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Distinctive Spectral and Potentiometric Studies of Some phenylhydrazonos Schiff base with metal complexes

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Abstract

The spectral behavior of some Schiff base compounds derived from 2-((2,4-dihydroxyphenyl) (hydroxy)methyl)-2-phenylhydrazono)propanal,2-(2-(hydroxy(2-hydroxy-4-methoxyphenyl)methyl)-2-phenylhydrazono)propanal,3-(2-(hydroxy (2-hydroxy-4-methoxyphenyl)methyl)-2-phenylhydrazono)butan-2-one and 2-(-(2,4-dihydroxybenzylidene) hydrazono)-1,2-diphenylethanone to investigate the acid ionization constants (pK_H) of these ligands using Half-height method and Modified limiting absorbance method. A series of new metal chelates of Co(II), Cu(II), Gd(III), Sm(III) and Tb(III) with Schiff base ligands derived from condensation of glyoxal, biacetyl or benzyl bishydrazone with 2,4 – dihydroxybenzaldhyde and 4-methoxysaliycaldhyde in ethanol and characterized via potentiometric titrations. Stability constants of these metal complexes were determined using a potentiometric method by calculating the values of $\bar{n}_A$, $\bar{n}$ and pL and found in the order Co(II)<Cu(II)<Tb(III)<Sm(III)<Gd(III). It has been found that ligand forms complexes in 1:1 ratio.

Keywords; Schiff base complexes; Potentiometry; Spectrophotometry; Stability constant

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1. Introduction

Schiff base ligands were considered ‘‘privileged ligands’’ [1,2] because they are easily prepared by the condensation between aldehydes and imines. Stereo genic centers or other elements of chirality (planes, axes) can be introduced in the synthetic design. Schiff base ligands are able to coordinate many different metals, and to stabilize them in various oxidation states, enabling the use of Schiff base metal complexes for a large variety of useful catalytic transformations. Our research has continued on bis-hydrazones with glyoxal, biacetyl and benzyl with 2,4-dihydroxybebzaldhyde and 4- methoxysalicaldhyde. Metal complexes derived from 2.4-dihydroxybenzaldhyde and 4-methoxysalicaldhyde have great interest as potential compartmental ligands capable of forming mono and binuclear coordination compounds with various metals because of several donor centers in their molecules. This nature of the Schiff bases has attracted our attention and aroused our interest in elucidating the structures of Cu(II), Co(II), Sm(III), Tb(III) and Gd(III) complexes. The acid ionization constants (pK_H) of the ligands under consideration are determined spectrophotometrically in universal buffer solutions covering the pH range 2.39 to 12.17. The absorption spectra of the Schiff base compounds in buffer solutions of varying pH values are recorded within the wave length range 200 to 800 nm.

The dissociation constants of Schiff base and metal-ligand stability constants of its complexes with some metal ions have been determined potentiometricaly against standard 0.1M NaOH in ethanol-water mixture (40vol %).

The present study aims to investigate 2-((2,4-dihydroxyphenyl) (hydroxy)methyl)-2-phenylhydrazono)propanal,2-(2-(hydroxy(2-hydroxy-4-methoxyphenyl)methyl)-2-phenylhydrazono)propanal,3-(2-(hydroxy(2-hydroxy-4-methoxyphenyl)methyl)-2-phenylhydrazono)butan-2-oneand 2-(-(2,4-dihydroxybenzylidene)hydrazono)-1,2-diphenylethanone using several techniques as well as determination of their dissociation constants using spectral and potentiometric methods. The study was extended to calculate the stability constants of complexes of these compounds with some transition metal ions in solution.

2. Experimental

Materials

All reagents used in the present study were of the highest quality (Merck, Aldrich, Fluka and Sigma Research Laboratories) and were used without further purification. Freshly bi distilled water was used whenever water is necessary.

Preparation of the organic ligands.

Preparation of dihydrazides of glyoxal, biacetyl and benzyl.

1- 0.1 mole of diketone derivatives (glyoxal "1.5ml", biacetyl "2.8gm" and benzyl"7.007gm") was dissolved in 25 ml of ethanolic solution in a condenser flask.
2- A 3.2 ml solution containing 0.2 mole of hydrazine hydrate or 6.56 ml solution containing 0.2 mole of phenyl hydrazine was added drop wise to the previous solution in ice bath. The resulting solutions were then refluxed for 4-5 hrs.
3- Up on cooling the reaction mixtures, the products formed were filtered of, washed by ethanol and dried in vacuum desiccator over anhydrous CaCl2.

Preparation of the metal ion complexes

The solid chelates of stoichiometric ratios (1:1) (M: L) for some selected metal were prepared by mixing the hydrated metal chlorides [$CuCl_2.2H_2O$, $CoCl_2.6H_2O$, $TbCl_3.6H_2O$, $GdCl_3.6H_2O$ and $SmCl_3.6H_2O$] with a hot alcoholic solution of each ligand. The mixture was then refluxed on a water bath for about 8-10hrs.and then allows cooling where by the solid chelates were separated and recrystallized from absolute ethanol, dried and preserved in a desiccator over an hydrous $CaCl_2$.

UV - visible spectra

Electronic spectra were carried out using Jasco V-530(UV-Vis) spectrophotometer (Japan) with scanning speed 400 nm/min, band width 2.0 nm and equipped with 10.0mm matched quartz cell in the range 800-200nm.

Potentiometric titration of metal ion solutions of Cu(II), Co(II), Sm(III), Gd(III) and Tb(III)

Potentiometric measurements were carried out using PH-meter type HI8014HANA instrument. The PH-meter was calibrated from time to time by means of buffer solution of pH=4.01 and pH=9.11. Metal ion solutions ($T_{M^{\circ}}$= 0.001 M) were prepared from analar metal chlorides in bidistilled water. The ligand solution ($T_{L^{\circ}}$=0.001 M) was prepared by dissolving the accurate mass of the solid in ethanol (Analar). Solutions of 0.1M HCl and 1M KCl were also prepared in double distilled water. A carbonate free sodium hydroxide in ethanol-water mixture (40vol %) was used to titrate and standardized against oxalic acid (Analar). The following mixtures (A-C) were prepared and titrated potentiometricaly against standard 0.1M NaOH in ethanol-water mixture (40vol %):

(A) 5ml 0.1M HCl +5ml 1M KCl +25ml absolute ethanol
(B) 5ml 0.1M- HCl + 5ml 1M KCl + 25ml 0.001M- ligand.
(C) 5ml 0.1M-HCl +5ml 1M KCl + 25ml 0.001M- ligand + 5ml 0.001M- Metal salt.

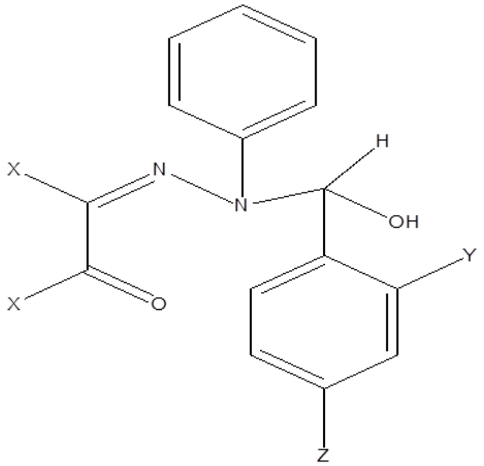
For each mixture, the volume was made up to 50ml with double distilled water before the titration.

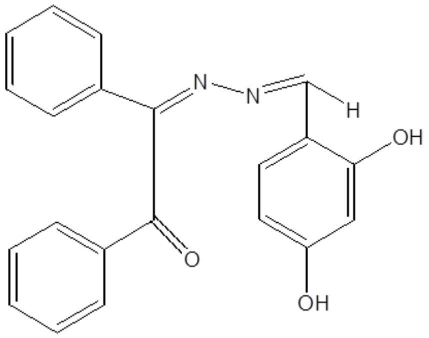
3. Results and discussion

Synthesis of glyoxal, biacetyl and benzyl bis- hydrazone Schiff bases

A mixture of 2,4-dihydroxybenzaldhyde"0.5gm" or 4-methoxysalicaldhyde"0.5gm" and each of the synthesized dihydrazide:(2-hddrazonoacetaldehyde) (0.1 mole;0.3gm),(3-hydrazonobutan-2-one)(0.1mole;0.4gm),(2-hydrazono-1,2-diphenylethanone (0.1mole;0.86gm)),(2-(2-phenylhydrazono)acetaldehyde)(0.1mole;.086gm),(3-(2-phenylhydrazono)butan-2-one)(0.1mole;0.96gm)and(1,2-diphenyl-2-(2-phenylhydrazono)ethanone)(0.1mole;1.4gm) in 2:2 molar ratio in an alcoholic medium containing a few drops of conc.HCl was refluxed for 3-4hrs.

The product separated on evaporation of the alcohol and was recrystallized from ethanol, the prepared ligands have the following structures:





L(IV)

2-(-(2,4-dihydroxybenzylidene)hydrazono)-1,2-diphenylethanone

If x = -H, y = -OH and z = -OH → L(I) 2-((2,4-dihydroxyphenyl)(hydroxy)methyl)-2-phenylhydrazono)propanal.
If x = -H, y = -OH and z = $-OCH_3$ → L(II) 2-(2-(hydroxy(2-hydroxy-4-methoxyphenyl)methyl)-2-phenylhydrazono)propanal.
If x = $-CH_3$, y = -OH and z = $-OCH_3$ → L(III) 3-(2-(hydroxy(2-hydroxy-4-methoxyphenyl)methyl)-2-phenylhydrazono)butan-2-one.

Spectrophotometric Studies

Electronic absorption spectra of Schiff base ligands in buffer solutions.

The acid ionization constants (pK_H) of the ligands under consideration are determined spectrophotometrically in universal buffer solutions covering the pH range 2.39 to 12.17. The absorption spectra of the Schiff base compounds in buffer solutions of varying pH values are recorded within the wave length range 200 to 800 nm. Fig. (1) & (2), represents the spectra of compound (IV) as a typical example of this series and absorbance – pH curve for this compound respectively.

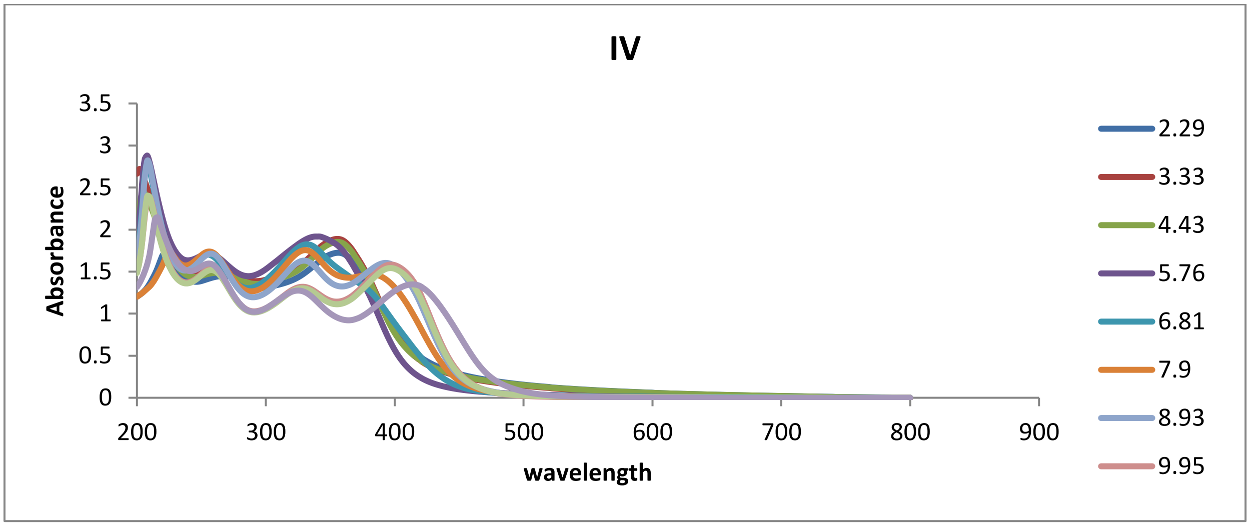


Fig (1): Absorption spectra of compound (IV) in buffer solutions.

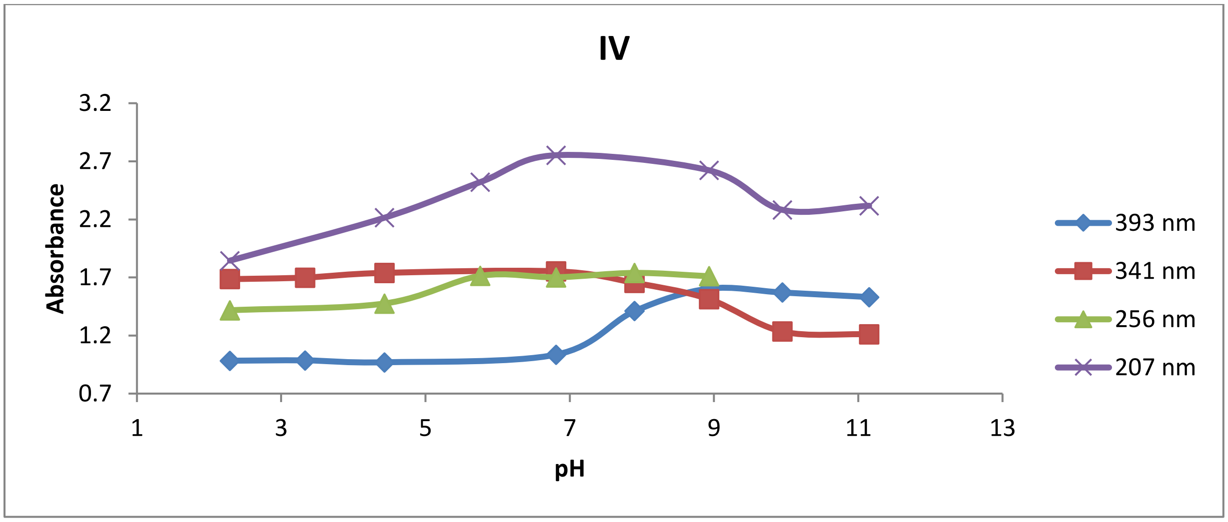


Fig (2): Absorbance – pH for compound (IV)

All the investigated compounds exhibited three bands; the first band (not shown) appeared at 230-250 nm is due to the local excitation of the π-π* transition of the aromatic moiety, while the second and third bands appeared within the range 380-450 nm are attributed to the charge transfer (C.T) interaction within the whole molecule. Also, a clear one or two isobestic points were observed indicating more than one species are present in equilibrium.

Determination of the dissociation constant values

To determine the dissociation constants of the compounds (I-IV); Half-height method (HHM) [3,4], and the modified limiting absorbance method (MLAM) [5,6] were used.

1- **Half-height method.**

At a constant wave length, a relation between the pH values and the absorbance of each ligand are drawn. The (pK_H) value for each ligand can be evaluated from the absorbance- pH curve depending on the fact that at the half-height of the absorbance- pH curve, the ionized and non-ionized forms exist in equivalent quantities, hence

$pK_H = pH$ at $A_{1/2}$

Where: $A_{1/2} = [(A_{max} – A_{min})/2] + A_{min}$.

2- **Modified limiting absorbance method.**

This method has the advantage of eliminating any overlaps between absorbance of two forms, for a ligand of formula HnA, its first ionization takes place as follows:

$$H_nA \rightleftharpoons H_{n-1}A^- + H^+$$

Hence, the pH value is given by the following relation:

$$pH = pKH + \log Y^1 + \log [(A- A_{min})/(A_{max}-A)]$$

Where,

A is the absorbance at a given pH value.

$\bar{Y}$: is the activity coefficient of the ions present at equilibrium.

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

The pK_H value can be evaluated by plotting the log $[(A- A_{min})/(A_{max}-A)]$ versus pH where a straight line is obtained. The pK_H value is that value corresponds to the pH at zero log $[(A- A_{min})/(A_{max}-A)]$. The pK_H values of compounds (I-IV) obtained from the two previous methods are given in Table (1). The results indicated that:

A. Two pK_H values for each compound (I, IV) were obtained; due to the dissociation of two protons of the two hydroxyl groups in the phenyl ring.
B. One pK_H value for each compound (II, III) was obtained; due to dissociation of the proton of the hydroxyl group in the phenyl ring.

Table (1). Dissociation constants of compounds (I-IV) determined using spectrophotometric method.

Compound	Spectrophotometry					
	HHM		MLAM		Mean value	
	pK_H^1	pK_H^2	pK_H^1	pK_H^2	pK_H^1	pK_H^2
I	4.1	4.8	4.3	4.5	4.2	4.65
II	5.2	-	5.5	-	5.35	-
III	6.2	-	6.4	-	6.3	-
IV	8.2	8.8	7.7	9	7.95	8.9

HHM = half-height method. **MLAM** = modified limiting absorbance method.

Potentiometric studies

Proton-ligand dissociation constant and Stability constants of metal complexes

Potentiometry is convenient and successful technique for studying ionic equilibria for metal complex equilibrium measurements it can be used to follow complex formation; M (metal ion), L (ligand) and H (proton). It can be also used to determine the proton ionization constant of the ligands and the stability constants of the formed complexes. Fig.(3,4&5), represents Potentiometric titration curve of ligand (IV) in present of metal ions as a typical example of this series, Formation curve of proton-ligand and Formation curves of metal ions with this ligand respectively.

The titration procedure used in this work is that developed by Calvin and Bjerrum [7,8]. The evaluation of ligand-proton and metal ligand stability constants can be evaluated as follows:

(i) The average number of the protons associated with the ligand molecule L, $\bar{n}_A$ was determined at different pH values applying the following equation [9,10].

$$\bar{n}_A = Y + \frac{(V_1-V_2)(N^\circ+E^\circ)}{(V^\circ+V_1)T_{L^\circ}} \quad (1)$$

Where Y is the number of available protons in Ligand and V_1 and V_2 are the volumes of alkali required to reach the same pH on the titration curve of hydrochloric acid and organic ligand respectively. V° is the initial volume (50 ml) of the mixture; N° is the concentration of sodium hydroxide solution and T_{L° is the initial concentration of free acid and finally E° is the initial concentration of the free acid (HCl aqueous solution). The titration curves ($\bar{n}_A$ vs. pH) for the proton- ligand systems were constructed and found to extend between 0 and 1 in case of ligand (II & III) and between 1 and 2 in case of ligand (I & IV) on the η_A scale. This means that ligands (II &III) have one ionisable proton and ligands (I &IV) have two ionisable protons. It can be seen that for same volume of NaOH added the ligand titration curves had a lower pH value than the acid titration curve. The displacement of a ligand titration curve along the volume axis with respect to the acid titration curve is an indication of proton dissociation. The proton-ligand stability constants were calculated using the method of Irving and Rossoti [11-14] as adapted by Fronaeus [15-17]. The plots of $\bar{n}_A$ against the pH of solutions give the proton-reagent formation curves (an S-shape) as shown in Fig (4) then the values of the proton-ligand stability constants K_1^H and K_2^H, can be calculated by interpolation at $\bar{n}_A$ half values. The data obtained are listed in table (2). It is important to noted that, the data obtained from spectrophotometric measurements are in agreement with those calculated by potentiometric ones.

(ii) The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ions ($\bar{n}$) vs. the free ligand exponent (pL), according to Irving and Rosotti [18]. The average number of the reagent molecules attached per metal ion, $\bar{n}$ and free ligand exponent, pL, can be calculated using the following equations [119].

$$\bar{n} = \frac{(V_3 - V_2)(N^\circ + E^\circ)}{(V^\circ + V_2)\bar{n}_A T_{M^\circ}} \qquad (2)$$

and

$$pL = \log_{10}\left[\frac{\sum_{n=0}^{n=1} \beta_n^H \left(\frac{1}{\text{anti logpH}}\right)^n}{T_{L^\circ} - \bar{n} T_{M^\circ}} \text{ x } \left(\frac{V^\circ + V_3}{V^\circ}\right)\right] \qquad (3)$$

Where T_{M° the total concentration of the metal ions present in the solution is β_n^H is the overall proton-reagent stability constant. V_1, V_2, V_3 are the volumes of alkali required to reach the same pH on the titration curves of hydrochloric acid, organic ligand and complex, respectively, at a giving pH. On plotting the values of $\bar{n}$ against the pL values give the formation curves of metal complexes (an S-shape) as shown in Fig (5) then interpolation at the half $\bar{n}$ values. These curves were analyzed, and the successive stability constants were determined using different computational methods [20]. The values of the stability constants (log {K1} and log {K2}) are given in table (2).

Potentiometric titration curves, as shown in Fig (3), are S-shaped with a sharp jump in mixtures (A) and (B) but with smooth one in mixture (C) containing the metal ions. From the titration curves it can be found that the end points of the mixtures increase in the order C < B < A. The titration curve of the metal ion complexes was displaced to the right-hand side of the ligand titration curves along the volume axis, indicating proton release upon complex formation of the metal ion and ligand. The large decrease in pH for the metal ion complexes titration curves relative to ligand titration curves points to the formation of strong metal ion complexes [21]. It had been found that the metal mixtures (C) of Cu(II), Co(II), Sm(III), Gd(III) and Tb(III) ions consumed larger volumes of the alkali during the titrations due to neutralization of the (H^+) giving off through the complex formation indicating that such types of ligands interact with the metal ions through simple covalent bonds in addition to the coordination ones. The stability constants of the metal complexes obtained $\log\beta_1$ and $\log \beta_2$ are given in table (2). Where $\log\beta_1$ is the stepwise constant for (1:1) complex and $\log \beta_2$ is the accumulative constant for the chelates of the (1:2) (M: L). It is clear that ligand (IV) has the greater value in chelation with Gd(III) ion indicating the strong and high stability of these complexes. The maximum value of $\bar{n}$ was 2 indicating the formation of 1:2 (n [metal]: n [ligand]) complexes. The metal ion solution used in the present study was very dilute (0.001M); hence there was no possibility of formation of polynuclear complexes [22].

Table (2): Proton-ligand stability constants and stepwise formation constants of chelates of Cu(II), Co(II), Sm(III), Gd(III) and Tb(III) with the Schiff base ligands.

Ligand	Proton ionization constant		Metal-ligand stability constant									
			Cu(II)		Co(II)		Sm(III)		Gd(III)		Tb(III)	
	$\log K_1^H$	$\log K_2^H$	$\log \beta_1$	$\log \beta_2$	$\log \beta_1$	$\log \beta_2$	$\log \beta_1$	$\log \beta_2$	$\log \beta_1$	$\log \beta_2$	$\log \beta_1$	$\log \beta_2$
I	4.7	5.6	6.77	3.85	6.61	3.95	6.82	3.96	5.71	3.45	5.8	3.37
II	5.5	-	4.75	-	4.13	-	5.91	-	6.47	-	5.87	-
III	6.95	-	5.73	-	4.11	-	6.53	-	6.11	-	6.65	-
IV	8.7	9.5	5.93	-	5.48	-	6.53	-	6.85	-	6.77	4.47

$\log\beta_1 = \log K_1$, $\log \beta_2 = \log K_1 K_2$

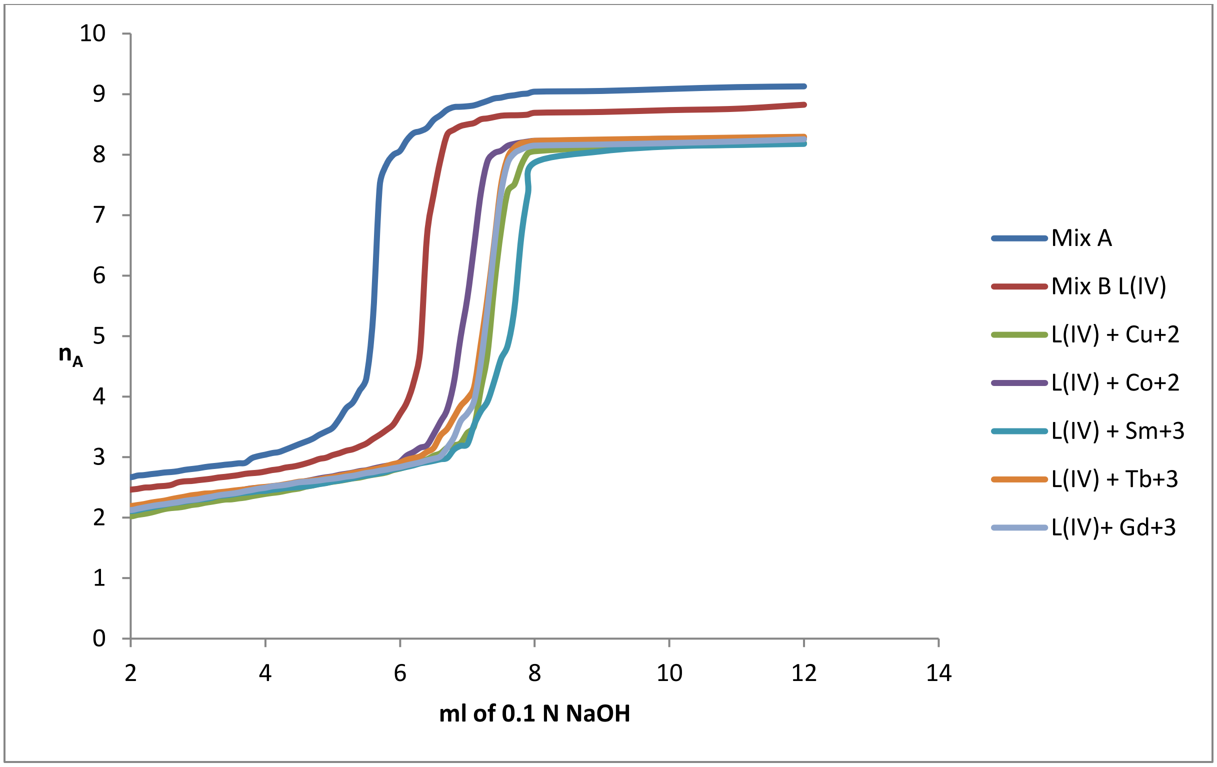


Fig (3): Potentiometric titration curve of ligand (IV) in present of metal ions

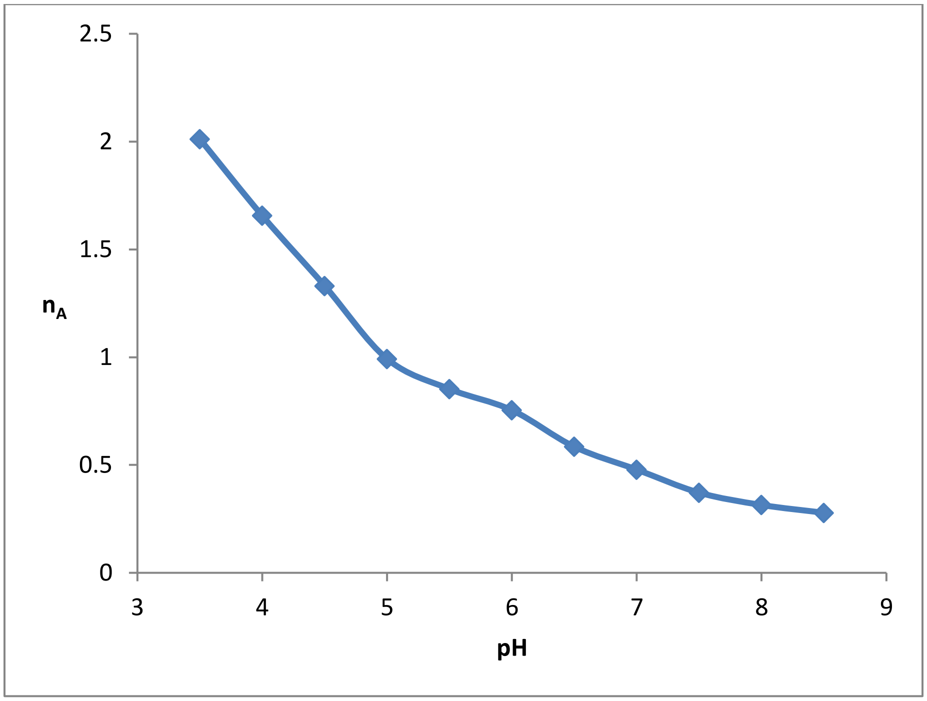


Fig (4): Formation curve of proton-ligand (IV)

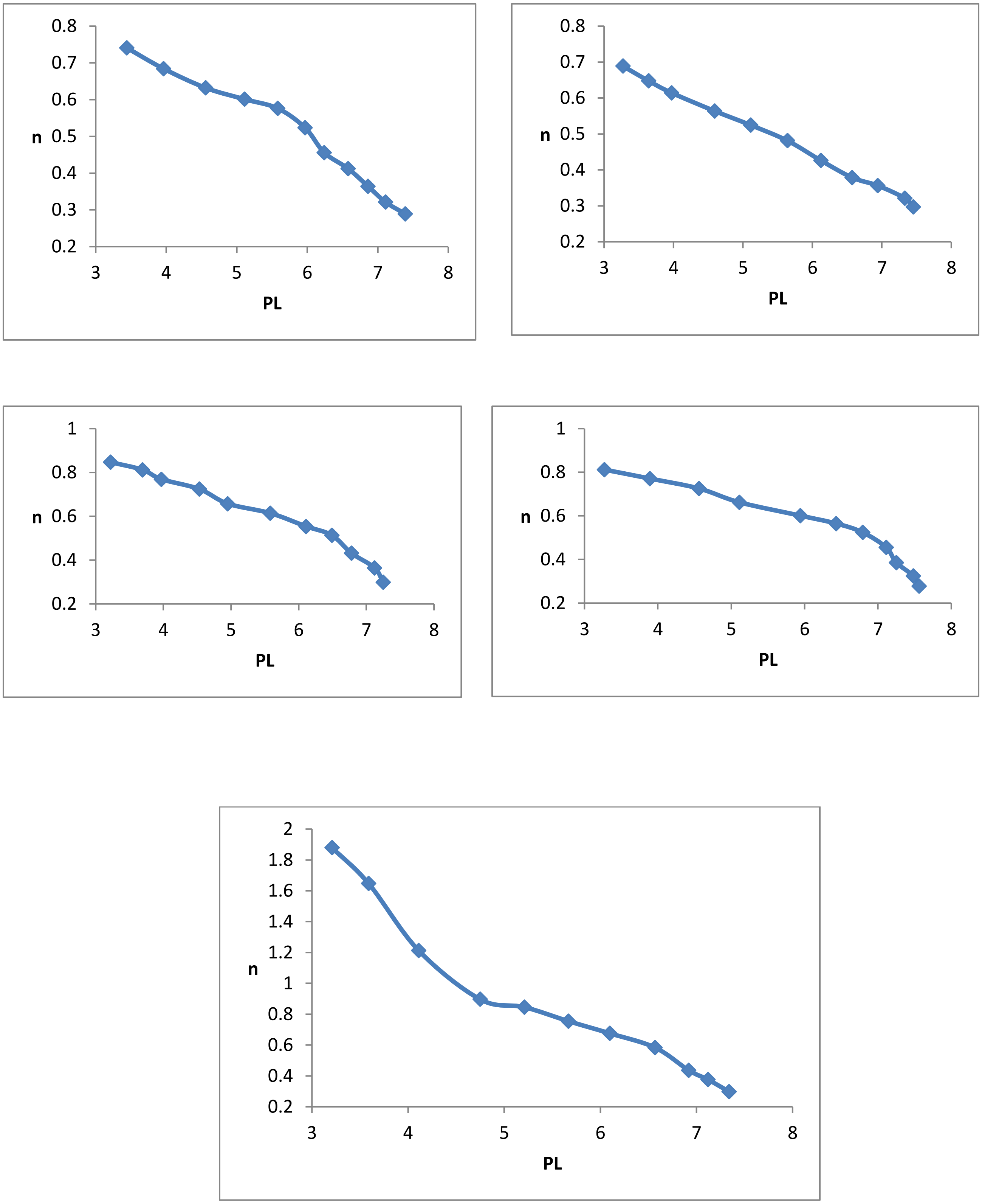
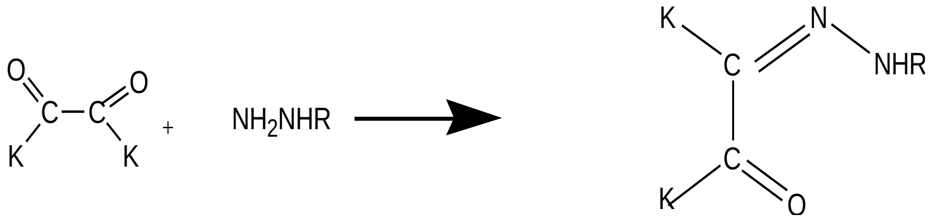


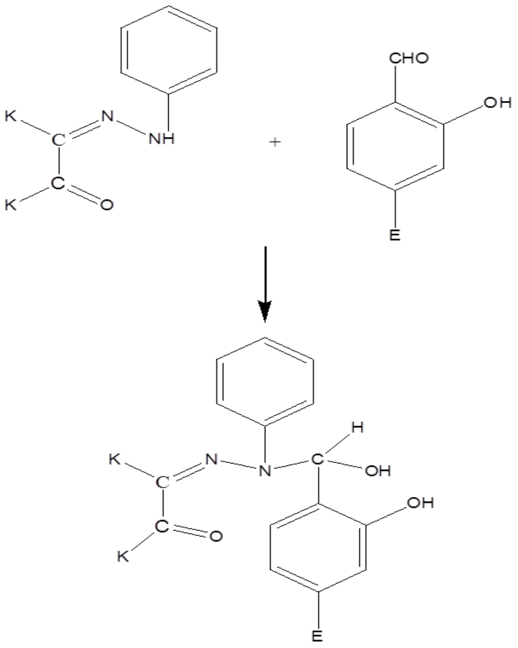
Fig (5): Formation curves of metal ions with ligand (IV)

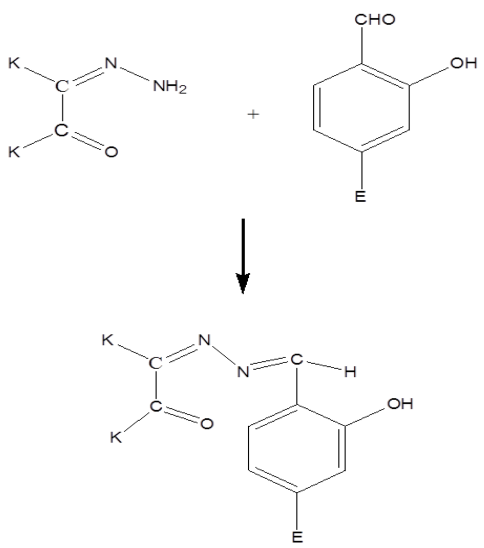
Mechanism of the reaction can be represented as follows:



R=-Ph in dihydrazide of ligand (I, II and III)

R=-H in dihydrazide of ligand (IV)





If K=-H, E=-OH→ L(I)

If K=-H, E=$-OCH_3$→ L(II)

If K=$-CH_3$, E=$-OCH_3$→ L(III)

If K=-Ph, E=-OH→ L(IV)

4. Conclusion

The metal chelates have been structurally characterized and ligand stoichiometry 1:1.The acid ionization constants (pK_H) of the ligands under consideration are determined spectrophotometrically in universal buffer solutions covering the pH range 2.39 to 12.17.To determine the dissociation constants of the compounds (I-IV); Half-height method (HHM), and the modified limiting absorbance method (MLAM) were used, the pK_H values of compounds (I-IV) obtained from the two previous methods indicated that two pK_H values for each compound (I, IV) were obtained; due to the dissociation of two protons of the two hydroxyl groups in the phenyl ring and one pK_H value for each compound (II, III) was obtained; due to dissociation of the proton of the hydroxyl group in the phenyl ring. Based on the potentiometric studies the order of stability constants with respect to metal ions is Co(II)<Cu(II)<Tb(III)<Sm(III)<Gd(III). It has been found that the order of stability constants of metal complexes with respect to ligands [(III)<(IV)]. It is clear that ligand (IV) has the greater value in chelation with Gd(III) ion indicating the strong and high stability of these complexes. The metal ion solution used in the present study was very dilute (0.001M); hence there was no possibility of formation of polynuclear complexes, several techniques as well as determination of their dissociation constants using spectral methods; the study was extended to suggest the reaction mechanism and calculate the stability constants of complexes of these compounds with some transition metal ions in solution.

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