
	٢	٥٦٥	٠.٩٥٦	21.17	16.55	$1.03x10^{4}$	173.3	$9.64x10^{4}$
	٣	700	0.998	34.87	29.05	$4.54x10^{4}$	162.88	١$.0x10^{4}$
Zn^{2+}-I_c (1:1)	١	363	٠.٩٢٩	17.05	14.03	$1.02x10^{2}$	212.06	$7.7x10^{4}$
	٢	530	0.995	33.9	29.49	$2.8x10^{2}$	185.21	$9.8x10^{4}$
	٣	648	٠.٩٢٨	14.92	10.04	$2.26x10^{3}$	146.48	$9.5x10^{4}$
	٤	788	0.991	48.52	41.97	$8.43x10^{4}$	158.71	$15.5x10^{4}$

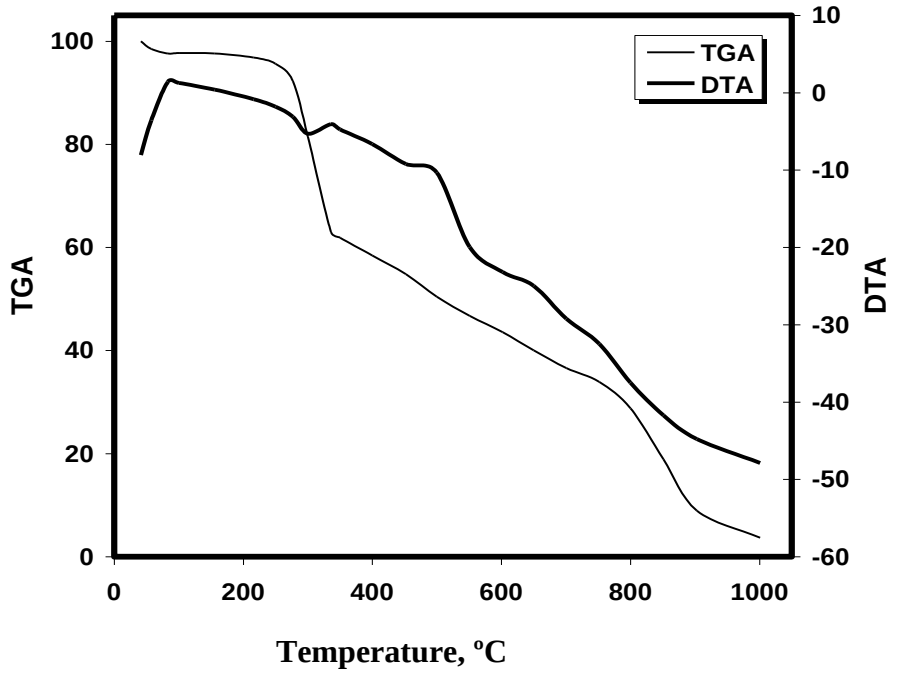


Fig. (60):Thermogravimetric and Differential thermal analysis of I_a ligand chelate with Ag(I) ion in ratio (1:1) (M:L) in a nitrogen gas with a heating rate of 10 °C/min

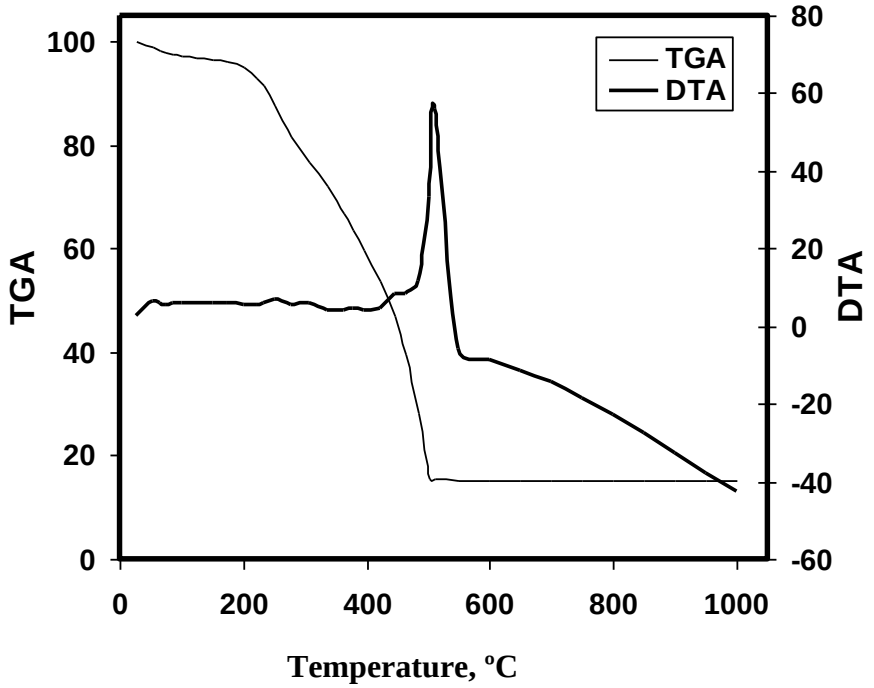


Fig. (61): Thermogravimetric and Differential thermal analysis of I_c ligand chelate with Zn(II) ion in ratio (1:1) (M:L) in a nitrogen gas with a heating rate of 10 °C/min.

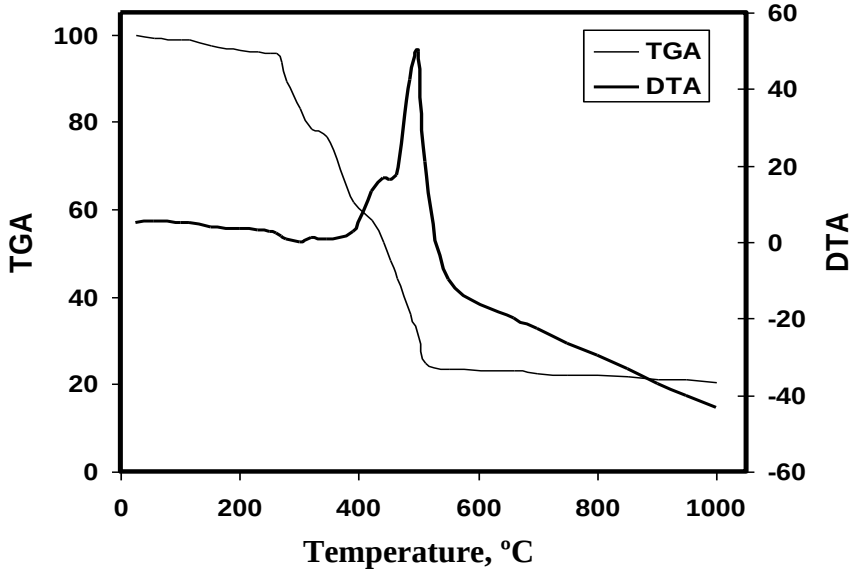


Fig (62): Thermogravimetric and Differential thermal analysis of I_a ligand chelate with Zn(II) ion in ratio (1:2) (M:L) in a nitrogen gas with a heating rate of 10 °C/min

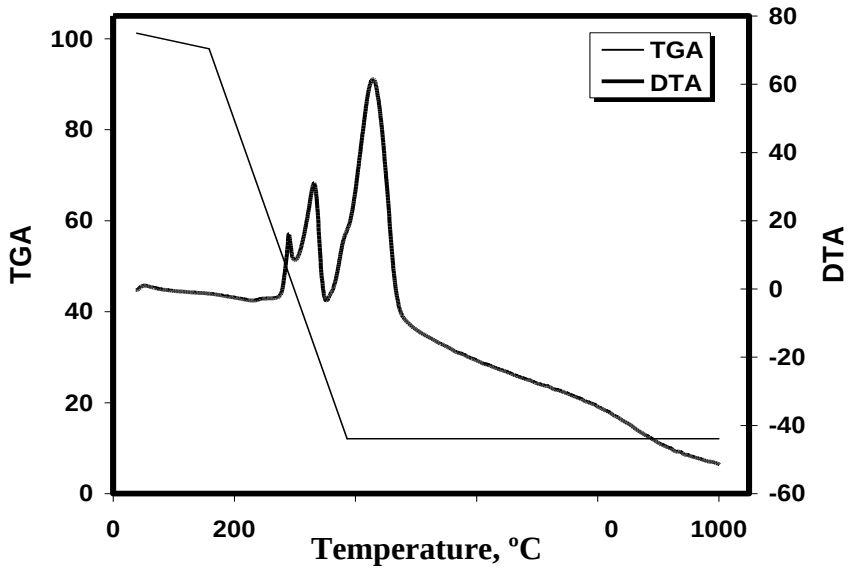


Fig. (63): Thermogravimetric and Differential thermal analysis of I_b ligand chelate with Cu(II) ion in ratio (1:2) (M:L) in a nitrogen gas with a heating rate of 10 °C/min

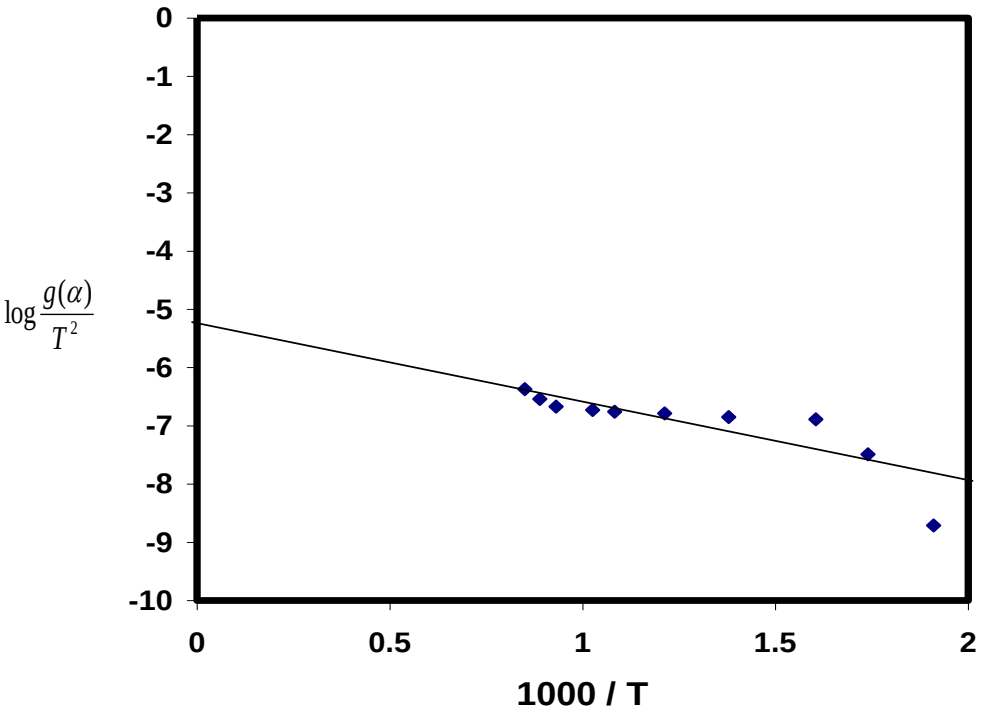


Fig. (64): The overall thermal degradation process of Ag(I)-I_a (1:1)

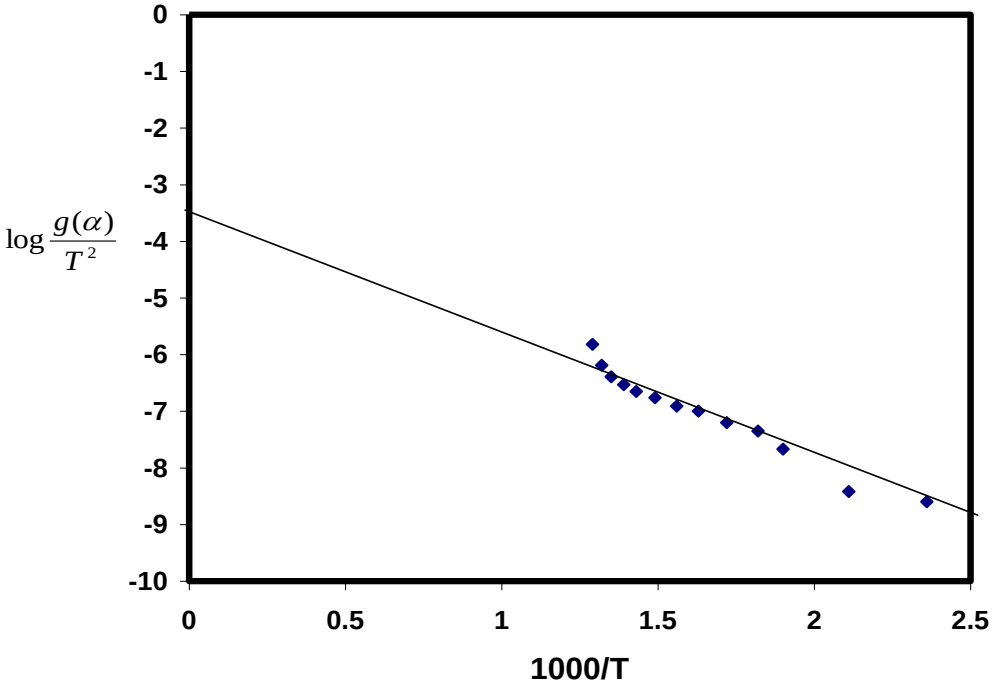


Fig. (65) : The overall thermal degradation process of Zn(II) –I_c (1:1)

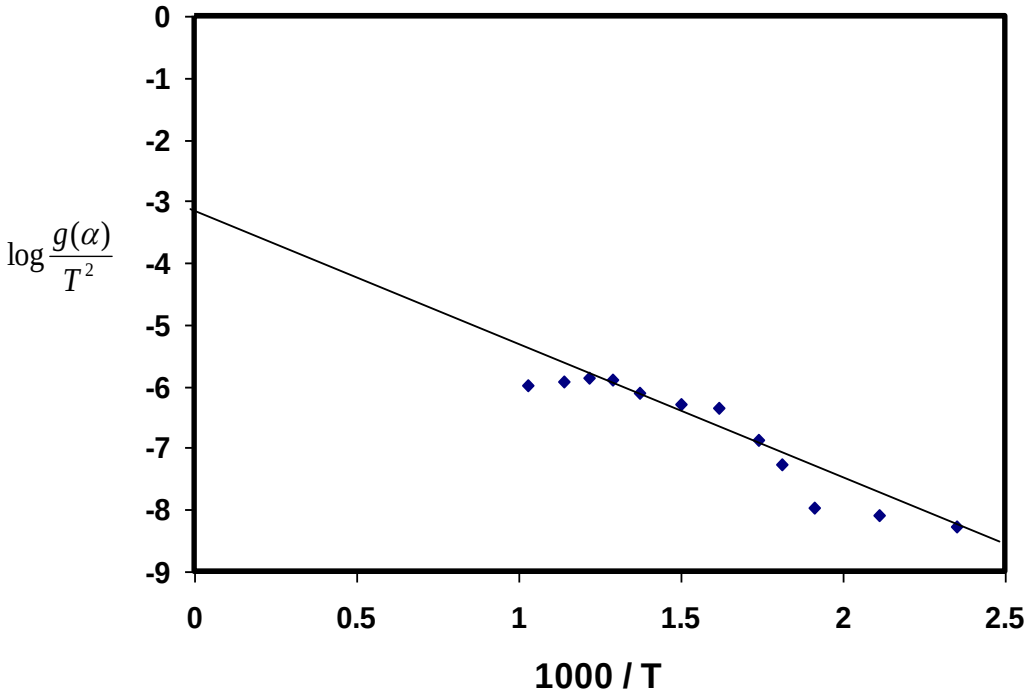


Fig. (66) The overall thermal degradation process of Zn(II)–I_a (1:2)

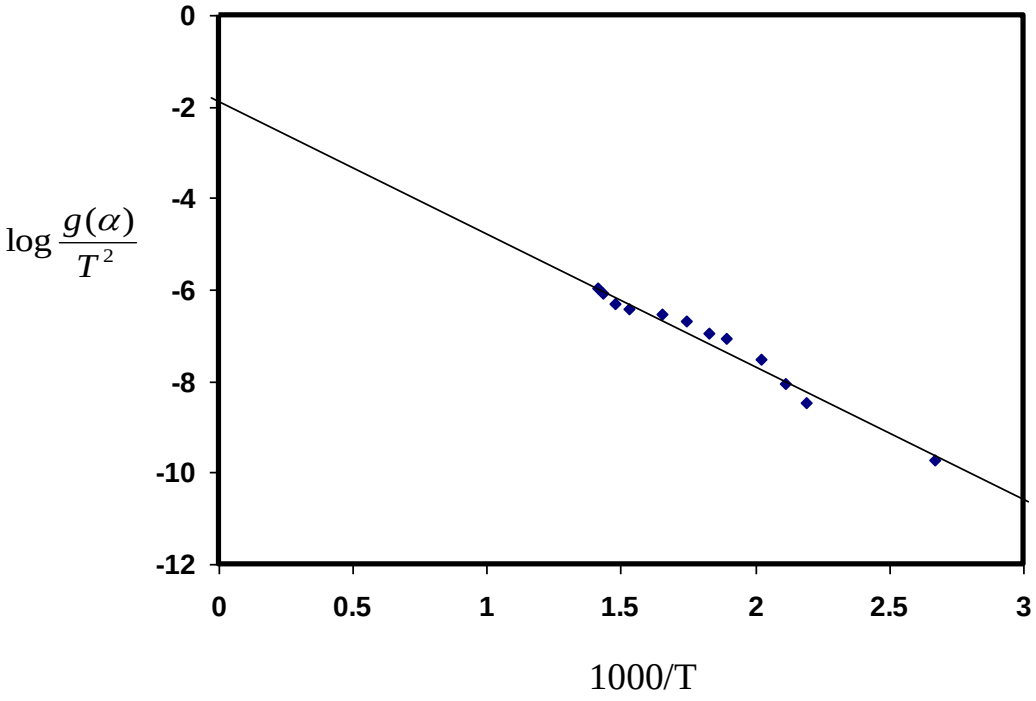


Fig. (67) The overall thermal degradation process of Cu(II)–I_b (1:2)

3.3.4. Infrared absorption spectra of metal chelates with ligands under consideration.

When a ligand coordinates to a metal ion M^{z+}, new modes of vibrations, is not present in the free state may become infrared active. For example, for a coordinated water molecules, rocking, twisting and wagging modes become possible and of course, this is in addition to the M-O and M-N bond which are due to the metal ligand bands stretching vibrations. In general, the frequencies of these new bands not only depend on the ligand involved but are also sensitive to the nature of the metal ion, its size and charge.

In true aquo complexes, the water molecules that firmly bound to the metal ion by means of a partial covalent bond and is known as coordinated water. However, in some other cases, the metal oxygen bond may be almost ionic in nature and in these hydrates the water molecule may be considered as crystal or lattice water. Since this type of water molecule is trapped, certain rotational and vibrational motions become partially hindered by environmental interactions and may in fact become infrared active. These bands are observed in the region 600-300 cm^{-1}**(192)**.

The azo group is non polar in nature hence exhibits weak absorption in the IR region. In addition, the weak absorptioin band of azo group occurs in the same region as the absorption of aromatic compounds, the cis-form have slightly stronger bands normally than the trans-form **(193)**.

Aromatic azo compounds absorb for ν N=N at 1410-1510 cm^{-1} and the compounds in trans-form absorb at the lower-frequency end of the range given if they are substituted with strong electron donors**(194)**.

Coordination complexes frequently contain oxygen or nitrogen metal bonds, but the absorption bands associated with these bonds are normally difficult to assign empirically, since their position is not dependant on the

metal ion but also on the ligand and in addition coupling with other vibration modes often occurs **(195)**.

By comparing the spectrum of the free ligand with that of the complex, metal-ligand vibrations may often be identified although, since some ligand vibrations may become infrared active on forming the complex, it is not uncommon for clear assignments to be made by this comparison. Also, metal-ligand vibrations may sometimes be identified by changing the central metal ion or its valency state.This technique is useful when a series of complexes with the same structure will be studied

3.3.4.1. The IR absorption spectra of the metal ion complexes with ligand I_a, I_b, I_c and I_d (1:1) (M:L) ratio of complexes.

The IR spectra of Cu(II), Hg(II), Ag(II),V(V) and Zn(II) complexes with I_a, I_b, I_c and I_d ligands are studied and compared with those of the freee ligands. The spectra are represented in Figs from (68) to (70) and the data are listed in Table (20).

The IR spectra of the ligands show a sharp strong band in the frequency range 3412-3440 cm^{-1} which is due to ν OH but these bands become broadened and suffer a frequency shift when the ligand is bonded with the metal ions to give the chelate. This indicate the deprotonation of the replacable hydrogen atom.

The IR spectra of reagents confirmed the presence of azo group due to the band in the frequency range 1475-1482 cm^{-1} . A weak band appears in the vicinity of 450 cm^{-1} which is attributed to a M-N bond in the reagents chelates.

The IR spectra of the solid complexes confirmed the presence of coordinated water molecules by the broad band in the frequency range 3400-3600 cm^{-1}.

3.3.4.2. The IR absorption spectra of the metal ion complexes with ligand I_a ,I_b.I_c and I_d (1:2) (M:L) ratio of complexes

The IR spectra of Cu(II), Hg(II), Ag(II),V(V) and Zn(II) ions with reagent I_a, I_b, I_c and I_d are studied. The IR spectra of these compounds are compared to those of the free ligands. The spectra are represented in Figs. (68 -70) and data are listed in Table (20).

The IR spectra of ligands show strong band in the frequency range 3412-3440 cm^{-1} due to the stretching vibration of hydroxyl group and this band shifted from the position by chelation indication the deprotonation of the hydrogen atom. Also bending vibratioin band of (OH) grouping the frequency range 1311-1399 cm^{-1} shifted by high degree than (1:1) chelates indicates the participation of the two groups of the (1:2) chelates in chelation .The appearance of a new band at far IR region 400-450 cm^{-1} due to ν M-O also support the formation of covalent bond between the metal ion and the oxygen of two (OH) groups while ν M-N exhibits a band in the vicinity of 450 cm^{-1}.

The infrared spectra of the selected ligands and their complexes exhibit strong band in the frequency range 1527-1596 cm^{-1} characteristic of ν C=N. The IR spectra of the solid complexes confirmed the presence of coordinated water by the strong broad band at 3400-3600 cm^{-1}.

Table (20) : Assignment of the important bands in the IR spectra of I_a, I_b, I_c and I_d, ligands and their metal chelates .

Compound	Ratio (M:L)	ν -OH	δ OH	ν -C=N	ν -N=N-	ν C-O	ν M-O	ν M-N
I_a Free	-	3412	1378	1573	1455	1156	-	-
Zn(II) -I_a	(1:1)	3680	1376	1576	1424	1150	408	448
Hg(II)-I_a	(1:1)	3738	1375	1576	1423	1155	412	448
Hg(II)-I_a	(1:2)	3742	1375	1575	1424	1150	410	449
Ag(I)-I_a	(1:1)	3427	1378	1574	1427	1159	404	447
Ag(I)-I_a	(1:2)	3614	1375	1573	1423	1156	447	520
V(V) -I_a	(1:1)	3742	1375	1599	1423	1149	409	453
V(V) -I_a	(1:2)	3742	1283	1596	1422	1148	408	450
Cu(II)-I_a	(1:1)	3742	1384	1527	1425	1150	408	449
I_b Free	-	3440	1366	1586	1482	1151	-	-
Hg(II)-I_b	(1:1)	3424	1370	1585	1482	1153	453	492
V(V) -I_b	(1:1)	3742	1366	1585	1483	1151	454	492
Ag(I)-I_b	(1:1)	3741	1375	1582	1482	1162	449	492
Ag(I)-I_b	(1:2)	3424	1366	1586	1484	1151	454	492
Zn(II) -I_b	(1:1)	3398	1393	1530	1478	1152	439	504
Zn(II) -I_b	(1:2)	3360	1394	1528	1480	1152	455	513
Cu(II)-I_b	(1:2)	3429	1394	1593	1463	1151	425	458
I_c Free	-	3742	1344	1576	1480	1145	-	-
Zn(II) -I_c	(1:1)	3314	1346	1622	1472	1150	523	584
Zn(II) -I_c	(1:2)	3742	1344	1579	1479	1144	449	523
I_d Free	-	3691	1380	1619	1475	1143	-	-
Hg(II)-I_d	(1:1)	3742	1374	1617	1472	1160	407	500
Hg(II)-I_d	(1:2)	3741	1384	1617	1471	1160	421	500

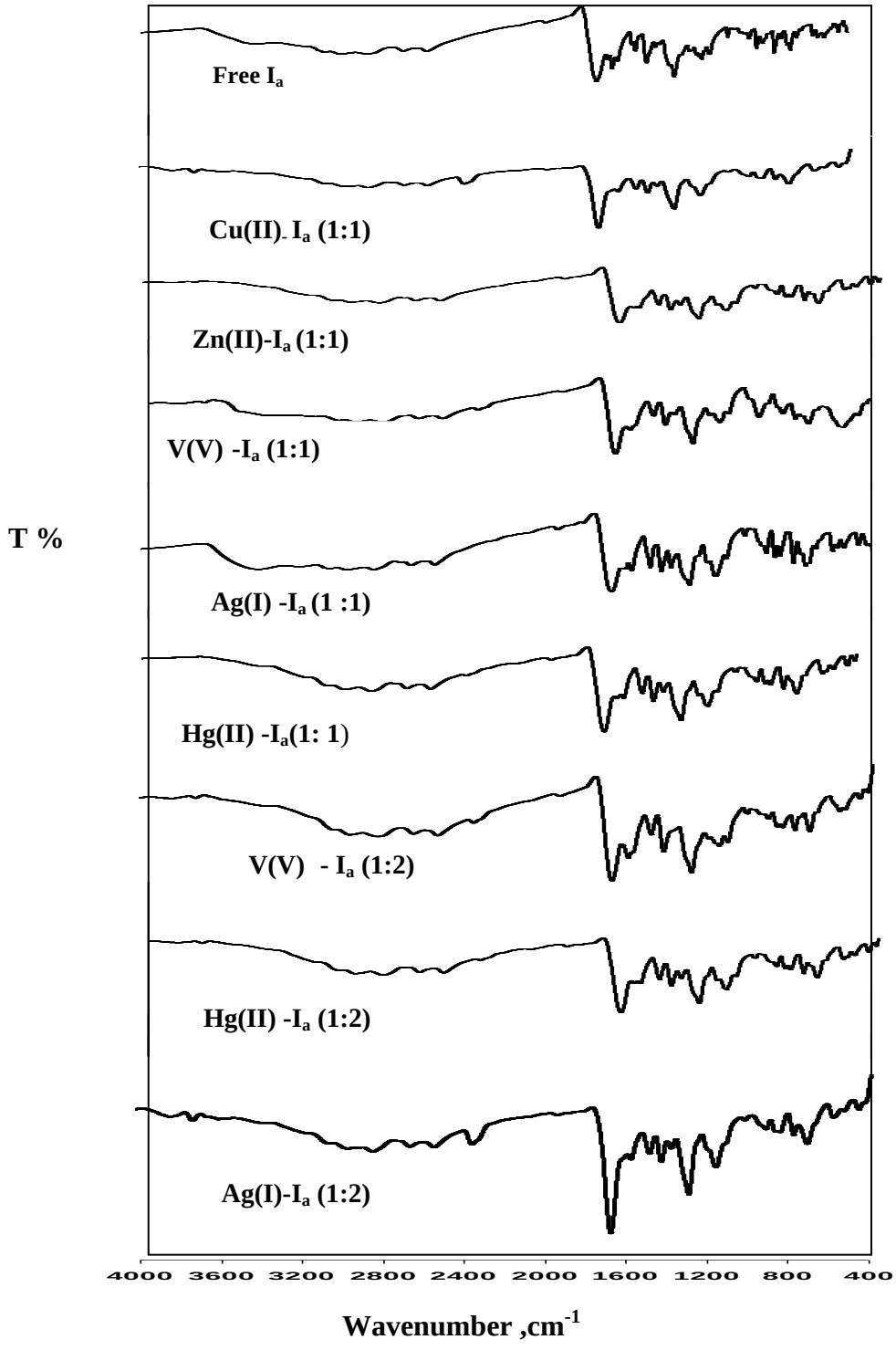


Fig. (68) IR spectra of I_a free ligand and its chelates

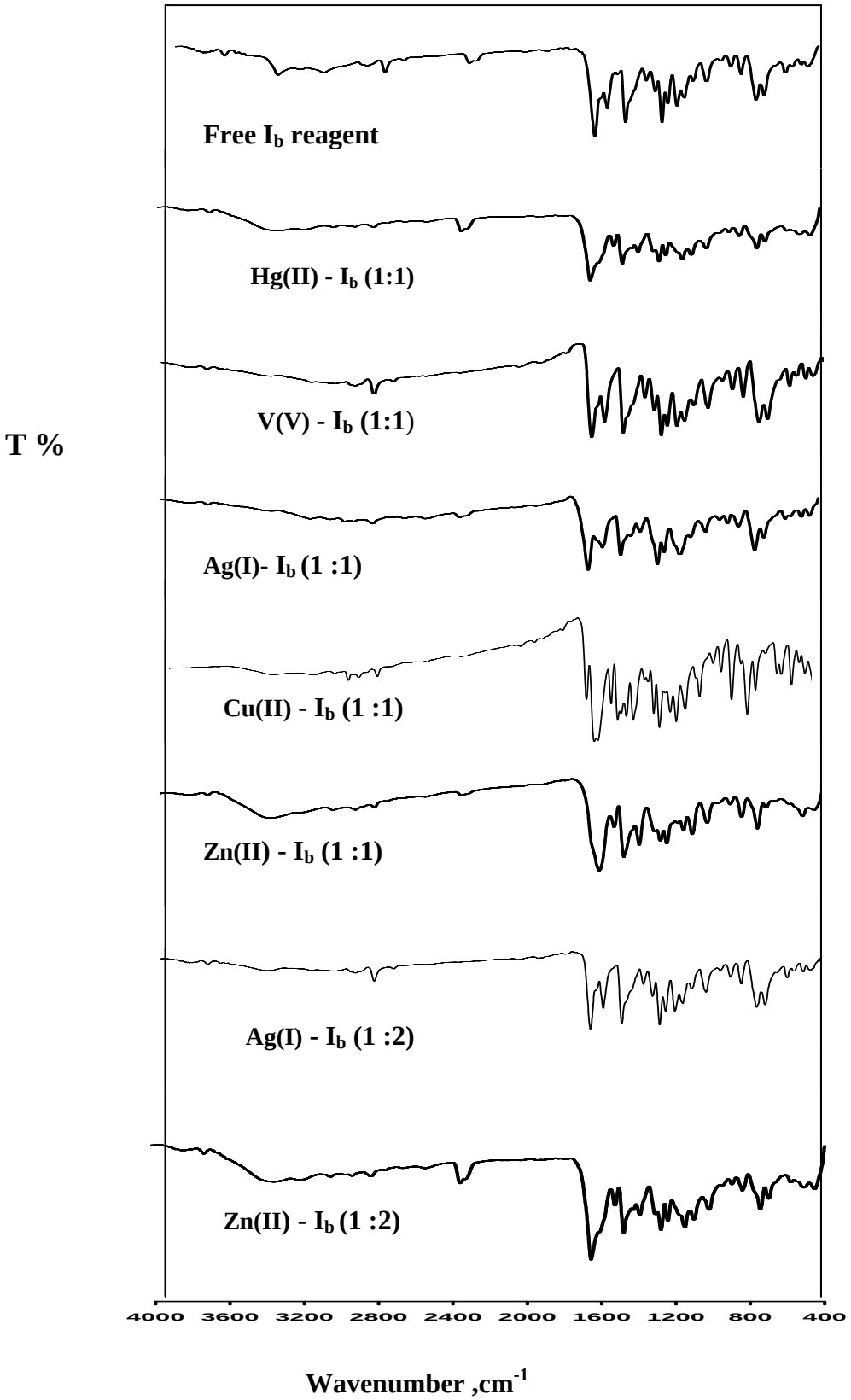


Fig. (69) IR spectra of $I_b$free ligand and its chelates

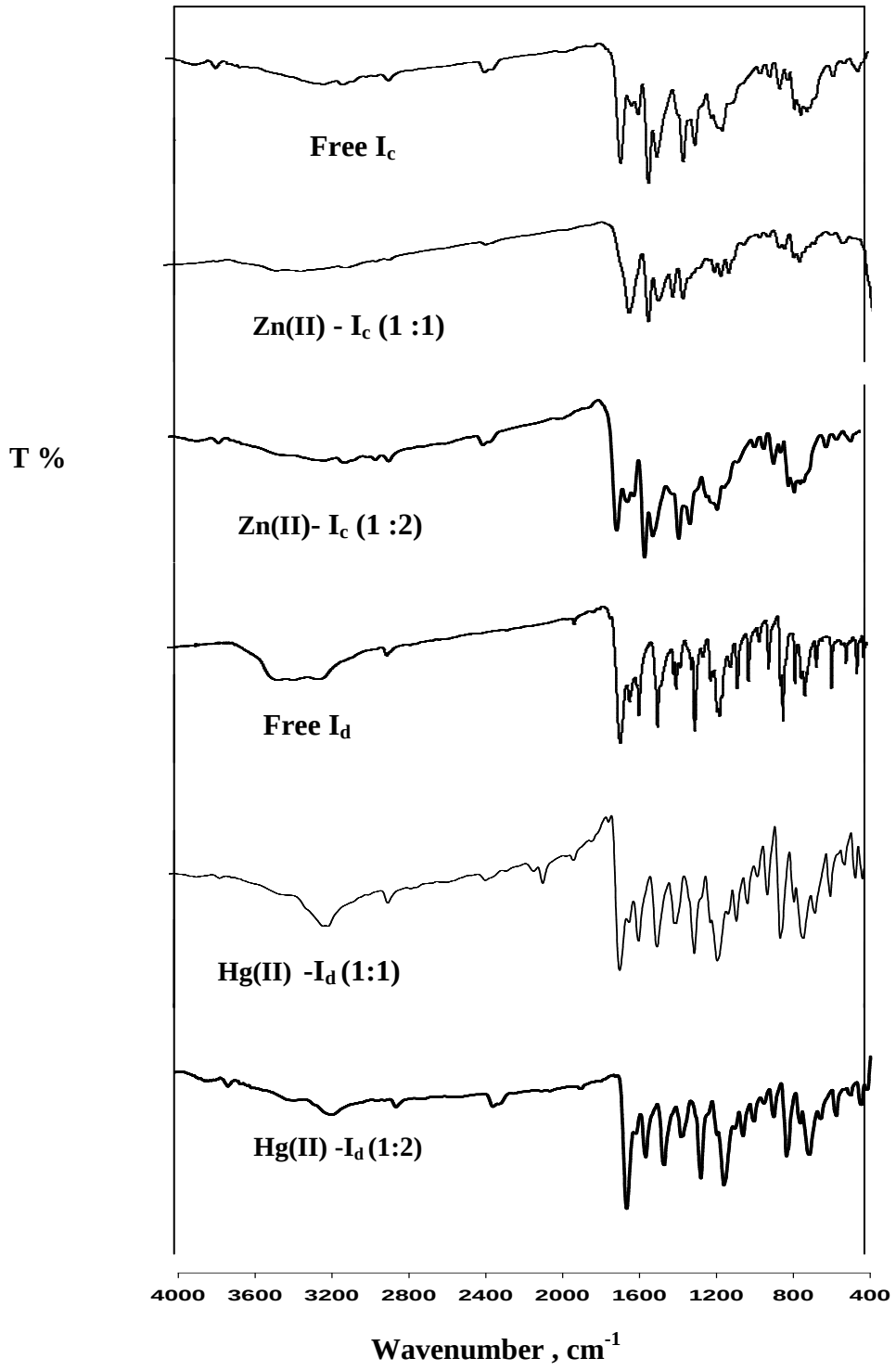


Fig. (70) IR spectra of I_c and I_d free ligands and their chelates

3.3.5. ^{1}H-NMR spectra of some complexes formed between I_b and I_c ligands and metal ions

^{1}H-NMR spectroscopy is considered now as a very helpful tool for investigation of both molecular structure of organic ligands and their metal chelates. It can be used to determine the position of replaceable proton of the function groups that contribute in complex formation.

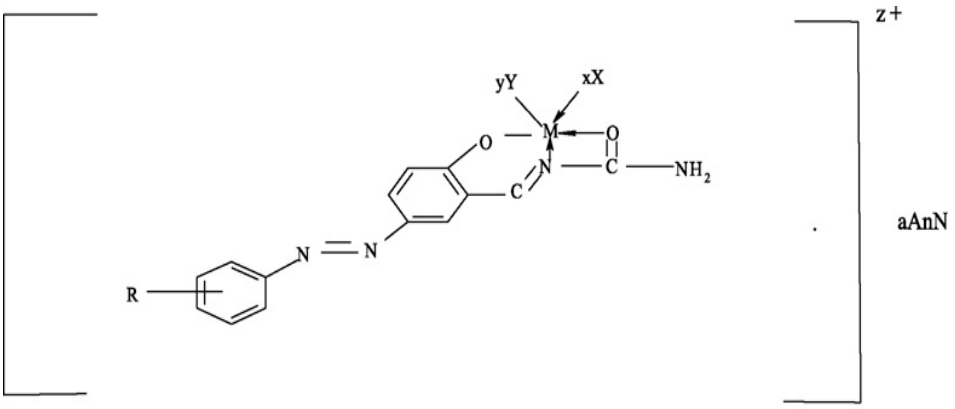
The representative samples of some (1:1) and (١:٢) (M:L) complexes reaction between ligands I_b and I_c with Zn(II), Cu(II) and Hg(II) ions are recorded as shown in Fig (71) and Fig.(72).

The spectra are then compared with those of the free ligand in order to identify the centers of chelation and replaceable protons in chelate molecules as shown in Fig (71, 72) and recorded the data in Table (21).

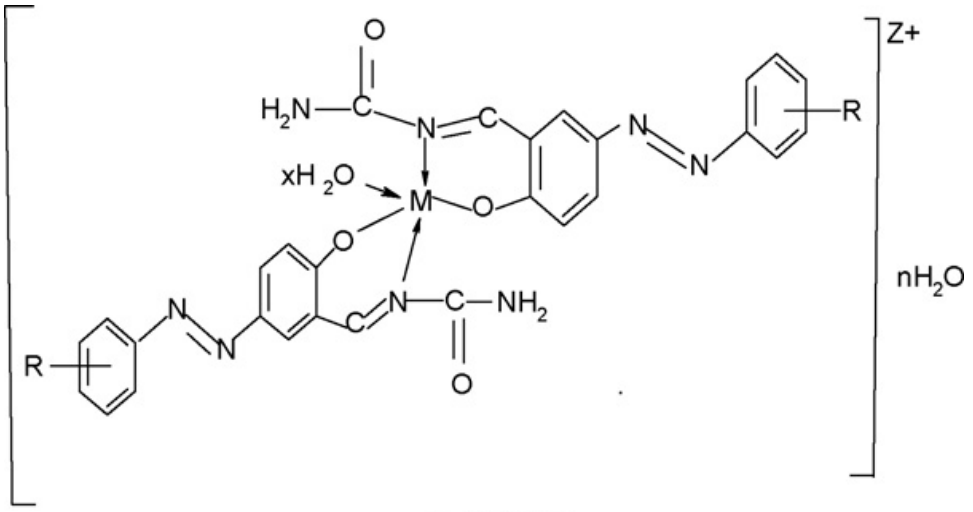
The signal of hydrogen (1) form OH group of free ligands for all complexes disappeared in the spectra.

The signals of all aromatic proton are shifted downfield with an observed decrease and broading in their appearance indicating the formation of a covalent bond between metal ions and oxygen atom of the hydroxyl group attached to the phenyl ring, where the formation of metal-nitrogen or metal-oxygen bonds withdraws electrons from the aromatic ring resulting in a deshielding of the hydrogen on the carbon atom adjacent to the azo group

From the studies of the data of elemental ,thermal analysis, IR and H-NMR- spectra of the chelates (1M:1L) and (1M:2L) ratios can be represented as :



(1:1) (M:L)



(1:2) (M:L)

Where :

R =p-COOH (**I_a**); o- OCH_3 (**I_b**); o- NO_2 (**I_c**) p-Br(**I_d**)

M= Cu(II), Hg(II), Ag(I) and Zn(II) ions

Y= OCOCH3, $SO4^{2-}$ or Cl^{-} anions coordinated to metal ion

X= Water molecules coordinated to metal ion

z = Overall charge on the chelate

N= number of crystalline water molecules

A= number of anion in outer sphere

Table (21): Assignment of signals of protons (ppm) of ligands I_b and I_c and their metal chelates

Compound	Ratio (M: L)	Chemical shift (δ), ppm of protons					
		H (1) OH	$H(2)_{NH2}$	H(3) CH=N	H(٤)	H(٥)	H(٦)
I_b Free	-	١٠.٣٩٢	٦.٠٥	8.13	٧.٩٠١	٧.٣٢	٣.٥
Cu(II)-I_b	1:1	---	٦.١	٨.١٣	٧.٤٨	٧.٢٥	٣.٩٤
Hg(II)-I_b	1:1	-----	٦.٠٧	٨.١٣	٧.٥	٧.٢٧	3.75
Zn(II)-I_b	1:1	----	٦.٠٥	٨.١٢	٧.٥	٧.٢٤	٣.٩٦
Zn(II)-I_b	1: ٢	-----	٦.١١	8.12	٨.٠٣	٧.٢٧	٣.٤٥
I_c Free	-	10.42	٦.٠٥	٨.١٨	7.84	7.30	--
Cu(II)-I_c	1:1	---	٦.١٢	٨.٠٥	٧.٧٢	٧.١٢	--
Hg(II)-I_c	1:1		٦.٠٦	٨.١٢	٧.٧٩	٧.٥١	---
Zn(II)-I_c	1:1	---	٦.٠٥	٨.١٦	٧.٧٨	٧.٥١	---
Zn(II)-I_c	1:2		٦.٠٧	٨.١٦	٧.٩٩	٧.١٧	---

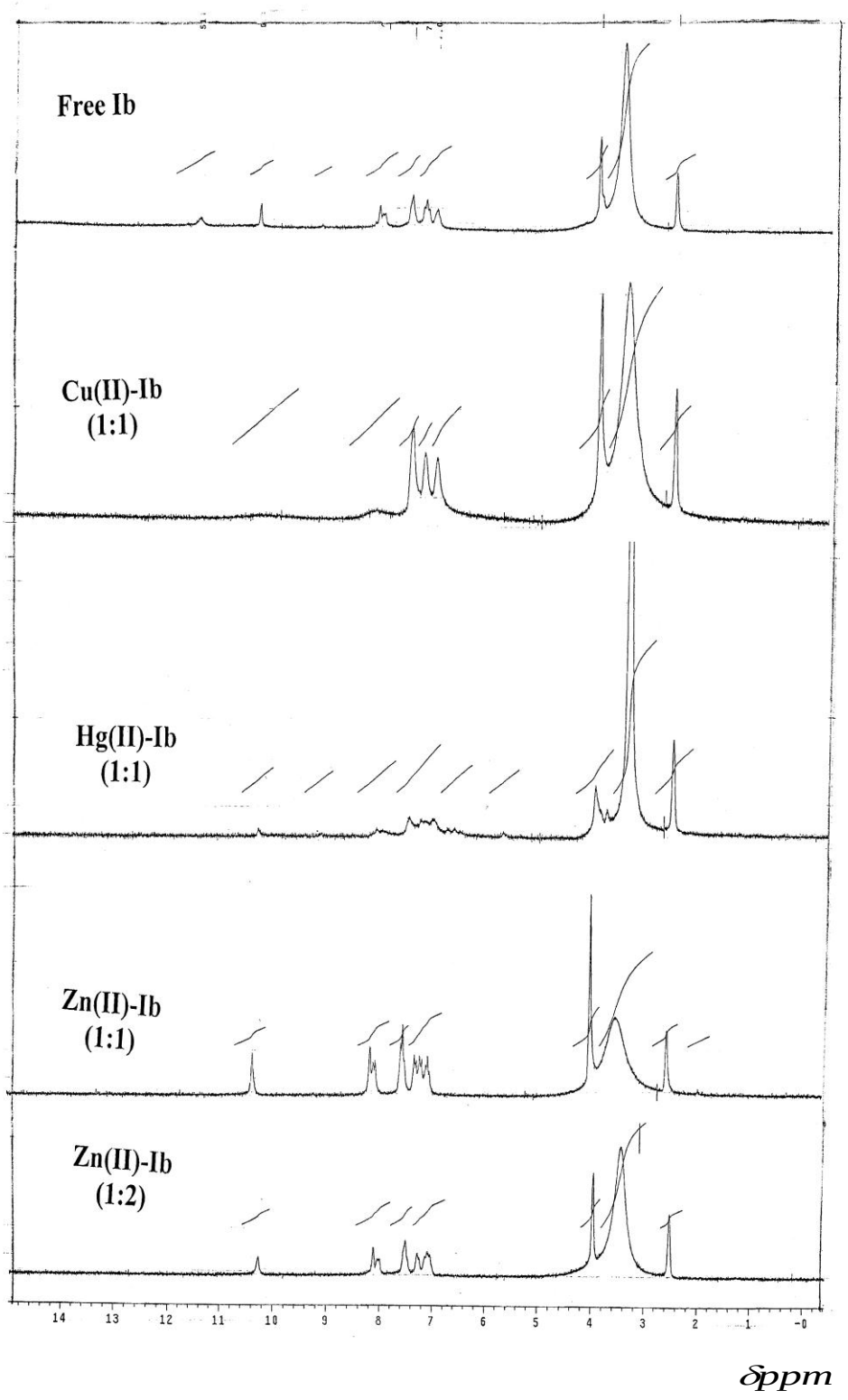


Fig. (71) H-NMR spectra of I_b ligand and its metal chelate

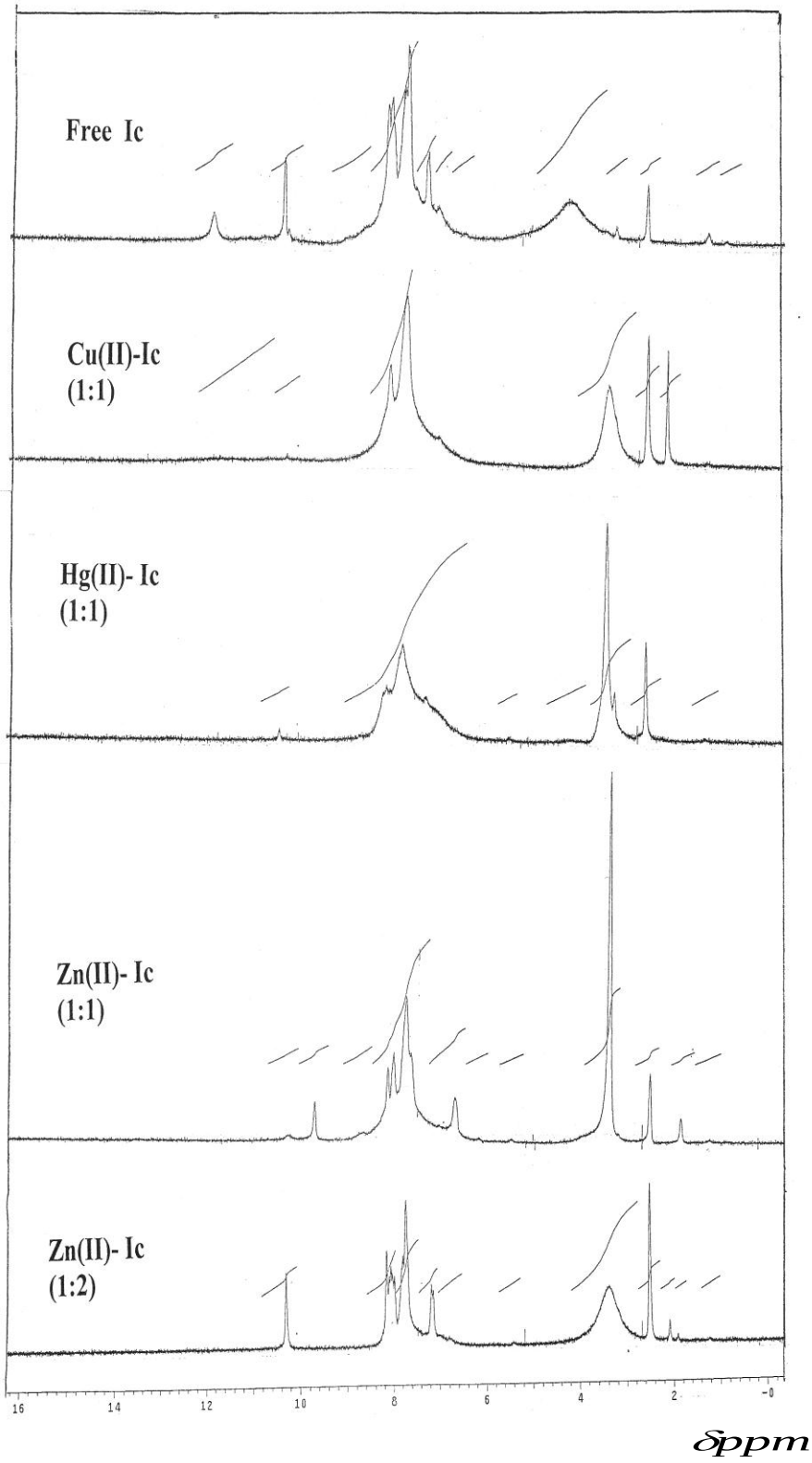


Fig. (72) H-NMR spectra of I_c ligand and its metal chelates

3.3.6. Electronic spectra of some selected metal chelates

Most complexes of the transition elements are highly coloured compounds which means that they are capable of absorbing radiant energy in the visible reigion of the spectrum. The study of the absorption spectra of these compounds reveal that they absorb energy in infrared (IR) and ultraviolet (UV) regions as well as in the visible. The study of electronic absorption spectra of transition metal complexes can be used to evaluate the stereochemistry of the transition metal complexes.

The electronic absorption spectra of metal complexes can be generally classified into four general types depending on the nature of the electronic transitions involved. These types are:

1-Transitions may occur between the splitted levels of the central ion giving rise to the so-called d-d or ligand field spectra.These transitions are the ones responsible for the great variety of colours found in transition metal complexes.The region is generally scanned from 10000 to 30000 cm^{-1}.

2-Transitions may occur from molecular orbitals located on the ligands, the metal-ligand bonding σ or π molecular orbitals, to nonbonding or antibonding molecular orbitals located on the metal ion.

3-The transitions which involve electrons being excited from nonbonding or antibonding orbitals located on the ligands are termed metal to ligand charge transfer (M→L) transitions.The bands generally occur in the UV region .

4-The electronic transitions which involve electrons being excited from one ligand orbital into another ligand orbital.These intraligand transitions generally occur with energies found in the UV region and they are often little affected by the coordination. In addition, their bands can usually be disentangled from the equally intense charge transfer bands in their neighborhood.

In the present work, the electronic absorption spectra of the prepared solid chelates are measured as nujol mull and in DMF solution within the range 340 -800 nm, based on the fact that the electronic absorption spectra are very diagnostic of the stereochemistry of metal chelates.

The spectral data of the metal chelates of Cu(II), Hg(II), Ag(II),V(V) and Zn(II) ions in comparison to those of the corresponding free ligands are shown in Tables (22) to(23).

The spectra of the free ligands I_{a-d} in DMF indicate that ν^- (cm^{-1}) of the CT band are 21186 ,26041, 23547 and 25687 cm^{-1} for I_a, I_b, I_c and I_d respectively whereas that taken in nujol mull are 24752 ,28011 ,27472 and 28818 cm^{-1} respectively .The ν^- (cm^{-1}) of the CT band of all metal chelates of such ligands displays a red or blue shift in nujol mull or DMF compard to that of the free ligands as shown in Figs (73, 74).

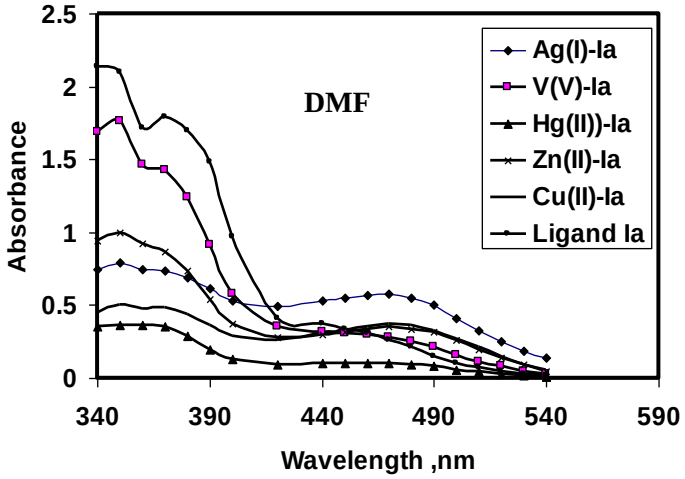
This confirms that such ligands interact with the metal ion. The difference in ν^- (cm^{-1}) values of the bands in DMF than in nujol mull indicates that the crystal state of the complexes differ in the solid state.

Table (22): Electronic spectra of I_a and I_b chelates in DMF and nujol mull

Metal ion	Ratio (M:L)	Band maxima (cm^{-1})		Assignment
		DMF	Nujoll mull	
Free I_a	----	21186	24752	CT
Zn(II)	1:1	20876,27322	21645,23094,24691	$\pi-\pi^*, n-\pi^*$
	1:2	27247,28169	27624,28248,29154	$\pi-\pi^*, n-\pi^*$
V(V)	1:2	21739,27472,28735	23529,24390,25000,26809	$\pi-\pi^*, n-\pi^*$
	1:1	20114,25447	235510,24519,26314	$\pi-\pi^*, n-\pi^*$
Cu(II)	1:2	25252,26737,27700	24570,27932,28735,29239, 31152	$^2T_{2g}\rightarrow{}^2E_g$
	1:1	21881,29411	24330,26455,27932,29585	$\pi-\pi^*, n-\pi^*$
Hg(II)	1:2	21551,27247,28089	23923,25974,27322,28328, 29239	$\pi-\pi^*, n-\pi^*$
	1:1	27322,28571	24813,26315,27548,28985, 30864	$\pi-\pi^*, n-\pi^*$
Ag(I)	1:1	21834,26954,28011 ,29154	25773,27933,29411,30395	$\pi-\pi^*, n-\pi^*$
Free I_b	----	26041	28011	CT
Zn(II)	1:1	24551,21739,28328	25906,26315,27777,28409	$\pi-\pi^*, n-\pi^*$
	1:2	26543,27541	25641,26737,28735,29411	$\pi-\pi^*, n-\pi^*$
V(V)	1:1	21786,27100,28571	25839,27027,28490,29154	$\pi-\pi^*, n-\pi^*$
	1:2	20112,26557	2391,25447,28456	$\pi-\pi^*, n-\pi^*$
Cu(II)	1:2	23541,27445	24154,26809,28169,29411	$^2T_{2g}\rightarrow{}^2E_g$
	1:1	21188,21929	25252,27855,29154,30864	$\pi-\pi^*, n-\pi^*$
Ag(I)	1:1	22558,23445,25487	27624,28011,29411,30211	$\pi-\pi^*, n-\pi^*$

Table(23): Electronic spectra of I_c and I_d chelates in DMF and nujol mull

Metal ion	Ratio (M:L)	Band maxima (cm^{-1})		Assignment
		DMF	Nujoll mull	
Ag (With I_b)	1:2	22534,22556	25252,27855,29154,30864	$\pi-\pi^*, n-\pi^*$
Free I_c	----	23547	27472	CT
Zn(II)	1:1	21881,25125	21598,23255,24271,25706	$\pi-\pi^*, n-\pi^*$
	1:2	24224,26354	22587,24874,25781,27771	$\pi-\pi^*, n-\pi^*$
Ag(I)	1:1	25664,27361	23564,26547,28314	$\pi-\pi^*, n-\pi^*$
	1:2	21225,24115,27112	22314,24524,26541,27415	$\pi-\pi^*, n-\pi^*$
Cu(II)	1:1	23222,24156	20154,23554,28235	$\pi-\pi^*, n-\pi^*$
	1:2	27351,28321,29321	23145,26547,28541,30154	$\pi-\pi^*, n-\pi^*$
Free I_d	----	25687	28818	CT
Hg(II)	1:1	22222,27277,29325	25062,27322,28089,29673	$\pi-\pi^*, n-\pi^*$
	1:2	23272,25271,26355	24031,26529,27142,28231	$\pi-\pi^*, n-\pi^*$
Cu(II)	1:1	2039,25471	21457,26547	$\pi-\pi^*, n-\pi^*$
	1:2	22147,26548	245177,26331,27445	$\pi-\pi^*, n-\pi^*$



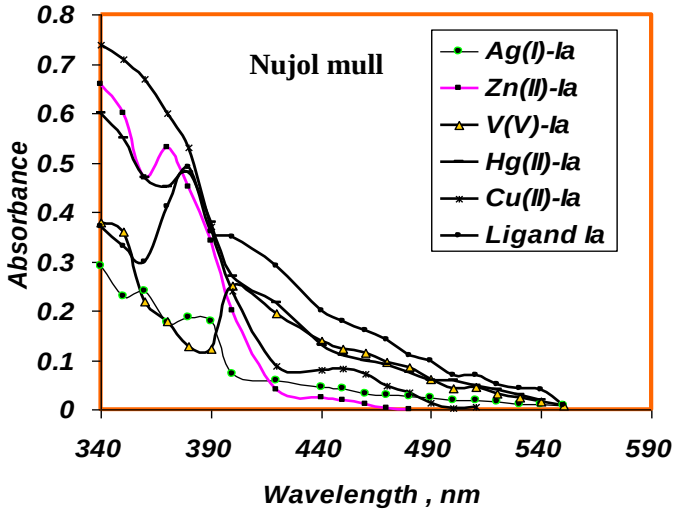
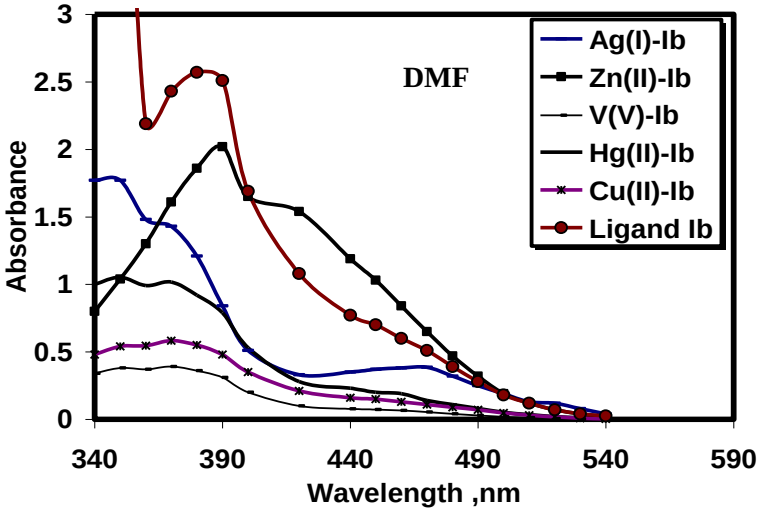


Fig. (73) Electronic spectra of reagent I_a and its metal chelates in DMF and nujol mull



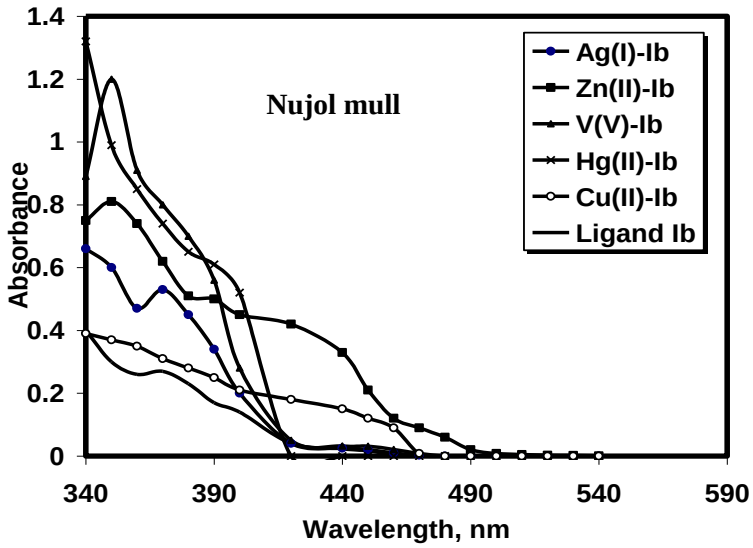


Fig. (74) Electronic spectra of reagent I_b and its metal chelates in DMF and nujol mull