# STUDY ON TERNARY COMPLEXES OF SOME HEAVY METAL IONS WITH BIOLOGICALLY IMPORTANT LIGANDS


BY

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## *DECLARATION*

*It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma.*


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# *CERTIFICATE*

*This is to certify that the research work embodying in this thesis has been carried out under my supervision. The work presented herein is original. This thesis has not been submitted elsewhere for the award of any other degree or diploma in any University or institution.*

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## CONTENTS

# Abstract

Ternary complexes are known to provide models for metalloenzymes and several other biological processes involving metal ions. The principles of coordination chemistry will thus allow an increasing understanding of the structure and dynamic features involved in biochemical processes.

Ternary metal complexes of type [MAL], where M=Cu(II), Ni(II), & Zn(II), A=Aspertic Acid(Asp), 1,10 Phenanthroline (1,10 ph) and L= Ethylenediamine (en),α-alanine(α-ala), Glycine(gly), Phenylalanine(ph-ala), Tyrosine(tyro) have been investigated potentiometrically at 25°C and at ionic strength of 0.2M ($NaClO_4$). The stability constants have been determined using SCOGS (Stability Constant of Generalized Species) computer program.

The stabilities in ternary complexes have been discussed in terms of ligand-ligand interaction, steric interaction, basicity of the ligands, nature of donor sites and charge neutralization factors. The stabilization is expressed in terms of ΔlogK. The ΔlogK values and percentage species computed gave parallel evidence for the stabilization of ternary complexes. The stabilities of ternary complexes have been quantitatively compared with each other.

It is observed that for the ternary complexes of Cu(II), Δlog K values are more negative than corresponding Ni(II) ternary complexes. This is due to the absence of Jahn-Teller distortion in Ni (II) complexes.

It is also observed that Δlog K values are positive when phenylalanine and tyrosine are coordinated with central metal ion. This is due to the intramolecular interligand interaction between non-coordinated side groups.

Another reason of extra stabilization of tyrosine is due to intramolecular interligand hydrogen bonding and stacking interation of phenylalanine and tyrosine with metal ion. Additional stabilization in the complexs can occur due to the noncovalent hydrophobic interaction between non-coordinated side group phenyl and hydroxyphenyl of phenylalanine and tyrosine respectively with A(Asp, 1,10 ph).

Hence, in the present investigation, the orders of the stability of the ternary complexes is as follows-

$$[Zn(A)(L)] > [Ni(A)(L)] > [Cu(A)(L)]$$

The formation of the complexes also has been confirmed by Cyclic Voltammogram.

# CHAPTER-1
# INTRODUCTION

# Introduction

**1.1: General Introduction:**

Mixed ligand complexes play an importent role in biological process as exemplified by many instance in which enzymes are known to be activated by metal ions.[1,2] Such complexes have been implicated in the strong and transport of active substances through membrance[3]. Many mixed ligand complexes are finding application in the microelectronic industry, chemical vapour deposition of metals and drugs[4]. Mixed ligand complexe have been used in the analysis of semi-conductor materials. Various mixed ligand complexes of Co(II) with salicylaldehyde and substituted salicylaldehydes have been synthesized. Earlier mixed ligand complexes of Ni(II), Co(II) and Zn(II) and alkaline earth metals with substituted salicylaldehydes have been reported.

Most of the transition metal form complex with ligand and this metal complexes play very important roles in biological system[5]. Metal complexes is a branch of biological inorganic chemistry. This field has important implications in many other sciences, ranging form medicine to the environment. It is an interdisciplinary science. Furthermore, studies of the roles of metal ions in biological system often involve development of relevant chemistry.

In a complex where two or more ligands of the same type are bonded with a metal ion is called a binary ligand complexes and if the different types of ligand are present, then the complex is said to be ternary complexes or mixed ligand complexes[6]. It is now generally agreed that in a solution containing metal ions and two different suitable ligands are

usually combined. Metal ions in living bodies are mostly coordinated to other chemical species present in the bodies. Not only many ligands compete for a metal ion but metal ions also compete for a species ligand. Metal ions displace one another in accordance with the formation constants of their coordinated compounds. It has been observed that the stability constant of the mixed complex depends on the nature of the metal ions[7] and the nature of the ligands[8].

Amino acids are a class of compounds occurring in living organism. These amino acids perform variety of biological functions and all the amino acids are good ligands too. Aspertic acid is extremely important because of its possible bindings sites for protons or metal ions. It is a tridented ligand. It is widely used as a metal chelating agent. On the other hand 1,10 Phenanthroline is also an important ligand. It is a bidented ligand. It forms stable complex with metal ions.

In a living tissue and fluid, strong coordinating metal ions and poteutial coordinating sites of organic molecules are responsible for biochemical reactions[9]. In such case the mixed ligands complex formation is to be expected[10,11]. In a biochemical system the ternary complexes [12-16] are also expected to be formed. The study of the ternary complexes in solution provides simpler models for more complicated biochemical reactions.[17] The biochemical reactions are models of ternary complex forming[18-21] systems. The systematic ternary complexes are formed when metal ion bonded with different carrier ligands and substrate[12,16,22-27]. The stability of the ternary complexes and associated binary complexes[13,15,28-35] have been extensively studied.

The biochemical reactions[36] taking places in solution involve organic molecules with potential coordinating sites and also strongly coordinating transition metal ions. In living tissues and fluids[37,38] the total ligand

concentration greatly exceeds the metal content, and hence the various complexion species compete for the metal ions present. Under these conditions formation of mixed ligand complexes are to be expected. Ternary complexes[39,40] have been implicated in the storage of metal ions and their transport through membranes in the biological system [38,41]. Taking every thing together, one is not surprised any more about Wood's conclusion[42], "If you think that biochemistry is the organic chemistry of living systems then you are misled; biochemistry is the coordination chemistry of living systems".

This understanding has directed the attention of chemists to the study of dynamic equilibriua in the formation of metal complexes, involving metal ion and ligands similar to those present in biological fluid and living tissues[36,37]. The formation[43] and stability[37,38] of such complexes have been extensively studied. For more than three decades metal interactions with nucleic acids and their constituents have received much attention because of their biological importance in nucleic acid processes[44] .This results in a large body of data involving metal binding sites or models[45] and structures formed[46]. The effect of structural features of the complexes and the natures of the ligand on the stability of the ternary complex and associated binary complexes is of great fundamental significance[47]. This has led to the study of mutual influence of two ligands bound to the same metal ion and the effect of the nature of the metal ion on the ternary complex stability.

It is known that transition metal ion with great acidic character and with vacant 'd' orbitals form more suitable complexes. Irrving and William suggested, the order of the stabilities of the bivalent metal ion complexes based on two factors, overall second ionization potential and inverse of

ionic radius. For the same ligand the stability of the bivalent metal ions of the 1st transition series can be arranged as follows.

$V^{2+} < Cr^{2+} > Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$

The order of the stability of Ni(II) and Cu(II) complexes depends on whether the ligands creates a week or strong field. $Cu^{2+}$ has anomalous position forming more stable complex than $Ni^{2+}$. This is because $Cu^{2+}$ with $d^9$ electronic configuration are subjected to Jahn-Teller effect.

The formation of ternary complex can be expressed in three different ways as follows[48].

$$M + A + L \rightarrow MAL \qquad K^{M}_{MAL} = [MAL] / [M][A][L] \qquad [1]$$

$$MA + L \rightarrow MAL \qquad K^{MA}_{MAL} = [MAL] / [MA][L] \qquad [2]$$

$$ML + A \rightarrow MAL \qquad K^{ML}_{MLA} = [MAL]/[ML][A] \qquad [3]$$

Hence

$$\log K^{MA}_{MAL} = \log K^{M}_{MAL} - \text{Log } K^{M}_{MA} \qquad [4]$$

$$\log K^{ML}_{MLA} = \log K^{M}_{MLA} - \text{Log } K^{M}_{ML} \qquad [5]$$

There are two common methods to express, a quantitative basis the stability of ternary complexes[13,49,50]. Firstly it can be expressed[51] in terms

$$\text{of } \Delta\log K = \log K^{MA}_{MAL} - \log K^{M}_{ML} = \log K^{ML}_{MLA} - \log K^{M}_{MA} \qquad [6]$$

i.e. the difference in the tendency of a ligand (A or L) to bind with free metal ion and with the metal ion already bound to another ligand (L or A). It is evident that from the relationship of eq. (6), the influence of both ligands is mutual and both ligands are either stabilized or destibilized in their co-ordination to the metal ion equally.

ΔlogK must be a constant because it is the result form substraction of two constants logK is a constant corresponding to the equilibrium constant of the reaction indicated in eqnation [7]

$$MA + ML \rightarrow MAL + M \qquad [7]$$

$$\log K = \log \frac{[MAL][M]}{[MA][ML]} \qquad [8]$$

From statistical consideration ΔlogK is expected to be negative. This is becanse when the first ligand (A) combines with a given mnltivalent (hydrated) metal ion, it has more co-ordination positions available for bonding than when it combines with metal already bound to another ligand (L). Hence, the order $\text{Log } K^{M}_{ML} > \text{Log } K^{ML}_{MLA}$ usually holds and one expects to observe negative values for ΔlogK.

The stabilization factor governing ΔlogK depends on the coordination number of the metal ion and the denticity of the ligand.

The difference, $(\log K^{ML}_{MAL} - \log K^{M}_{MA})$ is generally about –0.5 to –0.8 log units for monodentate ligands and about –1 to –2 log units for bidentate ligands[52]. In the case where A and L are bidentate ligands, there are twelve edges of a regular octahedron$_{oh}$ available for the first entering ligand, but only five for the second[53] i.e. the statistical factor is 5/12 and accordingly - Δlog $K_{oh}$ = -0.4. For square plane (sp) a factor of ¼. i.e. $\Delta\log K_{sp}$ = -0.6 is obtained. However for the distorted octahedron(do) of $Cu^{2+}$ the statistical value is more difficult to assess. Considering the John-Teller inversion to be rapid[52], there are eight (or even twelve) equivalent attacking positions for the first ligand while the value for the second ligand can vary from one to four (or even five) depending on the relative rates of iuversion. Hence, the statistical value is between 1/8 (or 1/12) and 4/8 and Δlog $K_{do}$ = -0.9 (or – 1.1) to –0.3. Incase of $Cu^{2+}$ and

the ligands that introduce a strong ligand field, the statistical expression $\Delta\log K_{do/Cu} = -0.9$ is considered to be most appropriate one[15]. Hence an experimentally determined value of ΔlogK, more or less negative than –0.9, indicates that in equation (7), the ternary complex is favored less or more, respectively. So the value of ΔlogK is affected by the non statistical factors depending on the natures of the ligands A and L and structure of the metal ion in some cases[20].

The other approach to express the stability of ternary complex on a quantitative basis is based on the "disproportionation constant" $K_{reprop}$ as defined by the following equation.

$MA_2 + ML_2 \leftrightarrows 2MAL$

$$K_{reprop} = \frac{[MAL]^2}{[MA_2][ML_2]} \qquad [9]$$

$$\log K_{reprop} = 2\log \beta^M_{MAL} - (\log \beta^M_{A_2} + \log \beta^M_{L_2})$$

From statistical consideration the value of $K_{reprop}$ is expected to be 4. Under purely statistical considerations the mixed ligand complex MAL is formed by two path ways (eqs. 2 and 3), whereas $MA_2$ and $ML_2$ are formed by one path way each. Hence there is a possibility of 50% formation of [MAL], while binary complexes $MA_2$ and $ML_2$ are formed to the extent of 25% each. Hence the value of $K_{reprop}$ should be equal to 4 as shown below.

$$K_{reprop} = \frac{[MAL]^2}{[MA_2][ML_2]} = \frac{50^2}{25 \times 25} = 4$$

or, $\log K_{reprop} = 0.6$

Hence $\log K_{reprop}$ will be 0.6 if only statistical factors were responsible for the formation constant. If for electrostatical reasons the stability of $MA_2$

or $ML_2$ complex is less, more of MAL is formed and the value $\log K_{reprop}$ is higher than 0.6.

Thus the stability of the ternary complexes can be evaluated either based on the values of ΔLogK or $\log K_{reprop}$. Each of the above two methods has its own merits and demerits[15,49] and preference to either approach has to depend on the kind of study. The main advantage of consideration of $\log K_{reprop}$ is in its firm statistical basis. It does not depend on the co-ordination number of the metal ion or the denticity of the ligand. This advantage is lost while using ΔLogK formulation. Since the statistical value depends upon the co-ordination nnmber of the metal ion and the denticity of the ligand. $\text{Log}K_{reprop}$ does not indicate absolute stability of the complex, but its relative stability with respect to the complexes $MA_2$ and $ML_2$. In a mixed ligand complex containing a neutral ligand A or a negatively charged ligand L, ΔLogK is not affected by the electrostatic or entropy factor. But steric hindrance between the two ligands in a $MA_2$ or $ML_2$, complex results in the distortions from a tetragonal geometry[54,55].

In the present chapter the formation constant of ternary complexes [MAL], where M = Cu(II), A = aspertic acid or 1,10 plenanthroline, L = glycine, or α - alaline, or phenylelanine or tryptophan have been determined and the values of ΔLogK have been calculated. The protonation constants and formation constants for binary complexes have been reported earlier[56,57,58], and present work has used those of previous constants.

## 1.2 Importance of Metal and Metal Complexes in Biological System:

Metal ions play very significant roles in biological system. Many metals are vital component of blood, bones, teeth, body pigments, nerves, some proteins and enzymes. The colouring pigments which impart colours to the plants and flowers contain ions likes Cu(II), Fe(II), Fe(III), Co(II) etc.

Among the vitally important biochemical processes[59] which are influenced by the various metal ions (i) transmission of the nerve pulses in the animal body, (ii) maintenance of the osmotic pressnre in the animal and plant bodies are controlled by various metal ions[60].

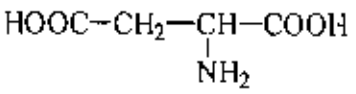
The activation of enzymes is controlled by varions metal ions. The enzymes from yeast and many bacteria is activated by $Fe^{2+}$, $Co^{2+}$ or $Zn^{2+}$ ions[61].

Some metal ions play remarkable contradictory physiological roles in different concentration and in different chemical form. Thus while Cu is found to play important nutritional and metabolic role in the body system, its imbalance may result in microcytic normochromic anemia, Wilson's disease etc, and number of other disease in man and animal[62]. Cu(II) complexes with DL aspetric acid, L- prolin, DL-methionine and L-glutamic acid have similar toxicities to mice[63].

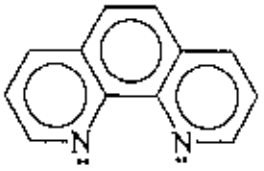
## 1.3 Ligands and Their Structure:

In the present investigation, the formation constant as well as stability constant of ternary complexes of the type [MAL] have been determined by using bidentate and tridentate ligands. In these complexes A refers to Aspertic acid and 1,10 plenanthroline and L refers to oxalic acid, ethylenediamine, glycine, α-alanine, phenylalanne and tyrosine. The structure of ligands (A and L) used in this study are as follows-

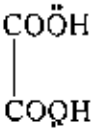
1. Aspertic Acid (Asp)



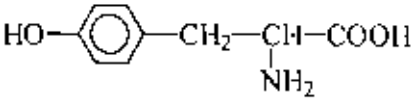
2. 1,10 Phenanthrolene (1,10 ph)



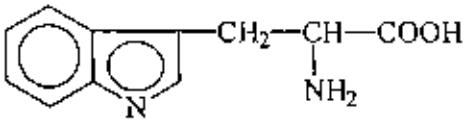
3. Oxalic acid (ox):



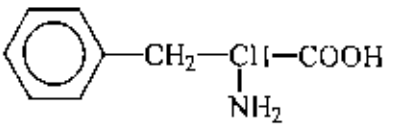
4. Tyrosin (Tyro) :



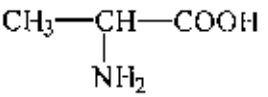
5. Tryptophans (Tryp) :



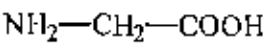
6. Phenyl Alanine (Ph-ala) :



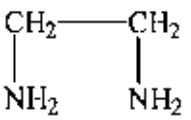
7. α- Alanine ( α-ala)



8. Glycine (Gly) :



9. Ethyldiamine (en):



# CHAPTER-2
# LITERATURE REVIEW

## 2.1: Literature Review:

The study of ternary complexes in solution provides simpler models for the more complicated biochemical reactions[64-67]. The synthetic ternary complexes with metal atom bound to two different ligand mimic the metalloenzymes with the metal ion bridging the carrier ligand and substrate[68-75].

The understanding has directed the attention of the chemists to the study of dyanamic equilibria in the formation of metal complexes, involving the metal ion and ligands similar to those present in biological fluids and living tissues.[76,77] The formation [78-81] and stability[82-84] of such complexes have been extensively studied.

The effect of structural features of the complexes and the natures of the ligand on the stability of the ternary complexes and associated binary complexes is of great fundamental significance. This has led to the study of mutual influence of two ligands bound to the same metal ion and the effect of the nature of the metal ion on the ternary complex stability. Various workers have reviewed excellently much of the wok done in this field[66,67,85-88].

The natures of the two ligands involved in the formation of ternary complex greatly affect its stability constant[89,90]. These effects vary with the nature of the metal ion involved [91]. Six main non-statistical factors have been observed to be of significance in determining the stability of a ternary complex. They are as follows:-

(1) Electronic repulsion[87,92], between L and L' of a ternary complex : Ternary complexes containing two negatively charged ligands like $O^{-}$ - $^{-}O$ and $^{-}O$- N are less stable. This is because second

negatively charged ligand faces electrostatic repulsion form the first charged ligand at the stage of the formation of the ternary complex.

(2) Steric hindrance [93,94] between the bulky side groups on the coordinating ligands L and L'; If the two ligands involved in the formation of the ternary complex have substituted groups on the front or back side of the ligands, there is steric hindrance when the second ligand coordinates with the metal ion forming the ternary complex resulting in less stable complex.

(3) Tridentate nature of the ligand[85,96] making Cu(II) complexes less stable. If one of the coordinating ligands is tridentate and the other is bidentate in character then Cu(II) complexes are much more destabilized due to Jahn- Teller effect.

(4) Size of the chelate ring[97] . The order of the stabilization observed by Sigel et.al and Bhattacharya et. al in ternary complexes containing two chaelate rings are two five-membered rings> one five-membered and one six-membered ring> two six-membered rings.

(5) π -acid character of one of the ligand[98,99] : It has been observed that the presence of an aromatic amine is crucial for high stability of a ternary complex. This has been repeatedly confirmed[66,68,89,100-102]. If a complex MA is considered where A is a tertiary diamine like 2,2' bipyridine, there is synergetic stabilization of N → M 6-bond and M → A π-bond. The $d_{\pi}$-$P_{\pi}$ interaction does not allow the electron density over the metal ion to increase significantly.

(6) Intermolecular inter-ligand interaction[103-106] : There can be direct interaction between the parts of the two ligands in ternary complex, leading to its stabilization, such interaction is known as intramolecular inter-ligand interaction and can be of two types. One is rigid intramolecular inter-ligand interaction and the other is flexible interaction in which interaction takes place between the ligands in complex through side groups not co-ordinated with the metal ion.

(7) Taqui Khan and coworkers have determined the formation constants of the complexes of adenine nucleotides with a variety of metal ions[107,108] . They have given the relative order of stabilities of metal adenine nucleotide complexes as ATP> ADP> AMP in accordance with the length of phosphate chain.

(8) Sigel and C.F. Naumanncoworkers[109] have also observed the intermolecular stacking interactions between covalently linked suitable groups like nicotinamide adenine dinucleotied $(NAD)^+$ and dihydronicotin amide (NADH).

(9) It has been shown by Bhattacharya and coworkers[111,112] that interligand interaction is dependent on the nature of the tertiary base. In case of [Cu(2,2′-dipyridyl) (ATP)] or [Cu (1,10 ph)(ATP)] the stacking interaction is less than that observed in case of [Cu(2,2′-dipyridyl) (benzimidaole) (ATP)].

(10) An interesting relationship of the stability of Cu(II) and Ni(II) ternary complexes is observed if one of the ligands is tridentate ligand[112-114] . It has been shown that in[M (NTA) (L)] where M = Cu (II) or Ni(II) and NTA = tridentate nitrilo triacetate anion, L =

ethylenediamine (en), 1,2- propanediamine, the Δlogk is more negative in case of Cu(II) as compared to Ni(II) complexes.

(11) Sigel and coworkers[115] have also observed that in the systems [Cu (DET) (L)] (DET = diethylenetriamine) where, L = bidentate L-alanineamide, Δlogk is more negative.

(12) (i) Israici studied[116] the formation constants of mixed ligand complexes of Cn(II) and Ni (II) with NTA and various amino acids.

(ii) Tandom and coworkers[117] reported formation constants of mixed ligand complexes [M (NTA) (hydroxy acids)] , where M = Cu(II) or Ni(II), the Δlogk is more negative in case of Cu(II) as compared to Ni(II) complexes.

(13) Watters and Yamauchi[118,119] carried out research work on the [Cu(ox) (L)] type ternary complexes where L = catecholate and ethylenediamine. They observed that ternary complexes containing two negatively charged ligands are less stable. Bhattacharya and coworkers[120-122] have further elaborated the effect of negatively charged on the stability constant in terms of electronic repulsion concept.

(14) The order of the stabilization observed by sigel et al[123] and Bhattacharya et al.[124] in ternary complexes containing two chelate rings are two five-membered ring> one five-membered and one six-membered ring> two six-membered rings.

(15) The presence of an acid character of one of the ligand in a ternary complex leads to a high stability. This phenomena has been studied by chidambaram et al.[125] and Patel et al[126]. This has been repeatedly confirmed[127-131].

(16) Study of [M(dpx)(pyrocatecholate)] complexes[132] of the later members of the first tranision series where dpx = bis (2-pyridyl) amine (dpa), bis (2-pyridyl) ketone (dpk) or bis (2-pyridyl) methane (dpm) has shown that the tendency for the formation of ternary complexes decreases within the series dpk> dpm> dpa.

(17) In another series of ternary diamines, Bhattahacrya and coworkers[120,121,126,133] have observed that the tendency of mixed ligand formation follows the order: 2,2′ pyridyl> benzimidazole> 2,2′ bipyridyl ≈1,10- phenanthroline> 2,2′- pyridyl> inidazoline.

(18) The complexes containing aromatic amines and pyrocatechol derivatives have been studies by Bhattacharya and cowrokers[133,134] also by sigel and coworkers[135]. Both groups conclude that the electron density over the ligand L, donor site has singnificant influence on the stability of the ternary [CuAL] complexes. Electron withdrawing snbstitution on L lower the stability of the complex and electron donating substitutents increases it.

(19) In ternary complex [M(bipyridyl)(ATP)][136-138] the nucleotide is coordinated from the phosphate end and the free base part comes over bipyridyl. This results in rigid stacking interaction between the coordinated tertiary amine and the non-coordinated base pat of the nucleotied as confirmed by formation constant studies and NMR studies.

(20) In the complex [Cu (ATP) (Try)][139] an aromatic ring stacking interaction has been observed between the purine moiety of ATP and the indole of tryptophane. In mixed amino acid ternary complexes such as [Cn (phenylalanine) (norvalinate)][141] a flexible hydrophobic interaction has been shown. Interligand interaction

has also been proposed in [Cu (phe) (Tyr)][142] (phe = phenylalanine, Tyr = Tyrosine) complexes due to non-coordinated side groups . In [M (ATP) (His)] type complexes there can be charge transfer flexible interaction between adenosine part of ATP and imidazole part of histamine in addition to the hydrophobic interaction between two ligands.

(21) M. M Taqui Khan and coworkers have determined the formation constants with complexes of adenine nucleotides with variety of metal ions.[143-149]They have given the relative order of stabilities of metal adenine nucleotide complexes as ATP> ADP > AMP in accordance with the length of the phosphate chain[143,149,150].

(22) A. Oriodi and coworkers[149] carried out X-ray study of [M(bipy) (ATP)] complex. According to them there are two types of stacking interactions (i) Intramolecular and (ii) Intermolecular.

(23) H. Sigel et al[150] synthesized the mixed ligand 2,2′- bipyridyl-$Cu^{2+}$ nucleotide complexes exist in a folded from that allows a charge transfer interaction between the pyridyl and purine moieties. The stability of these adducts is increased by the formation of a metal ion bridge between the two involved aromatic moieties.

(24) An interesting research on synthesis, crystal structure and maganitic properties of tetrakis [diaqua (μ- 1,3-dimethylviolurato) Copper(II)] tetraperchlorate dihydrate have been investigated by Enrique Colacio et al.[151] The structnre of this complex is square planar. From variable temperature magnetic susceptibility measurements the compound was found to exhibit a very strong antiferromagnetic character.

(25) Two new ferromagnetic end on azide-bridged Nickel (II) dimers $[\{Ni(terpy)(N_3)_2\}_2]$. $H_2O$ and $[Ni(terpy)_2(N_3)_3(H_2O)]$ $ClO_4.H_2O$ (terpy = 2,2′:6′,2′′- terpyridine) have been synthesized and characterized through X-ray single crystal analysis. IR spectroscopy and magnetic susceptibility measurements by Gotzone Barandika et al[152]. The results indicate that the antiferromagnetic contribution of the global coupling constant is decreased.

(26) Most of the theoretical approaches concern simple architectures such as dimers among which those of dibridged $Cu^{II}$ have been particularly studied. In this respect, Thompson and coworkers[152-155] experimentally confirmed the angle dependence of the crossover between ferro and antiferromagnetic couplings for a variety of copper (II) dimers.

(27) According to a recent study by Kahn and coworkers[156] based on experimentally obtained spin density maps for a particular copper (II) dimer exhibiting di- $\mu$-$N_3$ bridges, neither of the mechanisms cited above is completely satisfactory both are co-operative.

(28) Murakami Tasuka et al[157] have investigation on the stabilities and spectral properties of five coordinate mixed ligand Cu (II) complexes containing penta- methyl diethylenetriamine and α-amino acid.

(29) The $\mu(\eta 1$- N: $\eta^2$O,O)- nitrito dinuclear compounds $[Ni(\mu\text{-}NO_2)(NCS)_3(Medpt)_2]$. $H_2O$ and $[Ni(\mu\text{-}NO_2)(NCS)_3((dpt)]$ and the mononuclear nitrito compounds $[Ni(NO_2)(NCS)(Medpt)]$ and $[Ni(NO_2)(NCS)$ Medien)] where Medpt = bis (3 aminopropyl)

methylamine dpt = bis (3-aminopropyl) amine and Medien = bis (2-aminoethyl) methylamine, have been synthesized and characterized by Albert Escure et al[158]. They reported that thiocyamate ligand appears to stabilise the tridentate coordination mode of the nitrito ligand and dinuclear compounds shows antiferromagnetic character.

(30) Hoffmann and Yeager[159] have examined the effect of various ligands coordinated to nickel(II) on the rates of formation and dissociation of the corresponding malonato complexes. Ring closure and ring opening, respectively appear to be the rate determining processes with this six-membered chelate ring system. The rates were found to increase steadily with an increase in the number of coordinated aliphatic amines; both [Ni (pn)] and (Ni (trien)] react faster than [Ni(dien]

(31) Cis-trans isomerism in complexes of the kinetically labile cupric ion was reported by Tomita[160], who suggested that while bis-glycinatocoper(II) monohydrate adopts a cis configuration, the dihydrate of this complex exists as the trans isomer.

(32) Synthesis and X-ray crystallographic studies on Cu (II) complexes with alanine have been investigated by Gillard et al[161] . They prepared light blue platelets and dark blue prismatic crystals of bisalaninatocoper (II) and they concluded that these respect trans and cis modifications respectively.

(33) D.L Leussing et al[162], studied mixed Ni(II) and zn (II) complexes involving glyoxalate and the amino acids e.g. glycine, α-alanine and α-Saminoisobutyric acid. They observed that glyoxalate reacts rapidly and cleanly in these systems and offers a smaller steric requirement than pyruvate. Besides, the mixed complexes formed

in nickel (II) pyruvate-glycinate mixtures do not have structures identical with those formed with nickel (II) glyoxalate-α -alanate.

(34) Mixed ligand complexes involving amio acid dithiocarbamates substituted phosphines and Ni (II) have been reported by Thirumaran et al[163] . They observed that all complexes are diamagnetic. Thermal decomposition of dithiocarbamart moiety proceeds through the formation of $[Ni(SCN)_2\ pph_3]$.

(35) Mohammad Enamullah et al[164] have determined the proton-ligand and metal-ligand formation constants of phthalic acid with some transition metal ions such as Zn (II), Ni(II) and Cd (II). It was found that the metal ions Zn (II) and Cd (II) form complexes at low ionic strength, $I \leq 0.1$ M. Above this ionic strength such as I = 0.15 M, these ions seem to be inactive towards.

(36) G. R. Cayley and Hague [165] studied the formation of several ternary complexes of Zn(II) of the type [Zn(L)(pada)] (pada = Pyridine-2-azo-p-dimethylaniline), L=(dien, trien, $cys^{2-}$ and $ida^{2-}$) at 25°C, I = 0.3M. The formation rates for all these ternary complexes were found to be similar to those of the binary complex, $[Zn(pada)]^{2+}$ . However, the dissociation rates for these ternary complexes are much higher than that of $[Zn(pada)]^{2+}$ .

(37) F. Nobuo et al[166] have studied an interesting research on trinuclear Mn(II),Cu(II) complexes of an oxamide dioxime ligand and finally these have been extended to a bimetallic magnetic compound.

(38) T. H. Tarafder[167] carried out a research work on complex compounds which contain a nitrogen sulfur donor ligand with lighter and heavier metal ions and he studied the biological activities of complexes.

(39) Addition stability of (MAL) was observed if L coordinates through $O^-,O^-$ (e.g. oxalic acid)[168]. It has been shown that ΔlogK is positive in the complex [CuAL], due to the repulsion between dπ electron and the ligand electrons and finally neutralization of the ternary complex result[169,170].

(40) Beda E. Fischer and co-worker[171] observed the perticipationof $Co^{2+}$ and $Ni^{2+}$ in biological system. They suggested that S ligands may have π accepting qualities.

(41) (i) P.G. More and co-worker studies the synthesis, spectral, thermal and antibacterial studies on Copper(II) andf Zinc (II)complexes using NNO donor Schiff bases[172]. It is observed that Copper(II) andf Zinc (II) complexes shows enhanced antibacterial activity as compare to the ligand.

(ii) Mixed ligand chelates of some multidentate heterocycles with Cobalt(II) and Nickel (II) have been studies by P.T. Araus et al[173].

The intramolecular stacking has been observed[109,174-176] in solution and also in solid[(66-68)] . In the solution it is considered[180] that there exists an intramolecular equilibrim of open and closed forms and it has been shown that about 35% to 75% intramolecular equilibrium exist in the stacked closed form.

The stability constants of the ternary Cu(II) complexes [Cu (A) (L)] where A refers to oxalic acid, malonic acid and L refers to glycine, β-alanine, α-alanine, phenyl alanine, tyrosine, and tryptophance have been determined potentiometrically using SCOGS computer programme. The tendency of the ligand L to form the ternary complex decrease in the following orde ; tryptophane> tyrosine> phenyl alanine> α-alanine > glycine > β-alanine. Probable reason for less negative Δlogk values and the order of stabilization have been discussed[181].

## 2.2:AIM OF THE PRESENT INVESTIGATION

Most of the transition metal form complex with ligand and this metal complexes play very important roles in biological system. This field has important implications in many other sciences, ranging form medicine to the environment. It is an interdisciplinary science. Scientists are working in different areas of Chemistry, Biochemistry, Biology, Physiology, Agriculture, Physics and even Mathematics. Furthermore, studies of the roles of metal ions is biological system often involve development of relevant chemistry.

This coordination chemistry phenomenon has tremendous significance to life science. This was observed [182] from the instances of a few common compounds of biological importance, such as hemoglobin, myoglobin, chlorophyll, metalloenzymes, metalloprophyrines etc. which are, by and large coordination compounds. Therefore it is necessary to investigate the action of metal ions with substances of biologically important ligands.

In the present research work we have determined the formation constants of ternary complexes [MAL], where M refers to transition metal ion e.g. Cu(II), Ni(II) and Zn(II). A refers to biological important ligands like Aspettic acid (Asp) and 1,10 phenanthroline (1,10 Ph) and L refers to glycine, α-alanine, phenylalanine, tyrosine, tryptophane, ethylenediamine and oxalic acid. The values of ΔlogK have also been calculated for the stability of ternary complexes. The protonation constant, binary constant and ternary constant have been determined potentiometrically using SCOGS (Stability Constant of Generalized Species) computer program[183,184]. The formations of the complexes have been confirmed by CV (Cyclic Voltammogram).

# CHAPTER-3
# EXPREMENTAL, RESULTS
# &
# DISCUSSION

# EXPERIMENTAL

## 3.1 Apparatus and Chemicals

**Apparatus:**

All glasswares used were of Pyrex glass. The microburette was calibrated to 0.01 mL by the method described by Vogel [185]. The measuring flask of various capacities, pipettes etc were also calibrated.

**Chemicals:**

All reagents are AR grade and their standard solution were prepared by directly dissolving the weighed quantity of them in known volume of aqueous solution, Copper perchlorate was prepared from analytical pure copper carbonate by treatuent with 70% perchloric acid (AR). The resulting solids were washed with ethanol till free from excess acid and recrystallized several times from ethanol. Copper perchlorate is partially soluble in alcohol.

Stock solution of copper perchlorate, perchloric acid, sodium hydroxide and sodium perchlorate were prepared in carbonate free double distilled deionized water. Copper perchlorate solution was also standardized by iodometric titration, carbonate free sodium hydroxide solution was prepared according to the literature method [186], standardized by standard oxalic acid solution. Standard perchloric acid solution was prepared from AR 70% acid by proper dilution and titrated with standard alkali, nickel perchlorate and zinc perchlorate were prepared with the same method.

### 3.2: Potentiometric Determination Stability Constant:

Irving Rossotti titration technique[186] has been used to determine the formation constants of the ternary complexes using SCOGS (Stability Constant of Generalized Species) computer program[183,184].

The activity coefficient of $H^+$ under experimental condition has been considered to be equal to unity and the value of the ionic product of water 14.167 has been used.

For the determination of formation constants all solutions were titrated potentiometrically against standard (0.02M) sodium hydroxide solution. In all the cases acid concentration was kept $2.00 \times 10^{-2}$ M and the total ionic strength (I) of the solution was maintained at 0.2M.

For the determination of the formation constants of the ternary complexes [MAL], the following solution ($50cm^3$) having M:A:L in the ratio 1:1:1 were prepared. 0.02M $HClO_4$, 0.002M metal perchlorate, 0.002M ligand (A), 0.002M ligand (L) and 0.174M $NaClO_4$ set was titrated against standard alkali. All the titrations were carried out in aqueous medium and the temperature was maintained at 25°C±1°C during the progress of titration. Titrations were carried out by using TOA pH-METER HM-2OS, having an accuracy of ±0.01 pH unit. The glass electrode was calibrated using buffer solutions of pH 6.86 and 4.01. Hence the stability constants calculated are stochiometric constants. The calculations were carried out by computer, Dell, Optiplex, GX 280.

A model input data required for the calculation of formation constant in the ternary system requires the following details.

1. No of jobs to be calculated.
2. No of experiments in the set experiments under study.

3. No of ligands (two), no. of metals (one) and the no. of complex species formed (including protonated forms of ligand, hydrolyzed metal species etc).
4. Composition of each species has to be described along with its approximate formation constant as the logarithm to base 10.
5. No. of displaceable protons on ligand (1) and ligand (2).
6. Title of the experiment.
7. Initial concentrations of the metal, ligands, mineral acid ($HCO_4$), titrant base and total initial volume concentrations are expressed in moles/L and volumes in mL.
8. For each titration reading bearing values of titre of base, of pH and of INDEX (a quantity which is zero for all but the last reading of experiment when INDEX = 1).
9. Then return to item 6 to read data for next experiment and repeat until data for all the experiments, indicated by item (2), have been read.
10. Logarithm to base 10 of the ionic product of water and the coefficient of hydrogen ion under the condition of experiment (e.g. at 25°C and I = 0.2M).
11. The no. of constants to be refined and the no. of calculation cycles to be repeated to get convergence in the formation constant values.
12. The particular constant to be varied given with serial no. as in (4) and the logarithm increment or decrement to be applied to the formation constant in the numerical differentiation.

In the case of calculation of proton-ligand formation constants the species L, [LH] and [$LH_2$] were considered. For the determination of formation constants of the binary complexes, the species L, [LH], [$LH_2$], M, [ML], [$ML_2$] were considered. These refined values were used as fixed parameters for the refinement of the formation constants of the ternary complexes. The values of protonation constant and the formation constants of binary complexes are in close agreement with the values

reported earlier in the literature[123,188]. The species considered for the calculation of formation constants of the ternary complexes were L, [LH], [$LH_2$], A, [AH], [$AH_2$], M, [ML], [$ML_2$], [MA], [$MA_2$] and [MAL].

The values of the protonation constants of the ligands and the formation constants of the binary complexes have been presented in Table (3.2.1 to 3.2.3). The values of formation constants for the ternary complexes and Δlog K have been presented in Table (3.2.4 to 3.2.9 ). pH titration curves have been presented in Fig. (3.2.1 to 3.2.9) for ternary complexes. Representative species distribution curves as a function of pH in the solution containing M, A and L in 1:1:1 ratio have been presented in Fig (3.2.10 to 3.2.21).

## 3.2: Potentiometric determination of stability constant :

## Experimental Data:

**Table – 3.2.1:** Proton ligand formation constant of ligands and formation constant of their Cu(II) binary complexes in aqueous medium with I = 0.2 M ($NaClO_4$) at 25°C ± 1°C.

| Ligands | log $K_1^H$ | Log $K_2^H$ | log $K_{CuL}^{Cu}$ | log $K_{CuL_2}^{Cu}$ |
|---|---|---|---|---|
| Oxalic acid | 3.89 | 5.13 | 5.01 | 6.83 |
| Ethylenediamine | 9.64 | 16.90 | 10.04 | 8.11 |
| Glycine | 9.08 | 11.68 | 6.99 | 12.44 |
| α-alanine | 9.88 | 12.06 | 7.71 | 13.65 |
| Phenylalanine | 9.23 | 10.95 | 7.58 | 14.21 |
| Tyrosine | 9.56 | 17.91 | 8.11 | 15.28 |
| Aspertic Acid | 4.33 | 6.38 | 8.87 | 16.25 |
| 1,10 Phenanthroline | 4.48 | 2.70 | 7.11 | 11.14 |

**Table – 3.2.2:** Proton ligand formation constant of ligands and formation constant of their Ni(II) binary complexes in aqueous medium with I = 0.2 M ($NaClO_4$) at 25°C ± 1°C.

| Ligands | log $K_1^H$ | Log $K_2^H$ | log $K_{NiL}^{Ni}$ | log $K_{NiL_2}^{Ni}$ |
|---|---|---|---|---|
| Oxalic acid | 3.89 | 5.13 | 4.25 | 6.44 |
| Ethylenediamine | 9.64 | 16.90 | 7.38 | 15.11 |
| Glycine | 9.08 | 11.68 | 6.76 | 10.58 |
| α-alanine | 9.88 | 12.06 | 6.12 | 10.03 |
| Phenylalanine | 9.23 | 10.95 | 5.23 | 9.11 |
| Tyrosine | 9.56 | 17.91 | 5.88 | 9.05 |
| Aspertic Acid | 4.33 | 6.38 | 6.01 | 13.80 |
| 1,10 Phenanthroline | 4.48 | 2.70 | 7.88 | 12.05 |

**Table – 3.2.3:** Proton ligand formation constant of ligands and formation constant of their Zn(II) binary complexes in aqueous medium with I = 0.2 M ($NaClO_4$) at 25°C ± 1°C.

| Ligands | log $K_1^H$ | Log $K_2^H$ | log $K_{ZnL}^{Zn}$ | log $K_{ZnL_2}^{Zn}$ |
|---|---|---|---|---|
| Oxalic acid | 3.89 | 5.13 | 4.78 | 6.02 |
| Ethylenediamine | 9.64 | 16.90 | 6.55 | 11.03 |
| Glycine | 9.08 | 11.68 | 5.02 | 10.11 |
| α-alanine | 9.88 | 12.06 | 4.88 | 8.78 |
| Phenylalanine | 9.23 | 10.95 | 4.32 | 8.41 |
| Tyrosine | 9.56 | 17.91 | 4.20 | 8.35 |
| Aspertic Acid | 4.33 | 6.38 | 6.55 | 12.12 |
| 1,10 Phenanthroline | 4.48 | 2.70 | 6.75 | 9.23 |

**Table-3.2.4:** Stability constant of mixed ligand complexes [Cu(Asp)(L)] in aqueous medium with I = 0.2 M ($NaClO_4$) at 25°C ± 1°C.

| System | log $K_{CuAL}^{Cu}$ | log $K_{CuA}^{Cu}$ | log $K_{CuAL}^{CuA}$ | log $K_{CuL}^{Cu}$ | ΔlogK |
|---|---|---|---|---|---|
| [Cu(Asp)(Ox)] | 12.01 | 8.87 | 3.14 | 5.01 | -1.87 |
| [Cu(Asp)(en)] | 18.61 | 8.87 | 9.74 | 10.04 | -0.30 |
| [Cu(Asp)(gly)] | 14.94 | 8.87 | 6.07 | 6.99 | -0.92 |
| [Cu(Asp)(α-ala)] | 16.13 | 8.87 | 7.26 | 7.71 | -0.45 |
| [Cu(Asp)(Ph-ala)] | 16.24 | 8.87 | 7.37 | 7.58 | -0.21 |
| [Cu(Asp)(Tyr)] | 16.98 | 8.87 | 7.99 | 8.11 | -0.12 |

**Table – 3.2.5:** Stability constant of mixed ligand complexes [Ni(Asp)(L)] in aqueous medium with I = 0.2 M ($NaClO_4$) at 25°C ± 1°C.

| System | log $K^{Ni}_{NiAL}$ | log $K^{Ni}_{NiA}$ | log $K^{NiA}_{NiAL}$ | log $K^{Ni}_{NiL}$ | ΔlogK |
|---|---|---|---|---|---|
| [Ni(Asp)(Ox)] | 9.84 | 6.01 | 3.83 | 4.25 | -0.42 |
| [Ni(Asp)(en)] | 13.28 | 6.01 | 7.27 | 7.38 | -0.11 |
| [Ni(Asp)(gly)] | 12.29 | 6.01 | 6.28 | 6.76 | -0.48 |
| [Ni(Asp)(α-ala)] | 12.09 | 6.01 | 6.08 | 6.12 | -0.04 |
| [Ni(Asp)(Ph-ala)] | 11.63 | 6.01 | 5.62 | 5.23 | +0.39 |
| [Ni(Asp)(Tyr)] | 12.32 | 6.01 | 6.31 | 5.88 | +0.43 |

**Table – 3.2.6:** Stability constant of mixed ligand complexes [Zn(Asp)(L)] in aqueous medium with I = 0.2 M ($NaClO_4$) at 25°C ± 1°C.

| System | log $K^{Zn}_{ZnAL}$ | log $K^{Zn}_{ZnA}$ | log $K^{ZnA}_{ZnAL}$ | log $K^{Zn}_{ZnL}$ | ΔlogK |
|---|---|---|---|---|---|
| [Zn(Asp)(Ox)] | 11.09 | 6.55 | 4.54 | 4.78 | -0.24 |
| [Zn (Asp)(en)] | 14.45 | 6.55 | 7.90 | 6.55 | +1.35 |
| [Zn(Asp)(gly)] | 13.38 | 6.55 | 5.83 | 5.02 | +0.81 |
| [Zn(Asp) (α-ala)] | 12.29 | 6.55 | 5.74 | 4.88 | +0.86 |
| [Zn(Asp)(Ph-ala)] | 11.78 | 6.55 | 5.23 | 4.32 | +0.91 |
| [Zn(Asp)(Tyr)] | 11.68 | 6.55 | 5.13 | 4.20 | +0.93 |

**Table – 3.2.7:** Stability constant of mixed ligand complexes [Cu(1,10 Ph)(L)] in aqueous medium with I = 0.2 M ($NaClO_4$) at 25°C ± 1°C.

| System | log $K^{Cu}_{CuAL}$ | log $K^{Cu}_{CuA}$ | log $K^{CuA}_{CuAL}$ | log $K^{Cu}_{CuL}$ | ΔlogK |
|---|---|---|---|---|---|
| [Cu(1,10 Ph)(Ox)] | 12.89 | 7.11 | 5.78 | 5.01 | +0.77 |
| [Cu(1,10 Ph)(en)] | 16.23 | 7.11 | 9.12 | 10.04 | -0.92 |
| [Cu(1,10 Ph)(gly)] | 13.80 | 7.11 | 6.69 | 6.99 | -0.30 |
| [Cu(1,10 Ph)(α-ala)] | 14.24 | 7.11 | 7.13 | 7.71 | -0.58 |
| [Cu(1,10 Ph)(Ph-ala)] | 14.25 | 7.11 | 7.12 | 7.58 | -0.46 |
| [Cu(1,10 Ph)(Tyr)] | 15.40 | 7.11 | 8.29 | 8.11 | +0.18 |

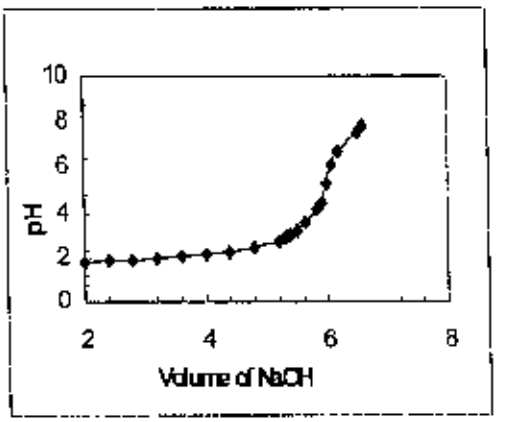
**Table – 3.2.8:** Stability constant of mixed ligand complexes [Ni(1,10 Ph)(L)] in aqueous medium with I = 0.2 M ($NaClO_4$) at 25°C ± 1°C.

| System | log $K^{Ni}_{NiAL}$ | log $K^{Ni}_{NiA}$ | log $K^{NiA}_{NiAL}$ | log $K^{Ni}_{NiL}$ | ΔlogK |
|---|---|---|---|---|---|
| [Ni(1,10 Ph)(Ox)] | 13.00 | 7.88 | 5.12 | 4.25 | +0.87 |
| [Ni(1,10 Ph)(en)] | 15.06 | 7.88 | 7.18 | 7.38 | -0.20 |
| [Ni(1,10 Ph)(gly)] | 14.36 | 7.88 | 6.48 | 6.76 | -0.28 |
| [Ni(1,10 Ph)(α-ala)] | 13.75 | 7.88 | 5.87 | 6.12 | -0.25 |
| [Ni(1,10 Ph)(Ph-ala)] | 12.99 | 7.88 | 5.11 | 5.23 | -0.12 |
| [Ni(1,10 Ph)(Tyr)] | 14.12 | 7.88 | 6.24 | 5.88 | +0.36 |

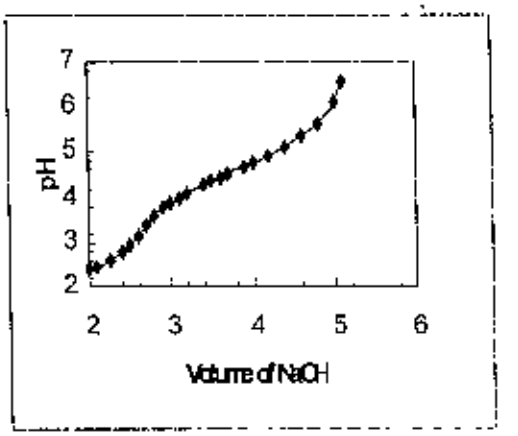
**Table –3.2.9:** Stability constant of mixed ligand complexes [Zn(1,10 Ph)(L)] in aqueous medium with I = 0.2 M ($NaClO_4$) at 25°C ± 1°C.

| System | log $K^{Zn}_{ZnAL}$ | log $K^{Zn}_{ZnA}$ | log $K^{ZnA}_{ZnAL}$ | log $K^{Zn}_{ZnL}$ | ΔlogK |
|---|---|---|---|---|---|
| [Zn(1,10 Ph)(Ox)] | 12.59 | 6.75 | 5.84 | 4.78 | +0.97 |
| [Zn(1,10 Ph)(en)] | 12.83 | 6.75 | 6.08 | 6.25 | -0.17 |
| [Zn(1,10 Ph)(gly)] | 11.39 | 6.75 | 4.64 | 4.79 | -0.15 |
| [Zn(1,10 Ph)(α-ala)] | 11.41 | 6.75 | 4.66 | 4.88 | -0.22 |
| [Zn(1,10 Ph)(Ph-ala)] | 10.92 | 6.75 | 4.17 | 4.32 | -0.15 |
| [Zn(1,10 Ph)(Tyr)] | 11.25 | 6.75 | 4.50 | 4.20 | +0.30 |

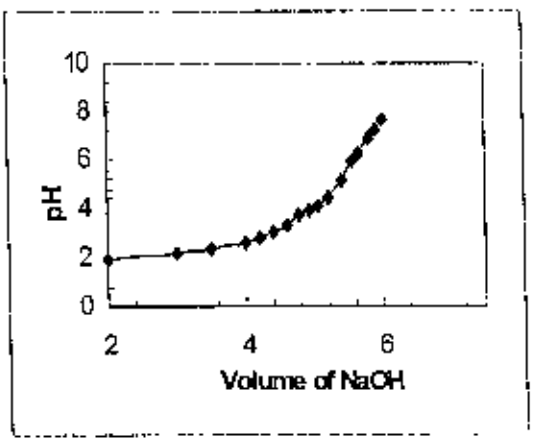
**Potentiometric titration curves:**



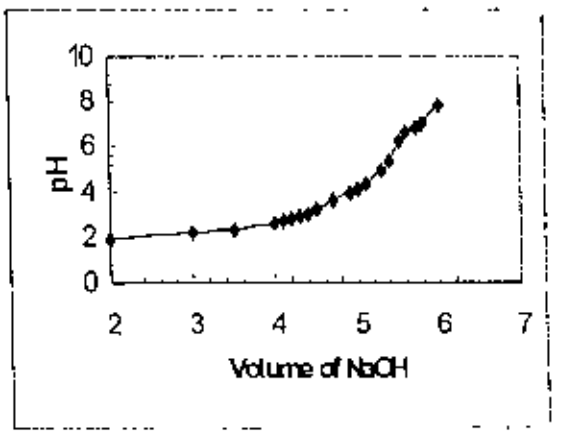

Curve-I




Curve-2

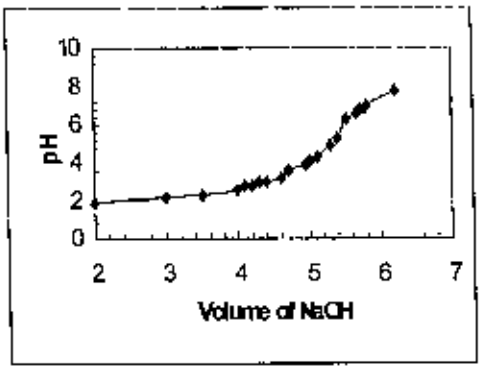



Curve-3

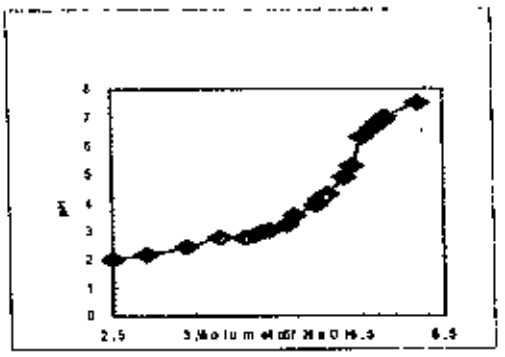



Curve-4

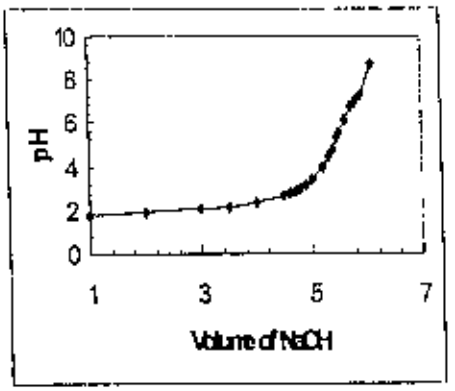
**Fig- 3.2.1:** Potentiometric titration curves of aqueous solutions containing metal ions, Aspertic Acid(Asp) and L. (each 0.001M).
Curve (1) : $Cu^{2+}$ + Aspertic Acid (Asp) + Oxalic Acid
Curve (2) :$Cu^{2+}$ + Aspertic Acid (Asp)+ Ethylenediamine
Curve (3) :$Cu^{2+}$ + Aspertic Acid (Asp)+ Glycine
Curve (4) :$Cu^{2+}$ + Aspertic Acid (Asp)+ α-alanine



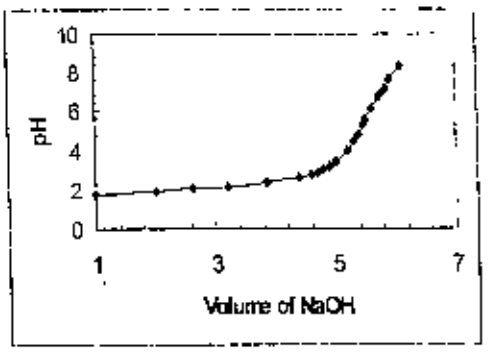

Curve-1



Curve-2

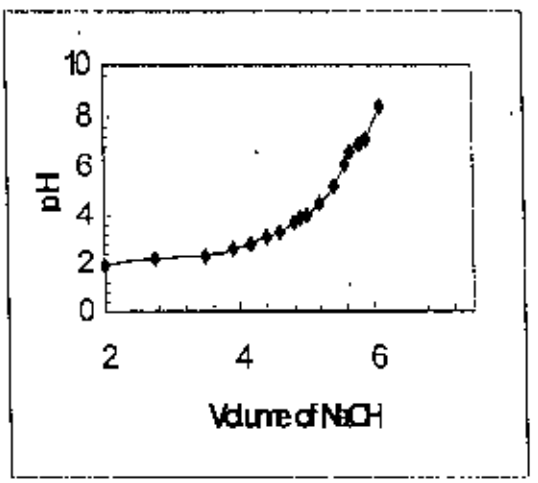



Cueve-3

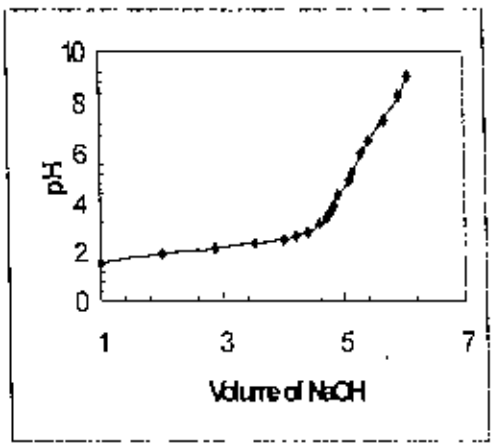



Cueve-4

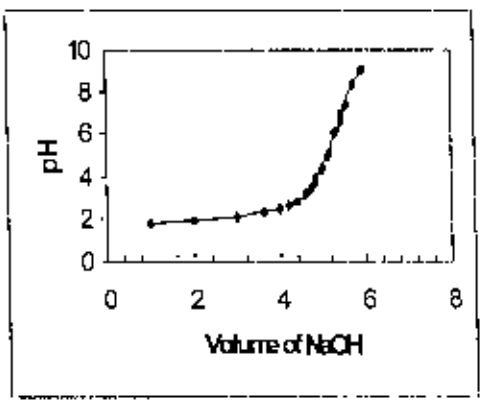
**Fig- 3.2..2:** Potentiometric titration curves of aqueous solutions containing metal ions, Aspertic Acid(Asp)and L. (each 0.001M).
Curve (1) : $Cu^{2+}$ + Aspertic Acid(Asp)+ Phenyl alanine
Curve (2) :$Cu^{2+}$ + Aspertic Acid(Asp)+ Tyrosine
Curve (3) : $Ni^{2+}$ + Aspertic Acid(Asp)+ Oxalic Acid
Curve (4) :$Ni^{2+}$ + Aspertic Acid(Asp)+ Ethylenediamine



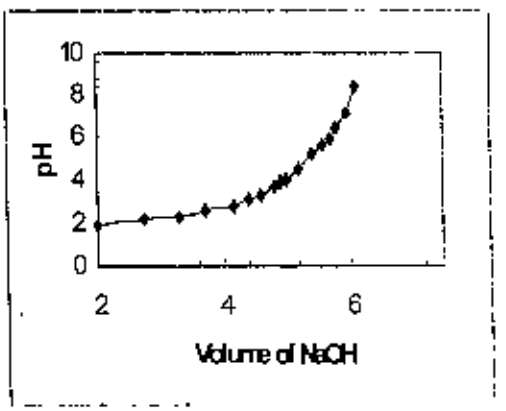

Curve-1




Curve-2

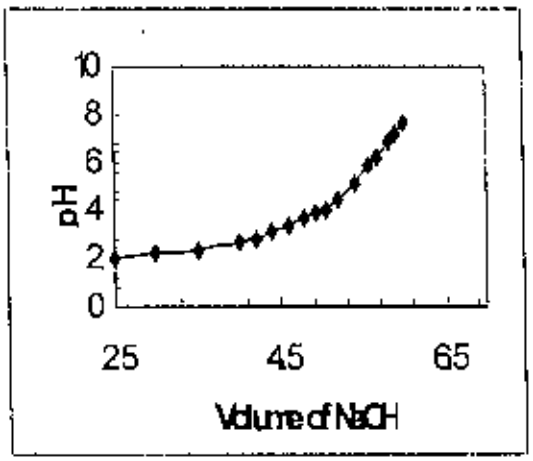



Curve-3

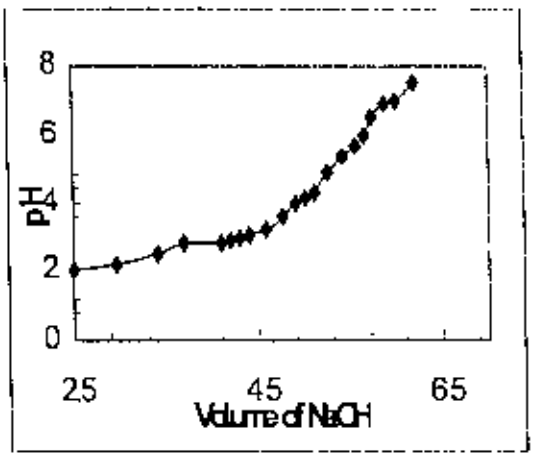



Curve-4

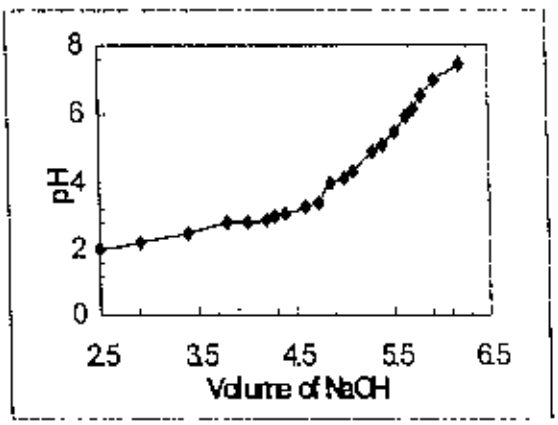
**Fig- 3.2..3**: Potentiometric titration curves of aqueous solutions containing metal ions, Aspertic Acid(Asp) and L. (each 0.001M).
Curve (1) :$Ni^{2+}$ + Aspertic Acid(Asp) + Glycine
Curve (2) :$Ni^{2+}$ + Aspertic Acid(Asp) + α-alanine
Curve (3) : $Ni^{2+}$ + Aspertic Acid(Asp) + Phenyl alanine
Curve (4) :$Ni^{2+}$ + Aspertic Acid(Asp) + Tyrosine



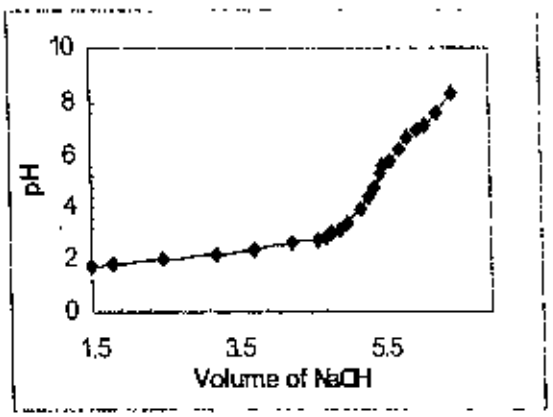

Curve-1




Curve-2

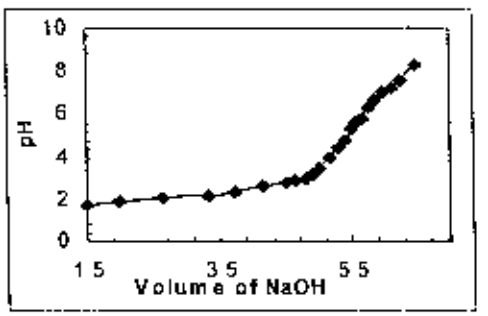



Curve-3

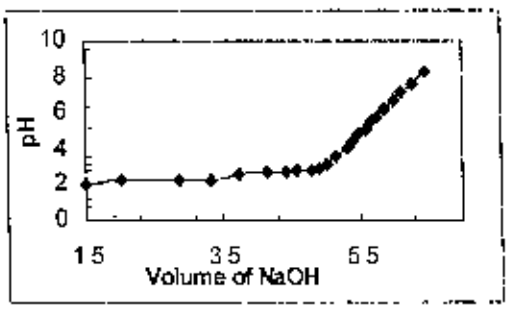



Curve-4

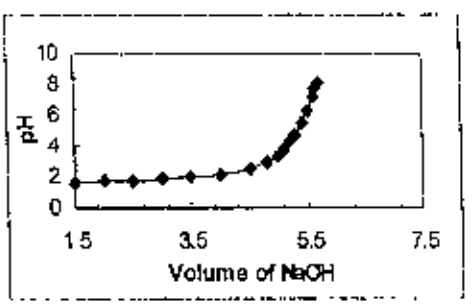
**Fig- 3.2..4:** Poteutiometric titration curves of aqueous solutions containing metal ions, Aspertic Acid(Asp) and L. (each 0.001M).
Curve (1) : $Zn^{2+}$ + Aspertic Acid(Asp) + Oxalic Acid
Curve (2) :$Zn^{2+}$ + Aspertic Acid(Asp) + Ethylenediamine
Curve (3) :$Zn^{2+}$ + Aspertic Acid(Asp) + Glycine
Curve (4) :$Zn^{2+}$ + Aspertic Acid(Asp) + α-alanine



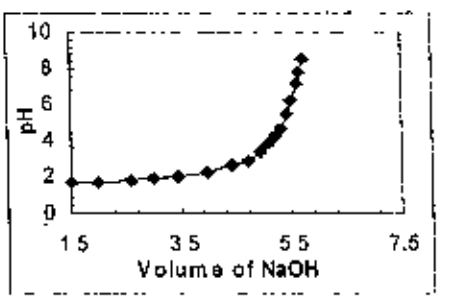

Curve-1




Curve-2




Curve-3




Curve-4

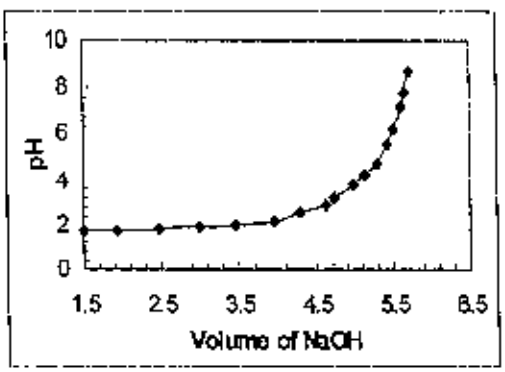
**Fig- 3.2.5:** Potentiometric titration curves of aqueous solutions containing metal ions, Aspertic Acid(Asp) / 1,10 Phenanthroline (1,10 Ph) and L. (each 0.001M).

Cnrve (1) : $Zn^{2+}$ + Aspertic Acid (Asp) + Phenyl alanine

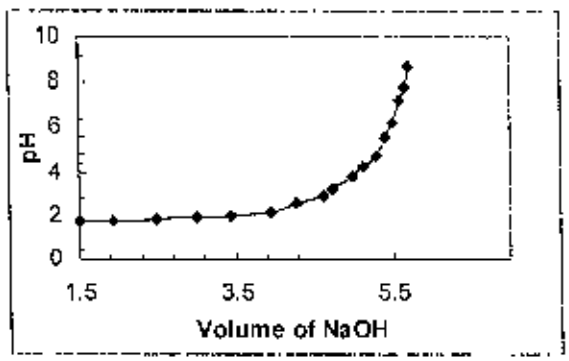
Curve (2) :$Zn^{2+}$ + Aspertic Acid (Asp) + Tyrosine

Curve (3) : $Cu^{2+}$ + 1,10 Phenanthroline (1,10 Ph)+ Oxalic Acid

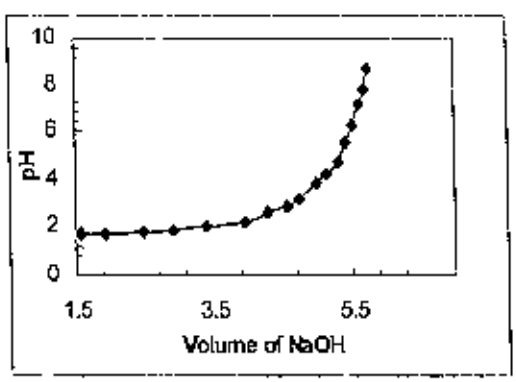
Curve (4) :$Cu^{2+}$ +1,10 Phenanthroline (1,10 Ph)+ Ethylenediamine



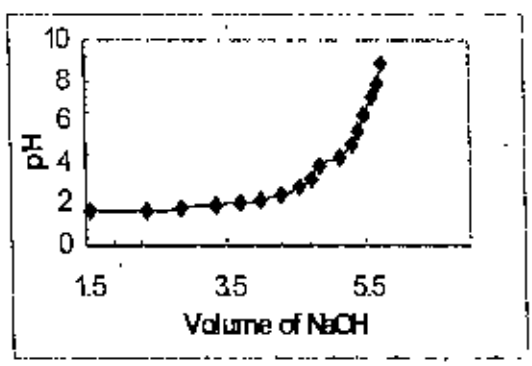

Curve-1




Curve-2

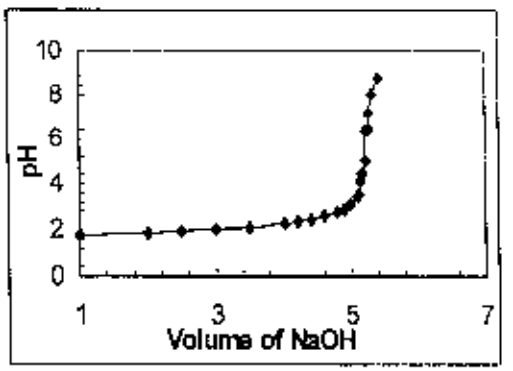



Curve-3

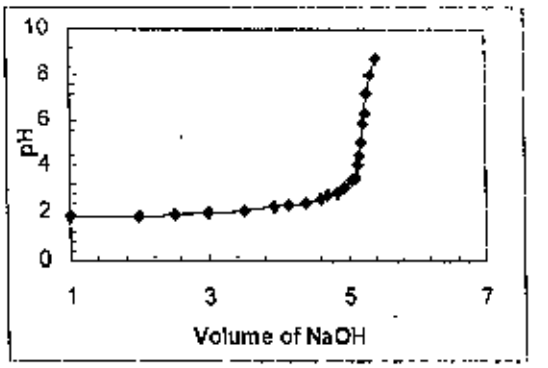



Curve-4

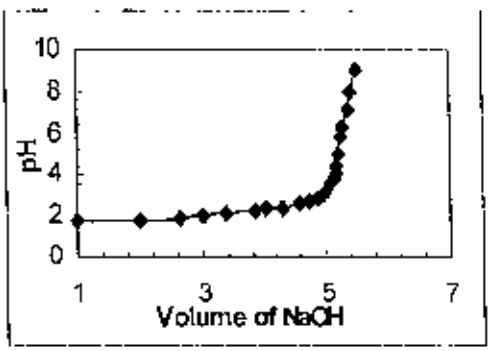
**Fig- 3.2.6:** Potentiometric titration curves of aqueous solutions containing metal ions, 1,10 Phenanthroline (1,10 Ph)and L. (each 0.001M).
Curve (1) :$Cu^{2+}$ + 1,10 Phenanthroline (1,10 Ph)+ Glycine
Curve (2) :$Cu^{2+}$ +1,10 Phenanthroline (1,10 Ph)+ α-alanine
Curve (3) : $Cu^{2+}$ + 1,10 Phenanthroline (1,10 Ph)+ Phenyl alanine
$Cu^{2+}$ +,10 Phenanthroline (1,10 Ph)+ Tyrosine



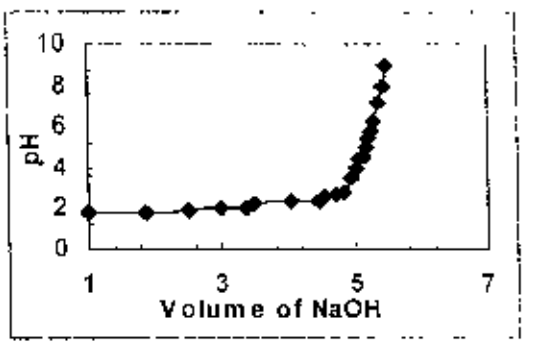

Curve-1




Curve-2

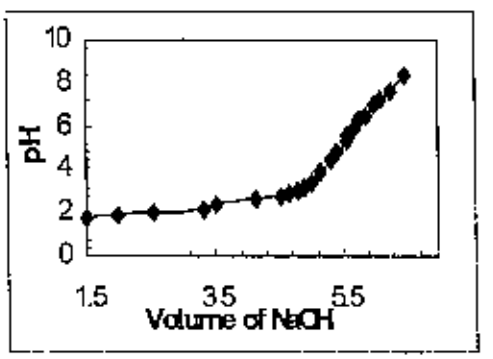



Curve-3

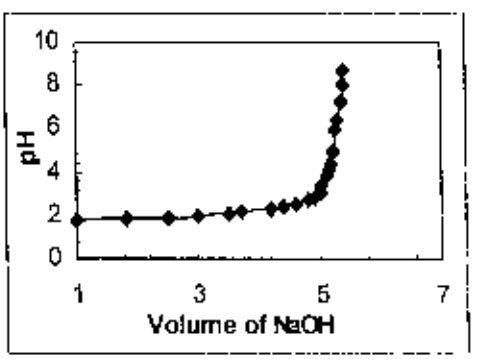



Curve-4

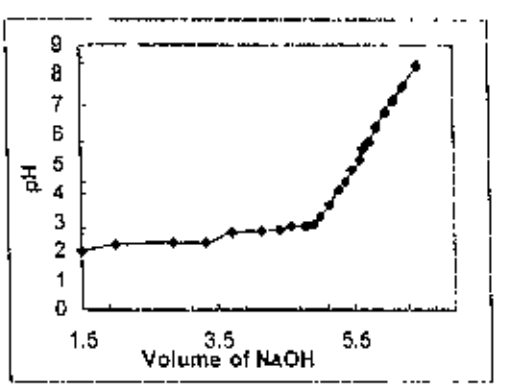
**Fig- 3.2.7:** Potentiometric titration curves of aqueous solutions containing metal ions, 1,10 Phenanthroline (1,10 Ph) and L. (each 0.001M).
Curve (1) : $Ni^{2+}$ + 1,10 Phenanthroline (1,10 Ph)+ Oxalic Acid
Curve (2) :$Ni^{2+}$ +1,10 Phenanthroline (1,10 Ph)+ Ethylenediamine
Curve (3) :$Ni^{2+}$ + 1,10 Phenanthroline (1,10 Ph)+ Glycine
Curve (4) :$Ni^{2+}$ + 1,10 Phenanthroline (1,10 Ph)+ α-alanine



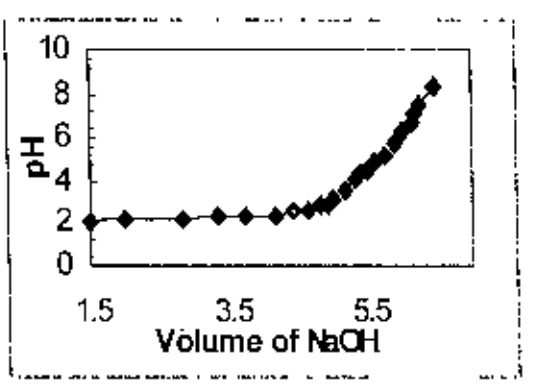

Curve-1




Curve-2

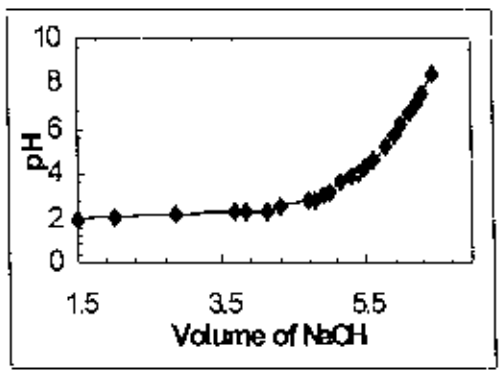



Curve-3

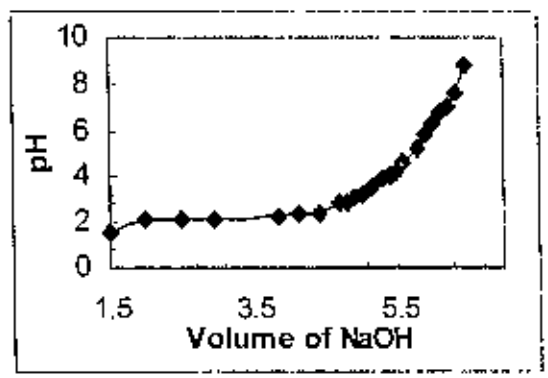



Curve-4

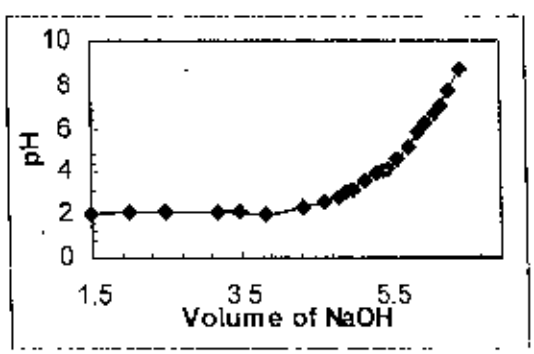
**Fig- 3.2.8:** Potentiometric titration curves of aqueous solutions containing metal ions, 1,10 Phenanthroline (1,10 Ph)and L. (each 0.001M).
Curve (1) : $Ni^{2+}$ + 1,10 Phenanthroline (1,10 Ph)+ Phenyl alanine
Curve (2) :$NI^{2+}$ + 1,10 Phenanthroline (1,10 Ph) + Tyrosine
Curve (3) : $Zn^{2+}$ 1,10 Phenanthroline (1,10 Ph)+ Oxalic Acid
Curve (4) :$Zn^{2+}$ + 1,10 Phenanthroline (1,10 Ph)+ Ethylenediamine



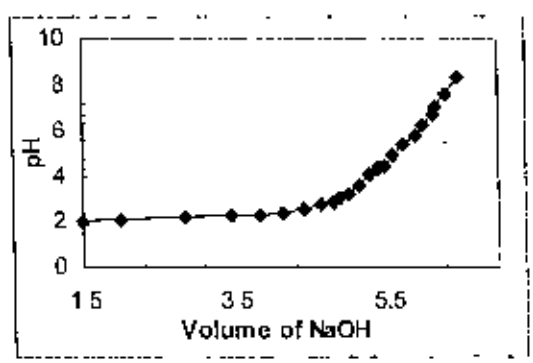

Curve-1




Curve-2




Curve-3




Curve-4

**Fig- 3.2.9:** Potentiometric titration curves of aqueous solutions containing metal ions, 1,10 Phenanthroline (1,10 Ph) and L. (each 0.001M).
Curve (1) :$Zn^{2+}$ + 1,10 Phenanthroline (1,10 Ph)+ Glycine
Curve (2) :$Zn^{2+}$ + 1,10 Phenanthroline (1,10 Ph)+ α-alanine
Curve (3) : $Zn^{2+}$ +1,10 Phenanthroline (1,10 Ph)+ Phenyl alanine
Curve (4) :$Zn^{2+}$ + 1,10 Phenanthroline (1,10 Ph)+ Tyrosine

**Species distribution curves:**

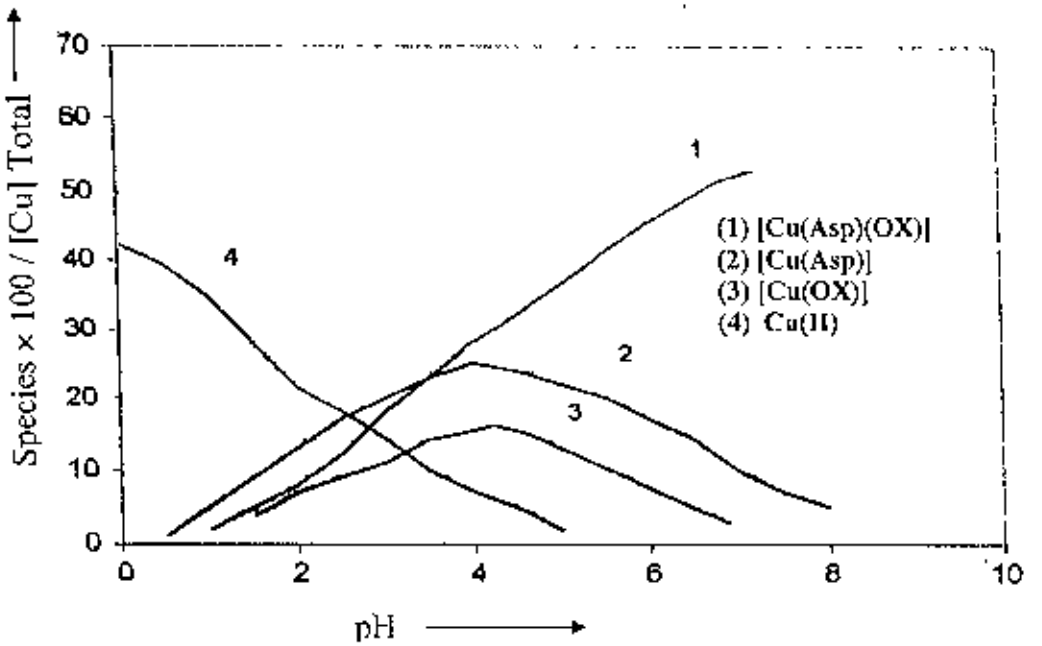



**Fig – 3.2.10:** Species distribution diagram for the [Cu (Asp) (Ox)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

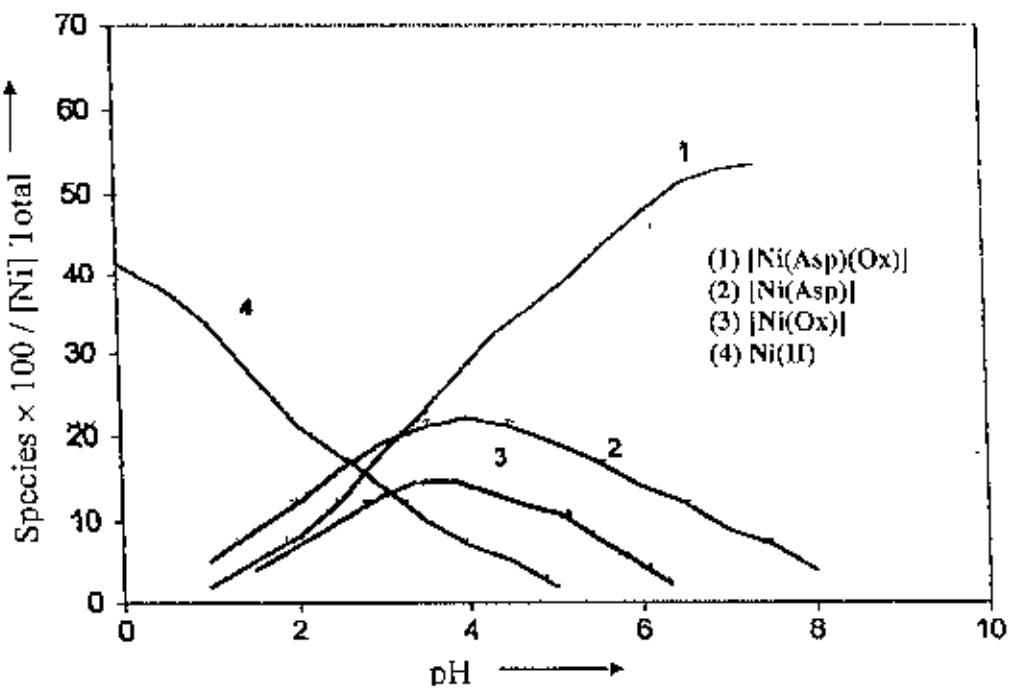



**Fig – 3.2.11:** Species distribution diagram for the [Ni (Asp) (Ox)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

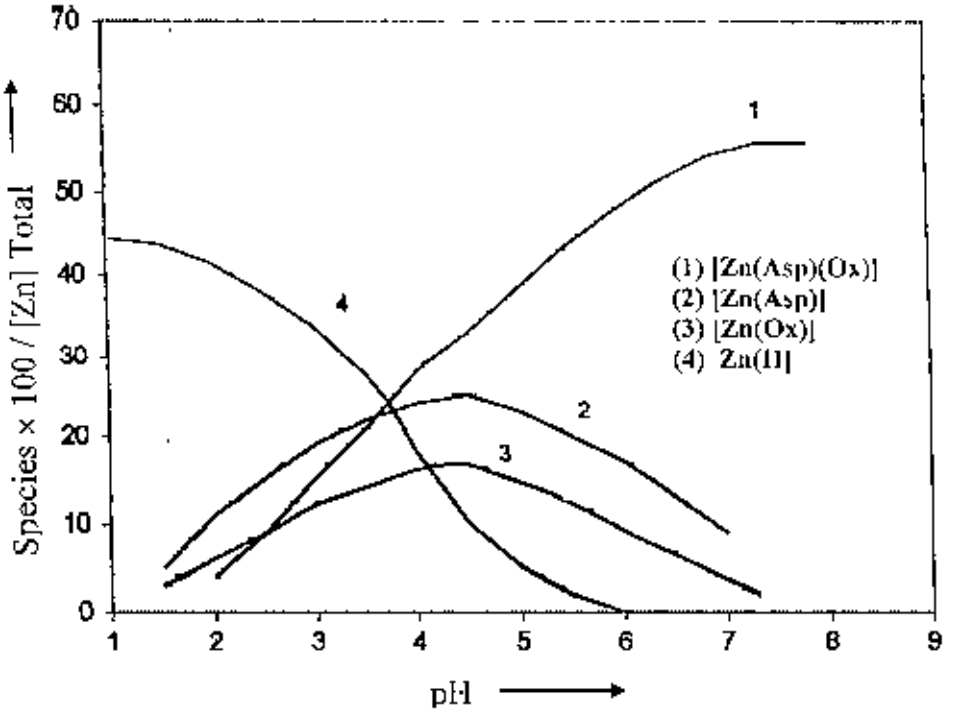



**Fig – 3.2.12:** Species distribution diagram for the [Zn (Asp) (Ox)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

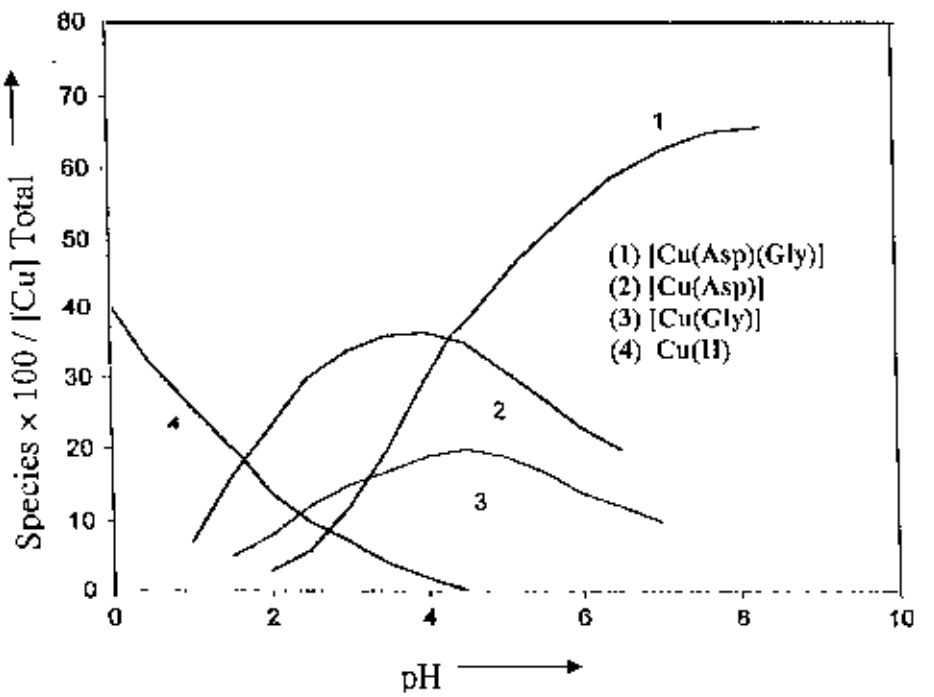



**Fig –3.2.13:** Species distribution diagram for the [Cu (Asp) (Gly)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

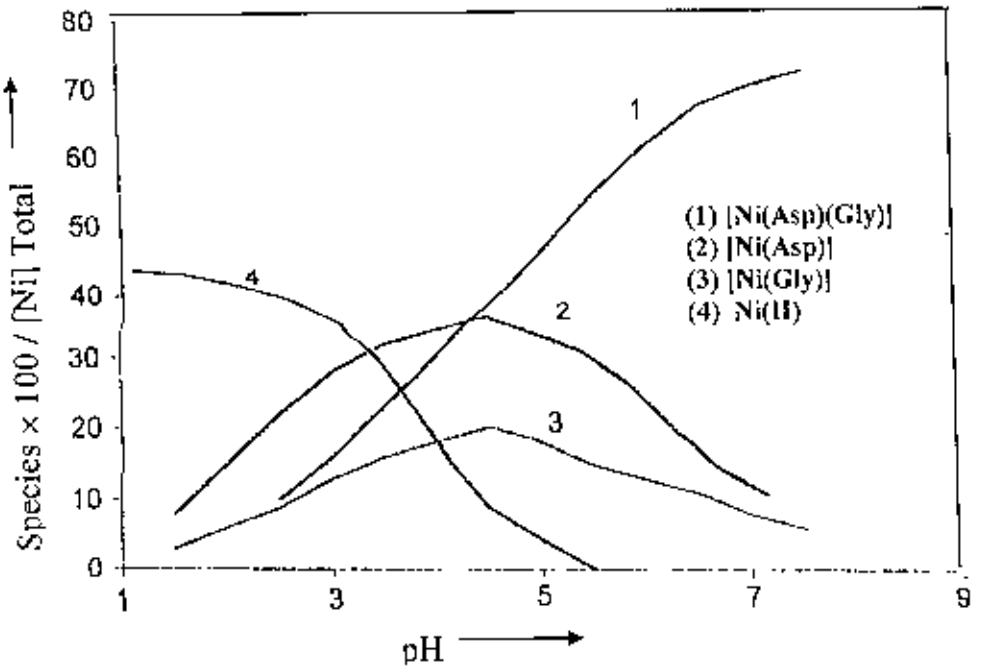



**Fig – 3.2.14:** Species distribution diagram for the [Ni (Asp) (Gly)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

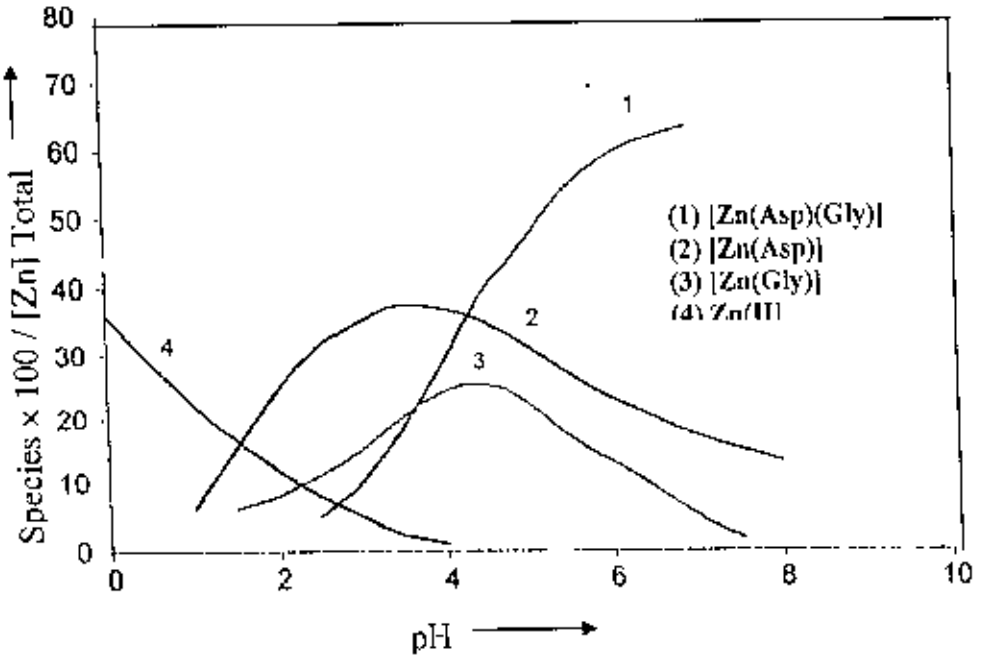



**Fig –3.2.15:** Species distribution diagram for the [Zn (Asp) (Gly)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

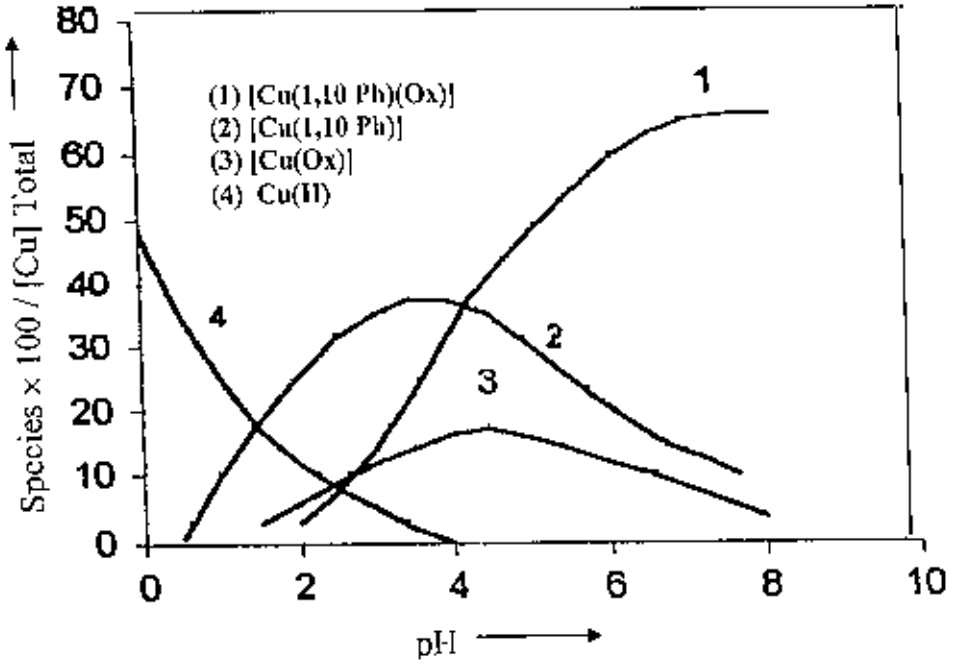



**Fig – 3.2.16:** Species distribution diagram for the [Cu (1,10 Ph) (Ox)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

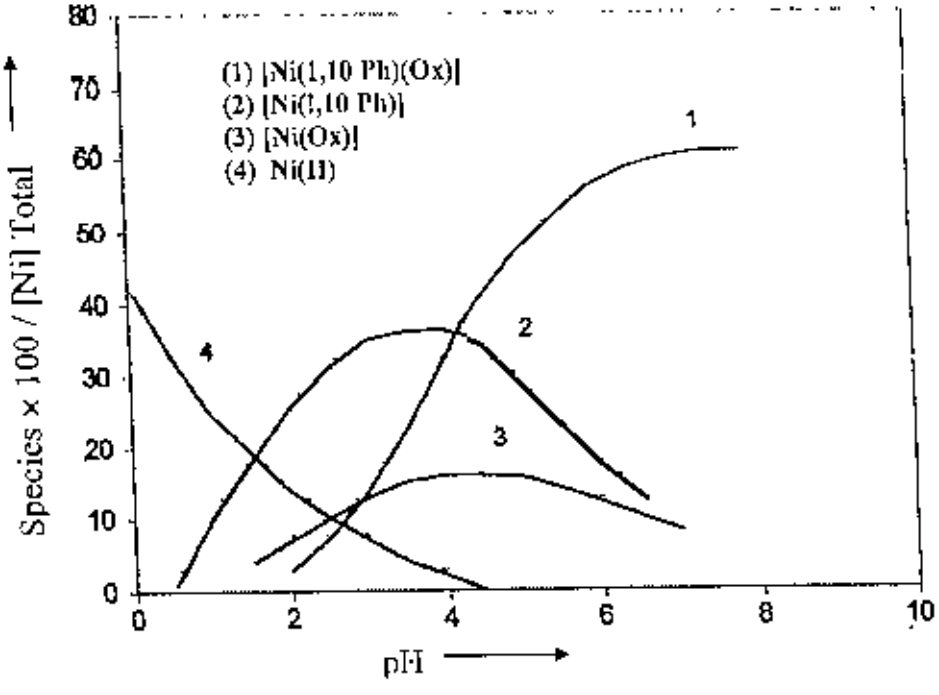



**Fig –3.2.17:** Species distribution diagram for the [Ni (1,10 Ph) (Ox)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

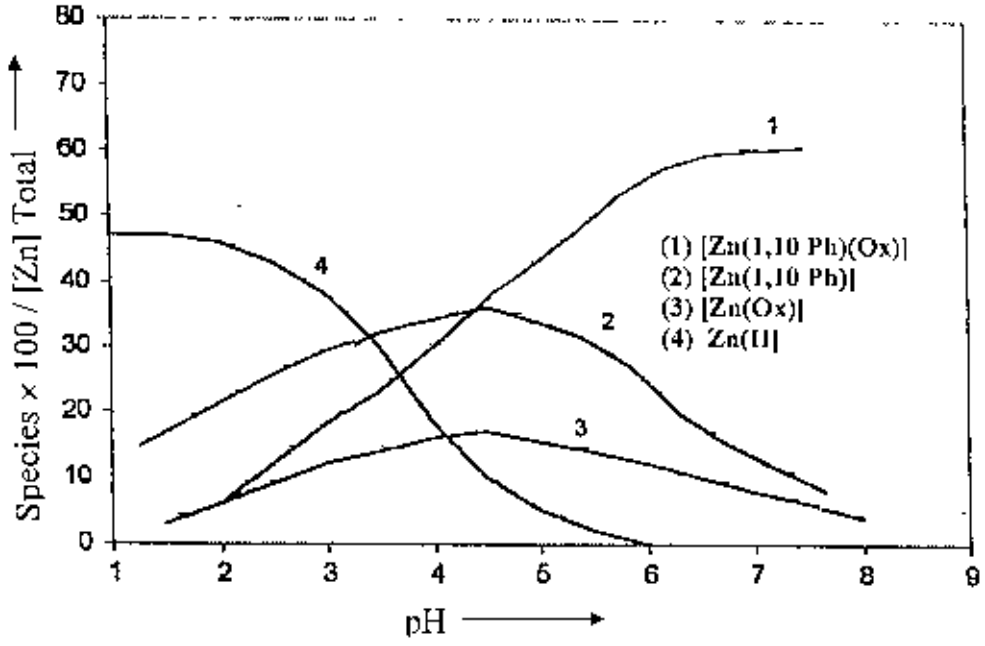



**Fig – 3.2.18:** Species distribution diagram for the [Zn (1,10 Ph) (Ox)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

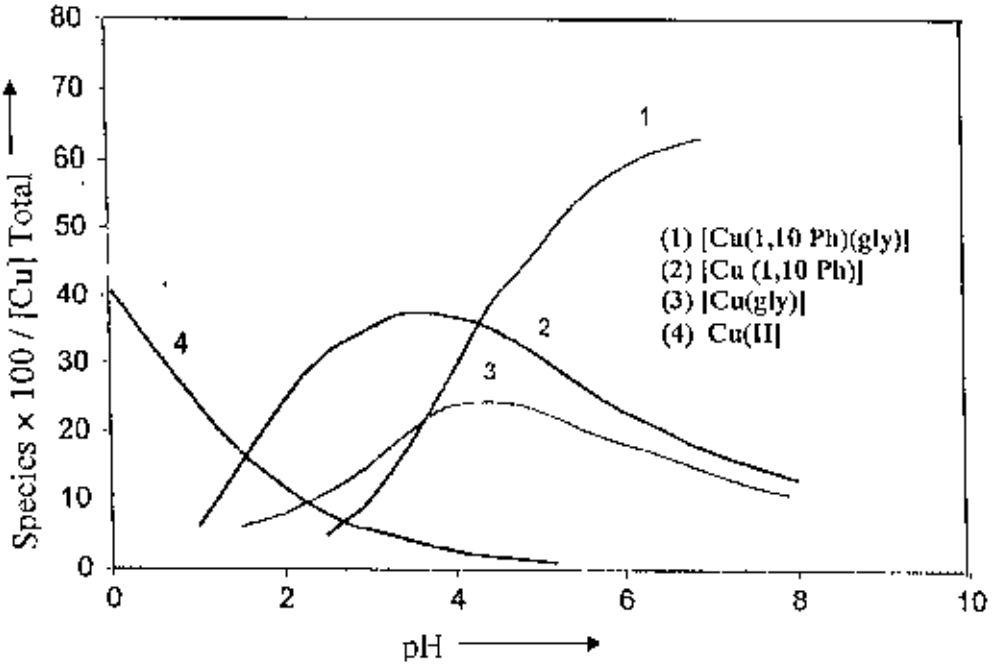



**Fig – 3.2.19:** Species distribution diagram for the [Cu(1,10 Ph) (gly)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

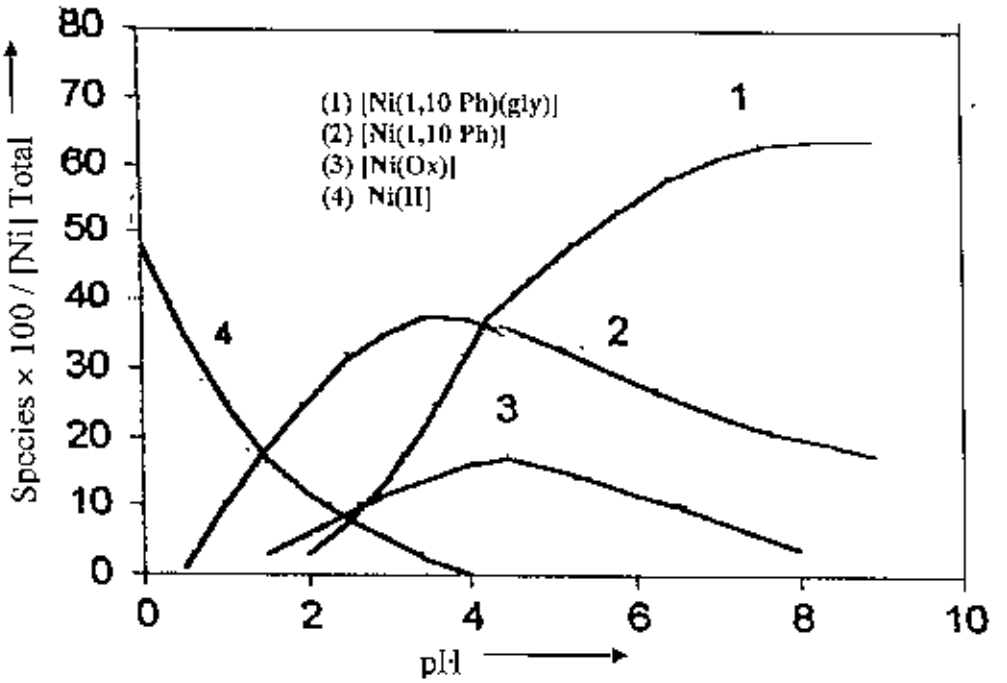



**Fig – 3.2.20:** Species distribution diagram for the [Ni (1,10 Ph) (gly)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

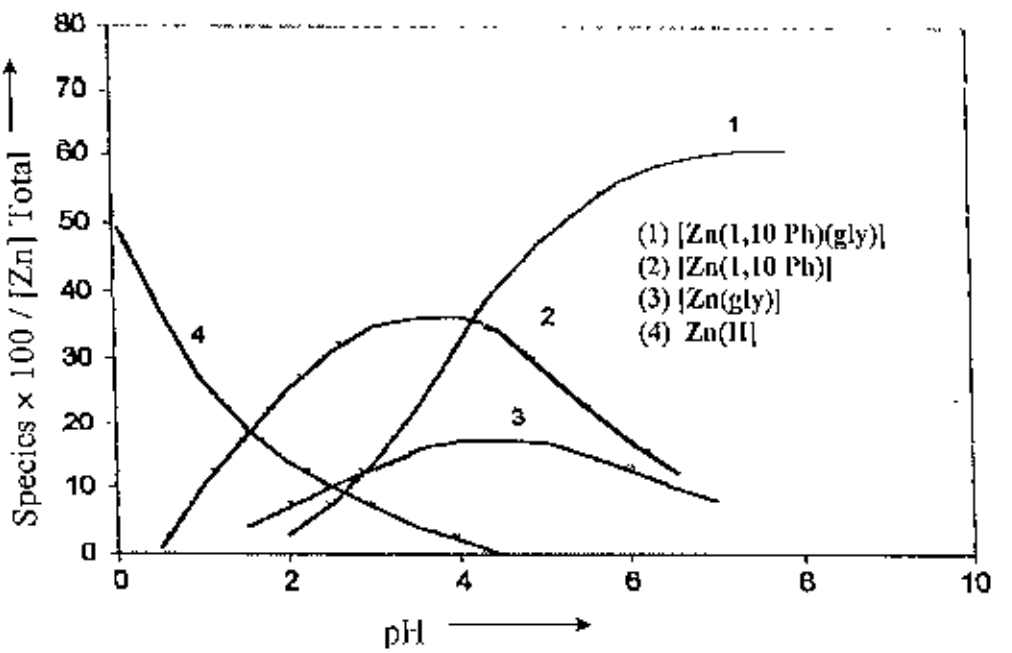



**Fig – 3.2.21:** Species distribution diagram for the [Zn (1,10 Ph) (gly)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

## Results & Discussion

**[M(Asp)L] system:**

**Stability constant of ternary complexes [MAL] type where M =Cu(II), Ni(II) & Zn(II), A =Aspertic Acid (asp), and L = Oxalic acid(ox), Ethylenediamine (en), glycine(gly), α-alanine (α-ala), phenylalanine (ph-ala), and tyrosine (tyro).**

The analysis of the representative species distribution curves (fig-3.2.10 to3.2.15) shows that in the pH range 3.5-5.5 [ML] and [MA] is predominating and in the pH range 5.5-6.0 the species [MAL] is exist. The percentage of all other species is less than 3% in case of [M(Asp)(L)] system. At low pH, L combines with [MA] to form [MAL] ternary complex.

The ΔlogK value is more negative with increasing charge on the ligand, i.e. oxalate>glycinate>en. The second negative charge ligand faces electronic repulsion in forming the ternary complexes. Hence, the tendency of $L^{n-}$ to get bound to neutral [MA] will be less than to get bound with charge $M^{2+}$ ion in the formation of binary complex [ML], leading to negative Δ logK values. The electronic repulsion is more with the increasing charge on $L^{n-}$, resulting the more negative Δ logK values.

It is observed that ΔlogK values are more negative in the case of Cu(II) complexes coupared to Ni(II) complexes. This is due to the presence of tridentate ligand Aspertic acid (Asp).The tridentate ligand Aspertic acid (Asp) occupy the three equitoriar position aroand the metal ion. Hence,in the formation of ternary complexes , the bidentate ligand (L) has to occupy one equitoriar and one axial position. Due to the John- Teller effect, in case of [Cu(Asp)] complexes, the ligand is strained in occnpying the axial position and hence its tendency to coordinate with the [MA] is mnch less than in binary complexes, where the bidentate ligand

occupies two equatorial positions. Hence $\log K_{MAL}^{MA}$ is much less than $\log K^{M}_{ML}$ and Δ logK value is more negative. In the absence of Jahn-Teller distortion in Ni(II) complexes, the bidented ligand does not feel any strain in occupying one eqnatorial and one axial position and hence Δ logK value is less negativc.

It is observed that for the complex [Cu(Asp)L], [Ni(Asp)L] and [Zn(Asp)L] where L= ph-alaninc and tyrocin, Δ logK value is less negative than the complexes L=ox, gly, α-ala. This is because of the intramolecular interligand interaction. More positive values of Δ logK for systems with L= tyrosine may be because of hydrogen bonding[190] between the phenolic –OH of the side group in tyrosine and thc carboxylate $O^-$ of the Aspertic acid (Asp). Howcver no such H-bonding interaction is possible between non-coordinate sides of Aspertic acid and phenyl group of phenylalanine. Therefore the stabilization of such ternary complexes is mainly due to the non-coordinate side group occupying a position in the vicinity of less hydrophilic M-A moiety. Additional stabilization of the complexes can occur due to the stacking interaction of tyrosine and phenylalanine with metal ion.

Thc non-coordinate side group phcnyl and hydroxyphenyl of phenylalanine and tyrosinc respectively come over the group of Asp and hence non-covalent hydrophobic interaction is possible.[189] This intramolecnlar interligand interaction stabilizes the ternary coinplexes, leading to the less negative Δ logK values.

It is also an interesting fact that for the complexes of [M(Asp)(L)] whcre, M = Zn(II), L = en, gly, α-ala, ph-ala and tyro shows positive ΔlogK values though these are unexpected phenomcna from the statistical consideration. This observation indicates the complexes [Zn(Asp)L] are more stable as compared to [Cu(Asp)(L)] and [Ni(Asp)(L)] complexes.

This observation can be explained on the basis of the following two factors:-

(1) Size of the metal atom

(2) Geometry of the complexes.

Ternary complexes are those complexes in which the metal ion has two or more type of legends in its coordination sphere. If different types of ligand coordinate to the central metal ion easily i.e. accommodate the space in their coordination sphere, the rate of the formation of ternary complexes will move in a favorable direction and stable complexes will be formed. When a bulky group is either attached to or present near the donor atom of a ligand mutual repulsion among the ligands occurs and consequently the metal-ligand bond is weakened. Thns large bulky ligands form less stable complexes than do the analogous smaller ligands. This effect is commonly referred to as steric hindrance (steric effect or steric strain). On the basis of the above discussion it can be said that with the increase in size of the metal atom, the ligand will coordinate more easily to the central metal ion to form ternary complex. The size of the metal atom is expressed in terms of atomic radii.

The atomic radii of Cu(II) Ni(II) and Zn(II) are as follows .

Zn (1.25A°) > Cu (1.17A° )> Ni (1.15 A°)

A mutual repulsion among the ligands in ternary complex decrease in the following order:-

[Ni(Asp)(L)] > [Cu(Asp)(L)] > [Zn(Asp)(L)]

For this reason in our present investigation [Zn(Asp)(L)] complexes acquire higher stability than [Ni(Asp)(L)] and [Cu(Asp)(L)] complex.

The shape of transition metal complexes is determined by the tendency of electron pairs to occupy position as far away from each other as possible. As also effected by whether the d orbitals are symmetrically or asymmetrically field.

Besides of the fact that Zn (II) have coordination number 4, and it forms $sp^3$ hybridization in forming complex.[191] i.e the complex fits into a tetrahedral structure. It prefers a tetrahedral geometry[192] over an octahedral or square planar, as the ligand-ligand repulsion is minimum in a tetrahedral geometry. This is due to the fact that the four ligands are situated at the four corners of a regular tetrahedron. The tetrahedral angle[193] is 109°28'. But in an octahedral and a square planar structure the ligands are situated at a 90° angle about the central metal ion. This leads to close proximity of ligands in an octahedral and a square planar structure. Hence octahedral and square planar structure shows higher ligand-ligand mutual repulsiou over ligand-ligand mutual repulsion in tetrahedral strueture.

Hence, the complex [Zn(Asp)L] attains higher stability than [Ni(Asp)L] and [Ni(Asp)L] is more stable than [Cu(Asp)L].

## [M(1,10 Ph)(L)] system:

**Stability constant of ternary complexes [MAL] type where M =Cu(II), Ni(II) & Zn(II), A =1,10 Phenanthrolcane (1,10 Ph) and L = Oxalic acid(Ox), Ethylenediamine (en), glycine (gly),α-alanine (α-ala), phenylalanine (ph-ala), and tyrosine (tyro).**

The analysis of the representative species distribution curves (Fig-3.2.16 to 3.2.21) shows that in the pH range 1-3, metal ion is the major species. In the pH range 3-5, the species [MA]and [ML] is predominating. In the pH range 5-7, the species [MAL] exists.

It is interesting fact that for the complexes of [M(1,10 Ph)(L)] where M =Cu(II), Ni(II) & Zn(II) and L= Ox and tryo the ΔlogK valne is positive. In this type of complexes M→A interaction of dπ-pπ results in an increases in class A character of transition metal ion in the comp!ex. This brings in discriminating behaviour of [MA] towards the secondary ligand L coordinating through N-N, N-O$^-$, O—O$^-$. This can also be explained on the basis of the electron repulsion between the metal d electrons and the additional lone pairs of electrons present over the O—O$^-$ coordinating ligands. In the ternary complexes M→A, π-bonding reduce the electron density over the metal ion and hence the lone pair of electrons over L has to face less repulsion while combining with [MA] than with the free metal ion. It is observed that ΔlogK values for the complexes of [M(1,10 Ph)L] increases. The complex [M(1,10 Ph)L] show more positive value when, L=tyr and M= Cu(II), Ni(II) & Zn(II). This is due to the fact that the intermolecular interligand interaction

involves the complex. The non- coordinated side group hydroxyphenol ring of tyrosin comes over the pyridyl ring of 1,10 Ph and hence non-covalent hydrophobic interaction is possible. This intramolecular interligand interaction stabilizes the ternary complex, leading the more positive ΔlogK value.

It is investigated that for the complexes of [M(1,10Ph)(L)] type the ΔlogK values are negative where L=Ethylenediamine(en), glycine(gly),α-alanine (α-ala), phenylalanine (ph-ala) and M= Cu(II), Ni(II) & Zn(II). The ΔlogK value are more negative in case of Cu(II) complexes compared to Ni(II) complexes. This is because of the presence of Jahn-Teller effect in case of Cu(II) complexes and because of the absence of Jahn-Teller effect in case of Ni(II) complexes.

It is also reported that for the complexes of [M(1,10 Ph)(L)] where M = Zn(II), L = gly, α-ala, ph-ala, tyro shows less negative ΔlogK values as compared to [Ni(1,10 Ph)(L)] and [Cu(1,10 Ph)(L)] complexes where, L =gly, α-ala, ph-ala & tyro. This observation can be explained on the basis of the following two factors:-

(1) Size of the metal atom

(2) Geometry of the complexes.

Ternary complexes are the complexes in which the metal ion has two or more type of ligands in its coordination sphere. If different type of ligands coordinated to the central metal ion easily i.e. accommodated the space in their coordination sphere, the rate of the formation of ternary complexes will move in favorable direction and stable complexes will be formed. On the basis of the above discussion it can be said that with the increase in size of the metal atom the ligand will coordinate more easily

## 3.3: CYCLIC VOLTAMMETRY MEASUREMENT

Cyclic Voltammetry (CV) comprises a group of electro-analytical methods in which information about the analyte derived form the measurement of current as a function of applied potential. The cell of cyclic voltammetry is made up of there electrodes immersed in a solution containing the analyte and also an excess of a non-reactive electrolyte called a supporting electrolyte .One of the three electrodes is the microelectrode or working electrode, whose potential is varied linearly with time. Its dimensions are kept small in order to enhance its tendency to become polarized. The second electrode is a reference electrode (commonly a saturated calomel electrode) whose potential remains constant throughout the experiment. The third electrode is a counter electrode, which is often a coil of platinum wire or a pool of mercury that simply serves to conduct electricity from the signal source through the solution to the microelectrode. The potential of the micro working electrode is varied (scanned slowly) and the resulting current is recorded as a function of applied potential. The recording is called a voltammogram. Cyclic voltammetry has become an important tool in the study of mechanisms and rates of redox processes particularly in organic and in inorganic systems. Now a-days this electrochemical technique is employed to study of the coordination chemistry which is the part of inorganic chemistry.

T. A. Petersen et al[194] have carried a piece of research work on reduction of $O_2$ on the basis of the cyclic voltammetry (CV). At an initial potential of –9.75V, the forward scan starts and at –1.15 V, $O_2$ begins to be reduced to super oxide ($O_2^-$) ion and the cathodic peak is reached at –1.25V. The anodic peak is obtained at about –1.25V and the oxidation of $O_2^-$ ion back to $O_2$ occurs.

A research work have been carried out on cyclic voltammetry for a solntion of 6.0mM in $K_3Fe(CN)_6$ and 1.0M in $KNO_3$ by P.T. Kissinger et al[126] . They observed that a cathodic current is developed at 0.4V and at point –0.15V the scan direction is switched.

Cyclic voltammograms of $B_{10}H_{14}$ and $B_{10}H_{12}^{2-}$solutions have been observed by Donald E. Smith et al[196]. Those voltammograms showed an irreversible oxidation wave at about –1.4V and a reversible conple centered at about –0.5V. The cyclic voltammetric oxidation waves at –1.4V were characterized by considerable distortion and erratic behavior, particularly at lower scan rates.

A shift in the half-wave potential of a metal ion in solution in the presence of an added ligand (anion or neutral molecnles) is indicative of complex formation. J. J. Lingane[197] observed that the half-wave potential for the reduction of a metal complex is generally more negative than that for reduction of the corresponding simple metal ion.

In the present investigation cyclic voltammograms of complexes of [MA], [$MA_2$], [$MA_4$], [ML], [$ML_2$], [$ML_4$] and [MAL] types have been studied where M=Cu(II), Ni(II) & Zn(II),; A=Aspertic acid (Asp), 1,10 Phenanthroline(1,10 ph) and L= Oxalic Acid(ox). Cyclic voltammograms of the Cu(II), Ni(II) & Zn(II) complexes were recorded at Pt electrode in aqueous media. Typical voltammograms are given in fig-3.3.1 to 3.3.36. The voltammograms were obtained at a scan rate of 100mV/S for all the voltammetric experiments studied in this work. Solution of [MA], [$MA_2$] & [$MA_4$] were prepared by mixing of M(II) & A in 1:1,1:2 & 1:4 ratio respectively. Solution of [ML], [$ML_2$] & [$ML_4$] were prepared also by mixing of M(II) & L in 1:1,1:2 & 1:4 ratio respectively.For [MAL] the

metal ion and two ligands were mixed in the ratio 1:1:1. The pH of each solution was adjusted at the optimum position of the formation of complexes. Optimum pH for the maximum formation of complexes was obtained from computer output and species distribution curves.The voltammograms exhibits one oxidation and one reduction peak for all the complex compounds and metal perchlorate (Copper perchlorate, Nickel perchlorate and Zinc perchlorate).

In the above cases the anodic peak potential of complexes shifted towards more positive potential from the peak of the metal perchlorate indicate the formation of the complex compounds. On the other hand, the cathodic peak potential of the formed complexes shifted towards the more negative potential indicating the breakdown of the formed complexes. This is because of the slow transfer of electrons. The slowness is due to the formation of complex compounds. The value of $\Delta E^0$ [$\Delta E^0 = (E_{pa}+E_{pc})/2$] is the mean potential indicate the transition potential between the oxidation and reduction process. The voltammetric characteristics are presented in Table-3.3.1 to 3.3.3.

**Table-3.3.1:** Results of cyclic Voltammetry of copper perchlorate and their different complexes.

| Compounds | $E_{pa}$ (Anodic) mV | $E_{pc}$ (Cathodic) mV | $\Delta Ep=E_{pa}- E_{pc}$ mV | $\Delta Ep=(E_{pa}+ E_{pc})/2$ mV |
|---|---|---|---|---|
| $[Cu(ClO_4)_2]$ | 200 | -250 | 450 | 225 |
| [Cu(ox)] | 310 | -175 | 485 | 242.50 |
| $[Cu(ox)_2]$ | 240 | -280 | 520 | 260 |
| $[Cu(ox)_4]$ | 240 | -280 | 520 | 260 |
| [Cu(1,10 Ph)] | 350 | -150 | 500 | 250 |
| $[Cu(1,10\ Ph)_2]$ | 250 | -280 | 530 | 265 |
| $[Cu(1,10\ Ph)_4]$ | 250 | -280 | 530 | 265 |
| [Cu(Asp)] | 260 | -300 | 560 | 280 |
| $[Cu(Asp)_2]$ | 360 | -210 | 570 | 285 |
| $[Cu(Asp)_4]$ | 240 | -330 | 570 | 285 |
| [Cu(1,10 Ph)(ox)] | 290 | -330 | 620 | 310 |
| [Cu(Asp)(ox)] | 350 | -320 | 670 | 335 |

**Table-3.3.2:** Results of cyclic Voltammetry of Nickel perchlorate and their different complexes.

| Compounds | $E_{pa}$ (Anodic) mV | $E_{pc}$ (Cathodic) mV | $\Delta Ep=E_{pa}- E_{pc}$ mV | $\Delta Ep=(E_{pa}+ E_{pc})/2$ mV |
|---|---|---|---|---|
| $[Ni(ClO_4)_2]$ | 220 | -240 | 460 | 230 |
| [Ni(ox)] | 160 | -520 | 680 | 340 |
| $[Ni (ox)_2]$ | 370 | -330 | 700 | 350 |
| $[Ni (ox)_4]$ | 370 | -330 | 700 | 350 |
| [Ni (1,10 Ph)] | 340 | -350 | 690 | 345 |
| $[Ni (1,10 Ph)_2]$ | 380 | -320 | 700 | 350 |
| $[Ni (1,10 Ph)_4]$ | 410 | -290 | 700 | 350 |
| [Ni (Asp)] | 450 | -280 | 730 | 365 |
| $[Ni (Asp)_2]$ | 280 | -470 | 750 | 375 |
| $[Ni (Asp)_4]$ | 330 | -420 | 750 | 375 |
| [Ni (1,10 Ph)(ox)] | 380 | -390 | 770 | 385 |
| [Ni (Asp)(ox)] | 375 | -410 | 785 | 392.50 |

**Table-3.3.3:** Results of cyclic Voltammetry of Zinc perchlorate and their different complexes.

| Compounds | $E_{pa}$ (Anodic) mV | $E_{pc}$ (Cathodic) mV | $\Delta Ep=E_{pa}- E_{pc}$ mV | $\Delta Ep=(E_{pa}+ E_{pc})/2$ mV |
|---|---|---|---|---|
| $[Zn(ClO_4)_2]$ | 300 | -280 | 580 | 290 |
| [Zn (ox)] | 440 | -340 | 780 | 390 |
| $[Zn (ox)_2]$ | 400 | -390 | 790 | 395 |
| $[Zn (ox)_4]$ | 405 | -385 | 790 | 395 |
| [Zn (1,10 Ph)] | 420 | -380 | 800 | 400 |
| $[Zn (1,10 Ph)_2]$ | 500 | -420 | 920 | 460 |
| $[Zn (1,10 Ph)_4]$ | 500 | -420 | 920 | 460 |
| [Zn (Asp)] | 420 | -380 | 800 | 400 |
| $[Zn (Asp)_2]$ | 520 | -420 | 940 | 470 |
| $[Zn (Asp)_4]$ | 520 | -420 | 940 | 470 |
| [Zn (1,10 Ph)(ox)] | 510 | -440 | 950 | 475 |
| [Zn (Asp)(ox)] | 520 | -420 | 940 | 470 |

## Cyclic Voltammograms:

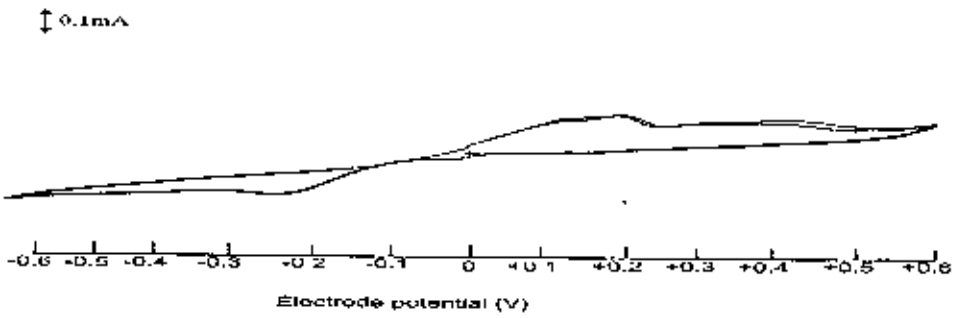



Fig. 3.3.1: Cyclic Voltammogram of $[Cu(ClO_4)_2]$ system in aqueous media at platinum electrode.

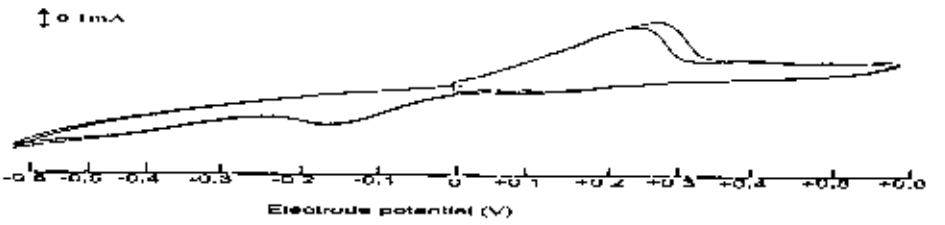



Fig. 3.3.2: Cyclic Voltammogram of [Cu (ox)] system in aqueous media at platinum electrode.

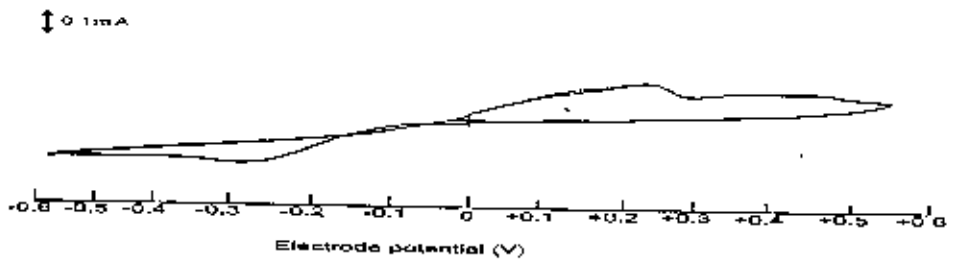



Fig. 3.3.3: Cyclic Voltammogram of [Cu $(ox)_2$] system in aqueous media at platinum electrode.

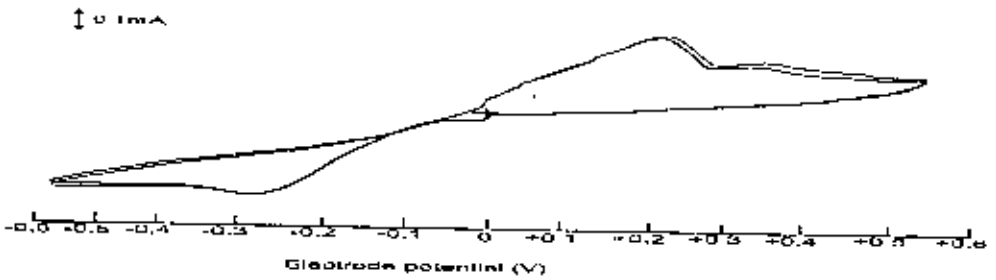



Fig. 3.3.4: Cyclic Voltammogram of [Cu $(ox)_4$] system in aqueous media at platinum electrode.

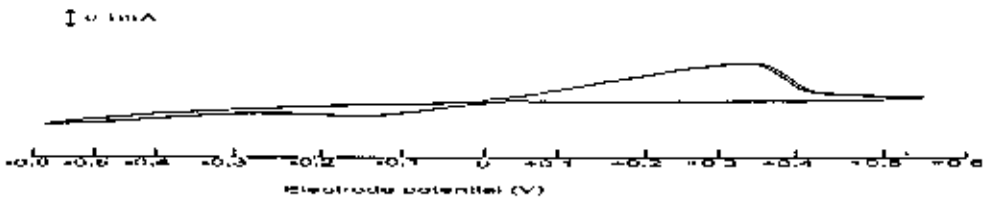
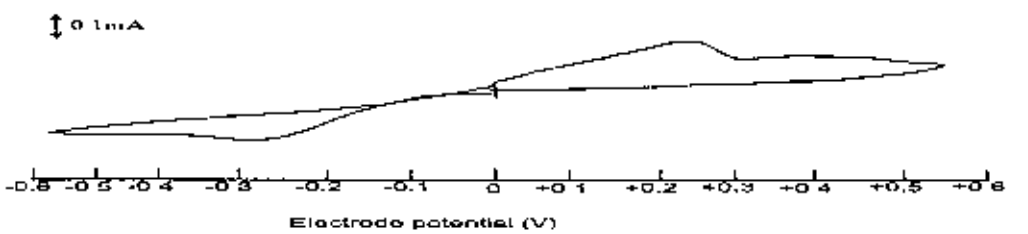


Fig. 3.3.5: Cyclic Voltammogram of [Cu (1,10 ph)] system in aqueous media at platinum electrode.






. Fig. 3.3.6: Cyclic Voltammogram of [Cu (1,10 $ph)_2$] system in aqueous media at platinum electrode.

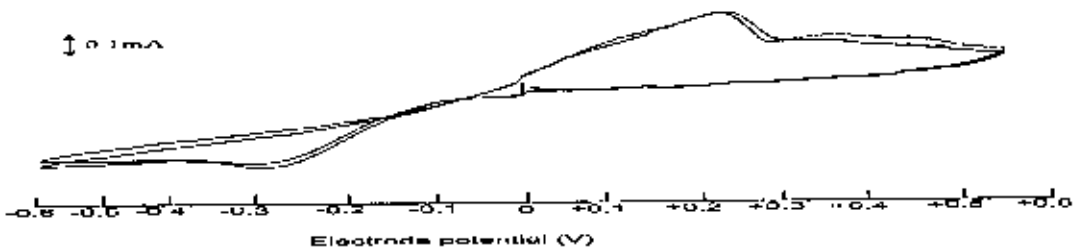



Fig. 3.3.7: Cyclic Voltammogram of [Cu (1,10 ph)$_4$] system in aqueous media at platinum electrode.

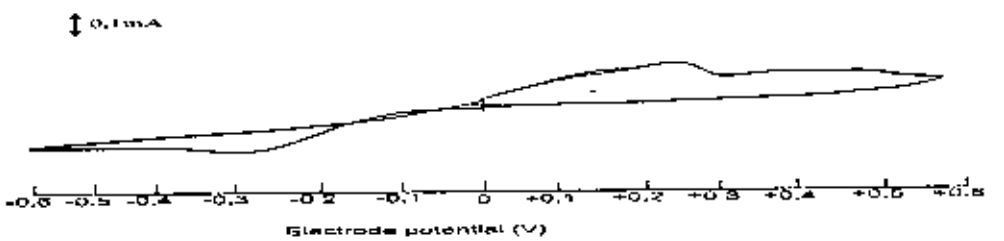



Fig. 3.3.8: Cyclic Voltammogram of [Cu (Asp)] system in aqueous media at platinum electrode.

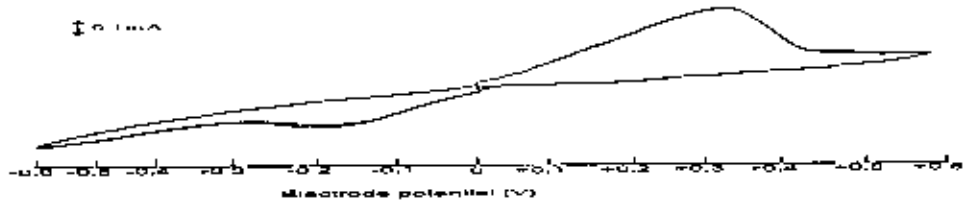


Fig. 3.3.9: Cyclic Voltammogram of [Cu $(Asp)_2$] system in aqueous media at platinum electrode.

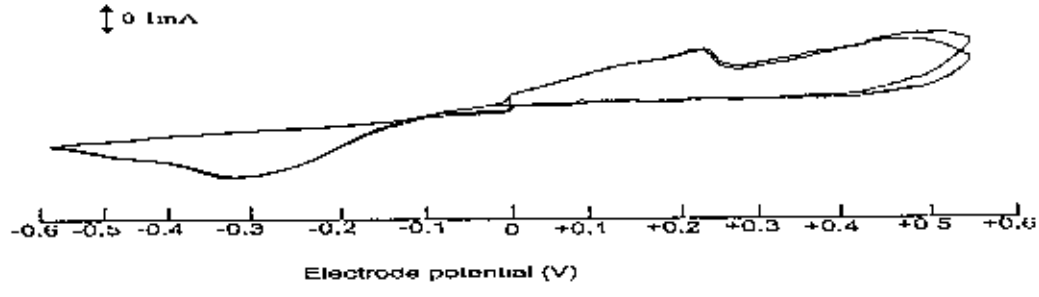



Fig. 3.3.10: Cyclic Voltammogram of [Cu $(Asp)_4$] system in aqueous media at platinum electrode

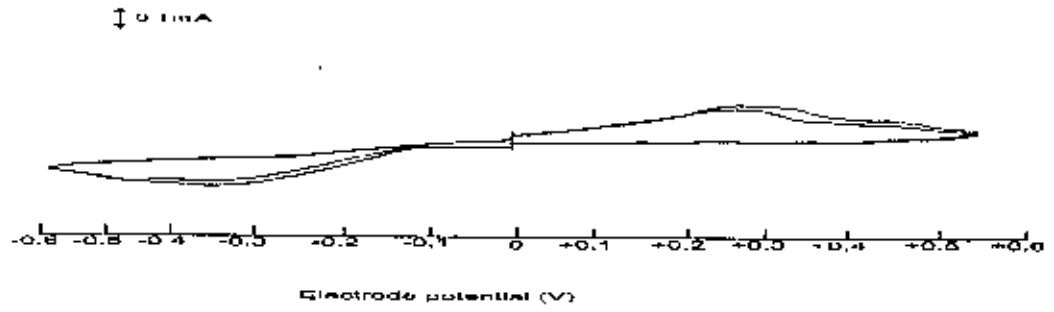



Fig. 3.3.11: Cyclic Voltammogram of [Cu (1,10 ph)(ox)] system in aqueous media at platinum electrode.

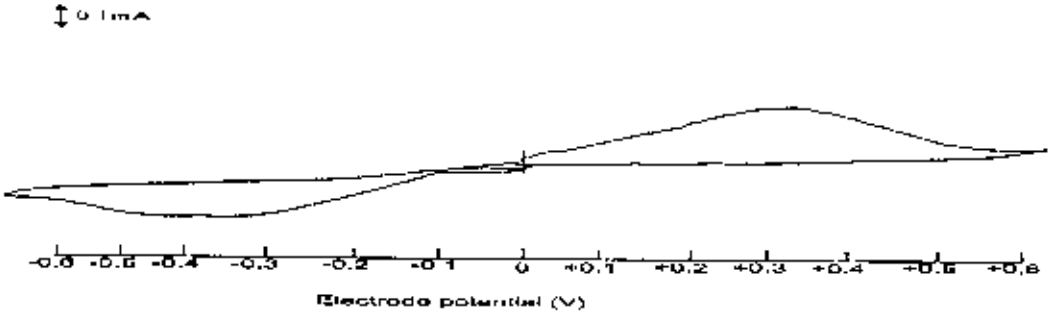



Fig. 3.3.12: Cyclic Voltammogram of [Cu (Asp)(ox)] system in aqueous media at platinum electrode.

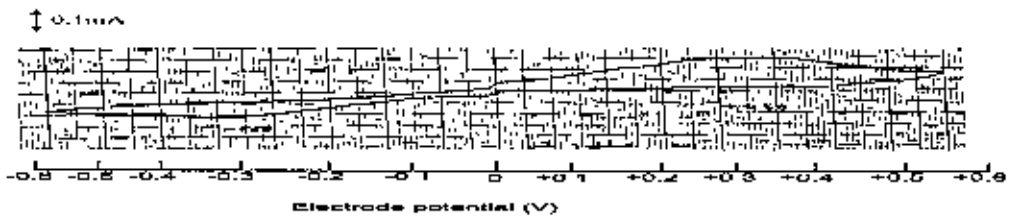



Fig. 3.3.15: Cyclic Voltammogram of [Ni $(ox)_2$] system in aqueous media at platinum electrode.

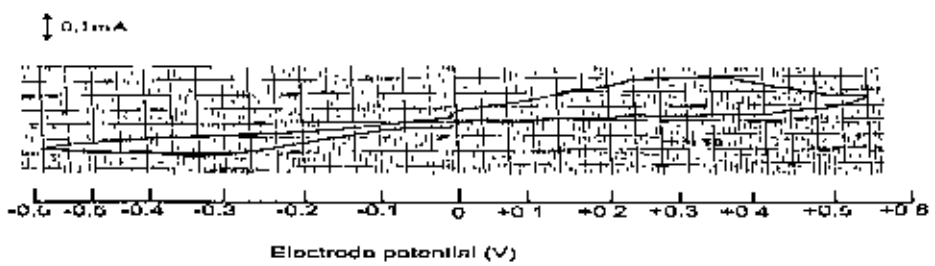



Fig. 3.3.16: Cyclic Voltammogram of [Ni $(ox)_4$] system in aqueous media at platinum electrode.

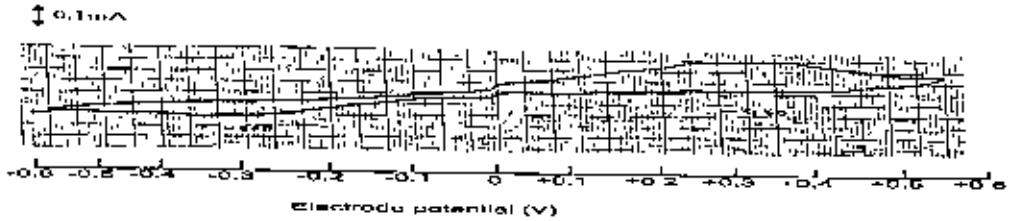



Fig. 3.3.15: Cyclic Voltammogram of [Ni $(ox)_2$] system in aqueous media at platinum electrode.

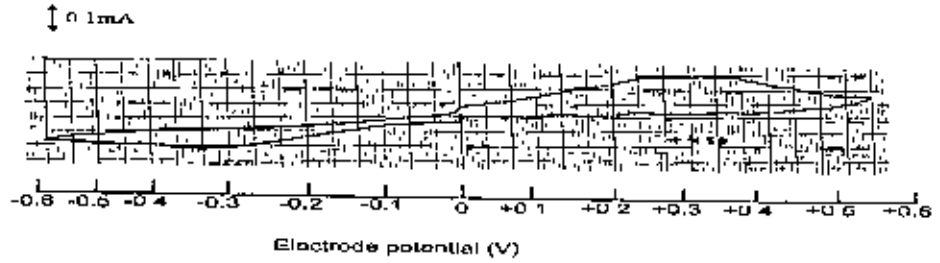



Fig. 3.3.16: Cyclic Voltammogram of [Ni $(ox)_4$] system in aqueous media at platinum electrode.

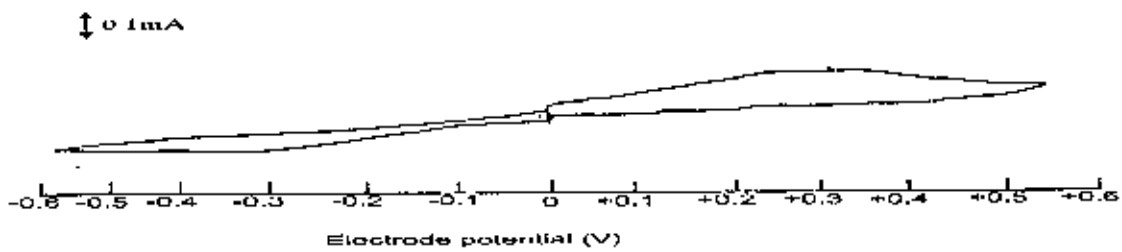



Fig. 3.3.17: Cyclic Voltammogram of [Ni (1,10 ph)] system in aqueous media at platinum electrode.

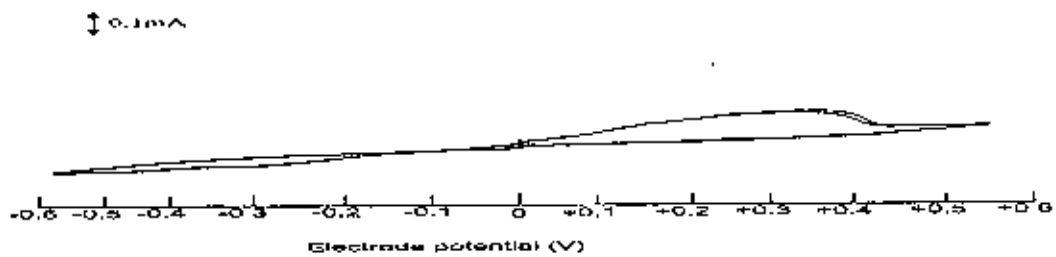



Fig. 3.3.18: Cyclic Voltammogram of [Ni (1,10 ph)$_2$] system in aqueous media at platinum electrode.

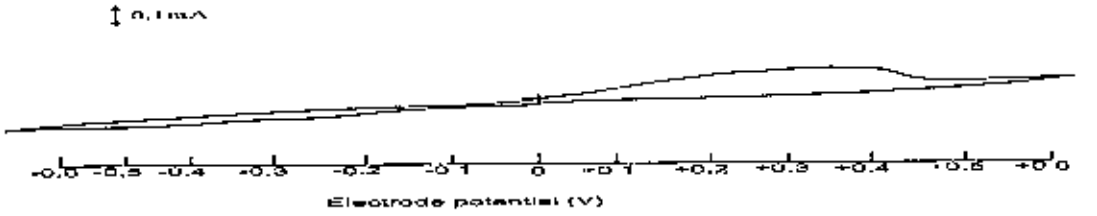



Fig. 3.3.19: Cyclic Voltammogram of [Ni (1,10 ph)$_4$] system in aqueous media at platinum electrode.

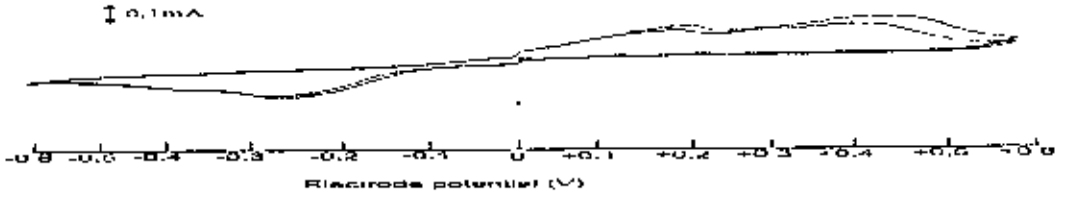



Fig. 3.3.20: Cyclic Voltammogram of [Ni (Asp)] system in aqueous media at platinum electrode.

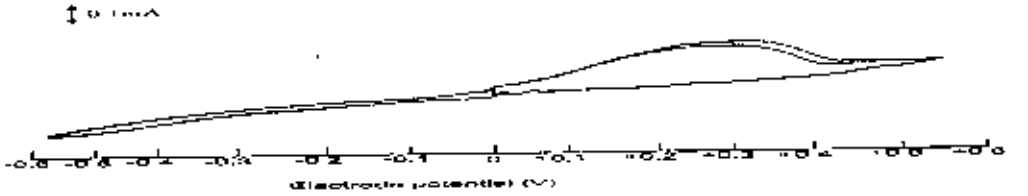


Fig. 3.3.21: Cyclic Voltammogram of [Ni $(Asp)_2$] system in aqueous media at platinum electrode.

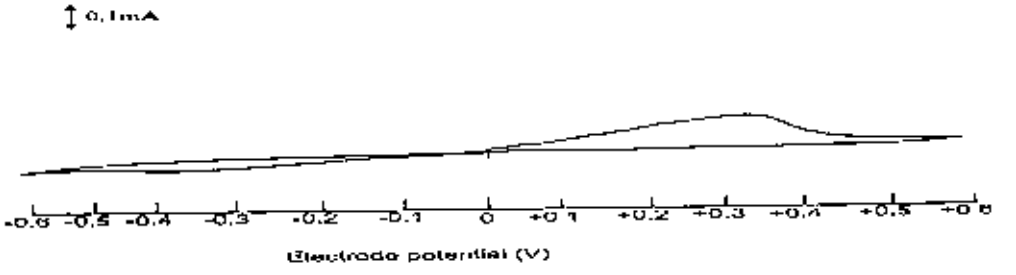



Fig. 3.3.22: Cyclic Voltammogram of [Ni $(Asp)_4$] system in aqueous media at platinum electrode.

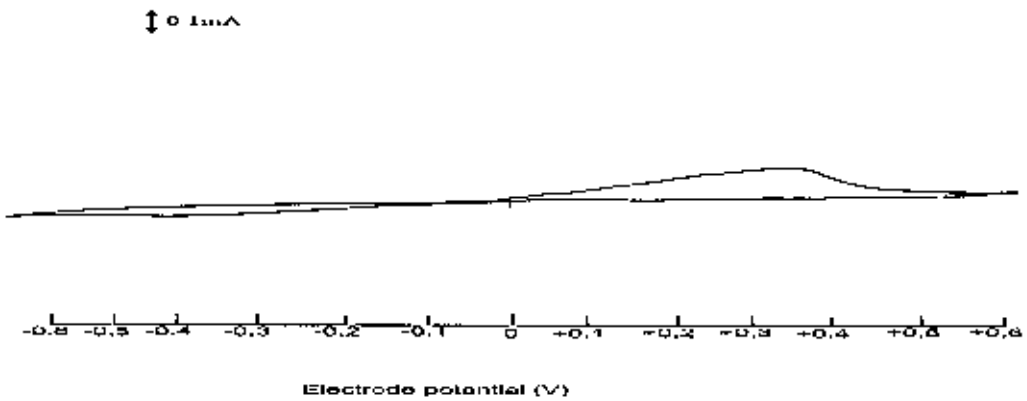



Fig. 3.3.23: Cyclic Voltammogram of [Ni (1,10 ph)(ox)] system in aqueous media at platinum electrode

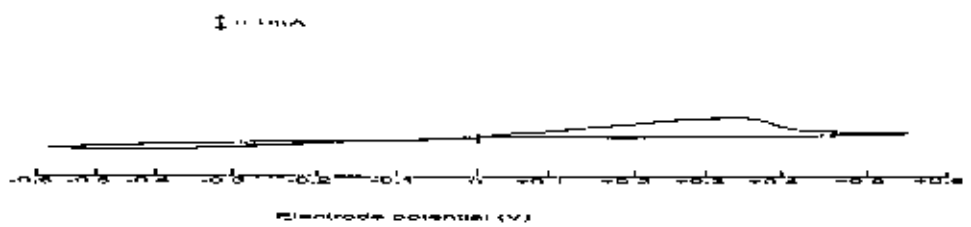


Fig. 3.3.24: Cyclic Voltammogram of [Ni (Asp)(ox)] system in aqueous media at platinum electrode.

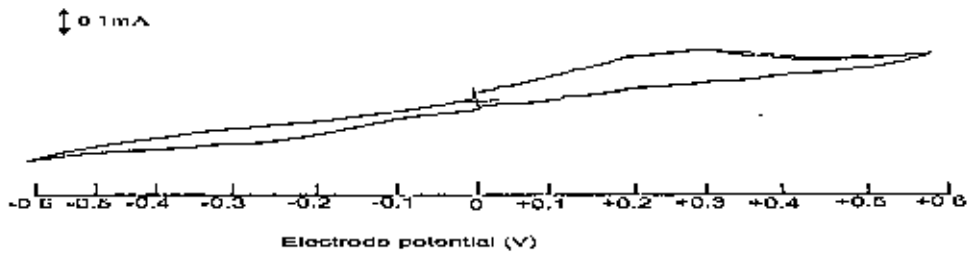



Fig. 3.3.25: Cyclic Voltammogram of [Zn $(ClO_4)_2$] system in aqueous media at platinum electrode.

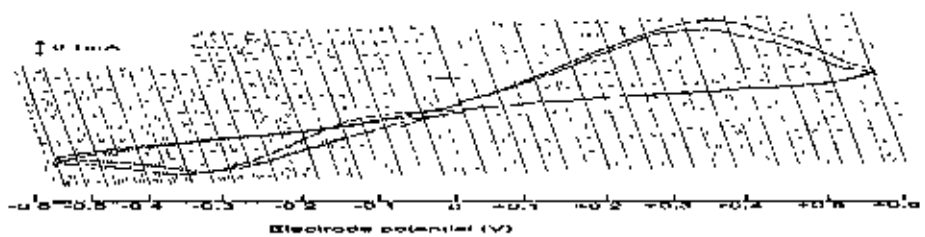


Fig. 3.3.26: Cyclic Voltammogram of [Zn (ox)] system in aqueous media at platinum electrode.

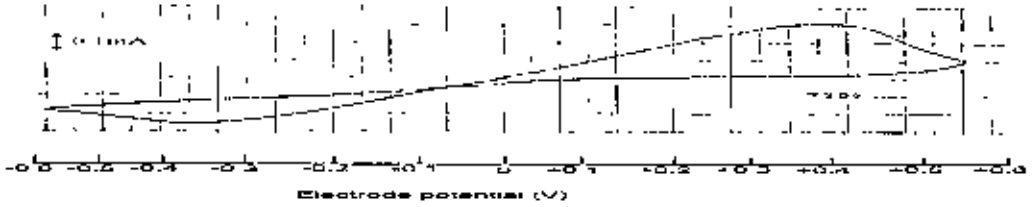


Fig. 3.3.27: Cyclic Voltammogram of [Zn $(ox)_2$] system in aqueous media at platinum electrode.

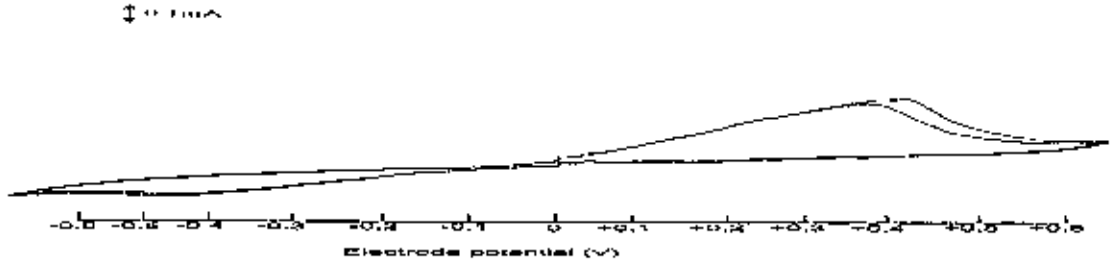


Fig. 3.3.28: Cyclic Voltammogram of [Ni $(ox)_4$] system in aqueous media at platinum electrode.

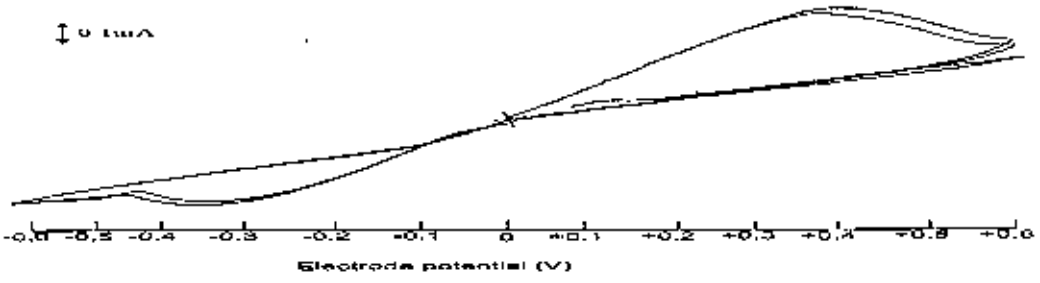


Fig. 3.3.29: Cyclic Voltammogram of [Zn (1,10 ph)] system in aqueous media at platinum electrode.

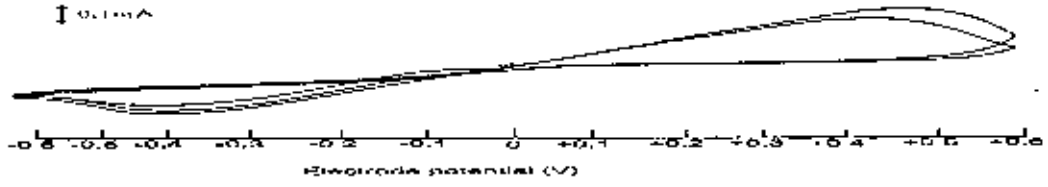


Fig. 3.3.30: Cyclic Voltammogram of [Zn (1,10 ph)$_2$] system in aqueous media at platinum electrode.

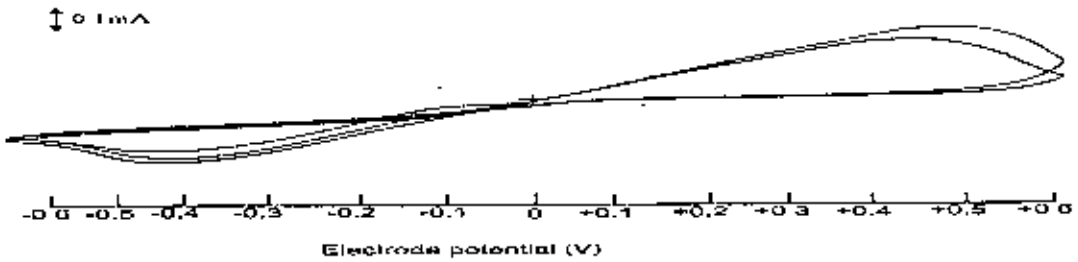



Fig. 3.3.31: Cyclic Voltammogram of [Zn (1,10 ph)$_4$] system in aqueous media at platinum electrode.

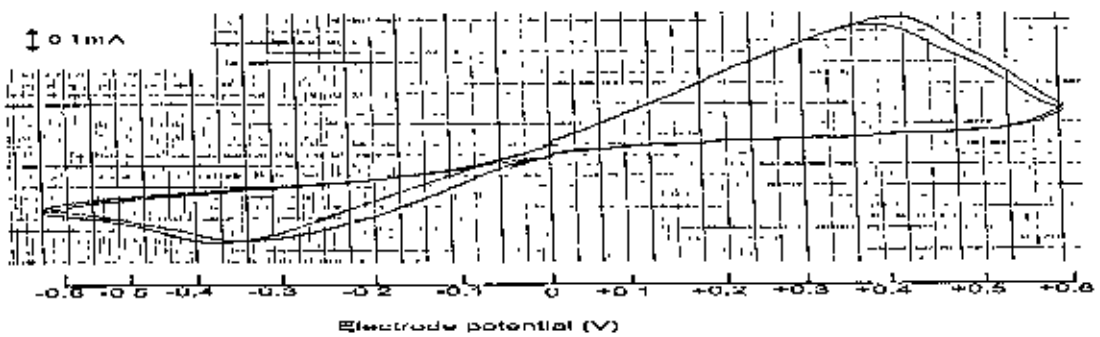



Fig. 3.3.32: Cyclic Voltammogram of [Zn (Asp)] system in aqueous media at platinum electrode.

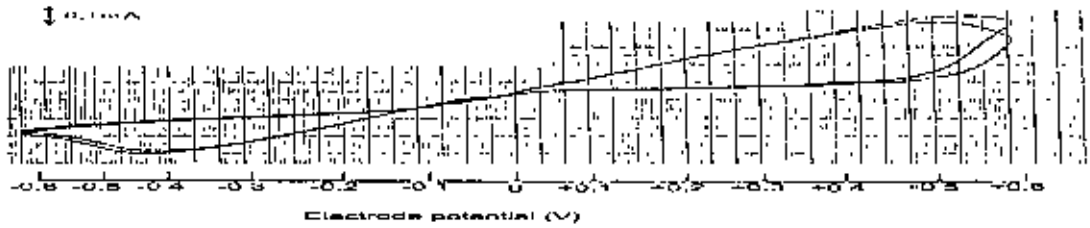


Fig. 3.3.33: Cyclic Voltammogram of [Zn $(Asp)_2$] system in aqueous media at platinum electrode.

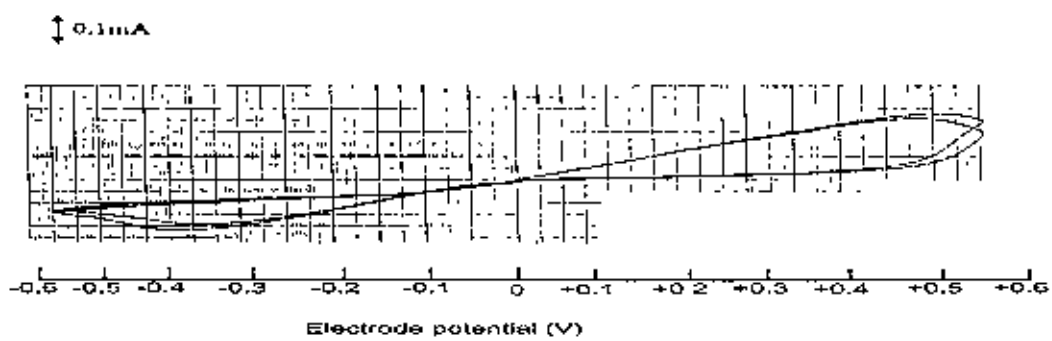



Fig. 3.3.34: Cyclic Voltammogram of [Zn $(Asp)_4$] system in aqueous media at platinum electrode.

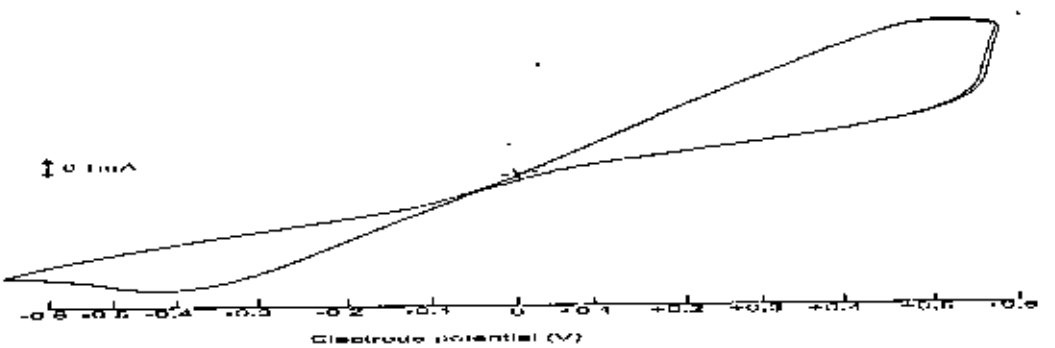


Fig. 3.3.35: Cyclic Voltammogram of [Zn (1,10 ph)(ox)] system in aqueous media at platinum electrode.

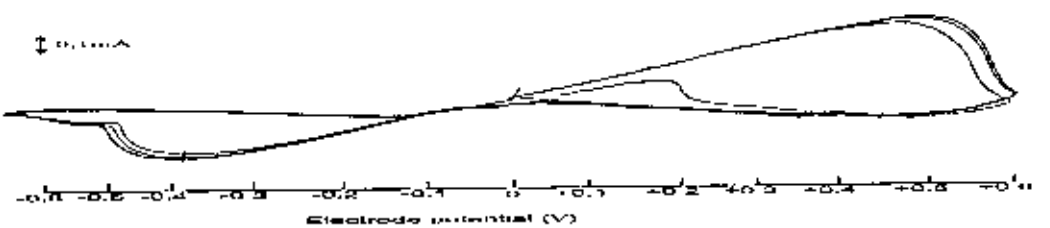


Fig. 3.3.36: Cyclic Voltammogram of [Zn (Asp)(ox)] system in aqueous media at platinum electrode.

# Result and Discussion for CV:

It is possible to explain the order of stability of ternary complexes. The anodic and cathodic potential gives us the informatiou about the relative stability of complexes. The potential is required to show anodic and cathodic peak is called anodic ($E_{pa}$) and cathodic potential ($E_{ca}$).Greater the value of cathodic and anodic potential, greater will bc the stability of the complexes. The potential difference between $E_{pa}$ and $E_{ca}$ also helps us to ascertain the relative stability of complexes. An increase in potential difference between $E_{pa}$ and $E_{ca}$ indicates the higher stability of the complex compound, i.e. the process is irreversible. In the light of the above discussion it is said that the order of stability of the ternary complexes is as follows:

[Zn(A)L]> [Ni(A)L]> [Cu(A)L]

Where, A= Aspertic Acid (Asp), 1,10 Phenanthroleane (1,10 Ph) and L = Oxalic acid(Ox).

An interesting fact that the study of the cyclic voltammograms of the complexes of [MA], [$MA_2$], [$MA_4$], [ML], [$ML_2$] and [$ML_4$] types predicts that [$MA_2$], [$MA_4$]; [$ML_2$] and [$ML_4$] complexes shows the similar $E_{pa}$ and $E_{ca}$ value in cyclic voltammograms. This indicates that the formation of complex compound is completed at [$MA_2$] and [$ML_2$]state, i.e. metal to A ratio 1:2 and metal to L ratio 1:2.

**Probable Structure of the ternary complexes:**

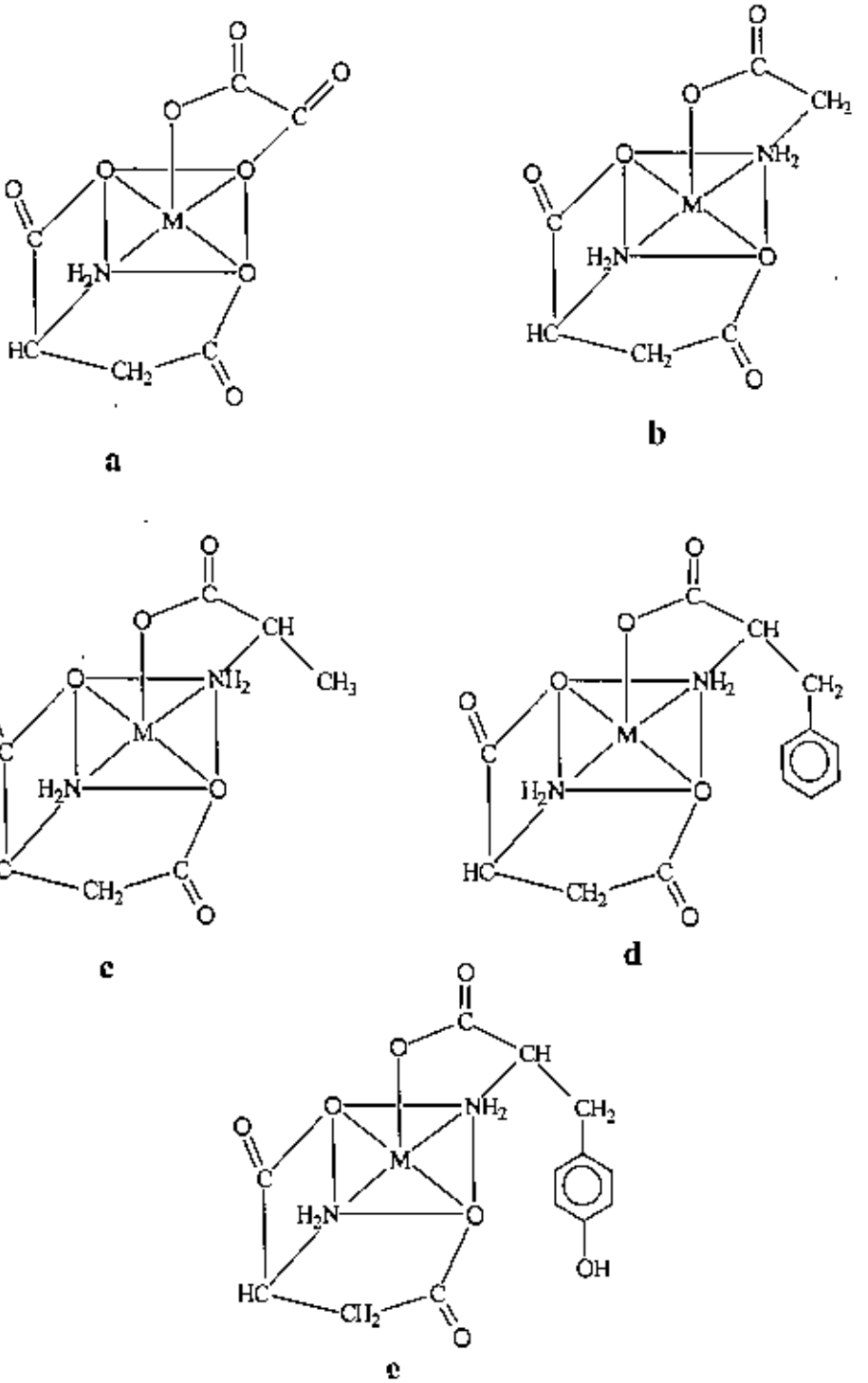
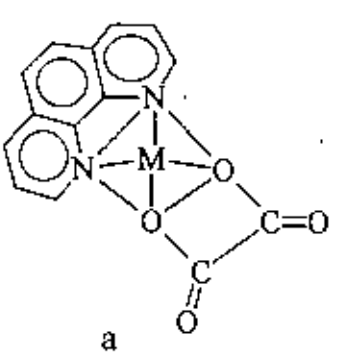
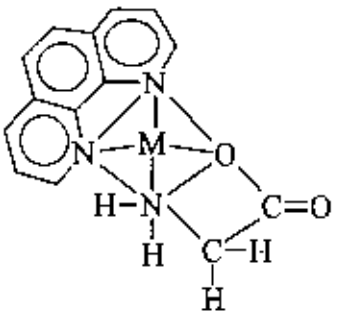


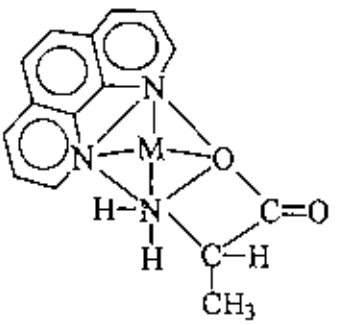

**Fig. :** Structure of **(a)** [M(Asp)(ox)] **(b)** [M(Asp)(gly)] **(c)** [M(Asp)(α-ala)] **(d)** M(Asp)(ph-ala)] **(e)** [M(Asp)(tyr)] complexes, where M= Cu(II), Ni(II).



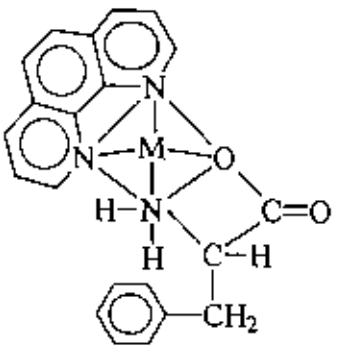
a



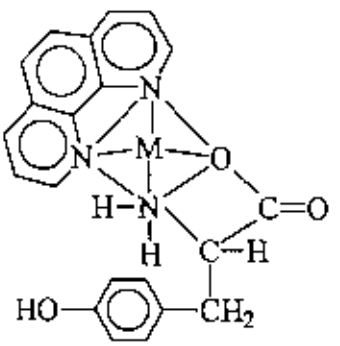
b



c



d



e

**Fig.** :Structure of **(a)** [M(1,10 Ph)(Ox)] **(b)** [M(1,10 Ph)(gly)] **(c)** [M(1,10 Ph)(α-ala)] **(d)** [M(1,10 Ph)(phy-ala)] **(e)** [M(1,10 Ph)(tyr)] complexes. where M= Zn(II).

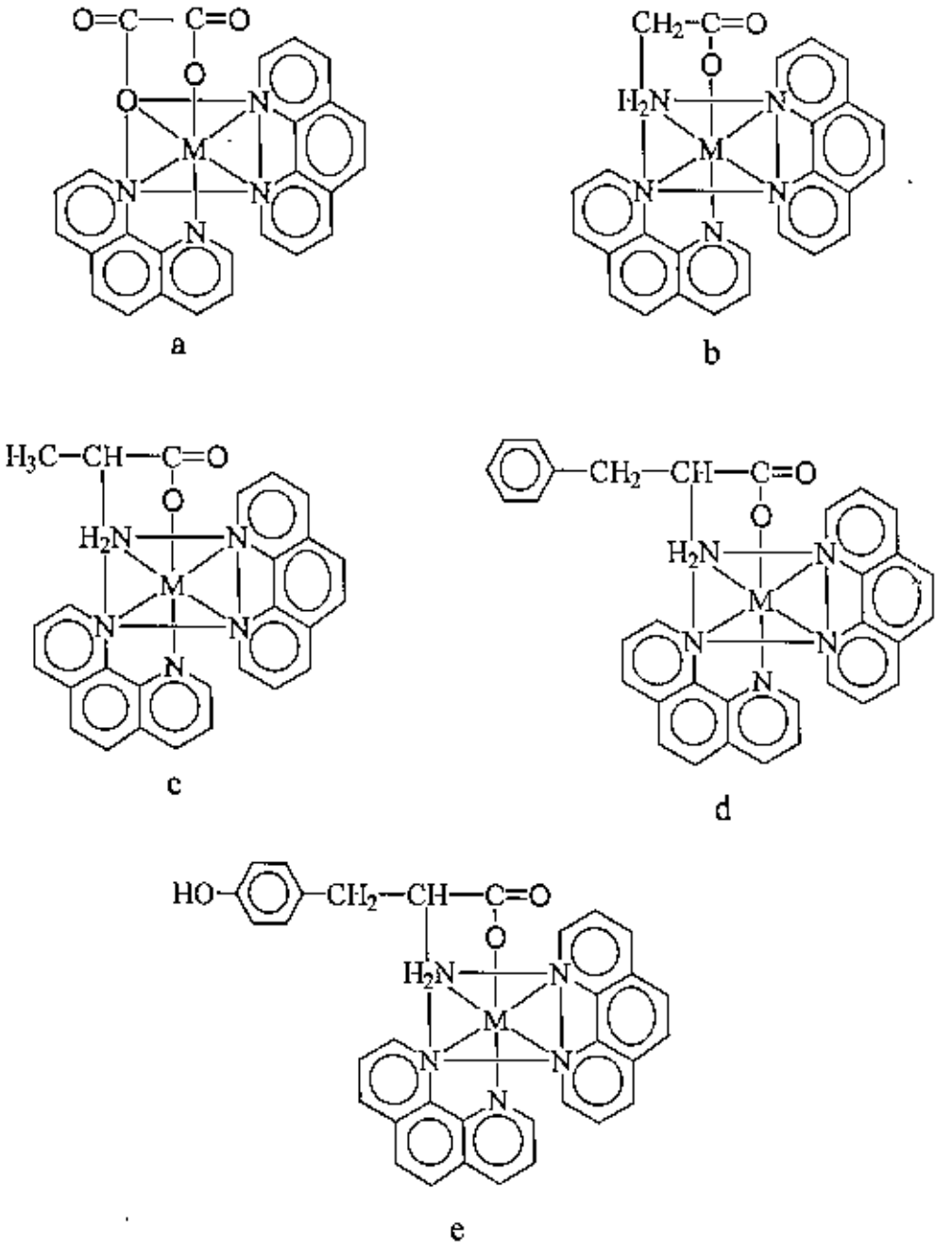



**Fig. :** Structure of **(a)** [M(1,10 $Ph)_2$(Ox)] **(b)** [M(1,10 $Ph)_2$(gly)] **(c)** [M(1,10 Ph)(α-ala)] **(d)** [M(1,10 $Ph)_2$(phy-ala)] (e) [M(1,10 $Ph)_2$(tyr)] complexes.
where M= Cu(II) and Ni(II).

# CHAPTER-4
# SUMMARY

## Summary

Ternary complexes play an important role in biological processes, as exemplified by many instances in which enzymes are known to be activated by metal ions. Such complexes have been implicated in the storage and transport of active substances through membranes. Many mixed ligand complexes are finding applications in the microelectronic indnstry, chemical vapour deposition of metals and as drugs. Ternary complexes have been used in the analysis of semi-conductor. Many biochemical are potential chelating ligands and several drugs have coordinating sites. This allows possible formation of complexes with the transition metal ions involved with life processes.

Study of ternary complexes is also important from fundamental chemistry point of view. The effect of the structnral features of the ligands on the stability of the ternary complexes and corresponding binary complexes is of great fundamental significance. Hence it is interesting to study the various factors which affect the stability of the ternary complex.

The stability of ternary complexes have been determined in terms of $\Delta\log K = \log K^{MA}_{MAL} - \log K^{M}_{ML}$ value, i.e. the difference in the tendencies of L to bind with the free metal ion and the metal ion already bound to another ligand. From statistical consideration ΔlogK is expected to be negative. Different type of ternary complexes of [MAL] type have been studids. Where M= Cu(II), Ni(II) and Zn(II) ;A=Aspertic acid (Asp), 1,10 Phenanthroline (1,10 Ph); L=ox,en,gly,α-ala, ph-ala, tyr.

The stability constants of ternary complex were determined by carrying out pH-metric titration in aqueous medium. The protonation constant, Binary constant and ternary constant have been determined potentiometrically nsing SCOGS compnter program. The proton-ligand formation constant and formation constant of binary complexes were first refined. These values were used as fixed parameters for the refinement of the formation constant of the ternary complexes.

It is also reported that for the ternary complexes of Cu(II), Δlog K values is more negative than corresponding Ni(II) ternary complexes. This is due to the absence of Jahn-Teller distortion in Ni (II) complexes. It is also observed that the Δlog K value is more negative with increasing the charge on the ligand L. This is because of the electrostatic repulsion between the dianionic tridentate ligand Aspertic acid (Asp) and the incoming charge of the second ligand.

It is observed that Δlog K value is positive when phenylalanine and tyrosine is coordinated with central metal ion. This is due to the intramolecular interligand interaction between non-coordinated side group. Another reason of extra stabilization of tyrosine is due to intramolecular interligand hydrogen bonding and stacking interation of phenylalanine and tyrosine with metal ion. Additional stabilization in the complexs can occur due to the noncovalent hydrophobic interaction between non-coordinated side group phenyl and hydroxyphenyl of phenylalanine and tyrosine respectivelr with A(Asp, 1,10 ph).

The greater stability of Zn(II) complex as compared to those of complexes of Cu(II) and Ni(II) is due to the fact that the complex of

Zn(II) prefer tetrahedral geometry in which ligand-ligand repulsion is minimum. More over larger size of Zn(II) metal is favourable for the accommodation of ligand more easily than Cu(II) and Ni(II).

Hence, in the present investigation, the orders of the stability of the ternary complexes are as follows-

$$[Zn(A)(L)] > [Ni(A)(L)] > [Cu(A)(L)]$$

The stability of ternary complexes has been confirmed by CV (Cyclic Voltammogram).

# *CHAPTER-5*
# *REFERENCE*

## REFERENCES


1. G. H. Bell, J. N. Davidson, *Text Book of Physiology and Biochemistry*, E. S. Livingstone, Edinburgh, 39, (1994).
2. R.B.Martin and R.Parados, J.Inor. Nucl, Chem 9,1238,1970.
3. Baran E J Biochemistry,65 (2000) 789.
4. Warad D U,Satish C D & Chandrasekhar S.Bajgus, Proc Indian Acad Sci, 112 (2000)400.
5. Dugas H,Bio-Organic Chemistry (Springer, New York) 1995,407.
6. Shin H K Chi K.M, Farkas J, Smith M J H, Kodas T T & Duesler E N, Inorg Chem, 31(1992)424.
7. Sigel H, " Metal iou in biological System" Mareel dekker,(2) 1973, (13) 1981, J Indian Chem. Soc. Vol-72, No.-1, November-1995.
8. K. Nakamoto, "IR and Ramann Spectra of Inorganic and Co-ordination Compounds" John Willy and sou, New York, 3rd edition,1978.
9. Charles C. Thoms, "An Introduction to Bio-Inorganic Chemistry". D.R.Williams, Ed.Spring field,(iii) 1976.
10. D. D. Perrin and R.P. Agarwal in "Metal ions in Biological system". H.Sigel,Ed.New York, Vol-2,p-167,1673.
11. R.P. Martin, M.M. Petit- Ramel and J.P. Scharff, "Metal ions in Biological system". H.Sigel, Ed. New York, Vol-2,1973.
12. H. Sigel D.B.MC Cormick, Ace. Chem. Res, 3,201,1970.
13. H. Sigel, Chimia, 21, 489, 1967.
14. Mercel Dekker, "Metal ions in Biological system". H.Sigel, Ed. New York, Vol-2, 63, 1973.
15. H Sigel, Angew, 87, 391,1975.

16. A.S. Mildvan and C.M. Grisham, Struct, Bopnding,1,20,1974.
17. M.R.Ullah, Ph.D. thesis "Solution and solid state studies of some ternary complexes" page-2, (1990).
18. A.E. Mertell, "Metal ions in Biological system" Elsevier Ed. Amsterdam, Vol.-2,1973.
19. Marcel Dekker, "Metal ions in Biological system" H.Sigel, Ed. New York, Vol-2, 1973.
20. H. Sigel, B.E. Fischer and B. Prij's *J. Am. Chem. Soc.*, **99**, (1977).
21. H.Sigel, Inor. Chem. 19,1411,1980.
22. B. C. Malmstron and R. Rosenberg. And Enzymol 21,121,1959.
23. M. Dixon and E.C. Webb, Enzyme,Longmans Green Ed., London, 1964.
24. D.L. Leussing, J. Am. Chem. Soc. 86,4846,1964.
25. B.L.Vallee and W.E.C. Waker, "Protein Cosumption, structure and function ". Neurath Ed. Acedemic Press, New York, Vol.-5,1966.
26. D.D. Perrin, Soumen Kemistilehti, 42,205,1969.
27. P.S. Haltmar D.D. Perrin and A.E. Watt. Biochem, J. 121,549,1971.
28. R.F. Pasternack and H. Sigel. J.Am.Chem.Soc.92,6146,1970.
29. R.F. Pasternack, P. R. Huber and H. Sigel, Inor.Chem 11,420,1972.
30. D.N. Hauge, S.R. Martin and M.S. Zetter, J.Chem. Soc. Faraday Trans, 68,37,1972.
31. D.N. Hauge, S.R. Martin, J. Chem. Soc. Dalton Trans.,254,1974.
32. P.K. Bhattacharya, J. Scient. Int. Res.( India),40,382,1981.
33. Y. Marcus and I. Eleizer, Co-ordinatiou Chemistry. Rev.4,273,1969.
34. R.Dewitt and J.I. Watters, J.Am. Chem.Soc.,76,3810,1954.
35. S.Kida, Bull. Chem..Soc.Japan, 29,805,1956.

36. D. R. Williams. Ed., *An Introduction to Bio-Inorganic Chemistry*, Charles C. Thomas, Springfield, (iii), (1976).

37. H. Sigel, *Metal Ions in Biological Systems*, Marcel Dekker Inc, New York, 2,167, (1973).

38. R. P. Martin, M. M. Petit-Ramel and J. P. Scharft, *Mixed ligand metal ion complexes of peptides in metal ions in biological systems*, Marcel Dekker Inc., New York), **2,** 1, (1973).

39. H. Sigel and D. B. Mc Conrmick. *Acc. Chem. Res.* **3**, 201, (1970).

40. H. Sigel, *Chimia*, **21**, 489, (1967).

41. A. S. Mildvan and M. Cohn, *adv. Enzymol.*, **33**, 1, (1970).

42. J. M. wood, *Naturwissens chaften*, **62**, 357, (1975).

43. R. F. Pasternack and H. Sigel *J. Am. Chem. Soc.*, **92**, 6146, (1970).

44. G. L. Eichhorn (Ed), *Inorganic Biochemisty,* Elsevier, Amsterdam, **2,** 1191-1243, (1973).

45. R. B. Martin, Y. M. Mariam, *Metal Ions Biol. Syst.*, **8**, 57, (1979).

46. K. Aoki, *Metal Ions Biol. Syst.*, **32**, 91, (1996).

47. P. K. Bhattacharya, *J. Scient. Ind. Res.* (India), **40,** 382, (1981).

48. Y. Marcus and I. Eleizer, *Coordination Chem. Rev.*,**4**, 273, (1969).

49. R.B. Martin and R. Parados, J. Inog. Nucl. Chem., 36,1665,1974.

50. R. Grisses and H. Sigel, Inorg. Chem. 9,1238,1970.

51. H. Sigel, K. Becker and D.B. MC Cormick, Biochem. Biophys. Acta, 148,655,1967.

52. L. G. Sillen and A. E. Martell: *Stability Constants of Metal Ion Complexes.* Spec. Publ. No, 17, The chemical Society of London, (1964); Suppl. No.1, London, (1971).

53. R. F. Pasternack and H. Huber and H. Sigel, *Inorg. Chem.*, **11**, 420, (1972).

54. I.M. Procter, B.J. Hathaway and P.G. Hodgson, J. Inog. Nucl. Chem.,34,3689,1972.

55. H Sigel, R. Caraco and B. Prijs, Inog. Chem. 13,462,1974.

56. A.E. Martell, R.M. smith, "Critical Stability Constant" Vol. (1-3), 1977, Plenum Press, New York.

57. A Odain and O. Yamauchi, Inorg. Chem. Acta. 93,13,1984.

58. A.I. Vogal, " A text book of Quantitative Inorganic Analysis" Longmans Green, London,204,1962.

59. V. R. Williums and H. D. Williams, *Basic physical Chemistry for the life Science* Freeman and Co. Sanfransisco, 185, (1959).

60. R. T. Morrison and R. N. Boyd, *Organic Chemistry*, Prentice Hall of India Pvt. Ltd. New Delhi, 6$^{th}$ed., 1208, (1992).

61. W. A. Holder, P. E. Spith, E. Hill, R. L. Lehman, *Principles of Bio Chemistry*, McGraw Hill, Kagakuska Ltd. 6$^{th}$ed., 87, (1959).

62. A. H. White, E. L. Smith, *Principles of Bio Chemistry* , International Student, 3$^{th}$ed., 189, (1964).

63. A. C. Beseme, F. I Shatgh, *Ann, Pharm* **45(6)**, 533-7(Fr).

64. H. Sigel, B.E. Fischer and B. Prij's J, Am. Chem. Soc..1977,99,4489.

65. A.E. Martell," Metal ions in Biological System",Elsevier, Amsterdam, Vol. 2, 1973.

66. H. Sigel' " Metal ions in Biological System," Marcel Dekker, New York, Vol. 2, 1973.

67. H. Sigel, Inorg.Chem, 1980,19,1411.

68. H. Sigel and D.B. Mc Cormick, Acc, Chem, Res, 1970,3201.

69. (a) A.S. Mildvan and M. Cohn, adv. Enzymol,1970,33,1.
(b)A.S. Mildvan and C.M. Grisham, struct, Bonding; 1974,20,1.

70. B.C. Malmstrong and R. Rosenberg, ad. Enzymol,1959,21,121.
71. M.Dixon and E.C. Webb, Enzymes, Longmans green, London,1964.
72. D.L. Leussiong, J. Ann. Chem.. Soc. 1964,86,4846.
73. B.L. Vallee and W.E.C. Wacker,"Proteins comsumption, structure and function," Ed. By Neurath, academic Press, New York, Vol.5,1966.
74. D.D. Perrin, Soumen Remistilehti, 1969,42,205.
75. P.S. Hallman, D.D. Perrin and A.E. Watt, Biochemistry. J. 1971,121,549.
76. D.R. Williams, Ed, "An Introduction to Biochemistry," Charles C. Thomas springfirld, (iii),1976.
77. D.D.Perrin and R.P. Agarwal in " Metal ions in Biochemical System,"H.Sigel, Ed. Marcel Dekker, New York, Vol.2,1973,P-167.
78. R.F.Pasternack and H. Sigel. J.Am. Chem.Soc.92,6146,1970.
79. R.F. Pasternack, P.R. Haber and H. Sigel, inorg. Chem. 1972,11,420.
80. D.N. Hague, S.R. Martin and M.S. Zetter, J. Chem. Soc., Faraday Trans., 1972,68,37.
81. D.N. Hauge and S.R. Martin, J. Chem. Soc. Dalton Trans, 1974,254.
82. R.P.Martin, M.M. Petit- Rauel and J.P. Scharff in ref.2, P-1.
83. H. Sigel, Ed, " Metal ions in Biochemical System,"Marcel Dekker, New York, Vol.2,1973,P-63.
84. M.M.Taquikhan and A.E. Martell, J. Phys. Chem..,1962,66,10.
85. A.E.Martell," " Metal ions in Biochemical System," Elservic Amsterdam, Vol.2,1978.
86. Y.Mocus and J. Eleizer, Co- ordination chem.. Rev.,1969,4,273.

87. R. Dewitt and J.I. Watters, J Am. Chem. Soc. 1954,76,9810.

88. S. Kida, Bull, Chem. Soc. Japan, 1956,29,805.

89. R. Griesser and H. Sigel, Inorg. Chem. 1970,9,1237.

90. H. Sigal, Vol. 13,1981 of Ref. 1.

91. F.A. Walker, H. Sigel and D.B. Mc-cormic, Inorg. Chem. 1972,11,2756.

92. O. Yamahchi and A. Odani, J. Am. Chem. Soc.,1981,103,391.

93. P.C. Parikh and P.K. Bhattacharya, Bull, Acad Polon. Sci.,1975,23,289.

94. W.E. Bennett, J. Am. Chem. Soc., 1957,79,1290.

95. H. Sigel, A.D. Zuberbahler and H. Gampp, Inorg. Chem., 1982,21,1190.

96. W.E. Hatfield and T.S. Piper, Inorg. Chem. 1964,3,841.

97. P.C. Parikh and P.K. Bhattacharya, Indian J. Chem., 1974,12,402.

98. M.V. Chidambaram and P.K. Bhattacharya, J. Inorg. Nucl. Chem. 1970,32,3271.

99. P.J. Patel, V.K. Patel and P.K. Bhattacharya and J. Chem. 1982,21,590.

100. H. Sigel in Proc, 3rd Symp. Cood. Chem. Ed. M.T. Beck Vol. 1,1970,P-191,Vol.-II, 1971,P-241.

101. H.Sigel, R. Griesser and B. Prijs, Z. Natur forsch, 1972,27b,353.

102. P.R. Hubber, R. Griesser and H.Sigel, Inorg. J, Chem., 1971,10,945.

103. H.Sigel, H. Tribolet and K.H. Scheller Inorg. Chem. Acta.,1985,100,151.

104. R. Frieden, J. Chem. Ed.1973,57,754.

105. A. Odari and O. Yamauchi, Inorg. Chem. Acta. 1984,93,13.

106. C.F. Naumann, B. Priji and H. Sigel, Eur. J. Biochem.1974,41,209.

107. M.M. Taquikhan and A.E. Martell, J. Am. Chem. Soc. 1967,89,5589,1962,84,3037.

108. M.M. Taquikhan and P.R. Reddy, J. Inorg. Nucl. Chem..1975,37,771.

109. H.Sigel and C.F. Naumann, J. Am. Chem. Soc., 1974,96,2750.

110. P. Orioli, R. Cini, D. Donati and S. Managani, J. Am. Soc., 1981,103,4446.

111. P.K. Bhattacharya, U.V. chudasama and V.K. Patel, J. Chem. Soc. Dalton. Tanas.1983,1901.

112. M. V. Chidambaram and P. K. Bhattacharya, *Acta. Chem. Hung.*, **75**, 123, (1973).

113. P. K. Bhattacharya, C. R. Jejurkar and I. P. Mavani, *Ind. J. Chem.*, **10**, 742, (1972).

114. P. K. Bhattacharya and J. D. Joshi, *J. Indian Chem. Soc.*, **50**, 344, (1973).

115. H. Sigel, A. D. zuberbuhler and H. Gampp, *Inorg. Chem.*, **21**, 1190, (1982).

116. Y. J. Israeli, *Can. J. Chem.*, **41**, 2710, (1963).

117. J. P. Tandon and G. Sharma, *J. Inorg. Nuclear Chem.*, **32**, 1273, (1970).

118. J. I. Watters and R. Dawitt, *J. Am. Chem. Soc.*, **82**, 1333, (1960).

119. O. Yamauchi and A. Odani. *J. Am. Chem. Soc.*, **103**, 391, (1981).

120. P. K. Bhattacharya P. J. Patel and V. K. Patel, *Inorg,. Chem.*, **21**, 3163, (1982).

121. P. K. Bhattacharya and K. Gopal Krishnan, *J. Chem. Soc.* Dalton Trans, 543, (1981).

122. K. P. K. Bhattacharya and Gopal Krishnan, *J. Chem. Soc.* Dalton Trans., 353, (1982).

123. H. Sigel, R. Caraco and B. Prijs, *Inorg, Chem.*, **13**, 462, (1974).

124. P. C. Parikh and P. K. Bhattacharya, *Indian. J. Chem.*, **12**, 402, (1974).

125. M. V. Chidambaram and P. K. Bhattacharya, *J. Inorg. Nucl. Chem.*, **2**, 3271, (1970).

126. P. J. Patel, V. K. Patel and P. K. Bhattacharya, *Ind. J. Chem.*, **21A**, 590, (1982).

127. H. Sigel in Proc. 3rd *Symp, Coord. Chem.* Ed. M. T. Beck Vol-1, 191, (1970), Vol-II, 241, (1971).

128. H. Sigel and D. B. McCormick, *Accounts Chem, Res.*, **3**, 210, (1970).

129. H. Sigel, K. Becker and D. B. Mc Cormick, *Biochem, Biophys. Acta*, **148**, 655, (1967).

130. H. Sigel, R. Griesser and B. Prijs, *Z. Naturforsch*, **27(b)**, 353, (1972).

131. P. R. Huber, R. Griesser and H. Sigel, *Inorg. Chem.* 1971, Vol-10, p-945.

132. B. E. Fisher and H. Sigel, *Inorg. Chem.*, **18**, 425, (1979).

133. P. K. Bhattacharya and V. K. patel, *Proc. Indian. Acad. Sci. (Chem. Sci.),* **94(3),** (1985).

134. P. K. Bhattacharya, N. A. Emanuel and N. D. Kulkarni, *Proc. Indian. Acad. Sci. (Chem. Sci.)*, **97(5,6),** 529, (1986).

135. H. Sigel, P. R. Huber, R. Griesser and B. Prijs. *Inorg. Chem*, **12**, 1198, (1973).

136. C. F. Naumann, B. Prujs and H. Sigel, *Fur. J. Biochem.*, **41**, 209, (1974).

137. M. S. Zetter, H. W. Dodgen and J. P. Hunt, Biochemistry, 1973, Vol-12, p-778.

138. H. Sigel, *Eur. J. Biochem.*, **3**, 530, (1968).

139. J. B. Orenberg. B. E. Fischer and H. Sigel, *J. Inorg. Nucl. Chem.*, **48**, 785, (1980).

140. P. K. Bhattacharya and V. Manjula, J. Chem. Soc. Dalton Trans., 1980, p-567.

141. A. Gergely, I. Sovago, I. Nagypal and R. Kiraly, *Inorg. Chem, Acta.*, **6**, 435, (1972).

142. H. Sigel, H. Tribolet and K. H. Scheller, *Inorg. Chem. Acta*, **100**, (1985).

143. M. M. Taqui Khan and A. E. Martell, *J. Am. Chem. Soc.*, **66**, 10, (1962).

144. M. M. Taqui Khan and A. E. Martell. *J. Am. Chem, Soc.*, **89**, 5589, (1967).

145. M. M. Taqui Khan and A. E. Martell. J. Am. Chem, Soc. 1962, Vol-84, p-3037.

146. M. M. Taqui Khan and P. R. Reddy, *J. Inorg. Nucl, Chem.*, **37**, 771, (1975).

147. M. M. Taqui Khan and P. R. Reddy, *J. Inorg. Nucl, Chem.*, **35**, 2183, (1973).

148. M. M. Taqui Khan and P. R. Reddy, *J. Inorg. Nucl, Chem.*, **38**, 1234, (1976).

149. A. Oriodi, M. M. Taqui Khan and A. E. Martell, *J. Am. Chem, Soc.*, **88**, 668, (1966).

150. H. Sigel and C. F. Naumann, *J. Am. Chem. Soc.* **96**, 2750, (1974).

151. L. E. Colcaeio, Carols, M. Vickie, R. Antonis, *J. Chem. Soc.*, Dalton Trans, **17**, 2923,(1999).

152. M. Barandika, C. Roberto, L. Lezama, M.Karmele, *J. Chem. Soc.* Dalton Trans, **17**, 2971, (1999).

153. L. K. Thompson, S. S. Tandon, M.E, Manuel and J. N. Bridson, *Inorg. Chem.*, **33**, 5555, (1994).

154. L. K. Thompson and S. S. Tandon and M. E. Mannel, *Inorg. Chem.*, **34**, 2356, (1995).

155. L. K. Thompson and S. S. Tandon, *Comments Inorg. Chem.*, **18**, 125, (1996).

156. O. Khan, A. Grand, M. A. Aebersold, B. Gillon, O. Plantevin, L. Parfi and E. Lelievre-Berna, *J. Am. Chem. Soc.*, **120**, 5238, (1998).

157. T. Murakami, Y. Ishikawa, *Inorg. Chem. Acta*, **244(1)**, 51, (1996).

158. A. Escuer, M. Font-Bardia, E. Penalba and Vicente. *J. Chem. Soc.* Dalton Trans, 3115, (1999).

159. H. Hoffinann and E. Yeager, Ber. Bunsenges, *Phys. Chem.* 74, 641, (1970).

160. K. Tomita, *Bull. Chem. Soc. Jap.*, **34**, 280, (1961).

161. R. D. Gillard, H. M. Irving, R. M. Parkins, N. C. Payne and L. D. Pettit, *J. Chem. Soc.* A, 1159, (1966).

162. D. L. Lenssing and E. M. Hanna, *J. Am, Chem, Soc.*, **88**, 696, (1966).

163. S. Thirumaran, K. Raenalingam, *Transition Met. Chem.* (Dordrecht, Neth) 25(1), (2000).

164. M. Enamullah, M. G. Ahmed and Akhtar, *J. Bangladesh Chem. Soc.*, 4(2), 129, (1991).

165. G. R. Cayley and D. N. Hague, *Trans. Faraday Soc.*, **62**, 1236, (1966).

166. F. Nobuo; O. Masaaki; and S. Taknya, *J. Chem. Soc.* Dalton Trans, **1**, 64-70, (2001).

167. T. H. Tarafder, *Transition Met, Chem* (Dordrecht Neth.), **2**, 1-2, (2001).

168. Paresh J, Patel & P. K. Bhyattacharya, *Indian J. Chem.* **21A**, 590-594, (1982).

169. H. M. Irrving and J. P. Williams, *Nature* (London),, **162**, 746, (1953).

170. J. I. Watters and R. Dawitt, *J. Am Chem. Soc.* **82**, 1333, (1960).

171. E. Beda, Sigel, Fischer, Prijs, *Biochemical implications from mixed ligand complexes*, University of Basel, Switzerland, (1976).

172. P. G. More & R. B. Dhalvakar, *J. Indian Chem. Soc.* **81**,14-16, (2004),

173. P. T. Arasn & E. J. Ukpong, *J. Indian Chem. Soc.*, **80**, 174-177, (2003).

174. G.Arena, R. Cali, V. Cacinotta, S. Mnsanseei and E. Rizzaveli, J. Chem. Soc. Dalton,Trans; 1984,1651.

175. P. Chaudhari and H. Sigel, J. Am. Chem. Soc.,1977,99,3142.

176. P.R. Mifchell, B. Prijs and H. Sigel, Helv. Chem.. Acta; 1979,62,1723.

177. P.R.Mitchel and H. Sigel, J. Am. Chem.Soc. 1978,100,1564.

178. W.S.Sheldrick, Angew chem..,1981,93,473.

179. W.S.Sheldrick, Z. Naturtorseh; Inorg. Chem., 1982,373,863.

180. H.F. Steger and A. Corsini, J.Inorg. Nucl. Chem. 1973,35,1637.

181. Dr. Rafique Ullah and B.K. Bhattacherya, Indian Jarnaln of Chemistry, Vol.29A, February 1990, PP. 150-153.

182. K. Nakamoto, *IR and Raman Spectra of Inarganic and co-ordination compounds*, John willy and sons, New York, 3rd ed, (1978).

183. I. G. Sayee, Talanta, **15**, 1398, (1968).

184. I. G. Sayee and G . Astacoli, P. Paoletti, L. S. Petti and S. Samonartano, *Pure and Appl. Chem.*, **59**, 172, (1987).

185. A. I. Vogel, *A Text book of Practical Organic Chemistry*, Longmans Green, London (1956).

186. H. M. Irving and H. S. Rossotti, *J. Chem. Soc.*2904, (1954).

187. M. V. Chidambaram and P. K. Bhattacharya, *J. Inorg. Nucl. Chem.*, **32**, 237, (1970).

188. A. E. Martell, R. M. Smith, *Critical Stability Constant*, **(1-3)**, (1977).

189. Helmut Sigel and Christoph F. Naumann, *J. Am. Chem. Soc.*, **98**, 3,(1976).

190. M. R. Ullah & P. K. Bhattacharya. Indian J. Chem. 1990, 29A, 150-153.

191. R. D. Madan, *Modern Inorganic Chemistry*, S. Chand & Company Ltd. 2nded. 1372, (1990).

192. G. N. Mukhergee & A. Das, *Elements of Bio-Inorganic Chemistry*, U. N. Dhur & Sons Pvt. Ltd. 1sted., 66.

193. W. U. Malik, G. D. Tule & R. D. Madan, *Selected Topics in Inorganic Chemistry*, S. Chand & Company Ltd. 5th ed, 183,189, (1989).

194. P. T. Kissinger, W. R. Heineman, T. A. Petersen, *Eds, N. Y.* Marcel Dekker, 117, (1984).

195. W P. T. Kissinger, W. R. Heineman, *J. Chem. Educ*, **60**, 702, (1983).

196. E. S. Donald, B. R. Elinore and F. S. Duward, *J. Am. Chem. Soc.*, **89**, 5569-70, (1967).

197. J. J. Lingane, *Chem. Rev.*, **1**, 29, (1941).